TITOV, A. G.

<u>Titov, A. G.</u> - "A region of colored stones," (The Il'men state forest imeni V. I. lenin) Geografiya v shkole, 1949, No. 2, p. 27-38

SO: U-4934, 29 Oct 53, (Letopis 'Zhurnal 'nykh Statey, No. 16, 1949).

TITOV, A.I.; GITEL', P.O.

Reaction of white phosphorus with alkyl halides as governed by ionic and radical mechanism. Dokl. AN SSSR 158 no.6 1380-1381 O '64. (MIRA 17:12)

1. Predstavleno akademikom M.M. Shemyakinym.

TITOW, A.I. [Titov, A.I.] prof.

Ionocomplex mechanism of nitration of aromatic and unsaturated compounds. Wiad chem 15 no.12:741-811 D '61.

1. Panstwowy Instytut Naukowo-Badawczy Organicznych Polproduktow i Barwnikow w Moskwie.

TITOV, A.I.

Primary loss of weight and some features of water exchange in newborn infants. Vop.okh.mat. i det. 1 no.3:19-23 My-Je '56.
(MLRA 9:9)

1. Iz kafedry gospital'noy pediatrii (zav. - deystvitel'nyy chlen Akademii meditsinskikh nauk SSSR prof. A.F.Tur) Leningradskogo gosudarstvennogo pediatricheskogo meditsinskogo instituta.
(INFANTS (NEWBORN))

TITOV, A.I.

Chronaxy during the first days of life in infants born prematurely and at term. Pediatriia 39 no.5:11-13 S-O '56. (MLRA 10:1)

1. Iz kafedry gospital'noy pediatrii (zav. - deystvitel'nyy chlen AMN SSSR zasluzhennyy deyatel' nauki prof. A.F.Tur) Leningradskogo pediatricheskogo meditsinskogo instituta (dir. - prof. N.T.Shutova)
(NERVOUS SYSTEM, physiology,
chronaxy in premature & normal newborn inf. (Rus))
(INFANT, NEWBORN, physiology,
chronaxy (Rus))
(INFANT, PREMATURE, physiology,
same)

KUZNETSOV, V.I., polkovnik med. sluzhby; BARONOV, V.A., polkovnik med. sluzhby; TITOV, A.I., polkovnik med. sluzhby, dots.; FIALKOVSKIY, V.V., polkovnik med. sluzhby; SMIRNOV, K.K., polkovnik med. sluzhby, kand. med. nauk; DOVZHENKO, G.I., polkovnik med. sluzhby; DIVNENKO, P.G., polkovnik med. sluzhby; GORYUSHIN, G.S., podpolkovnik med. sluzhby; SHCHERBEKOV, N.I. podpolkovnik med. sluzhby; ZHUK, Ye. G., podpolkovnik med. sluzhby; BUTOMO, N.V., mayor med. sluzhby; PREOBRAZNEHSKIY, P.V., mayor med. sluzhby; TIKHONOV, K.B., mayor med. sluzhby

Clinical manifestations in subjects exposed to prolonged ionizing irradiation. Voen. med. zhur. no.2:40-43 F '57 (MIRA 12:7)
(RADIATIONS, effects,
clin. manifest. in subjects exposed to prolonged ionizing irradiation (Rus))

TUR, A.F., prof., zasluzhennyy deyatel' nauki, otv.red.(Leningrad); VOLOTOV, A.N., dotsent, red. (Leningrad); KVASNAYA, L.G., dotsent, red.; KOTIKOV, Yu.A., prof., red.; LIBOV, A.L., prof., red. (Leningrad); MALYSHEVA-MAKSIMENKOVA, Ye.S., dotsent; red.; MIRONOVICH, V.K., dotsent, red. (Leningrad); TERNOVSKIY, S.D., prof., red. (Moskva); TITOV, A.I., kand.med.nauk, red. (Leningrad); NATAROVA, N.V., red.; LIVSHITS, D.A., tekhn.red.

[Proceedings of the Seventh All-Union Congress of Pediatricians in Leningrad, 1957; abridged stenographic report] Trudy VII Vsesoyuznogo s"ezda detskikh vrachei; sokrashchennaia stenogramma. Otv.red. A.F.Tur. Leningrad, Gos.izd-vo med.lit-ry, Leningr.otd-nie, 1959. 654 p. (MIRA 13:5)

1. Vsesoyuznyy s"yezd detskikh vrachey, 7th, Leningrad, 1957.
2. Deystvitel'nyy chlen Akademii meditsinskikh nauk SSSR (for Tur).
3. Chlen-korrespondent Akademii meditsinskikh nauk (for Ternovskiy).

(PEDIATRICS--CONGRESSES)

TITOV, A.I., kand.med.nauk; POTANIN, N.V., kand.med.nauk

Case of erroneous diagnosis of eosinophilic reactions in children.
Sov.med. 24 no.11:111-114 N '60. (MIRA 14:3)

1. Iz kafedry gospital'noy pediatrii (zav. - deystvitel'nyy chlen AMN SSSR prof. A.F.Tur) Leningradskogo pediatricheskogo meditsinskogo instituta (dir. - prof. N.T.Shutova).
(EOSINOPHILES) (LEUKEMIA)

TITOV, A.I.

Erythrocytometric data in anemia in premature children. Vop. okhr. mat. i det. 6 no. 1:22-25 Ja '61. (MIRA 14:4)

1. Iz kafedry gospital'noy pediatrii (zav. - deystvitel'nyy chlen AMN SSSR prof. A.F. Tur) Leningradskogo pediatricheskogo meditsinskogo instituta (dir. - kand.med.nauk Ye.P. Semenova).
(INFANTS (PREMATURE)—DISEASES) (ANEMIA)
(ERYTHROCYTES)

DYMSHITS, L. A., prof.; DROZDOVA, M. V., dotsent; BELEVSKIY, A. G.,
kand. med. nauk; TITOV, A. I.

Lesion of the eyes in marble disease (Albers-Schonberg disease).
Vest. oft. no.2:52-55 '62. (MIRA 15:4)

1. Gospital'naya pediatricheskaya klinika (zav. - deystvitel'nyy chlen AMN SSSR prof. A. F. Tur) i kafedra glaznykh bolezney (zav. - prof. V. I. Grigor'yeva) Leningradskogo pediatricheskogo meditsinskogo instituta.

(BONES--DISEASES) (EYE--DISEASES AND DEFECTS)

TITOV, A.I.; BARYSHNIKOVA, A.N.

Chlorosulfichlorination and chlorosulfochlorination of ethylene. Conversion of β-chlotoethanesulfinic acid to thio ether. Dokl. AN SSSR 157 no.1:139-142 Jl '64. (MIRA 17:8)

1. Predstavleno akademikom M.M. Shemyakinym.

ACCESSION NR: AP5[illegible]

AUTHOR: Gitel', P. O.; 55 Titov, A. I.; 55 Sizova, M. V. 55

55 B

TITLE: A method for producing β-chloralkyl (alkenyl) dichlorophosphines. Class 12, No. 172322

SOURCE: Byulleten' izobreteniy i tovarnykh znakov, no. 13, 1965, 20

TOPIC TAGS: aklyl phosphine, chlorinated organic compound

ABSTRACT: This Author's Certificate introduces a method for producing β-chloralkyl (alkenyl) dichlorophosphines. Phosphorus trichloride is interacted with the proper [illegible]

ASSOCIATION: none

SUBMITTED: 04Dec62 ENCL: 00 SUB CODE: OC, GC

NO REF SOV: 000 OTHER: 000

Card 1/1 dm

SHILOV, P.M., doktor tekhn.nauk; KRIVOSHEYEV, A.Ye., doktor tekhn.nauk; DEMIDOVICH, N.S., kand.tekhn.nauk; RUDNITSKIY, L.S., kand.tekhn.nauk; FLOROV, K.V., kand.tekhn.nauk; SHAPOVAL, I.M., kand.tekhn.nauk; OLEYNICHENKO, V.G., inzh.; ZAIKIN, N.A., inzh.; TITOV, A.I., inzh.

Replacing alloyed steels by high-strength cast iron in manufacturing machine parts. Mashinostroenie no.4:59-61 Jl-Ag '65. (MIRA 18:8)

L 5409-66 EWT(l)/EWT(m)/T/EWP(t)/EWP(b)/EWA(c) IJP(c) JD

ACC NR: AP5027386 SOURCE CODE: UR/0181/65/007/011/3159/3162

41

AUTHOR: Abroyan, I. A.; Lavrov, V. P.; Titov, A. I. 37
55 55 55

ORG: Leningrad Polytechnic Institute (Leningradskiy politekhnicheskiy institut 18
im. M. I. Kalinina)
55

TITLE: Secondary emission of germanium bombarded along various cyrstallographic axes by potassium ions

SOURCE: Fizika tverdogo tela, v. 7, no. 11, 1965, 3159-3162

TOPIC TAGS: semiconductor single crystal, single crystal, secondary emission, germanium single crystal 14
55, 27 21, 44, 55

ABSTRACT: The ion-electron emission of germanium single crystals is studied to determine the effect which the crystal structure of the target has on secondary emission. Germanium specimens were bombarded with potassium ions at energies up to 7 kev, and secondary emission was measured as a function of the angle of incidence. It was found that the coefficient $\delta_{0.1}$ (the ratio of the number of ions reflected from the target at energies greater than 0.1 kev to the total number of

Card 1/2

0701 1304

L 5409-66

ACC NR: AP5027386

4

primary particles incident on the target in the same time interval) has a strong direct relationship to the temperature of the target. At 750° with primary particles in the 0.5-1.5 kev range, $\delta_{0,1}$ = 6-7.5% at angles of incidence between -30 and +24°. The experimental data show that the angle of ion incidence affects secondary emission in the semiconductor single crystals in a manner similar to that observed in the case of metals. It is suggested that all single crystals regardless of conductivity type (insulators, semiconductors and conductors) or type of chemical bond should show a non-monotonic relationship between the angle of incident radiation and secondary emission. The authors are grateful to N. A. Yeremeyev 55 and N. N. Petrov 55 for constant interest in the work and useful consultation. Orig. art. has: 2 figures.

SUB CODE: SS/ SUBM DATE: 23Feb65/ ORIG REF: 006/ OTH REF: 003

BVK

Card 2/2

L 18754-66 EWT(1)/EWT(m)/EWP(t) IJP(c) JD/JG/AT

ACC NR: AP6003770 SOURCE CODE: UR/0181/66/008/001/0111/0114

AUTHORS: Abroyan, I. A.; Makarova, T. N.; Pukshanskiy, A. L.; Titov, A. I.

ORG: Leningrad Polytechnic Institute im. M. I. Kalinin (Leningradskiy politekhnicheskiy institut) 84 B

TITLE: Excitation of electrons in germanium by alkaline metal ions
21, 44, 55 55 27 27

SOURCE: Fizika tverdogo tela, v. 8, no. 1, 1966, 111-114

TOPIC TAGS: germanium, single crystal, alkali metal, ion bombardment, electric conductivity, pair production, electron interaction

ABSTRACT: The authors investigated the increase in the conductivity of germanium single crystals upon excitation of electron-hole pairs by lithium and sodium ions of energy up to 6 kev. The induced conductivity was investigated by a pulse technique described in detail earlier (FTT v. 4, 2719, 1962). The target preparation procedure is also described elsewhere. To compare the pair-production efficiencies of electron and ion bombardment, two guns, one emitting electrons and 2

Card 1/2

L 18754-66
ACC NR: AP6003770

0

the other ions, were installed in the apparatus. The germanium used was n-type with resistivity ~38 ohm-cm. In all cases when the ion beam struck the surface of the germanium, its electric conductivity increased. The total number of electron-hole pairs excited by an ion of given energy before it is completely stopped in the target is estimated with the aid of Fermi-Dirac statistics at ~500 pairs when bombarded with 3-keV sodium ions and ~2000 pairs when bombarded with lithium ions of the same energy. The number of pairs is found to decrease with increasing atomic number of the bombarding ions and to increase monotonically with increase in the ion energy. The values obtained experimentally agree with the theoretical estimate. Orig. art. has: 3 figures and 2 formulas.

SUB CODE: 20/ SUBM DATE: 01Jul65/ ORIG REF: 004/ OTH REF: 001

Card 2/2 Sm

TITOV, A.I., inzh.

Compensation of the voltage dissymmetry with the aid of the capacitance of the DPR (two additional wires-rail) system. Vest. TSNII MPS 24 no.6:40-43 '65. (MIRA 18:9)

L 63925-65

ACCESSION NR: AP5021554

AUTHOR: Gitel', P. O.; Titov, A. I.; Sizova, M. V.

55 E

TITLE: A method for producing β-chloralkyl (alkenyl) dichlorophosphines. Class 12, No. 172322

SOURCE: Byulleten' izobreteniy i tovarnykh znakov, no. 13, 1965, 20

TOPIC TAGS: aklyl phosphine, chlorinated organic compound

ABSTRACT: This Author's Certificate introduces a method for producing β-chloralkyl (alkenyl) dichlorophosphines. Phosphorus trichloride is interacted with the proper olefin or halogen olefin in the presence of [illegible]

ASSOCIATION: none

SUBMITTED: [illegible]Dec62 ENCL: [illegible] SUB CODE: OC, GC

NO REF SOV: 000 OTHER: 000

Card 1/1 dm

L 56049-65 EWT(m)/EPF(c)/EWP(j)/T Pc-4/Pr-4 RM
ACCESSION NR: AP5018360

UR/0020/64/159/002/0385/0388
27
25
B

AUTHOR: Titov, A. I.; Sizova, M. V.; Gitel', P. O.

TITLE: New reaction for producing beta-chloroalkyldichlorophosphines from olefins according to an ionic mechanism

SOURCE: AN SSSR. Doklady, v. 159, no. 2, 1964, 385-388

TOPIC TAGS: chlorinated organic compound, organic phosphorus compound, ionization, reaction mechanism

ABSTRACT: Beta-chloroalkyldichlorophosphenes were produced by addition of PCl_3 to olefins in the presence of aluminum chloride, analogously to the scheme of its electron analog $SOCl_2$. The reaction mechanism is discussed through the formation of [illegible] acid, and the formation of [illegible]

Card 1/2

ACCESSION NR: AP5018360

PCl$_3$ and olefin were used to shift the equilibria in the necessary direction. Specific reactions with ethylene, vinyl chloride, propylene, isobutylene and cyclohexene are described. Literature data on the [illegible] with higher isoolefins are discussed. Orig. art. has: [illegible]

ASSOCIATION: none

SUBMITTED: 06May64 ENCL: 00 SUB CODE: OC, GC

NR REF SOV: 006 OTHER: 003 JPRS

Card 2/2

L 58874-65 EWT(l)/EWT(m)/T/EWP(t)/EWP(b)/EWA(h) Pz-6/Peb IJP(c)
JD/AT
ACCESSION NR: AP5017290 UR/0181/65/007/007/2007/2012

AUTHOR: Abroyan, I. A.; Titov, A. I.

TITLE: Induced conductivity in germanium during bombardment by potassium ions in different crystallographic directions

SOURCE: Fizika tverdogo tela, v. 7, no. 7, 1965, 2007-2012

TOPIC TAGS: anisotropy, electrical anisotropy, electric field, electric conductivity, semiconductor, germanium

ABSTRACT: The induced conductivity in single crystals of germanium was investigated as they were bombarded with potassium ions with energies up to 7 kev. The experimental device consisted of a sphere with two mutually perpendicular extensions. One of these contained a source of alkaline ions while the other contained the single crystal germanium target. The target was oriented in such a way that the electric field in the [illegible] angle of incidence of the primary beam was varied by rotating the target. A flat screen covered with willemite was placed in front of the target and controlled by an electromagnet.

Card 1/2

L 58874-65
ACCESSION NR: AP5017290

3

This made it possible to observe the ion beam visually and prevented the radiation destruction of the sample when the primary current was measured (the screen was lifted only while the current pulse of induced conductivity was measured) and also protected the surface of the target from contaminations which evaporated from the ion source during [illegible] the angle of incidence of primary particles on the surface of the sample. The maximum value of induced conductivity corresponds to the direction of maximum crystal "transparency" to the ions. "The authors are grateful to M. A. Yeremeyev for constant interest in the work and useful advice and to N. B. Grigor'yeva for help in making the measurements." Orig. art. has: 5 figures.

ASSOCIATION: Leningradskiy politekhnicheskiy institut im. M. I. Kalinina (Leningrad Polytechnic Institute)

SUBMITTED: 29Dec64 ENCL: 00 SUB CODE: NP, EM

NO REF SOV: 003 OTHER: 005

Card 2/2

1. TITOV, A.I.
2. USSR (600)
4. Agriculture
7. Production of butter of improved quality, Moskva. Pishchepromizdat,1952

9. <u>Monthly List of Russian Accessions</u>, Library of Congress, March,1953.Unclassified.

14

USSR.

The stability of different kinds of butter. A. I. Titov. *Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Molochnoi Prom.* 1953, No. 13, 39–59; *Referat. Zhur., Khim.* 1954, No. 37129.—Fresh butter, put to storage just after its prepn., preserves its original qualities for a long period of time when stored at temps. not higher than +1°. Melted butter is best stored at temps. approx. −5°; at lower temps. the undesirable pistachio-green color can be developed, at high temps. the liquid phase can be sepd. Milk fat and refined butter have to be stored at temps. not lower than −5°, and not higher than 6°; under these conditions the storage can be as long as 2 years. Pasteurized butter can be stored for 3 years at temps. not higher than 6°; when the butter is made from fat + milk it can be stored for 2 years at minus temps. only. The product made from fat + salt water is stable also at plus temps. up to 6°; such a product is usually not attacked by molds. Dry butter stored in hermetically sealed containers preserves its natural freshness for 12 months even when kept at 18–20°; at lower temps. it is stable for 16 months. When butter contains yeasts it can be stored without any significant changes for 2 years. B. W.

Titov, A.I.

AUTHORS: Titov, A.I.; Vlodavets, I.N.; Rebinder, P.A. 69-20-1-13/20

TITLE: The Processes of Structure Formation in Milk Fat and Their Significance in the Manufacture of Butter (Protsessy strukturoobrazovaniya v molochnom zhire i ikh znacheniye dlya proizvodstva slivochnogo masla)

PERIODICAL: Kolloidnyy Zhurnal, 1958, Vol XX, # 1, pp 92-101 (USSR)

ABSTRACT: A study has been made of the strength characteristics of milk fat and butter. It was found that in order to satisfy the consistency of butter, the fat must form a mixed crystallization-coagulation type of structure with the coagulation structure predominating. The specificities of structure formation in the production of butter by churning, and by the continuous chilling of high fat content cream, have been examined. Two major ways have been indicated for improving the butter consistency: controlling the crystallization temperature of the milk fat, which allows changes to be made in the total solid phase content of the system, and regulating the mechanical treatment in the hardening process, which allows changes to be made in the character of the structure formed so as to bring it closer to the crystallization or to the

Card 1/2

69-20-1-13/20

The Processes of Structure Formation in Milk Fat and Their Sifnificance in the Manufacture of Butter

coagulation type.

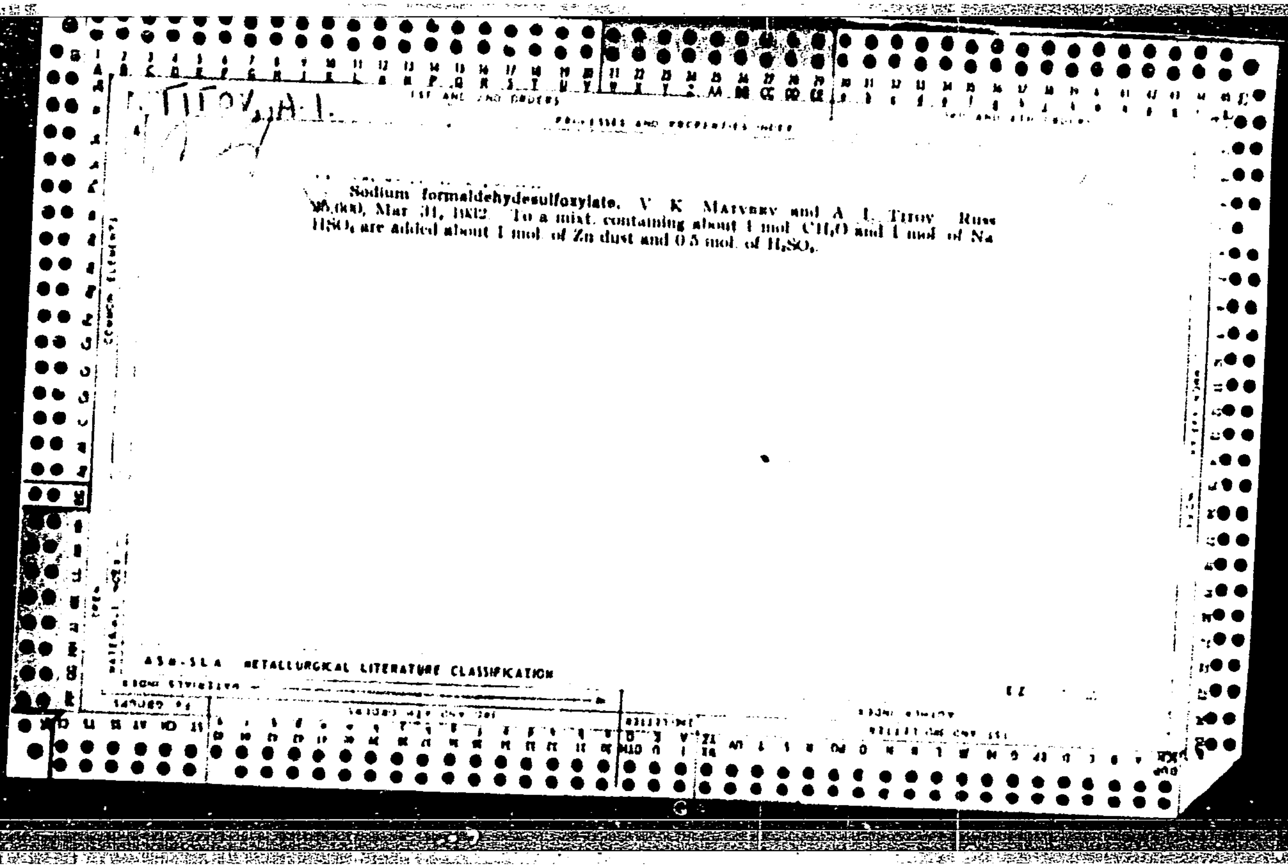
There are 6 figures, and 15 references, 11 of which are Soviet, 3 English and 1 Dutch.

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut molochnoy promyshlennosti, Moskva (All-Union Scientific Research Institute of the Milk Industry, Moscow)

SUBMITTED: July 19, 1957

AVAILABLE: Library of Congress

Card 2/2



TITOV, A.I.

Sodium formaldehydesulfoxylate. V. K. Matveev and A. I. Titov. Russ. 59,[illegible], Mar. 31, 1942. To a mixt. containing about 1 mol. CH_2O and 1 mol. of $NaHSO_3$ are added about 1 mol. of Zn dust and 0.5 mol. of H_2SO_4.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

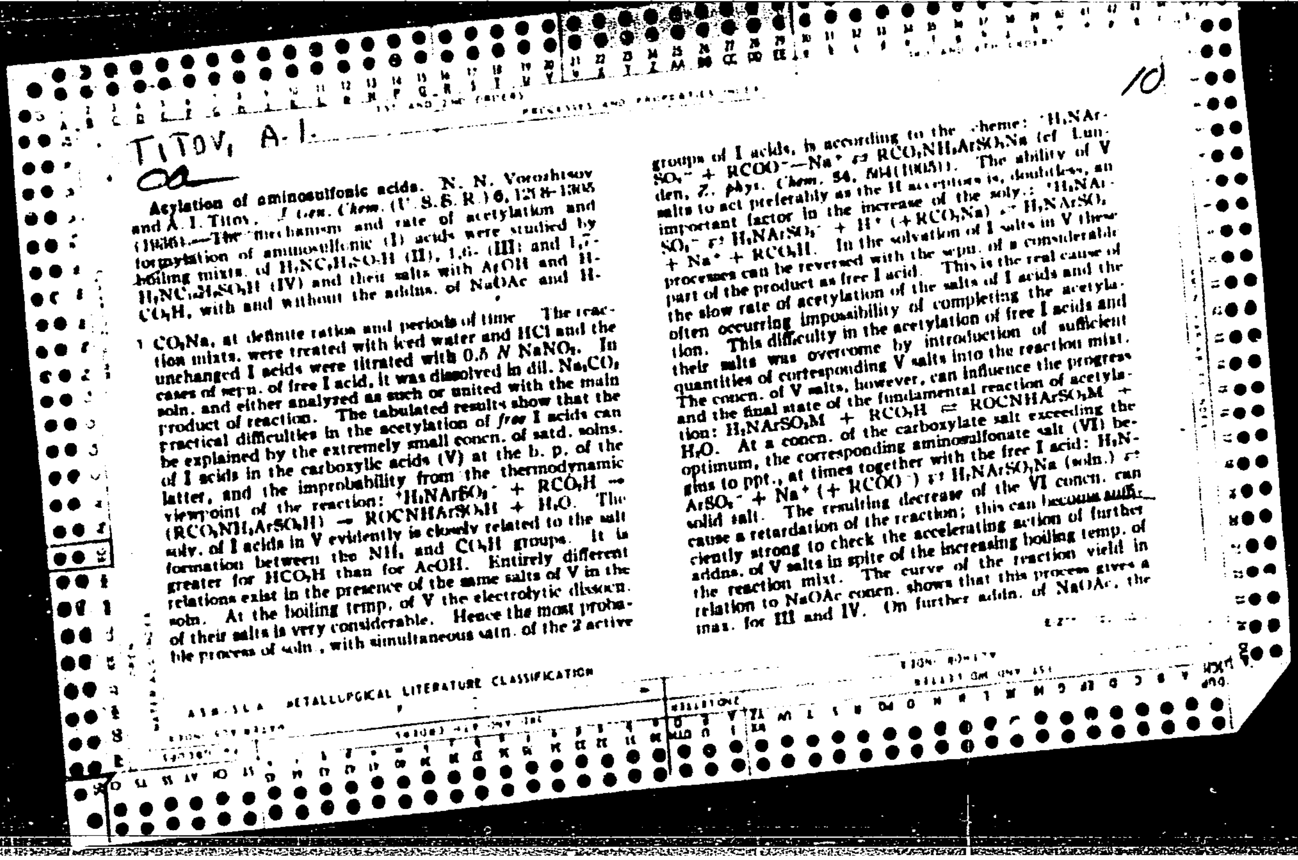
Titov, A.I.

ca

10

Acetylating aromatic amino sulfonic acids. A. I. Titov and N. N. Vorozhtsov. Russ. 40,272, March 31, 1938. Amino sulfonic acids and their salts are acetylated in the presence of sol. salts of corresponding carboxylic acids used in excess of one equiv. calcd. on free amino sulfonic acid.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



TITOV, A. I.

Ca

10

Acylation of aminosulfonic acids. N. N. Vorozhtsov and A. I. Titov. *J. Gen. Chem.* (U.S.S.R.) 6, 1278-1305 (1936).—The mechanism and rate of acetylation and formylation of aminosulfonic (I) acids were studied by boiling mixts. of $H_2NC_6H_4SO_3H$ (II), 1,6- (III) and 1,7-$H_2NC_{10}H_6SO_3H$ (IV) and their salts with AcOH and H-CO_2H, with and without the addns. of NaOAc and H-

The reac-

CO_2Na, at definite ratios and periods of time tion mixts. were treated with iced water and HCl and the unchanged I acids were titrated with 0.5 *N* $NaNO_2$. In cases of sepn. of free I acid, it was dissolved in dil. Na_2CO_3 soln. and either analyzed as such or united with the main product of reaction. The tabulated results show that the practical difficulties in the acetylation of *free* I acids can be explained by the extremely small concn. of satd. solns. of I acids in the carboxylic acids (V) at the b. p. of the latter, and the improbability from the thermodynamic viewpoint of the reaction: $^+H_3NArSO_3^- + RCO_2H \rightarrow$ $(RCO_2NH_3ArSO_3H) \rightarrow ROCNHArSO_3H + H_2O$. The soly. of I acids in V evidently is closely related to the salt formation between the NH_2 and CO_2H groups. It is greater for HCO_2H than for AcOH. Entirely different relations exist in the presence of the same salts of V in the soln. At the boiling temp. of V the electrolytic dissocn. of their salts is very considerable. Hence the most probable process of soln., with simultaneous satn. of the 2 active groups of I acids, is according to the scheme: ^+H_3NAr-$SO_3^- + RCOO^-—Na^+ \rightleftarrows RCO_2NH_3ArSO_3Na$ (cf. Lunden, *Z. phys. Chem.* 54, 564 (1905)). The ability of V salts to act preferably as the H acceptors is, doubtless, an important factor in the increase of the soly.: ^+H_3NAr-$SO_3^- \rightleftarrows H_2NArSO_3^- + H^+ (+RCO_2Na) \rightleftarrows H_2NArSO_3$ $+ Na^+ + RCO_2H$. In the solvation of I salts in V these processes can be reversed with the sepn. of a considerable part of the product as free I acid. This is the real cause of the slow rate of acetylation of the salts of I acids and the often occurring impossibility of completing the acetylation. This difficulty in the acetylation of free I acids and their salts was overcome by introduction of sufficient quantities of corresponding V salts into the reaction mixt. The concn. of V salts, however, can influence the progress and the final state of the fundamental reaction of acetylation: $H_2NArSO_3M + RCO_2H \rightleftarrows ROCNHArSO_3M +$ H_2O. At a concn. of the carboxylate salt exceeding the optimum, the corresponding aminosulfonate salt (VI) begins to ppt., at times together with the free I acid: H_2N-$ArSO_3^- + Na^+ (+ RCOO^-) \rightleftarrows H_2NArSO_3Na$ (soln.) $\rightleftarrows$ solid salt. The resulting decrease of the VI concn. can cause a retardation of the reaction; this can become sufficiently strong to check the accelerating action of further addns. of V salts in spite of the increasing boiling temp. of the reaction mixt. The curve of the reaction yield in relation to NaOAc concn. shows that this process gives a max. for III and IV. On further addn. of NaOAc, the increasing temp. again accelerates the action, and the yield, after reaching a min., begins to increase. I acids (II), giving well-sol. salts, gave no max. Because of the salting-out effect of the cations of V salts, the acetylation product is gradually pptd.: ROCNHArSO$_3^-$ + Na$^+$ (+RCOO$^-$) ⇄ ROCNHArSO$_3$Na ⇄ solid salt. This action causes a shift toward the desirable side of the reaction: H$_2$NArSO$_3$Na + RCO$_2$H ⇄ ROCNHArSO$_3$Na (+ H$_2$O) → solid salt, making it practicable to increase the yield above that possible by the conditions of the equil. in a homogenous medium. The accelerating action of the cations of V salts decreases in the order of K, Na, Mg. The rate of acylation is somewhat influenced by the structure of I acids, and increases with the greater consts. of electrolytic dissocn. of I acids. Thus, acetylation of II ($K_{18} = 6.2 \times 10^{-4}$) proceeds at a greater velocity than that of III ($K_{18} = 1.95 \times 10^{-4}$). The reaction of formylation proceeds at a greater rate than acetylation, because of the greater shift of the equil. toward the right side. The concn. of H$_2$NArSO$_3$ ion cannot attain the satn. point at which VI are salted out by the cations of V salts. The pptn. of formylated products proceeds as in the case of the acetylation products.

Chas. Blanc

B

Titov, A. I.

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

3RD AND 4TH ORDERS

C/P

The action of nitrogen dioxide on benzene, toluene and chlorobenzene. I. Nitration with nitrogen dioxide in the presence of sulfuric and phosphoric acids. A. I. Titov and A. N. Baryshnikova. *J. Gen. Chem.* (U. S. S. R.) 6, 1801-5(1936). On the assumption that HNO_3, formed by reaction of N_2O_4 (I) with H_2SO_4 (II), is the sole nitrating agent when aromatic hydrocarbons are nitrated with I in the presence of II, the following equation, supported by exptl. data, is offered to explain the course of the reaction: $RH + N_2O_4 + n\ H_2SO_4.m\ H_2O \rightarrow RNO_2 + HSNO_5 + (n - 1)\ H_2SO_4.(m + 1)\ H_2O$. To attain complete utilization of I the ratio toward the end of the reaction between free II and water, $(n - 1):(m + 1)$, must exceed a certain min. value, characteristic for each compd. The great tendency of II to transfer protons to compds. which normally in aq. medium are not proton acceptors explains its marked activating effect. Neither anhyd. H_3PO_4 nor P_2O_5 appreciably activates the reaction, indicating that they do not react with I to form HNO_3. To 29.2 g. C_6H_6 (III), vigorously stirred, is added at 40° over a period of 20 min. a soln. of 13.8 g. I in 39.25 g. II (94%). Stirring is continued 1 hr. at 50° and the reaction mixt. worked up to yield on distn. 18.15 g. (98.4%) nitrobenzene (IV), m. 6°, and 16.6 g. III. The reaction proceeds best when the concn. of free II is 78-85%. Below this concn. I does not completely react, above this concn. side reactions sharply lower the yield of IV. Hg and HgO, in small amts., cause almost explosive reaction. The greater resistance of PhCl (V) to nitration necessitates use of slightly more concd. II and a slightly higher temp. to give 98-100% $ClC_6H_4NO_2$ (VI). Toluene (VII) best nitrated at 0-15° with a soln. of 30.4% I in 94% II, gives 98% of mixed $MeC_6H_4NO_2$ (VIII). About 2% 2,6-di-

1C

nitro-*p*-cresol is also formed. Prolonged nitration of VII with I at room temp. gives ill-defined dark colored products. II. Preliminary communication. A. I. Titov. *Ibid.* 1855-62. In the absence of special activators I does not react with III, IV, V, and VII at room temp. At 108° I bubbled into V (50 cc.) for 14 hrs. gives a mixt. of VI (0.85 g.). In the nitration of VII the factors that favor dissocn. of I, namely, low concn. of I, elevated temp. and illumination, direct substitution in the side-chain. This is explained by inability of monomeric NO_2 to add to a double bond. Depending on the duration of the reaction and the concn. of I, VII treated with I at 12° in the absence of illumination for 6-20 days gives 1-21% phenylnitromethane (IX), 3-74% phenyldinitromethane (X), 0-18% BzH (XI), 0-51% BzOH (XII), and 5-25% VIII; exposure of the reaction mixt. to direct illumination (sunlight or Hg lamp) accelerates all of the reactions and cuts down VIII to 4-9%. at 108° and in the absence of illumination the yields are 25-30% IX, 7-21% X, 5-9% XI, 43-58% XII and 2% VIII. XI and XII are probably formed by hydrolytic cleavage of IX and X and oxidation of VII. I. L.

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TITOV, A-I.

CA

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Acylation of aromatic aminosulfonic acids. II. Method of multiple acylation. N. N. Vorozhtsov and A. I. Titov. *J. Applied Chem.* (U. S. S. R.) 9, 1852-7(1936); cf. *C. A.* 31, 1377⁷.—The acylation of 1,8-$C_{10}H_6(NH_2)SO_3H$ was carried out by the method of multiple acylation, in the following manner: the acid was dissolved in a hot satd. soln. of NaOAc in 98% AcOH and the soln. was allowed to boil (quietly) to the end of the reaction. Then, after slow cooling, the ppt. formed was filtered and the mother liquor was again used in the process instead of AcOH, together with a fresh portion of an amino acid and NaOAc. It is possible to carry out about 10 operations before reaching the limit of acid diln. The yield of the acylation product increased with each operation (77.1–105.0% of theory), because of the increase of concn. of the AcOH at the cost of the NaOAc, i. e., the acylation was carried out, practically, at the cost of the NaOAc. The 2nd and following operations differ from the first in that the acylation product is washed with dil. AcOH, sepd. from the product of the preceding operation during its drying. The formylation of the same compd. by this method yielded about 94% of the product. A. A. P.

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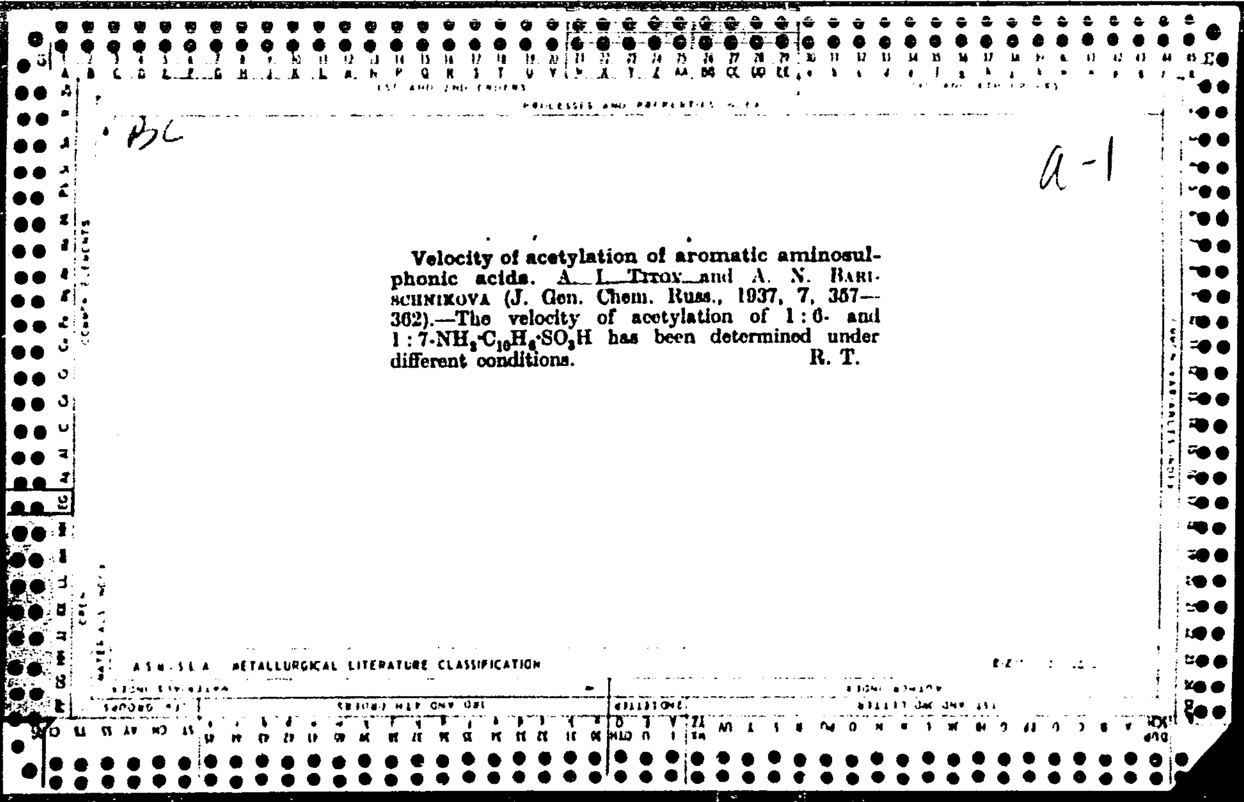

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a-1

Velocity of acetylation of aromatic aminosulphonic acids. A. I. TITOV and A. N. BARISCHNIKOVA (J. Gen. Chem. Russ., 1937, 7, 357—362).—The velocity of acetylation of 1 : 6- and 1 : 7-$NH_2 \cdot C_{10}H_6 \cdot SO_3H$ has been determined under different conditions. R. T.

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The action of nitrogen dioxide on benzene, toluene and chlorobenzene. III. Nitration with nitrogen oxide in the presence of aluminum chloride, phosphorus pentachloride and mercury nitrate. A. I. Titov. *J. Gen. Chem.* (U. S. S. R.) 7, 591-4(1937); cf. *C. A.* 31, 4281. According to Schaarschmidt (*C. A.* 19, 2930) the nitration of aromatic hydrocarbons with N_2O_4 in the presence of $AlCl_3$ proceeds by the formation of the complex $2AlCl_3 \cdot 3C_6H_5(NO_2)ONO$ (I), sol. in the excess of hydrocarbon, and its decompn. by the action of H_2O into $AlCl_3$, $PhNO_2$ and HNO_3. Exptl. data showed that $AlCl_3$ is dissolved by the action of 1/3 of the amt. of N_2O_4 that would be required for the formation of I; with further addn. of N_2O_4 the reaction proceeds much less energetically, and the action of H_2O is not indispensable to the formation of nitro compds. The reaction proceeds by heating in the absence of H_2O according to the formula: $2AlCl_3 + 3RH + 3N_2O_4 \rightarrow 3RNO_2 + 3NOCl + Al_2Cl_3(OH)_3$ (*1*). It is postulated that the course of the reaction is closely connected with the various phases of coördinated satn. of $AlCl_3$, and that the moment of $AlCl_3$ soln. corresponds with the end of the reaction: $RH + N_2O_4 + 2AlCl_3 \rightarrow RNO_2.AlCl_3 + AlCl_2(OH).NOCl \rightleftarrows RNO_2.AlCl_2(OH) + AlCl_3.NOCl$ (*2*). The intense color of the soln. is identical with that of a $AlCl_3$ soln. in the presence of NOCl. The following stages of the reaction are related to less energetically proceeding satn. of the Al field of force, and can approx. be represented by the schemes: $RNO_2.AlCl_3 + N_2O_4 + RH \rightarrow AlCl_2(OH).(2RNO_2)(NOCl)$; $AlCl_2(OH).NOCl + N_2O_4 + RH \rightarrow AlCl(OH)_2.(RNO_2)(2NOCl)$. When this high degree of satn. of the Al field of force has been attained, the formed compds. are more or less completely pptd. (cf. Dougherty, *C. A.* 23, 1399; Wohl and Wertyporoch, *C. A.* 25, 4230). N_2O_4 was gradually introduced, with shaking, into a mixt. of 55 g. (0.35 mol.) PhCl and 10.72 g. (0.08 mol.) $AlCl_3$ at 0°. $AlCl_3$ was completely dissolved when 3.74 g. (0.04 mol.) N_2O_4 was absorbed, i. e., exactly according to the formula (*2*). Further absorption of N_2O_4 was accompanied by less energetic liberation of heat. After absorption of 10.5 g. N_2O_4 (0.114 mol.) (95% of the theory), the $CaCl_2$-tube was replaced by a reflux condenser connected with a flask contg. 10% KOH, and a current of dry CO_2 was passed through the gelatin-like reaction mixt. heated gradually to boiling. The detn. of HNO_3 and Cl_2 in the adsorbent showed a loss of 7.44 g. NOCl (7.40 g. calcd. according to the formula (*1*)). The filter residue gave 8.25 g. of basic Al salts dried in a vacuum desiccator at room temp. (8.45 g. by the formula (*1*)). The filtrate contained 17.2 g. (90%) of mixed $ClC_6H_4NO_2$. The nitration of C_6H_6 gave analogous results. Conducting N_2O_4 at 100° for 8 hrs. into the reaction mixt. increased the yield of nitro products by 23%. Nitration of $PhNO_2$, BzCl and *p*-MeC_6H_4Me with N_2O_4 in the presence of $AlCl_3$ failed to give pos. results. The Schaarschmidt method of nitration of PhMe was improved by the reversed order of addn. of $AlCl_3$ to the mixt. of N_2O_4 and PhMe, resulting in 88% nitrotoluenes, b. 220-40°. Nitration of PhCl with N_2O_4 in the presence of PCl_5 gave 50% of isomeric $ClC_6H_4NO_2$. $HgNO_3$ with PhMe and N_2O_4 at 0° gave rapidly a dark brown ppt. and at room temp. explosive-like ignition. **IV. Nitration of benzaldehyde and nitro derivatives of benzene, toluene and chlorobenzene.** *Ibid.* 667-72.—Aromatic compds. contg. a *m*-orienting substituent, such as NO_2 and aldehyde groups, do not react with N_2O_4 even under pressure at

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high temps. and in the presence of $AlCl_3$. The formation of di- and trinitro compds. is easily effected with N_2O_4 in the presence of fuming H_2SO_4 (cf. Pinck, *C. A.* 21, 3804, Battegay, *C. A.* 22, 1061). In the nitration of aromatic compds. with N_2O_4 in the presence of H_2SO_4, 50% of combined N is converted into HNO_2 which is not used in the reaction. A complete use of N_2O_4 is possible in the lab. tests by the addn. of $K_2S_2O_8$ to the reaction mixt. after the completion of the 1st stage of the reaction: $RH + N_2O_4 + H_2SO_4 = RNO_2 + HSNO_5 + H_2O$; $RH + HSNO_5 + K_2S_2O_8 = RNO_2 + H_2SO_4 + SO_3 + K_2SO_4$. Hence, the reaction is completed without addnl. H_2SO_4 or SO_3. $C_6H_4(NO_2)_2$ was obtained in 97.6% yield by adding dropwise, with stirring, 10.1 g. N_2O_4 in 25 g. 45% fuming H_2SO_4 to 12.3 g. $PhNO_2$ at 5-7°. After standing for 1 hr., the temp. of the reaction mixt. was raised to 100° (1 hr.), then cooled to 40° and dild. with 100 cc. H_2O. By this method, $MeC_6H_4NO_2$ gave 98% 2,4-$(O_2N)_2C_6H_3Me$ and 85% 2,4,6-$(O_2N)_3C_6H_2Me$, and *p*-$ClC_6H_4NO_2$ gave 98.5% $ClC_6H_3(NO_2)_2$. Variations in the reaction temp. (5-140°) showed no effect on the nature and the yields of the nitration products. From 10.6 g. BzH, 10 g. N_2O_4 and 23 g. of 35% fuming H_2SO_4 at 3° resulted 9.5 g. of a nitro product, solidifying at 46-60°. Treating 13.7 g. (0.1 mol.) *p*-$MeC_6H_4NO_2$ at 70° with 4.9 g. N_2O_4 (0.054 mol.) in 12.4 g. of 35% fuming H_2SO_4 inside of 30 min., and then at the same temp. with 13.5 g. (0.05 mol.) $K_2S_2O_8$ and stirring for an addnl. hr., resulted in 97.1% 2,4-$(O_2N)_2C_6H_3Me$, solidifying point 69.1°.

Chas. Blanc

1ST AND 2ND ORDERS

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A 3

Mechanism of M. I. Konovalov's reaction. I. A. I. Titov (J. Gen. Chem. Russ., 1937, 7, 1695—1703).—PhMe and NO_2 yield mixtures of $CHPh(NO_2)_2$, $CH_2Ph\cdot NO_2$, $C_6H_4Me\cdot NO_2$, and BzOH, the yields and relative proportions of the products varying according to the temp. and duration of the reaction, and to the $[NO_2]$. Analogous results are obtained with PhMe and HNO_3 (d 1·4). The mechanism of the reaction is discussed.

R. T.

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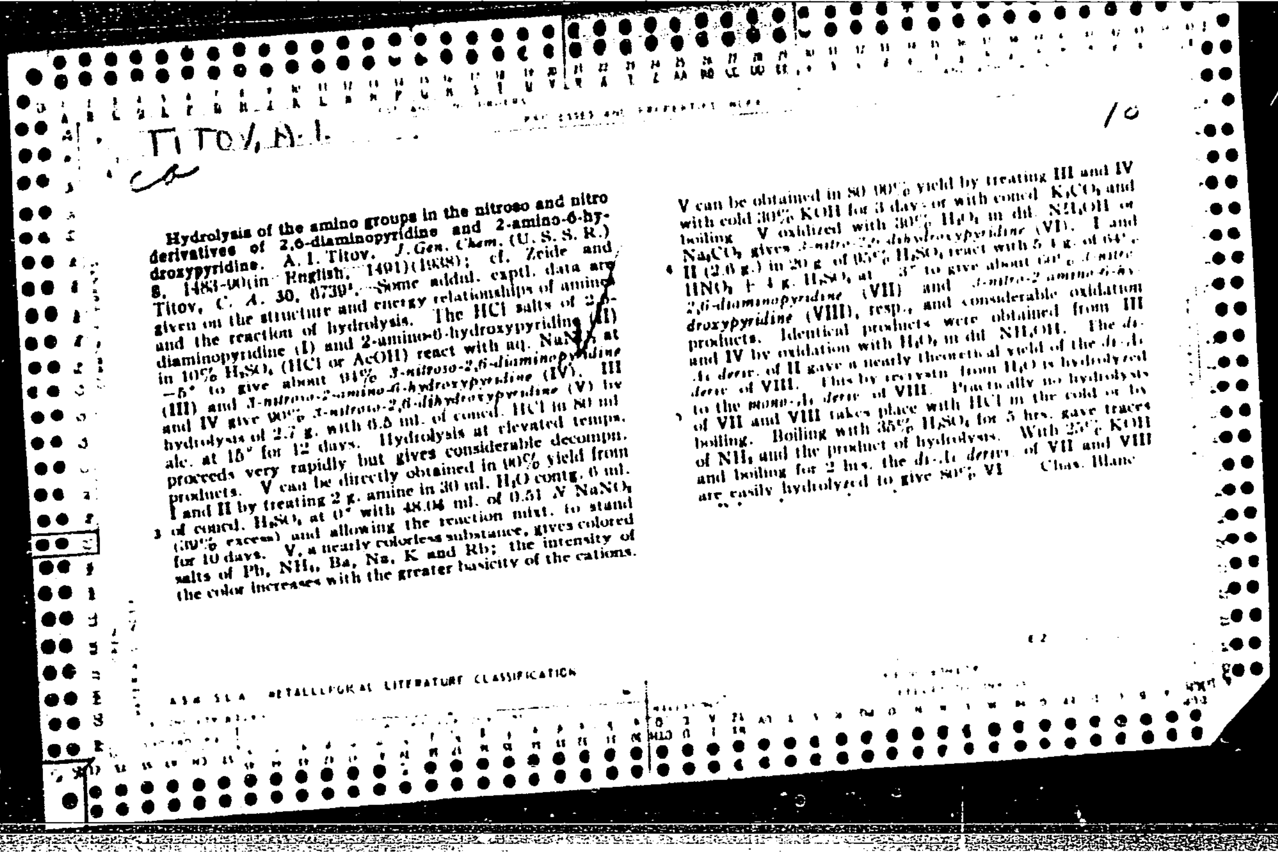

TITOV, A.I.

Ca

10

Hydrolysis of the amino groups in the nitroso and nitro derivatives of 2,6-diaminopyridine and 2-amino-6-hydroxypyridine. A. I. Titov. *J. Gen. Chem.* (U. S. S. R.) 8, 1483-90(in English, 1491)(1938); cf. Zeide and Titov, *C. A.* 30, 6739¹.—Some addnl. exptl. data are given on the structure and energy relationships of amines and the reaction of hydrolysis. The HCl salts of 2,6-diaminopyridine (I) and 2-amino-6-hydroxypyridine (II) react with aq. $NaNO_2$ at −5° in 10% H_2SO_4 (HCl or AcOH) to give about 94% *3-nitroso-2,6-diaminopyridine* (III) and *3-nitroso-2-amino-6-hydroxypyridine* (IV). III and IV give 90% *3-nitroso-2,6-dihydroxypyridine* (V) by hydrolysis of 2.7 g. with 0.5 ml. of concd. HCl in 80 ml alc. at 15° for 12 days. Hydrolysis at elevated temps. proceeds very rapidly but gives considerable decompn. products. V can be directly obtained in 90% yield from I and II by treating 2 g. amine in 30 ml. H_2O contg. 6 ml. of concd. H_2SO_4 at 0° with 48.06 ml. of 0.51 *N* $NaNO_2$ (30% excess) and allowing the reaction mixt. to stand for 10 days. V, a nearly colorless substance, gives colored salts of Pb, NH_4, Ba, Na, K and Rb; the intensity of the color increases with the greater basicity of the cations. V can be obtained in 80-90% yield by treating III and IV with cold 30% KOH for 3 days or with concd. K_2CO_3 and boiling. V oxidized with 30% H_2O_2 in dil. NH_4OH or Na_2CO_3 gives *3-nitro-2,6-dihydroxypyridine* (VI). I and II (2.6 g.) in 20 g. of 95% H_2SO_4 react with 5.4 g. of 64% HNO_3 + 4 g. H_2SO_4 at −3° to give about 60% *3-nitro-2,6-diaminopyridine* (VII) and *3-nitro-2-amino-6-hydroxypyridine* (VIII), resp., and considerable oxidation products. Identical products were obtained from III and IV by oxidation with H_2O_2 in dil. NH_4OH. The di-Ac deriv. of II gave a nearly theoretical yield of the di-Ac deriv. of VIII. This by recrystn. from H_2O is hydrolyzed to the mono-Ac deriv. of VIII. Practically no hydrolysis of VII and VIII takes place with HCl in the cold or by boiling. Boiling with 35% H_2SO_4 for 5 hrs. gave traces of NH_3 and the product of hydrolysis. With 25% KOH and boiling for 2 hrs. the di-Ac derivs. of VII and VIII are easily hydrolyzed to give 80% VI. Chas. Blanc

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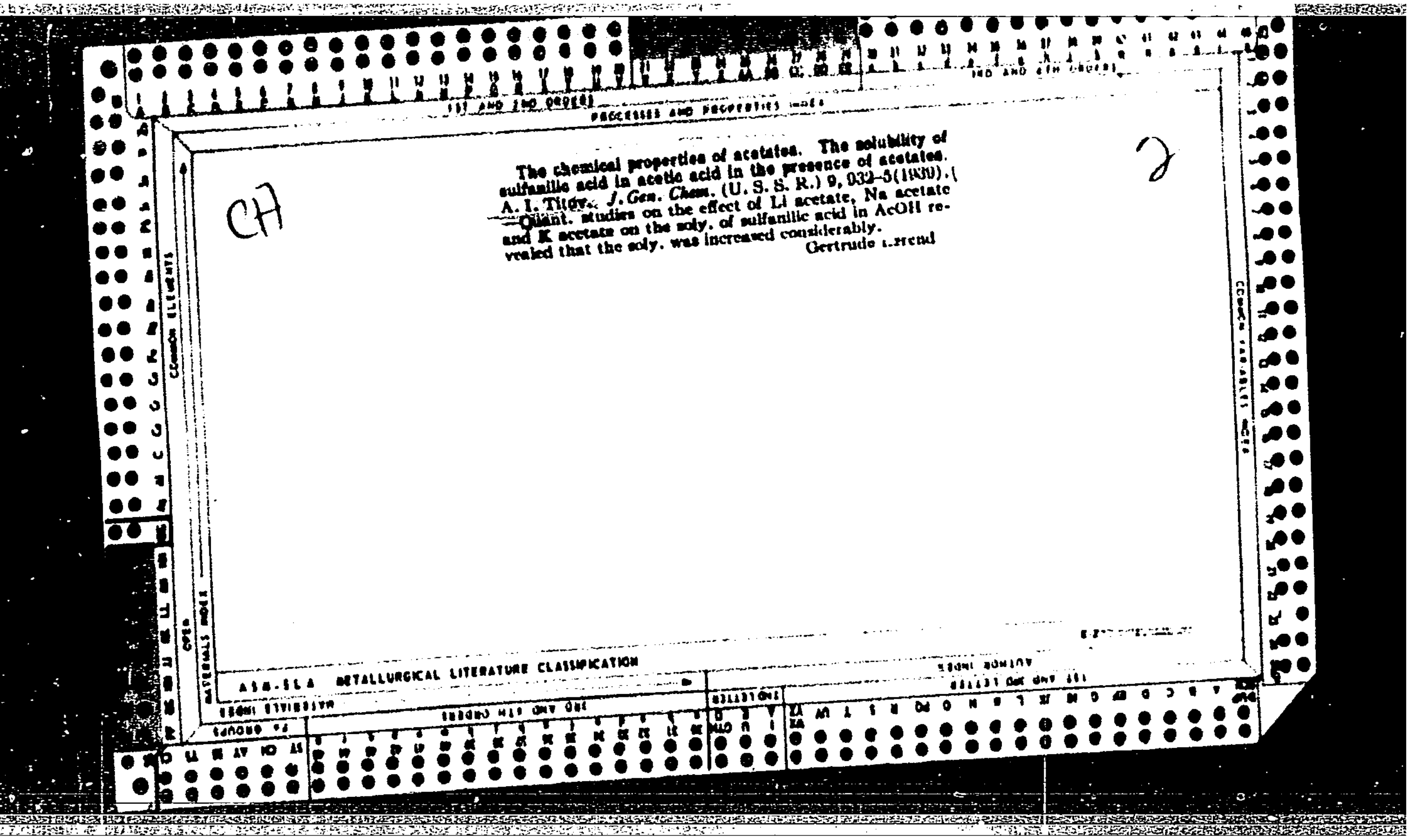

CH

2

The chemical properties of acetates. The solubility of sulfanilic acid in acetic acid in the presence of acetates. A. I. Titov. *J. Gen. Chem.* (U. S. S. R.) 9, 932-5(1939). Quant. studies on the effect of Li acetate, Na acetate and K acetate on the soly. of sulfanilic acid in AcOH revealed that the soly. was increased considerably.

Gertrude Berend

1ST AND 2ND ORDERS

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3RD AND 4TH ORDERS

Titov, A.I.

ca

10

The mechanism of the Konovalov reaction (nitration of saturated hydrocarbons). II. A. I. Titov. *J. Gen. Chem.* (U. S. S. R.) 10, 1878-84(1940); cf. C. A. 31, 8516⁸.—NO_2 acts on MePh at 100° to give chiefly $PhCH_2NO_2$ (I) and, by oxidation, BzH and BzOH. Some $PhCH(NO_2)_2$ (II) and nitrotoluenes are also formed, but NO_2 has a very slight nitrating action on the ring. Conversely, HNO_3 acts only to nitrate the ring when it is pure, but if it contains some NO, NO_2 is formed and the side chain is also nitrated. Thus, if urea is added to HNO_3 to remove all NO before nitrating, 2,6-dinitro-*p*-cresol is the chief product, and the side chain is neither nitrated nor oxidized, although the latter reactions predominate when NO is left in the acid. Neither HNO_3 nor NO_2 converts I into II. II is produced when the $PhCH_2$ radical, formed by reaction of PhMe and NO_2, reacts with NO to form $PhCH_2NO$ which isomerizes to PhCH:NOH and then reacts with NO_2 to form II.

H. M. Leicester

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1ST AND 2ND ORDERS

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TITOV, A.I.

ca

10

Theory of amine hydrolysis. Investigation of the hydrolysis of 2,6-diaminopyridine and 2,6-aminohydroxypyridine. A. I. Titov and B. B. Levin. *J. Gen. Chem.* (U.S.S.R.) 11, 9-15(1941).--In continuation of previous work (*C. A.* 30, 6730^{9}) on compds. contg. an aminovinyl grouping, the ease of hydrolysis of 2,6-diaminopyridine (I) was studied. On the basis of resonant structures the relative ease of hydrolysis of this compd. to 2,6-aminohydroxypyridine is explained, as well as the comparative difficulty of further hydrolysis to the 2,6-dihydroxypyridine (II). The rate of hydrolysis by dil. H_2SO_4 was studied and from the data obtained a set of preparative conditions for II was detd. as follows: 10 g. I and 70.5 g. 65% H_2SO_4 are heated at 155° for 4.5 hrs., dild. with 80 cc. H_2O, let stand at 7-10° and the anhyd. sulfate of II is filtered off in 4.6-g. yield. On diln. of the mother liquor a further 2.6 g. is obtained, giving a total yield of 50%. To obtain the free base, the sulfate (5 g.) in 25 cc. boiling water is treated slowly with NaOAc or $NaHSO_3$ until neutral to Congo red, boiled for several mins., filtered and cooled. The pptd. product is the hydrate of II (59.5% yield), m. 203.5-204°. By treatment with Ac_2O it is converted into the 2,6-diacetate, m. 69° (from Et_2O). Prolonged hydrolysis of I in 70% H_2SO_4 at 175° yields more NH_3 than the theoretical amt. from hydrolysis of the NH_2 groups, indicating hydrolysis of the pyridine ring. A small quantity of an acid was isolated from this hydrolysis mixt., but could not be identified positively. G. M. K.

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Mechanism of nitration of naphthalene by nitric acid. A. I. Titov (*J. Gen. Chem. Russ.*, 1941, 11, [illegible]; cf. A., 1938, II, 48).—Nitration of $C_{10}H_8$ to $1-C_{10}H_7\cdot NO_2$ by HNO_3 (*d* 1·36 and 1·33) takes place, at room temp., only in the presence of N oxides, and is prevented by the presence of [illegible] HNO_3. The rate of nitration increases with increase [illegible] HNO_3 of *d* 1·18 does not nitrate [illegible]. The function of HNO_3 is [illegible] and regeneration of N_2O_4, which [illegible] agent. Nitration by highly conc. [illegible] is ascribed to the action of N_2O_5. [illegible] G. W.

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Ca

2

Inductive, mesomeric, and steric effects in unsaturated and aromatic acids. A. I. Titov (Lab. Org. Chem., K. E. Voroshilov Milit. Acad., Moscow). *J. Gen. Chem.* (U.S.S.R.) 16, 1801-6(1946)(in Russian).--The fact that α,β-unsatd. acids are weaker than the corresponding β,γ-unsatd. acids (e.g., $CH_3CH_2CH:CHCOOH$, $10^5K = 1.5$; $CH_3CH:CHCH_2COOH$, $10^5K = 3.4$) is interpreted by the superposition of a pos. mesomeric (+*M*) effect on the neg. inductive (−*I*) effect, resulting in an increase of the neg. charge on the carboxyl and a lessening of the tendency to ionization. The +*M* effect explains also the increased basic properties of $PhNO_2$ as compared with $MeNO_2$, whereas the decrease of the basic properties in $PhNH_2$ as compared with $MeNH_2$ is due to the −*M* effect. The strong increase of acidity from $CH_3CH:CHCOOH$ to $CH_3C:CCOOH$ ($10^5K = 250$ as against 3.4) is understandable from the fact that the two π-bonds of C:C lie in different planes only one of which can be the seat of an *M* effect, whereas in the other inductive attraction of electrons remains uncompensated. The lowered electrophilism of the carboxyl C, due to the *M* and the electromeric effects, dets. the much lower rates of esterification of α,β-olefincarboxylic acids in comparison with the corresponding satd. acids, whereas the somewhat greater rate in β,γ-unsatd. acids is explained by the sole occurrence of the *I*-effect. Inasmuch as full realization of the *M*-effect of π-bonds depends on location of the corresponding atoms in one plane, substituents that disrupt the plane structure on steric grounds will hinder resonance and result in higher acid dissocn.; for steric reasons, the cis forms of $CH_3CH:CHCOOH$ and of $PhCH:CHCOOH$ are stronger acids than the trans forms; the same steric factor also underlies the increase of acidity from PhCOOH to *o*-MeC_6H_4COOH to 2,6-$Me_2C_6H_3COOH$ as contrasted with the acidity-decreasing +*I*-effect of introduction of Me groups in *m* and *p* positions. The combined action of the steric and the +*I* effect is detd. for the stability of the 2,4,6-$Me_3C_6H_2CO^+$ carbonium ion in soln. in H_2SO_4.

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TITOV, A.I.

Ca

10

Theory of nitration of saturated hydrocarbons and their derivatives. I. General conclusions on the primary elementary stage of the reaction. A. I. Titov (Lab. Org. Chem., K. E. Voroshilov Milit. Acad., Moscow). *J. Gen. Chem.* (U.S.S.R.) **16**, 1896-1906(1946)(in Russian).—The ineffectiveness of pure HNO_3 for the nitration of paraffins, paraffinic side chains, and cycloparaffins, was demonstrated in 60-day expts. at room temp. with C_6H_{14}, 2,7-dimethyloctane, cyclohexane, and PhMe, and HNO_3 d. 1.40-1.42; results were also neg. with C_6H_{14} and cyclohexane at 100°, 10 hrs. Nitration proceeds not with HNO_3 but with NO_2 which forms to some extent above 300°; 50 ml. cyclohexane nitrated with HNO_3 (d. 1.4) at 320-40° gave only 0.8 g. product while the same amt. reacting with 12 g. NO_2 gave 7.5 g. nitrated products. Further proof is derived from expts. on the nitration of PhMe with N_2O_4 with excess of either NO or O_2. In the first case, due to suppressed dissocn., $N_2O_4 \rightarrow NO_2 + NO$, nitration is very slight; in the presence of O_2 due to the oxidation of NO to NO_2, nitration is significant. Only the monomer NO_2 is effective, N_2O_4 is not. The primary reaction is assumed to be $RH + NO_2 \rightarrow R + HNO_2$, giving rise to free radicals R; by its electrophilic nature, NO_2 is analogous to at. halogens, being energetically closest to the iodine atom. Values of the energies of stabilization E_R of radicals R are derived from the differences of kinetic energies of activation *E* of hydrocarbons RH and of CH_4, assuming the difference to be approx. = E_R; for the nitration of CH_4, E = 43 kcal., and hence values of E_R are tabulated for a no. of radicals R (for R = Et, Pr, iso-Pr, Bu, *sec*-Bu, Me_3C, $PhCH_2$, Ph_2CH, Ph_3C, E_R = 2.0, 3.0, 4.0, 3.5, 4.7, 3.3, 15, 26, 38 kcal.) and the *E* values for the nitration of the corresponding hydrocarbons, *RH*. That nitration by NO_2 is of the radical reaction type is further corroborated by such facts as its localization in the hydrocarbon phase, absence of an influence of the polarity of the medium and of the presence of strong acids (H_2SO_4, $AlCl_3$, $TiCl_4$). The assumed mechanism, $RH + NO_2 \rightarrow R + HNO_2$, is further supported by considerations of energetic and steric improbability of other mechanisms, such as $RH + NO_2 \rightarrow RNO_2 + H$ or C—C rupture. Primary formation of compds. of the type RNOOH is improbable on steric grounds and on account of cis-trans conversion under the action of NO_2.

N. Thon

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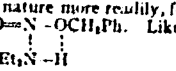
ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

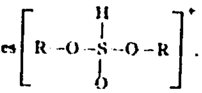
PROCESSES

The significance of steric factors in alkylation, acylation, and related chemical reactions. A. I. Titov (K. E. Voroshilov Milit. Acad., Moscow). *J. Gen. Chem.* (U.S.S.R.) 16, 2011-18(1946)(in Russian); cf. *C.A.* 41, 6000h.—(1) Velocities of reactions of this type are detd. not only by the pos. elec. charge on the corresponding electrophilic centers but also, to a large extent, by the "coördinative unsatn." of these centers, expressing the degree of their steric accessibility and their capacity of forming compds. with a higher coördination no. without substantially altering the elec. nature of the rest of the mol.; thus, in NO_2, RCHO, $SOCl_2$, the N, C, and S atoms are coördinatively unsatd. and ready to form intermediate complexes without substantial activation. The nucleophilic atom *A* (charge $-e$) in the mol. M-A-N will react faster with either the electrophilic center B_1 or with that at B_2 (charges $+e_1$ and $+e_2$, steric resistances R_1 and R_2) in the mol. (Q)(T)(X) B_1-B_2 (Y)(Z), depending on the sign of the difference of the driving forces *f* of the two reactions, approx. equal to the difference of the two rate consts.: $\Delta k \approx f_1 - f_2 = Pe(e_1 - e_2) - (R_1 - R_2)$ where *P* is a function of the distance. (2) These considerations are applied to the reactions of Et_2NH with the nitrite $PhCH_2NO_2$ (I) and with the nitrate $PhCH_2NO_3$ (II): 37.4 g. I reacted with 60 g. Et_2NH under cooling, giving, after 2 days' standing and twice repeated distn., 94% nitrosodimethylamine, Et_2NNO, b. 175-8°, and 88% $PhCH_2OH$; no alkylation took place. On the other hand, 5.8 g. II reacted with 10 g. Et_2NH with a spontaneous temp. rise to 65°; soln. in 30 ml. HCl (1:2), stirring with ether, alkalinization, extn. with ether, and distn. of the ext. gave 80% $(PhCH_2)Et_2N$, b. 209-13°, identical with the product synthesized by boiling on a water bath 3 hrs. 12.5 g. $PhCH_2Cl$, 25 g. Et_2NH, 10 g. K_2CO_3, extn. with 30 ml. C_6H_6, and fractionation (yield 80%), aurate m. 90-1°; picrate m. 121-2° (alc.). The 2 reactions, acylation by I and alkylation by II, proceed with approx. the same velocity. The pos. elec. charge on the N atom is undoubtedly greater in the nitrate than in the nitrite, but owing to greater steric accessibility the latter N exhibits its electrophilic nature more readily, forming the intermediate complex



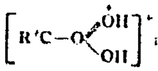
$$\begin{matrix} O{=}N & -OCH_2Ph \\ \vdots & \vdots \\ Et_2N & -H \end{matrix}$$

Likewise, phenols react readily with nitrites (in neutral or slightly alk. medium), forming nitroso compds., but are inert to alkyl nitrates. (3) Further examples of the effect of steric unsatn. are the alkylating action of alkyl sulfates and the acylating action of most carboxylic acid esters. The enhancement of the alkylating ability of sulfurous acid esters by addns. of strong inorg. acids may be due to the formation of intermediate complexes



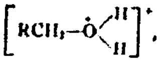
$$\left[R-O-\overset{\displaystyle H}{\underset{\displaystyle O}{S}}-O-R \right]^+$$

The esterification by way of acylation of primary aliphatic alcohols is due to a large extent to the greater steric accessibility of the C atom in



$$\left[R'C-\dot{O}\begin{matrix} OH \\ OH \end{matrix} \right]^+$$

as compared with



$$\left[RCH_2-\dot{O}\begin{matrix} H \\ H \end{matrix} \right]^+$$

, the reaction proceeding over the in-

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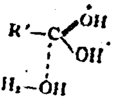
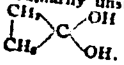
termediate  The enhancement of the alkyl-

ating ability of esters R_3CX as a result of increased wt. of
ionic structures in the resonance is not only due to an in-
creased charge of the C atom but also to the coordinative
unsatn. linked with the nearly plane configuration $[R_3C]^+$.
The same factor plays a role in the reactions between H_2O
and $SOCl_2$ and SO_2Cl_2. On cyclopropanone, due to the
closeness of the CH_2 groups, the carbonyl C is "laid bare"
thanks to which it becomes sterically readily accessible
and chemically reactive; hence the unusual stability of
ordinarily unstable addn. products such as the hydrate



N. Thon

TITOV, A. I.

"On Chemical Properties of Acetates. II." by A. I. Titov (p. 2[illegible]19)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1946, Volume 16, No. 12

TITOV, A. I.

PA 15T58

USSR/Chemistry - Nitration
Chemistry - Nitric acid

Feb 1947

"The Mechanism of Nitration of Aromatic Compounds With Nitric Acid," A. I. Titov, 3 pp

"Zhur Obshch Khim" Vol XVII, No 2

General statements on the diversity of nitrating agents, motive forces, reaction mechanism and influence of the steric-energetic factors.

15T58

1ST AND 2ND ORDERS

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3RD AND 4TH ORDERS

TITOV, A. I.

CA

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Mechanism of the catalytic nitration of aromatic compounds in the presence of mercury salts. I. A. I. Titov and A. N. Baryshnikova. *J. Gen. Chem.* (U.S.S.R.) 17, 829-35(1947)(in Russian).—With dil. HNO_3 free of oxides of N, the Hg aromatic compds. (I) undergo a reversible acid hydrolysis reaction leading to aromatic hydrocarbons (II) and a mercuric salt. When the reaction is carried out with 50-70% HNO_3 contg. oxides of N, the same mixt. of nitro aromatic hydrocarbons (III) and nitrophenols (IV) is obtained as when the aromatic hydrocarbon (II) itself is nitrated in the presence of Hg salts. The initial stage of the catalytic nitration involves formation of a mixed Hg aromatic compd. which is then converted to the mixt. of III and IV. In the absence of oxides of N, Hg salts do not catalyze the conjugate reactions of nitration and oxidation. When 2 g. Ph_2Hg or PhHgOAc (or $(C_{10}H_7)_2Hg$, etc.) is treated at 15° with HNO_3 of sp. gr. 1.33 in 5 ml. HOAc contg. 0.3 g. urea nitrate, no nitration takes place and 70% benzene is obtained. When 9 g. of PhHgOAc is treated with 15 ml. HNO_3 of sp. gr. 1.4 and 0.05 g. trioxymethylene, self-heating to 55° takes place and the reaction mixt. yields 0.06 g. $PhNO_2$, 0.11 g. p-$C_6H_4(NO_2)_2$, 0.03 g. p-nitrophenol, 1.08 g. 2,4-dinitrophenol, and 2.1 g. picric acid. Similar results are obtained with $(o\text{-}MeC_6H_4)_2Hg$, o-MeC_6H_4HgOAc, 1-$C_{10}H_7HgCl$, $PhHgNO_3$, etc. When 10 ml. benzene was treated at room temp. 10 days with 50 ml. HNO_3 of sp. gr. 1.33 and 5 g. $Hg(NO_3)_2$: with (1) 0.5 g. urea nitrate, and (2) 0.5 g. $NaNO_2$, the 1st reaction yielded 9 ml. benzene, a trace of $PhNO_2$, and no picric acid. Reaction (2) yielded 6.1 g. benzene, 0.08 g. $PhNO_2$, 0.06 g. p-$C_6H_4(NO_2)_2$, 0.42 g. 2,4-dinitrophenol, and 2.0 g. picric acid. Similar results were obtained using acid of sp. gr. 1.5 and HOAc as a solvent except that in (2) the yield of nitrophenols was higher.

P. H. Rathmann

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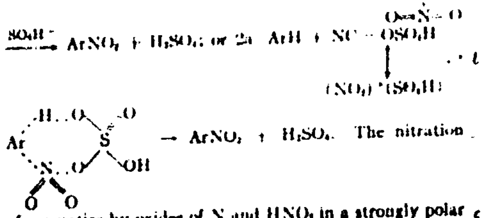
CA

TITOV, A.I.

Differences in the nitration of aromatic and saturated hydrocarbons. A. I. Titov. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 18, 100-3(1948).—The fundamental difference in the nitration of aromatic and satd. hydrocarbons is that the reaction with aromatic compds. is of an ion-complex or crypto-ionic character, while that with the satd. hydrocarbons is of the radical-reaction type. Monomer NO_2 is the effective nitrating agent for paraffins, while nitrating or nitrosating mixts. are required for the most efficient nitration of aromatics. If the same nitrating agent is used for both a satd. and an aromatic hydrocarbon, it is shown that the interaction of the nitrating agent and the satd. hydrocarbon involves an atom of H from the hydrocarbon and the agent, while in the case of the aromatic compd. the reaction is with a C atom. The mechanism for the nitration of satd. hydrocarbons is given in a previous paper (cf. C.A. 41, 6520b). The mechanism for the nitration of aromatic hydrocarbons with a H_2SO_4-HNO_3 mixt. is: 1. $NO_2OH + 2H_2SO_4 \rightleftharpoons (O{=}N{=}O)^+ + H_3O^+ + 2SO_4H^-$; $NO_2^+ + SO_4H^- \rightleftharpoons NO_2{-}OSO_3H$; 2. $Ar{-}H + (O{=}N{=}O)^+ \rightleftharpoons$

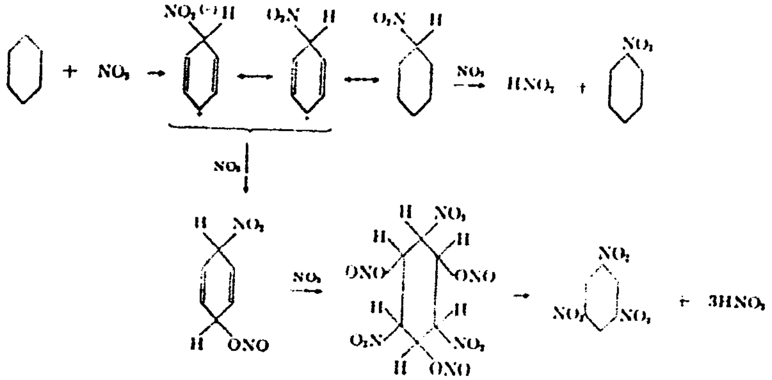


$$\overset{O=\dot{N}-O}{Ar{-}H}{}^{+} \xrightarrow{SO_4H^-} ArNO_2 + H_2SO_4; \text{ or 2a. } ArH + NO_2{-}OSO_3H \updownarrow (NO_2)^+(SO_4H)^-$$

$$\rightarrow ArNO_2 + H_2SO_4.$$

The nitration of aromatics by oxides of N and HNO_3 in a strongly polar medium at low or ordinary temps. can occur through interaction with the nitrosyl cation, $(O{=}N)^+$, or the nitrosyl nitrate form of N_2O_4, $O{=}N{-}ONO_2 \longleftrightarrow (O{=}N)^+ \cdot (NO_3)^-$, by a procedure analogous to the nitration of satd. hydrocarbons. The nitration of aromatics through primary interaction with monomer NO_2, such as the formation of $PhNO_2$, *sym*-$C_6H_3(NO_2)_3$, or *picric acid*, takes place at elevated temps. in a sealed tube. The mechanism of the formation of $PhNO_2$ or *sym*-$C_6H_3(NO_2)_3$ from C_6H_6 and monomer NO_2 is:

Lab. Org. Chem.
Mil. acad. im. K. Ye. Voroshilov



Paul W. Howerton

Note on their paper: "The reaction of chloral with phenyl thiocyanate." Theodor Wagner-Jauregg, Hermann Vonderbank, and Herbert Witzel. *Chem. Ber.* 82, 248(1949); cf. *C.A.* 43, 4657f. —The constitution of the reaction product of CCl_3CHO and PhSCN is corrected to $(PhS.CO.NH)_2CHCCl_3$, corresponding to that of $[(Ph.CO.NH)_2CHCCl_3]$, obtained from I and PhCN.

F. K. B.

TITOV, A. I.

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Theory of nitration of saturated hydrocarbons and their derivatives. II. Mechanism of formation of *gem*-dinitro derivatives. A. I. Titov (Voroshilov Military Acad., Moscow). *J. Gen. Chem.* (U.S.S.R.) **18**, 465-72(1948)(in Russian); cf. *C.A.* **41**, 6526*b*.—Radicals which originally arise in the interaction of a nitrating reagent with paraffins or alkyl side-chains of aromatic hydrocarbons, react preferentially with NO and monomeric NO_2, giving rise to the primary reaction products: nitroso compds., alkyl nitrites, and nitro derivs. The final transformation products of primary and secondary α-nitrosoalkylbenzenes under conditions of nitration are *gem*-dinitro derivs. In the absence of NO no *gem*-dinitro compds. are formed. N_2O_4 (25 ml.) and 20 g. dry $CuSO_4$ were mixed with various amts. of PhMe and allowed to stand 30 days at 20°; the isolation as described before (*C.A.* **35**, 4350^9) gave the following results: 1000 ml. MePh gave 21.5 g. $PhCH(NO_2)_2$ and 5 g. $PhCH_2NO_2$; 250 ml. MePh gave 7.3 and 3.0 g., resp.; 50 ml. MePh gave 2.0 and 2.1 g., resp. Parallel expts. in which gaseous N_2O_4 was passed into the mixts. at 40°, 70°, and 95°, gave, at 40°, 18.4 g. di-NO_2 deriv., 7.2 g. mono-NO_2 deriv. in 40 hrs.; at 70° (10 hrs.), 6.8 g. di-NO_2 deriv. and 15.9 g. mono-NO_2 deriv.; at 95°, 1.4 g. di-NO_2 deriv. and 13.4 g. mono-NO_2 deriv. (1 hr.). $PhCH_2NO_2$ is unreactive to NO_2 on heating in AcOH; HNO_3 under the same conditions gives much BzOH and no $PhCH(NO_2)_2$. Parallel expts. in which 18.4 g. NO_2 and 2 l. MePh were treated (*a*) as described in the earlier paper, (*b*) preliminarily satd. with NO, and (*c*) continuously treated with O with periodic shaking, gave the following results: (*a*) turned green from N_2O_3, (*b*) had the same color from the start, and (*c*) retained the brown color of NO_2; after 6 days at room temp. there were obtained from: (*a*) 3.7 g. $PhCH_2NO_2$, 14.8 g. $PhCH(NO_2)_2$, 0.1 g. BzOH, and 10.8 g. residual oil; (*b*) 2.4, 11.7, 0.1, 8.7; (*c*) 1.8, , 0.1, 20.4. Extn. of (*c*) with $NaHCO_3$ gave about 0.1 g. 2,4,6-trinitro-*m*-cresol, m. 105°. The residual oil in all cases was benzyl alc. and its derivs. The best prepn. of $PhCH(NO_2)_2$ was: 1500 ml. MePh, 10 g. NO_2, and 30 g. dry $CuSO_4$ were satd with NO until 1 g. was absorbed and let stand at 25-30 with 3 addns. of 10 g. NO_2 every 4 days, total time 15 days. After washing with H_2O, 20% $KHCO_3$, and 50% K_2CO_3, there was obtained 25 g. K salt of $PhC(NO_2)_2$, which was filtered and washed; the product remaining in soln. was treated with Br and isolated as the Br deriv., which on treatment with alc. KOH or Na_2SO_3 in the presence of KI gave the original $PhCH(NO_2)_2$; acidification of the mother liquor after sepn. of the Br deriv. gave 10.6% BzOH, while stirring the soln. with 100 ml. 10% NaOH 4 hrs. with addn. of 20 g. Et_2NH yielded 10.3% $PhCH_2NO_2$ (isolated as the di-Br deriv. after bromination); there was obtained a total of 46.7% $PhCH(NO_2)_2$, and 32.4% of the above-described residual oil. *If* the temp. is raised to 50° the reaction is complete in less than 24 hrs. but the yield is lower. As mentioned in the earlier paper, the 1st reaction is $RH + NO_2 \rightarrow$ $R^{\cdot} + HNO_2$; the radicals can undergo the following reactions: $R^{\cdot} + NO \rightarrow RNO$; $R^{\cdot} + NO_2 \rightarrow RNO_2$; $R^{\cdot} + NO_2 \rightarrow RONO$, which are the primary products of the completed reaction step. The nitroso derivs. are responsible for formation of the *gem*-dinitro compds., probably by conversion to oximes and rapid reaction of the latter with N_2O_4, which proceeds very rapidly even in very dil. solns. at temps. as low as 0°, or lower. Thus,

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the mononitro compd. is not an intermediate in the formation of the *gem* derivs. This is further confirmed by the nonformation of the *gem*-dinitro deriv. in the expt. in which NO was excluded. The nitroso derivs., under nitration conditions, are capable of giving a variety of products (*gem*-dinitro, *gem*-trinitro, ψ-dinitroles, nitrolic acids, nitrile oxides, nitrimines, nitriles, aldehydes, ketones, N-alkylamides, lactams) formed through the oxime intermediate, and mononitro derivs. directly by the action of NO_2. **III. General theory of the formation of mononitro derivatives. The nitration of toluene to phenylnitromethane.** *Ibid.* 473-8(in Russian). The formation of mononitro derivs. on a paraffin chain proceeds through: $RH + NO_2 \rightarrow R^{\cdot} + HNO_2$; $R^{\cdot} + NO_2 \rightarrow RNO_2$. The conversion of pseudo acids into salts of aci forms is accelerated by the addn. of amine to the mixt. in the course of isolation of the primary and secondary mono-NO_2 derivs. The expts. were conducted by the technique described earlier (see preceding abstr.), the isolation of $PhCH_2NO_2$ being facilitated by the addn. of a few g. Et_2NH, which rapidly forms the salt of the aci form, which on entering the alk. layer reverted to the Na salt and the amine was regenerated; this made it possible to complete the extn. even with large vols. of PhMe in 1 hr., instead of 20-30 hrs. The distn. of $PhCH_2NO_2$ was shown to depend on unknown factors for success, as occasional batches decompd. The pure substance was best isolated as follows: the alk. ext. was evapd. on a steam bath and the resulting Na salt of the aci form was washed with 20% NaCl; this, with working up the mother liquor, gave 80% recovery; pure *$PhCH_2NO_2$* is yellow, b_{16} 105-7°, n_D^{20} 1.5341. After extn. of the $PhCH_2NO_2$ the residual soln. was freed of excess MePh *in vacuo*; the residual matter is referred to as residue in the following expts. Nitration with NO_2 was shown to give higher yields of $PhCH_2NO_2$ with higher temp., max. at 100°; bubbling O into a mixt. of 1750 ml. MePh and 20 g. dry $CuSO_4$ on a steam bath with addn. of 43 g. NO_2 over 4 hrs. and subsequent heating 30 min. gave 56.1 g. $PhCH_2NO_2$ (3.2 g. without O bubbling), 3.8 g. $PhCH(NO_2)_2$ (2.7 g. without O), 10.6 g. BzOH (4.3 g. without O), 35.8 g. residue (28.2 g. without O). Use of 175 ml. MePh at 100° (other conditions as above) with O bubbling gave in 2 hrs. 15.3 g. $PhCH_2NO_2$, 1.5 g. $PhCH(NO_2)_2$, 2.5 g. BzH, 7.5 g. BzOH, and 4.4 g. residue; 1750 ml. MePh gave 41.7, 4.7, 2.4, 3.6, and 32.3 g., resp. To 8 g. HNO_3 (d. 1.38), 40 g. 80% H_2SO_4, 0.5 g. trioxymethylene, and PhMe on a steam bath was added over 3.5 hrs. 50 ml. HNO_3 (d. 1.5) with O being bubbled into the mixt. The $PhCH_2NO_2$ was extd. with 200 ml. 20% NaOH with addn. of 5-10 ml. Et_2NH, and $PhCH(NO_2)_2$ was extd. along with BzOH by means of 200 ml. 20% $NaHCO_3$. The following results were obtained on variation of the conditions used: (*a*) 200 ml. MePh, without O, gave 44.6% $PhCH_2NO_2$, 2.6% $PhCH(NO_2)_2$, 33.9% BzOH, and 18.9% residue; (*b*) 500 ml. MePh, without O, 50.1, 3.5, 23.5, and 22.9%, resp.; (*c*) 1750 ml. MePh, without O, 54.6, 3.8, 10.1, and 31.5%, resp.; (*d*) 500 ml. MePh, 8 l. O used, 48.7, 2.8, 27.5, and 21%, resp.; (*e*) 1750 ml. MePh, 8 l. O used, 55.2, 3.7, 11.9, and 29.2%, resp. Conversion to the mononitro compd. is seen to be rather const. and is lowered with smaller amts. of MePh, probably because of more intense decompn. of the nitro compds. in the acid layer. Successful side-chain nitration by HNO_3 is conditioned by initial presence of N oxides, support of concn. of NO_2 throughout the course of reaction, repression of nuclear nitration, and maintenance of conditions previously elaborated for nitration by N oxides. G. M. Kosolapoff

TITOV, A. I.

PA 69T11

USSR/Chemistry - Toluene
Chemistry - Nitration

Mar 1948

"Theory of Nitrating Saturated Hydrocarbons and Their Derivatives. III. General Theory of the Formation of Mononitro Derivatives. Nitrating Toluene With a Phenyl-Nitromethane Catalyst," A. I. Titov, Lab Org Chem, Mil Acad imeni K. E. Voroshilov, Moscow, 6 pp

"Zhur Obshch Khim" Vol XVIII (LXXX), No 3

Due to fact that mechanism of reaction was represented incorrectly author was unable to give a good description of nitrating of paraffin chains to obtain mononitro compounds. Tests conducted to deter-

[redacted] 69T11

USSR/Chemistry - Toluene (Contd) Mar 1948

mine true course of nitrating process. Submits a rapid method for changing pseudoacids into aciform salts with aid of ammonium additions, and stresses value for production of primary and secondary mononitro compounds. Submitted 8 Feb 1945.

[redacted] 69T11

CA TITOV, A.I.

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Theory of nitration of saturated hydrocarbons and their derivatives. IV. Mechanism of oxidation of the paraffin chain by nitrogen oxides and nitric acid. A. I. Titov. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 18, 534–43(1948); cf. *C.A.* 42, 7261g.—The main primary oxidation product in the action of HNO_3 or N oxides on a paraffin chain is the corresponding alkyl nitrite, which forms by the reaction $RH + NO_2\cdot \rightarrow R\cdot + NO_2 \rightarrow RONO$. The formation of alcs. and their derivs. thus can also arise from the radical interaction with N_2O_4, N_2O_3, HNO_3, and with O. In liquid-phase nitration, equil. is established between the alc., ether, and the N esters and the formation of further products depends on transformations of alcs. and nitrites primarily; the nitroso compds. participate to a slight extent, and nitro derivs. only to an insignificant extent. The action of NO_2 in the activation of the oxidation of paraffins by O is that of radical initiator, starting the chain reaction, on the one hand, and of chain terminator, on the other hand. The expts. on the nitration of PhMe, which are the basis for this work, are reported in Part III. Working up of the reaction mixts. with isolation of the products by reaction with Et_2NH, which reacts readily with $PhCH_2ONO$ to give Et_2NNO and with $PhCH_2ONO_2$ to give Et_2NCH_2Ph, the following results were obtained: nitrations in which the NO_2 reaction predominated (NO_2 nitration at 90-100°, using O) gave 34% residual oil, which gave: 52.5% $PhCH_2NO_2$, 2.7% dinitro deriv., 11.2% BzOH, 1.8% $PhCH_2ONO_2$, 6.4% PhONO, 7.1% $PhCH_2OH$, 2.4% BzH, 1% each of 2- and 4-nitrotoluenes; loss 10%. Use of NO_2 at room temp. with diln. by PhMe to 1-3% and using O to remove residual NO_2 gave mainly $PhCH_2OH$ (in 1 expt. up to 30% was isolated) and its derivs.; a summary of these reactions is: 11.2% $PhCH_2NO_2$, 43.2% $PhCH_2OH$ and its esters, 14.2% BzH, 4.4% BzOH, 13.6% 2- and 4-nitrotoluenes, 2.2% nitrocresols, 11.2% residue; the high yield of nitroaromatics is caused by increased HNO_3 concn. through the binding of NO by O and shifting of the NO_2-H_2O equil. to the right. In expts. with a high order of diln. either without O or with satn. by NO, the reaction was slow and mainly $PhCH_2NO_2$ resulted (up to 50%); the residual oil (35%) consisted mainly of $PhCH_2OH$ and its esters, with traces of nitroaryl derivs. Use of a small excess of PhMe (50 ml. PhMe, 40 g. NO_2, 15 g. $CuSO_4$, let stand 30 days) gave 7.2% $PhCH_2NO_2$, 9% dinitro deriv., 0.2% trinitro deriv., 15.5% BzOH, 10.3% $PhCH_2OH$ and its esters, and 36% nitrotoluenes, with 15.5% other products. Nitration by HNO_3 (d. 1.5; cf. Part III), with or without the use of O, gave comparable results. The isolation of the products was conducted as follows: after stirring the reaction mixt. with $KHCO_3$ to ext. BzOH, $PhCH_2NO_2$ and nitrocresols, the residual oil was concd. *in vacuo* at 50°, treated with excess Et_2NH and 50% KOH, warmed to 100°, dild., and sepd.; Et_2NCH_2Ph was extd. with 10% HCl-10% NaCl, followed by alkali and either distn. or isolation as the picrate. The residue after amine removal was shaken 3 hrs. with $NaHSO_3$ to sep. BzH, and the org. layer on distn. gave $PhCH_2OH$. For separate identification of

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$PhCH_2ONO$, the residue, after amine removal, was rapidly washed with concd. HCl in the cold; the oxonium deriv. of the alc. on standing gave $PhCH_2Cl$; the acid ext. treated with alkali gave the Et_2NNO, isolated by distn. $PhCH_2$-ONO decomp. on standing and in 30 days yields mainly BzH (60%) and BzOH; on warming much NO forms. On the other hand $PhCH_2ONO_2$ is stable to storage or heating. V. **Nitration of diphenylmethane by nitrogen dioxide.** *Ibid.* 1312-18.—As shown earlier, the 1st step of the nitration of a paraffin chain by NO_2 or by HNO_3 is the action of NO_2 monomer, yielding the radical R · of the paraffin. The more reactive Ph_2CH_2 confirms this view (rough calcn. shows a lowering of energy of activation in comparison with paraffins by 20 kcal.). The reaction with NO_2 is complete on 2 days' standing and the products include Ph_2CHNO_2, $Ph_2C(NO_2)_2$, Ph_2CHOH and its derivs., and Ph_2CO. Ph_2CH_2 (8.4 g.) in 100 ml. CCl_4 satd. with NO, treated with 9.2 g. N_2O_4 and 3 g. $Ca(NO_3)_2$ and let stand 5 days, then dild. with water, washed with Na_2CO_3, and treated with 10 ml. 28% KOH-15 ml. Et_2NH (for the detection of benzhydryl nitrate and sepn. of Ph_2CHNO_2) gave 22.4% Ph_2CHNO_2 (as K salt), 27.9% *$Ph_2C(NO_2)_2$*, m. 79-80° (from EtOH), 0.1 g. *Et_2NCHPh_2 picrate*, m. 100-1° [from 50% EtOH; authentic sample made from Ph_2CHOH (9 g.) by warming 2 hrs. with 40 ml. 48% HBr and treating the product with Et_2NH (25 ml.); the *amine*, m. 60-1° (from MeOH)], and traces of Ph_2CO and Ph_2CH_2. Ph_2CH_2 (16.8 g.) in 200 ml. CCl_4 with 10 g. $CuSO_4$, treated in 3 hrs. at 70-75° with 20 g. NO_2 in 50 ml. CCl_4, with bubbling of 2 l. O, gave 13.5 g. residual NO_2, 53.4% Ph_2CHNO_2 [treatment of K salt of the aci form with Br at 0° in the presence of K_2CO_3 readily gave *Ph_2CBrNO_2*, m. 44-4.5° (from MeOH), while the residue after washing with acid and concn. was let stand 24 hrs. with 48% HBr (and a little $NaHSO_3$), then washed with $NaHCO_3$ and treated with Et_2NH at 50°, giving 0.96 g. Et_2NCHPh_2, m. 60-1°, and 7.8 g. Ph_2CO. G. M. K.

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CA TITOV, A-I.

Mechanism of the nitration of aromatic compounds by mixtures of sulfuric and nitric acids and by other energetically nitrating agents. A. I. Titov. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 18, [illegible] (1948); cf. C. A. 42, 515, 3340.—Theoretical. The nitration of aromatic compds. by HNO$_3$ mixts. proceeds by way of addn. of an active nitronium cation, [NO$_2$]$^+$, in equil. concn. with the nitrating acid, to the aromatic nucleus to form a transition complex

The activating influence of substances such as H$_2$SO$_4$, AlCl$_3$, BF$_3$, TiCl$_4$, and of other strongly protonic and aprotonic acids, is due not to an activation of the aromatic compd. but to the production of HNO$_3$ complexes which readily break up to yield the nitronium cation. F. H. R.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

TITOV, A. I.

Titov, A. I., Laptev, N. G., "Oxide nitration of aromatic nitrogen compounds and arylhydroxy-lamines." (p. 741)

SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1948, Volume 18, No. 4

TITOV, A. I.

A. I. Titov, The theory of nitration of saturated hydrocarbons and their derivatives. V. Nitration of diphenylmethane with nitrogen dioxide. P. 1312.

The main product of nitration depending on the conditions of the reaction is diphenylnitromethane or diphenyldinitromethane.

Lab. of Organic Chemistry of the
Voroshilov Military Academy
Moscow
May 17, 1946.

SO: Journal of General Chemistry (USSR) 18, (80) No. 7 (1948).

TITOV, A. I.

PA 19/49T29

USSR/Chemistry - Angelic Acid Aug 48
Chemistry - Tiglic Acid

"Structures of Angelic Acid and Tiglic Acid," A. I. Titov, Lab of Org Chem, Mil Acad imeni K. Ye. Voroshilov, Moscow, 2 3/4 pp

"Zhur Obshch Khimii" Vol XVIII (LXXX), No 8

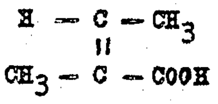
Examines relative energetic stability of cis- and trans- forms. Shows that principle of lability of cis- forms is of limited application. The rules of effect of steric factors on establishment of resonance may be used to determine configuration of α and β

[redacted] 19/49T29

USSR/Chemistry - Angelic Acid (Contd) Aug 48

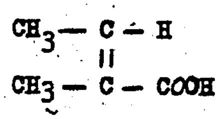
unsaturated acids from their dissociation constants. Above conclusions and application of principle of correspondence of properties and configurations of ethylene and aromatic compounds lead to acceptance of configuration (I) for angelic acid and configuration (II) for tiglic acid:

(I)



$$\begin{array}{c} H - C - CH_3 \\ \| \\ CH_3 - C - COOH \end{array}$$

(II)



$$\begin{array}{c} CH_3 - C - H \\ \| \\ CH_3 - C - COOH \end{array}$$

Submitted 7 Apr 47.

[redacted] 19/49T29

TITOV, A. I.

27630. N I Trovanie, 2, 7 - Dimetiloktana dvuokis'yu azota. Zhurnal obshchey khimii, 1949, VYP. 8, S. 1461 - 63. Bibliogr: S. 1463.

SO: Knizhaya Letopis, Vol. 1, 1955

27629. TITOV, A. I. Nitrovanie azotnoy kislotoy n. - geptaha 12, 7 - dimetiloktana. Zhurnal obshchey khimii, 1949, vyp. 8, s. 1464 - 66. -- bibliogr: s. 1466.

SO: Knizhaya Letopis, Vol. 1, 1955

TITOV, A. I.

27631. TITOV, A. I. Nitrovanie n. - pentana dvuokis'yu azota v gazovoy faze. zhurnal obshchey khimii 1949, vyp. 8, s. 1472 - 74. bibliogr: s. 1474

SO: Knizhaya Letopis, Vol. 1, 1955

Titov A. I

38337 TITOV, A. I. AND BARKOV, B. A.

Anatomicheskiye obosnovaniya poyasnichnykh boley posle kolopeksii po sposoby kyummelya. Sbornik trudov (Arkhang. gos. med. in-t), vyp. 9, 1949, s. 46-50. - Bibliogr: 12 nazv.

TITOV, A. I.

USSR/Chemistry - Nitration
Chemistry - Hydrocarbons

Feb 49

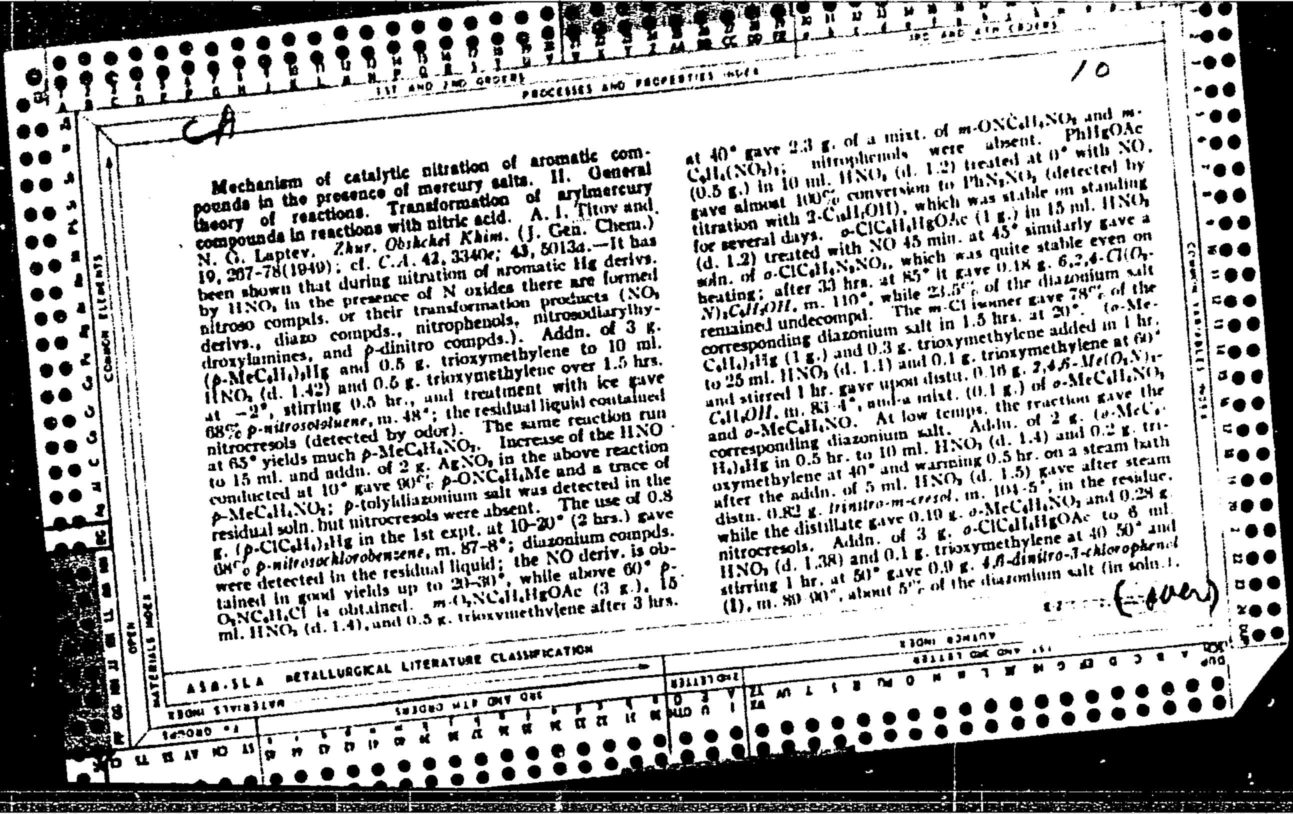
"Theory of Nitrating Saturated Hydrocarbons and Their Derivatives," A. I. Titov, 9 pp

"Zhur Obshch Khim" Vol XIX, No 2

Studies mechanism of activating action of methyl groups on reaction of side chains of polymethylbenzenes with a nitrogen peroxide monomer. Investigates reaction of nitrogen peroxide with m-xylene under conditions favorable for formation of . m-tolylnitromethane and m-tolylinitromethane. Gives easy method to obtain m-tolylnitromethane by nitration of m-xylene with concentrated nitric acid. Submitted 7 Apr 47.

[redacted]

46/49T23



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Mechanism of catalytic nitration of aromatic compounds in the presence of mercury salts. II. General theory of reactions. Transformation of arylmercury compounds in reactions with nitric acid. A. I. Titov and N. G. Laptev. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 19, 267-78(1949); cf. *C.A.* 42, 3340e; 43, 5013a.—It has been shown that during nitration of aromatic Hg derivs. by HNO_3 in the presence of N oxides there are formed nitroso compds. or their transformation products (NO_2 derivs., diazo compds., nitrophenols, nitrosodiarylhydroxylamines, and *p*-dinitro compds.). Addn. of 3 g. (*p*-$MeC_6H_4)_2Hg$ and 0.5 g. trioxymethylene to 10 ml. HNO_3 (d. 1.42) and 0.5 g. trioxymethylene over 1.5 hrs. at −2°, stirring 0.5 hr., and treatment with ice gave 68% *p-nitrosotoluene*, m. 48°; the residual liquid contained nitrocresols (detected by odor). The same reaction run at 65° yields much *p*-$MeC_6H_4NO_2$. Increase of the HNO to 15 ml. and addn. of 2 g. $AgNO_3$ in the above reaction conducted at 10° gave 90% *p*-ONC_6H_4Me and a trace of *p*-$MeC_6H_4NO_2$; *p*-tolyldiazonium salt was detected in the residual soln. but nitrocresols were absent. The use of 0.8 g. (*p*-$ClC_6H_4)_2Hg$ in the 1st expt. at 10-20° (2 hrs.) gave 98% *p-nitrosochlorobenzene*, m. 87-8°; diazonium compds. were detected in the residual liquid; the NO deriv. is obtained in good yields up to 20-30°, while above 60° *p*-$O_2NC_6H_4Cl$ is obtained. *m*-$O_2NC_6H_4HgOAc$ (3 g.), 15 ml. HNO_3 (d. 1.4), and 0.5 g. trioxymethylene after 3 hrs. at 40° gave 2.3 g. of a mixt. of *m*-$ONC_6H_4NO_2$ and *m*-$C_6H_4(NO_2)_2$; nitrophenols were absent. PhHgOAc (0.5 g.) in 10 ml. HNO_3 (d. 1.2) treated at 0° with NO, gave almost 100% conversion to PhN_2NO_3 (detected by titration with 2-$C_{10}H_7OH$), which was stable on standing for several days. *o*-ClC_6H_4HgOAc (1 g.) in 15 ml. HNO_3 (d. 1.2) treated with NO 45 min. at 45° similarly gave a soln. of *o*-$ClC_6H_4N_2NO_3$, which was quite stable even on heating; after 33 hrs. at 85° it gave 0.18 g. *6,2,4-Cl(O₂N)₂C₆H₂OH*, m. 110°, while 23.5% of the diazonium salt remained undecompd. The *m*-Cl isomer gave 78% of the corresponding diazonium salt in 1.5 hrs. at 20°. (*o*-$MeC_6H_4)_2Hg$ (1 g.) and 0.3 g. trioxymethylene added in 1 hr. to 25 ml. HNO_3 (d. 1.1) and 0.1 g. trioxymethylene at 60° and stirred 1 hr. gave upon distn. 0.16 g. *2,4,6-Me(O₂N)₂C₆H₂OH*, m. 83-4°, and a mixt. (0.1 g.) of *o*-$MeC_6H_4NO_2$ and *o*-MeC_6H_4NO. At low temps. the fraction gave the corresponding diazonium salt. Addn. of 2 g. (*o*-$MeC_6H_4)_2Hg$ in 0.5 hr. to 10 ml. HNO_3 (d. 1.4) and 0.2 g. trioxymethylene at 40° and warming 0.5 hr. on a steam bath after the addn. of 5 ml. HNO_3 (d. 1.5) gave after steam distn. 0.82 g. *trinitro-m-cresol*, m. 104-5°, in the residue, while the distillate gave 0.10 g. *o*-$MeC_6H_4NO_2$ and 0.28 g. nitrocresols. Addn. of 3 g. *o*-ClC_6H_4HgOAc to 8 ml. HNO_3 (d. 1.38) and 0.1 g. trioxymethylene at 40-50° and stirring 1 hr. at 50° gave 0.9 g. *4,6-dinitro-3-chlorophenol* (I), m. 80-90°, about 5% of the diazonium salt (in soln.).

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TITOV, A. I.
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Mechanism of the nitration of aromatic compounds by nitric acid. II. Relative electron potentials in aromatic compounds. Mechanism of the nitration of nitrophenols. A. I. Titov. *Zhur. Obshchei Khim.* 19, 517-26(1949); *J. Gen. Chem. U.S.S.R.* 19, 467-75(1949)(Engl. translation); cf. *C.A.* 43, 5012*h*.--Nitration by HNO_3 via intermediate reaction with NO_2 is possible only for aromatic compds. with a high relative electron potential (~0.1 v.).

As the introduction of a NO_2 group lowers this potential, no reaction is obtained from $1\text{-}C_{10}H_7NO_2$ or $p\text{-}O_2NC_6H_4OEt$ and HNO_3 (d. 1.2-1.4) contg. N oxides. The apparent contradiction that *o*-, *m*-, and $p\text{-}O_2NC_6H_4OH$ and $2,4\text{-}(O_2N)_2C_6H_3OH$ are easily nitrated by HNO_3 under similar conditions if NO_2 is present is explained by an initial reaction step occurring between NO_2 and the nucleophilic anion $(O_2NC_6H_4O)^-$ which has a higher relative electron potential than $O_2NC_6H_4OH$. Expts. showed that (a) nitrophenolates of alkali metals react rapidly with NO_2 to give di- and trinitro derivs., while free nitrophenols react sluggishly or not at all; (b) in $MeNO_2$, an ionizing solvent, nitration of $o\text{-}O_2NC_6H_4OH$ by NO_2 proceeds rapidly, but in CCl_4, a nonionizing solvent, the reaction goes only 50%. Formation of picric acid from $2,4\text{-}(O_2N)_2C_6H_3OH$ in $MeNO_2$ is nearly quant., while in CCl_4 the yield is below 10%. On the basis of electronic structures, a parallel is drawn between nitration and the conversion of hydroquinones to quinones, both being considered oxidation processes. $p\text{-}O_2NC_6H_4OEt$ or $1\text{-}C_{10}H_7NO_2$ (1 g.) treated with 5 ml. HNO_3 (d. 1.37) did not react when either $N_2H_4.H_2SO_4$ (0.05 g., to remove traces of N oxides) or trioxymethylene (0.05 g., to insure the presence of NO_2) was added. $p\text{-}O_2NC_6H_4OH$ (1 g.) with 5 ml. HNO_3 (d. 1.36) and 0.05 g. trioxymethylene gave 0.73 g. $2,4\text{-}(O_2N)_2C_6H_3OH$; addn. of 0.3 g. $N_2H_4.H_2SO_4$ to another sample gave no reaction. Similar results were obtained from the *m*- and *o*-isomers. To 3 samples of 1 g. $2,4\text{-}(O_2N)_2C_6H_3OH$ and 40 ml. HNO_3 (d. 1.2) was added 0.05 g. trioxymethylene, 0.5 g. $(H_2N)_2CO.HNO_3$, and 2 g. NH_4NO_3; in the 1st case was obtained 0.88 g. picric acid, in the 2nd case 0.92 g. starting material, and in the 3rd case, due to incomplete removal of N oxides, some nitration occurred. A mixt. (0.43 g.) of dinitrophenols, mainly $2,4\text{-}(O_2N)_2C_6H_3OH$, was obtained from 0.5 g. anhyd. $o\text{-}O_2NC_6H_4ONa$ in 20 ml. dry CCl_4 and 1 ml. liquid NO_2. Similarly, 0.31 g. picric acid was formed from 0.5 g. $2,4\text{-}(O_2N)_2C_6H_3ONa$ in 10 ml. dry $MeNO_2$ and 1 ml. NO_2; no reaction occurred with the free phenols.

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3RD AND 4TH ORDER

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Theory of nitration of saturated hydrocarbons and their derivatives. VI. Nitration in the side chain of *o*- and *m*-xylenes and mesitylene. A. I. Titov. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 19, 259-60(1949); cf. *C.A.* 43, 4217*a*.—The activation by Me groups of side-chain reaction with NO_2 monomer was examd. The reaction with *m*-xylene yields *m*-$MeC_6H_4CH(NO_2)_2$ (I) and *m*-$MeC_6H_4CH_2NO_2$ (II), while *m*-xylyl nitrate, *m*-MeC_6H_4CHO, *m*-toluic acid, and *m*-$MeC_6H_4C(NO_2)_3$ (III) were isolated among the products. *o*-Xylene and mesitylene react at room temp. and yield *gem*-dinitro derivs., as well as acids and aldehydes. *m*-Xylene (600 ml.), 20 g. $CuSO_4$, and 10 ml. NO_2 on standing 25 days with addn. of 10 ml. NO_2 every 8 days and treatment according to the previously given scheme (T., *C.A.* 42, 7262*g*) gave 25.8 g. *K salt of* I after stirring the hydrocarbon layer with 30% $KHCO_3$ and 60% K_2CO_3; the bicarbonate soln. with Br gave 8.6 g. *m-tolylbromodinitromethane*, which with alc. KOH gave 7.1 g. *K deriv. of ω-gem-dinitroxylene*. Acidification of the mother liquor yielded 11.8 g. *3-$MeC_6H_4CO_2H$*, m. 108-10°. Treatment of the residual solns. with 20% KOH and Et_2NH gave after 24 hrs. standing 1.6 g. K nitroxylenol while bromination of the soln. gave 6.1 g. *m*-$MeC_6H_4CH(NO_2)Br$. Sepn. of the remaining products gave the total compn. of the products: III 0.3, I 33.4, II 6.2, *m*-xylyl nitrate 4.9, *m*-MeC_6H_4CHO 4.1, 3-$MeC_6H_4CO_2H$ 20.4, residuals 30.7%. Passage of 38 g. NO_2 and 0.5 l. O_2 into 200 ml. *m*-xylene and 20 g. $CuSO_4$ in 3 hrs. gave: III 0.7, I 6.9, II 54.7, *m*-xylyl nitrate 1.6, *m*-MeC_6H_4CHO 4.1, *m*-$MeC_6H_4CO_2H$ 24.8, and residual oil 6.9%. II may be steam-distd. without decompn. upon addn. of $OC(NH_2)_2$ and it is distillable almost without decompn., b_{18} 112-14°, n_D^{20} 1.5300. Addn. over 2 hrs. of 50 ml. HNO_3 (d. 1.5) to 100 ml. *m*-xylene and 10 ml. HNO_3 (d. 1.4) in the presence of 1 g. trioxymethylene on a steam bath and stirring 0.5 hr. gave: I 5.6, II 29.1, *m*-MeC_6H_4CHO 1.2, *m*-$MeC_6H_4CO_2H$ 12.8, and residual oil 8.7 g. *m-Xylyldiethylamine*, prepd. from *m*-xylyl bromide, b_{756} 229°, d_4^{20} 0.8966, n_D^{20} 1.5072; *picrate*, m. 128° (from EtOH). Treatment of the K deriv. of I with dil. HCl gave the *free* I, prisms, m. 54.5° (from EtOH or petr. ether); it is a monobasic acid and the K deriv. is readily obtained by treatment with carbonates or bicarbonates; on heating 2 hrs. with 90% H_2SO_4 to 100° it yields *m*-toluic acid; addn. of Br to the alk. soln. of I immediately yields the oily Br deriv. which gives the K deriv. with alc. KOH. Allowing 100 ml. *o*-xylene, 10 g. $CuSO_4$, and 5 ml. NO_2 to stand 25 days at 15-20° with addns. of 5 ml. NO_2 every 7 days gave, after aq. washing and treatment with 10% $KHCO_3$, the *K salt of o-tolyldinitromethane*, yellow needles from the concd. bicarbonate

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est.; addn. of dil. HCl gave a total of 9.5 g. *ω,ω'-dinitro-o-xylene*, yellow prisms, m. 42° (from petr. ether); treatment of the residual solns. with 10% KOH and Et_2NH, followed by bromination, gave 2.6 g. of presumably o-tolylnitrodibromomethane as an oily liquid; heating the residue with Et_2NH 3 hrs. to 100° gave 1.1 g. of presumably o-xylyldiethylamine; distn. of the residual oil gave a small amt. of *o-tolualdehyde*, identified as the *semicarbazone*, m. 216-17°. Mesitylene reacts vigorously with NO_2 even at room temp. After allowing 150 ml. mesitylene and 10 ml. NO_2 to stand overnight there were obtained: 0.6 g. *3,5-*$Me_2C_6H_3CHO$ (identified as the semicarbazone), 1.1 g. *3,5-*$Me_2C_6H_3CH(NO_2)_2$ (isolated as the *K deriv.*; free substance, prisms, m. 81-2°), 1.0 g. carboxylic acids, and 1.6 g. ar-nitromesitylene. Reaction of HNO_3 with mesitylene in AcOH leads to nitration and oxidation of the side chains only in the presence of NO_2.

G. M. Kosolapoff

TITOV, A. I.

Nitration of 2,7-dimethyloctane by nitrogen dioxide. A. I. Titov. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 19, 1461-3(1949); cf. *C.A.* 41, 6526b. Nitration of *2,7-dimethyloctane* (I) by NO_2 in liquid phase proceeds according to the procedure outlined for alkylated benzenes. The radical formation in the initial step is much more rapid than in the vapor-phase nitration and the over-all operation is, hence, more rapid. Addn. of 200 g. iso-AmBr to Na wire in Et_2O gave 70% I, b. 156°. This (150 g.) and 30 g. dry $CuSO_4$ were treated on a water bath over 4 hrs. with 21 g. NO_2 dild. with 15 ml. I, with simultaneous passage of 3 l. O (for app., cf. *C.A.* 42, 7262g). After washing with H_2O, the mixt. was extd. with $KHCO_3$ and K_2CO_3, which extd. 1 g. org. acids. Extn. with 100 ml. 10% NaOH and passage of CO_2 into the ext. gave 10.6 g. nitro derivs., while acidification by AcOH gave 3.1 g. viscous oil, with an addnl. 1 g. obtained on acidification with HCl. Steam distn. of the crude product gave 10.7 g. substantially *1-nitro-2,7-dimethyloctane*, b_{11} 124-9°, n_D^{20} 1.4431. The residual liquid after alk. extns. gave some unreacted I (removed by distn.), and the residual 19 g. oil with 40% $NaHSO_3$ gave 0.8 g. aldehyde, probably *2,7-dimethyloctanal*. The residual org. matter upon distn. gave a series of fractions, b_{11} 90-125°, from which 7.6 g. *2-nitro-2,7-dimethyloctane*, b_{11} 125°, n_D^{20} 1.4371, was isolated. The low-boiling fractions were probably ROH and its esters. Nitration as above at 130-40° with 40 ml. I and 20 ml. N_2O_4 gave 0.8 g. carboxylic acids, 5.7 g. primary and secondary nitro derivs., and 12.2 g. crude *tertiary nitro derivs.*, which on fractionation gave a small amt. of *2,7-dinitro-2,7-dimethyloctane* as a distn. residue (b_{11} above 111°), m. 101°. G. M. Kosolapoff

TiTov, A.I.

Nitration of heptane and 2,7 dimethyloctane with nitric acid. A. I. Titov. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 19, 1461-6(1949); cf. C.A. 42, 7261g.—Paraffins are not nitrated by HNO_3 in absence of NO_2. *2,7-Dimethyloctane* (20 g.), allowed to stand 50 days at 12-15° with 50 ml. HNO_3 (d. 1.42), gave only a trace of carboxylic acids and no NO_2 derivs. if 2 g. urea nitrate was present to suppress NO_2 formation. Addn. of 5 ml. NO_2 to such a reaction mixt. gave 1.6 g. *primary NO_2 deriv.*, 0.8 g. *tertiary NO_2 deriv.*, and 1.5 g. carboxylic acids. NO_2 (5 ml.) without HNO_3 gave 2.5 g. primary NO_2 deriv., 1.4 g. tertiary NO_2 deriv., and 0.3 g. carboxylic acids; the primary deriv. was extd. with the aid of Et_2NH; an aldehyde was detected by $NaHSO_3$ extn. Heating 8 ml. *heptane* with 10 ml. HNO_3 (d. 1.2) with 1 g. NO_2 in a sealed tube 3 hrs. on a steam bath gave 2.52 g. crude nitro derivs. which yielded 1.37 g. *secondary NO_2 deriv.*, b_{10} 100-5°, b. 193-7°, contg. only a trace of primary analog; some 1.06 g. undistillable residue was obtained as well as 0.8 g. crude carboxylic acids. Repetition with substitution of 1 g. $(NH_4)_2SO_4$ for NO_2 gave only traces of reaction. G. M. K.

FA149T24

TITOV, A. I.

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USSR/Chemistry - Nitration
Heptane

"Nitration of n-Heptane With Nitrogen Dioxide in the Gaseous Phase," A. I. Titov, Mil Med Acad imeni K. Ye. Voroshilov, 3 pp

"Zhur Obshch Khim" Vol XIX, No 8

Main product of nitration is secondary nitropentane, which is in accordance with Titov's theory and M. I. Konovalov's principle. Submitted 26 Apr 48.

149T24

Titov, A. I.
CA

Oxidative nitration of 1- and 2-naphthylmercury nitrates. Mechanism of nitration of naphthalene by nitric acid. A. I. Titov and N. G. Laptev. *Doklady Akad. Nauk S.S.S.R.* **66,** 1101-3(1949); cf. C.A. **43,** 6585. 1- and 2-$C_{10}H_7HgNO_3$ under the action of concd. HNO_3 in the presence of N oxides are transformed into 2,4-dinitro-1-naphthol in over 50% yields; nitration of $C_{10}H_8$ by HNO_3, which proceeds via intermediate reaction with NO_2, does not go through a nitroso deriv. Equimolar amts. of 1-$C_{10}H_7HgCl$ and $AgNO_3$ in warm Me_2CO-EtOH give the corresponding nitrate, m. 137-8°. This (2 g.) added at 30-40° in 0.5 hr. to 13 ml. HNO_3 (d. 1.3) with 0.2 g. trioxymethylene, kept 1 hr. at 40-50°, and cooled, gave 0.8 g. crude 2,4-$(O_2N)_2C_{10}H_5OH$ (pure, m. 134-6°), isolated by extn. with 5% NaOH and acidification; the residual soln. gave on steam distn. 6.8% (0.08 g.) 1-$O_2NC_{10}H_7$, m. 53-5°. 2-$C_{10}H_7HgNO_3$, m. 203°, similarly gave 55.1% 2,4-dinitro-1-naphthol and no $O_2NC_{10}H_7$. The following reaction mechanism is proposed (R = $C_{10}H_6$ nucleus): 1-$RHgNO_3$ + (N_2O_4) → 1-RNO + (H^+) → 1-RHNO + (H_2O) → 1,4-R(HNOH)(OH) + (NO_2) → 1,4-R(NO)-OH + (NO_2) → 1,4-$R(NO_2)OH$ + (NO_2) → 1,2,4-$R(NO_2)_2OH$; with the 2-$HgNO_3$ isomer the process is similar and a 1,2-(NHOH)OH intermediate forms. The results indicate that nitration of $C_{10}H_8$ occurs by means of NO_2 monomer, as it takes place readily at 100° in HNO_3 of d. 1.2 at low NO_2 concn. (cf. C.A. **42,** 5450); if the active form were dimeric NO_2, the dinitronaphthol should have been detected; this is not the case, except in minute amts.

G. M. Kosolapoff

USSR/Chemistry - Oxidants, Fuels, Propellants 21 Dec 51

"Mechanism of the Nitration of Paraffins and Cycloparaffins With Nitrogen Pentoxide," A. I. Titov, I. V. Shchitov

"Dok Ak Nauk SSSR" Vol LXXXI, No 6, pp 1085-1088

N_2O_5 reacts with the paraffin chain in an inert solvent at temps below 0° to form alkylnitrates, nitroalkanes, and carboxylic acids. According to the authors' theory, the paraffin loses a hydrogen atom to form a free alkyl group upon the

215T16

action of a suitable agent. This agent, the NO_3 group arising from the equil dissocn $N_2O_5 \rightleftarrows NO_2 + NO_3$, is more active than NO_2. NO_2 has an inhibiting influence on the rate of the reaction. Nitration of n-octane at 0° yielded sec-octane and n-octylnitrate.

Translation W-23128, 20 Jun 52

215T16

TITOV, A.I.

TITOV, A. I.

"Theory of the Nitration of Saturated Hydrocarbons and of Side Chains of Aryl Paraffins," Usp. Khim., 21, No.8, pp 881-913, 1952

Trabslation W-27185, 11 Aug 53

Military Medical Academy im. Voroshilov during 1947-1950

TITOV, A.I.

Mechanism of reaction of nitrogen dioxide with aromatic hydrocarbons.
Zhur. Obshchey Khim. 22, 1329-35 '52.
(CA 47 no.13:6360) MLRA 5:8)

TITOV, A.I.; BARYSHNIKOVA, A.N.

Mechanism of nitration of aromatic compounds with nitric acid. III. Nitration of benzene by dilute nitric acid. Zhur. Obshchey Khim. 22, 1335-8 '52. (MLRA 5:8)
(CA 47 no.13:6361 '53)

TITOV, A. I. and Rusanov, D. Ye.

"The Action of Oxides of Nitrogen and Nitric Acid on Mercury Paraffinic Compounds. Utilization of the Reaction for the Investigation of the Nitration of Paraffins," Dokl. AN SSSR, 82, No.1, pp 65-68, 1952

Translation W-23139, 20 Jun 52

BTR

9411* Mechanism of Nitration and Oxidation of Cyclohexane. (In Russian.) A. I. Titov and M. K. Matveeva. *Doklady Akademii Nauk SSSR*, new ser., v. 83, Mar. 1, 1952, p. 101-104.

TITOV, A.I., SMIRNOV, V.V.

Chemistry, Organic - Synthesis

Effect of complex formation, ionization, and isomerization of organic substances on their chemical activity during nitration. Synthesis of phenyltrinitromethane and its properties. Dokl AN SSSR 83 No. 2 (1952)

Monthly List of Russian Accessions, Library of Cangress, August, 1952. Unclassifed.

TITOV, A.I.

Theory of nitration of saturated hydrocarbons and their derivatives. VII. Processes of diffusion and the role of hermetically sealed reactors in nitration with nitric acid in the liquid phase. A. I. Titov and M. K. Matveeva. *Sbornik Statei Obshchei Khim., Akad. Nauk S.S.S.R.* 1, 241-5(1953); cf. *C.A.* 43, 6584*d*; 47, 2716*b*.—In nitration of paraffins with HNO_3 the closure of the reaction vessels (usually sealing of tubes) is an essential factor in nitration since it assures the preservation of NO_2 and NO in the reaction zone. In liquid phase nitration there occurs a lag of the diffusion processes behind the actual course of the reaction; this causes a slowing down of the reaction proper and manifests itself in alteration of the quant. amts. of products: the relative yield of mono- and *gem*-dinitro derivs. rise, while oxidation products decline. This lag increases with the more reactive hydrocarbons and with elevation of temp., although it depends on the design of the app. and the mechanical conditions. The liquid phase nitration in sealed tubes gives a much better yield of total products if the tubes are placed horizontally rather than vertically; particularly great is the increase of the oxidation products. As the reaction tubes are increased in cross section, the same effect is observed and yield factors of 2 or 3 are not uncommon in reactions with xylene and cyclohexane. Nitration with NO_2 gave similar results. G. M. K.

TITOV, A.I.

Mechanism of oxidation and nitration of cyclohexane by nitric acid and nitrogen oxides. II. Formation of cyclohexyl nitrite and intermediate products in its transformation into adipic acid. A. I. Titov and M. K. Matveeva, *Sbornik Statei Obshchei Khim., Akad. Nauk S.S.S.R.* 1, 240-51; cf. *C.A.* 47, 2715*b*.—In nitration of cyclohexane by 1453 HNO$_3$ or N oxides the initial step is the formation of cyclohexyl radical and HNO$_2$; the radical reacts rapidly with NO$_2$ monomer yielding RNO$_2$ and RONO; as the ratio of N$_2$O$_4$/NO$_2$ increases, the formation of RONO becomes more important; for the cyclohexyl radical also reacts with N$_2$O$_4$ yielding RONO (with NO$_2$) and RONO$_2$ (with NO by-product). RONO hydrolyzes to ROH and HNO$_2$; the ROH is readily oxidized to the ketone and to the acid (adipic), and on the other hand ROH is also esterified and yields cyclohexyl adipate, nitrate, and dicyclohexyl ether. All these substances were identified in the reaction mixts. In a similar nitration of pentane, AmONO was detected. Generally an increase of concn. of NO$_2$ increases the yield of oxidation products, as expected from the above theory. Cyclohexyl nitrite was prepd. by addn. of 62 ml. concd. HCl to 70 g. C$_6$H$_{11}$OH, 90 ml. H$_2$O, and 53 g. NaNO$_2$ at 0°; a 90% yield of product, b$_{24}$ 54°, d$_{20}$ 0.991, d$_4$ 0.982, n^{20}_D 1.4370, was obtained. Heating C$_6$H$_{11}$OH and (CH$_2$)$_4$(CO$_2$H)$_2$ 10 hrs. to 130-40° gave dicyclohexyl adipate, b$_7$ 218-19°, m. 36°, along with oily monocyclohexyl ester. Allowing C$_6$H$_{11}$ONO to stand several days at 20-5° in loosely stoppered flask gave (CH$_2$)$_4$(CO$_2$H)$_2$, C$_6$H$_{11}$ONO, C$_6$H$_{11}$OH, cyclohexanone, dicyclohexyl ether, dicyclohexyl adipate, and monocyclohexyl adipate. When cyclohexane was heated in sealed tubes (horizontal) with NO$_2$ 1 hr. at 100°, the products contained (CH$_2$)$_4$(CO$_2$H)$_2$, monocyclohexyl adipate, C$_6$H$_{11}$ONO, C$_6$H$_{11}$OH, and C$_6$H$_{11}$NO$_2$. Similar reaction with HNO$_3$ (d. 1.3) also gave C$_6$H$_{11}$ONO and (CH$_2$)$_4$(CO$_2$H)$_2$.

G. M. Kosolapoff

Titov, A. I.

USSR.

New reaction for preparation of organoarsenic compounds. I. Synthesis of derivatives of methylenediarsine. A. I. Titov and B. B. Levin. *Sbornik Statei Obshchei Khim.* 2, 1469-72(1953); cf. *C.A.* 42, 528*i*.—Heating 40 g. As_2O_3, 10 g. K_2CO_3, 200 ml. Ac_2O and 50 ml. AcOH 1.3 hrs. at 135–38°, cooling, addn. of 150 ml. AcOH and 40 ml. H_2O, boiling 0.5 hr. and filtering hot, gave a ppt. which was washed with 200 ml. AcOH, the filtrates evapd. *in vacuo*, the residue treated with 200 ml. H_2O and dried gave *methylenediarsine oxide*, 12.3 g., 64% (from AcOH), $CH_2(AsO)_2$ (I), in 2 forms one of which is sol. in C_6H_6, the other insol.; both forms m. 214–20° (decompn.); possibly one is a dimer of the other; both are reduced by aq. NaH_2PO_2 to yellow arseno compd. CH_2As_2. I (3 g.) in 20 ml. concd. HCl heated 0.5 hr. to 60–70° and cooled gave 4.0 g. $CH_2As_2Cl_4$, m. 72–2.5° (from CCl_4), which is attacked by H_2O. Treatment with dry NH_3 in $CHCl_3$ gave $CH_2As_2N_2$, yellow, decomp. 122–4°. I with 48% HBr heated 0.5 hr. to 100° gave on cooling $CH_2As_2Br_4$, m. 87.5° (from CCl_4). Treatment of 5 g. I with 80 ml. H_2O and 18 ml. 30% H_2O_2 and heating to 70° gave on evapn. 100% $CH_2(AsO_3H_2)_2$, m. 184° (decompn.) (from 50% EtOH); in presence of phenolphthalein this titrates as a tribasic acid. The acid is reduced by NaH_2PO_2 to the yellow arseno deriv. cited above. The synthesis is believed to proceed through reaction of unsatd. oppositely charged atoms: As of $As(OAc)_3$, and nucleophilic C of the anion or enolate of Ac_2O. Mechanism of the reaction is discussed in detail, the last stage of the process being $CH_2[As(OAc)_2]_2$. II. Structure of high molecular weight products of reaction. Understanding of Cadet reaction. *Ibid.* 1473–7; cf. Cadet de Gassicourt, *Mem. savants étrangers* 3, 363(1760).—Reaction of s_2O_3

with Ac_2O in the presence of AcOK or other bases yields
polymeric or high mol. wt. As derivs. such [illegible] $(CH_2AsO_3H)_n$.
The reaction mechanism is [illegible] and the forma-
tion of the polymer is [illegible] to [illegible]
CH [illegible] OAc [illegible]
in [illegible] AcO [illegible] AcOH and As [illegible] AcOK,
leads to formation of [illegible]
the acetate then yields [illegible] which with
As_2O_3 yields AsO_2 ion and $OAsCH_2CO_2AsO$, which with
AcO ion yields $OAsCH_2CO_2$ ion and AcOAsO; loss of CO_2
yields $OAsCH_2$ carbanion, which reacts with As_2O_3 and gives
$CH_2(AsO)_2$ and AsO_2 ion. Heating 100 g. As_2O_3, 10 g.
K_2CO_3 and 500 ml. Ac_2O 6.5 hrs. on a steam bath, treatment
of the product with 200 ml. H_2O, refluxing 0.5 hr., filtration
(hot) and cooling gave a little $CH_2(AsO)_2$ from the filtrate.
The ppt. was extd. with H_2O leaving [illegible] solid which
treated with 150 ml. 10% H_2O_2 [illegible] completely
brought into soln. Diln. with MeOH gave a ppt. of poly-
meric $(CH_2AsO_3H)_n$, 20 g., which was purified by reduction
with NaH_2PO_2 to the arseno deriv., which was reoxidized
with H_2O_2 to the arsinic acid polymer, decomp. 182-4°,
partly sol. in hot H_2O. Longer duration of the original
reaction gives more polymer. The polymer also formed on
heating $CH_2As_2O_3$ with $As(OAc)_3$ in the presence of bases,
or on heating with Ac_2O-AcOK. In the presence of As-
$(OAc)_3$, the polymer consists of secondary acids, but with-
out the triacetate the product is a mixture of equal amount of
secondary and tertiary derivs., possibly cycles with CH_2
bridges. Heating As_2O_3 (10 g.), KOAc (30 g.) and 20 ml.
AcOH 5 hrs. at 200° also gave polymer of the arsinic acid.
Heating $CH_2As_2O_3$ with the unoxidized polymer and KOAc
gave homogeneous product, which with $HgCl_2$ gave $(Me_2As)_2O.2HgCl_2$, m. 210-12°. Heating the above mixt. with

As[illegible] also gave this material along [illegible] Me[illegible] 250-5°. III. Syntheses of tetraphenylmethylenediarsine and alkyldiarylarsines. *Ibid.* 1478-82.—Heating 62.8 g. $Ph_2AsOAsPh_2$ with 128 g. KOAc and 50 ml. Ac_2O 6 hrs. at 125°, cooling, adding 50 ml. H_2O, followed by 25% KOH until weakly basic, heating 15 min., cooling and extg. with Et_2O gave on evapn. of the ext. 8 g. $(Ph_2As)_2O$, while the filtrate gave Ph_2MeAs, b_{19} 168-72°. The residue was treated with hot EtOH yielding 13.2% $CH_2(AsPh_2)_2$, m. 97-7.5° (from EtOH); concd. HNO_3 oxidizes this to *Ph_2-AsO_2H*, m. 174°. To PhMgBr from 27.6 g. PhBr was added 5 g. $CH_2As_2Cl_4$ in C_6H_6; after 0.5 hr. reflux the mixture was hydrolyzed conventionally with dil. HCl and the evapd. org. layer was heated with EtOH to 60-70° to dissolve Ph_2, leaving behind 71.4% $CH_2(AsPh_2)_2$, m. 97°. This with excess MeI refluxed 5 hrs. gave 72% *dimethiodide*, m. 172° (from dil. EtOH). Heating $(Ph_2As)_2O$ (70 g.) with 69 g. K_2CO_3 and 250 g. Ac_2O 11 hrs. at 100° followed by neutralization with 25% NaOH, extn. with Et_2O and evapn. gave 15 g. $(Ph_2As)_2O$, while the residual oil gave 65% *Ph_2-$MeAs$*, b_{14} 165-70°; *methiodide*, m. 190°. Heating 40 g. $(Ph_2As)_2O$ with 50 g. KO_2CEt and 10 ml. $(EtCO_2)_2O$ 8 hrs. at 150° gave 53.6% *Ph_2EtAs*, b_{19} 162-5°; *methiodide*, m. 170°. Similarly KO_2CPr and $(PrCO_2)_2O$ gave 50% *Ph_2-$PrAs$*, b_{15} 178-81°. G. M. Kosolapoff

<u>TITOV A. I.</u>; and LEVIN B. B.

New Reaction for the Production of Organic Arsenic Compounds. II. Structure of High Molecular Reaction Products. On the Reaction of Cadet, Page 1473, Sbornik statey po obshchey khimii (Collection of Papers on General Chemistry), Vol II, Moscow-Leningrad, 1953, pages 1680-1686.

TITOV A. I.; and LEVIN B. B.

New Reaction for the Production of Organic Arsenic Compounds. III. Syntheses of Tetraphenyl Methylene Diarsine and Allyldiphenyl Arsines, Page 1475, Sbornik statey po obshchey khimii (Collection of Papers on General Chemistry), Vol II, Moscow-Leningrad, 1953, pages 1680-1686.

TITOV, A. I.

"Mechanism of oxidation and nitration of cyclohexane with nitric acid and nitrogen oxides. Part 1." Titov, A. I., Matveeva, M. K. (p. 238)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1953, Volume No. 23, No. 2.

USSR.

Mechanism of methylation of 2-aminopyridine according to Leuckart and condensation of dimethylaminopyridine with formaldehyde. A. I. Titov and A. N. Baryshnikova. *J. Gen. Chem. U.S.S* [redacted]53)(Engl. translation). —See *C.A* 48, 2704g. H. L. H.

TITOV, A. I.

5

USSR.

Mechanism of nitration and oxidation of cyclohexane. A. I. Titov and M. K. Matveeva. *J. Gen. Chem. U.S.S.R.* 23, 249-53(1953)(Engl. translation).—See *C.A.* 47, 2715b.

H. L. H.

TITOV, A. I.

Chemical Abst.
Vol. 48 No. 5
Mar. 10, 1954
Organic Chemistry

A new method of introduction of fluorine into an aromatic nucleus. A. I. Titov and A. N. Baryshnikova. *Zhur. Obshchei Khim.* 23, 340-7(1953).—Gradual addn. of 8 g. PhNHOH at 0° to 35 ml. abs. HF in a Cu crucible, followed by 2 days at 10°, treatment with K_2CO_3 soln., and steam distn. gave 3.8 g. *p*-$FC_6H_4NH_2$, b_{20} 80°, d_{20} 1.156; *Ac deriv.*, m. 150.5°. The reaction may occur by addn. of F^- ion to $PhNH^+$ ion, resulting from dehydration on the initially formed $PhNHOH_2^+$, followed by prototropic rearrangement to the final product. G. M. Kosolapoff

TITOV, A.I.

USSR.

A new method of introduction of fluorine into an aromatic nucleus. A. I. Titov and A. N. Ba[illegible]. J. Gen. Chem. U.S.S.R. 21, 291 [illegible] (Engl. [illegible]). See C.A. 45, 2623f.

TITOV, A.I. and BARYSHNIKOVA, A.N.

A New Method of Sybthesizing Ortho-Derivatives of Benzioc Acid Trifluoride, Zhurnal Obshchey Khimii, Vol.23, No 6, 1953, pp 966- 971.

I

Mechanism of nitration of unsaturated compounds. A. N. Baryshnikova and A. I. Titov. *Doklady Akad. Nauk S.S.S.R.* 91, 1099-102(1953).—The information on the nitration of olefins is reviewed (14 references). The nitration of olefins by N oxides in the absence of strong acids proceeds through a complex of the olefin with the radical NO_2, which is in equil. with the $O_2NCHRCR_2$ radical; the latter can react in a variety of paths: with NO it forms oximes, with NO_2 it forms dinitro derivs., nitro nitrites, and by elimination of HNO_2, nitroölefins. In reactions of styrene or cyclohexene with NO_2 or dil. HNO_3 in $PhNO_2$ satd. with N oxides, it is possible to detect PhN_2NO_3 (identified by coupling with 2-naphthol); the reaction involves O and addnl. amts. of the olefins. The reaction of NO_2 at low concn. with the olefin (satd. with O) probably proceeds by formation of the radical adduct (see above) which adds O, forming a peroxide radical, which with more olefin yields high-mol. materials. At low concns. of styrene in CCl_4 there is formed the "monomol." product, which with H_2O or EtOH gives up to 50% $BzCH_2NO_2$, formed presumably as follows: $PhCH(OO.)CH_2NO_2 \rightarrow PhCH(OONO_2)CH_2NO_2$, which reacts with H_3O^+, yielding the final product and NO_3^- ion. O was absorbed only during the reaction of olefin and NO_2 and nitroacetophenone formed only after satn. of the mixt. with O. A low concn. of NO_2 in cyclohexene in the presence of $CHBr_3$ gave mainly bromonitrocyclohexane, in a reaction which apparently involved $CHBr_3$ in a reaction with the radical adduct of the olefin and NO_2. If the concn. of NO_2 is kept low and the mixt. satd. with NO, up to 65% yields of nitrosite and pseudonitrosite can be attained [cf. Wieland, *Ber.* 36, 2550(1903)]. The structure of styrene pseudonitrosite, $PhCH(NO)CH_2NO_2$ corresponds to that expected from a radical-reaction course, since on ionic reaction, it should yield $PhCH(ONO)CH_2NO_2$ (i.e. nitrosonitrite), and in an ionic reaction in AcOH one would expect $PhCH(OAc)CH_2NO_2$, while actually only the pseudonitrosite is actually formed.
orbital overlap in cyclopropane can be expected to b
than normal, the nature of C-C links in this substan
be more akin to ordinary π-bonds, which correspon
phys. and chem. properties of this hydrocarbon
the reaction with NO_2 should proceed similarly to that
the olefins, forming an intermediate radical O_2NCH
the olefins, forming an intermediate radical O_2NCH
$CH_2\cdot$, with NO_2, giving $CH_2(CH_2NO_2)_2$ and $O_2N(CH$
this is confirmed by formation of color between
pane compds. and $C(NO_2)_4$ and by the nitration
clene (Nametkin *et al. J. Russ. Phys. Chem. Soc.*
(1926)). Typical expts. follow. NO_2 (4 g.) was
dropwise in 50 ml. $PhNO_2$ and Et_2O to 5.2 g. PhCH
in 50 ml. $PhNO_2$-Et_2O at 0° with percolation by NO
aq. ext. of the mixt. coupled with 2-naphthol gave the
dye, m. 132-3°; when a mixt. of 10 g. cyclohexen
ml. $PhNO_2$ and 20 ml. HNO_3 (d. 1.1) was satd. with
2 hrs., the aq. ext. gave similarly 0.3 g. of the dye. Pass
of 2.2 l. O into 20.7 g. $PhCH:CH_2$ at −5°, with the entering O carrying NO_2 from a bubbler, yielded 13.4 g. viscous, high-mol. product. When CO_2 was used instead of O, only 6.8 g. polymer was formed. When 2.45 g. NO_2 in CCl_4 was added at −5° over 35 min. to 3 g. $PhCH:CH_2$ in CCl_4 with the mixt. percolated with O, 47% $BzCH_2NO_2$, m. 105-6°, was obtained after treatment with EtOH. A stream of CO_2 carrying NO_2 (from a N_2O_4 container) passed into cyclohexene in $CHBr_3$ gave largely a product, b_{2-3} 95°, contg. 35.4% Br. NO_2 (3 ml.) in cold Et_2O added to 5.2 g. $PhCH:CH_2$ in Et_2O, and kept satd. with NO at −5° gave 5.8 g. styrene pseudonitrosite.

G. M. K.

Titov, A.I.

USSR/Chemistry - Addition reactions

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Authors : Titov, A. I., and Maklyaev, F. L.

Title : Conjugated addition reactions of halogens to olefins. Part 1.-

Periodical : Zhur. ob. khim. 24/9, 1624-1630, Sep 1954

Abstract : The idea of conjugated addition reactions of halogens over multiple bonds is introduced and reviewed. Experiments showed that halogen molecules display the characteristics of strong aprotonic acids (effective electrophilic nature), and olefins (in a somewhat less effective form) possess these basic characteristics only as result of the relatively weakly bound pi-electrons. The initial stages of reaction, between halogens and olefins, are explained. The general laws and the special cases where halogens react with unsaturated compounds, in accordance with the ion mechanism, are listed. Forty-five references: 23-USA; 18-USSR and 4-German (1905-1948).

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Submitted : March 19, 1954

TiTOV, A.I.

USSR/Chemistry - Addition reactions

Card 1/1	Pub. 151 - 29/42
Authors	Titov, A. I., and Maklyaev, F. L.
Title	Conjugated addition reactions of halogens to olefins. Part 2.-
Periodical	Zhur. ob. khim. 24/9, 1631-1635, Sep 1954
Abstract	Investigations were conducted for the purpose of finding suitable methods of synthesizing beta-halogenated ethyl ethers of benzene-and p-toluene sulfonic acids, beta-chlorethyl sulphate, chlorosulfonate, phosphate and mixed 1,2-dihalogenated ethanes by the conjugated reaction method by directing the alkylating action of the complex to proper third component. The results obtained are described in detail. Seven references: 2-USA; 2-USSR and 3-German (1920-1954). Tables.
Institution	...
Submitted	March 19, 1954

Titov, A.I.

USSR/Chemistry - Addition reactions

Card 1/1 Pub. 151 - 30/37

Authors : Titov, A. I., and Maklyaev, F. L.

Title : Conjugated addition reactions of halides to olefines. Part 3.- Order of addition to nonsymmetrical olefines.

Periodical : Zhur. ob. khim. 24/10, 1860-1862, Oct 1954

Abstract : A method determining the order of addition of halides to other nonsymmetrical olefines, in the case of conjugated reactions, is briefly described. The products obtained from the reaction of Cl with propylene, in a medium of homologous acids, are listed. The order of addition of olefines (e. g., to propylene) in conjugated reactions can be determined by considering the effect of substitutes on the distribution of the positive charge in the intermediate halide-olefine complex. Five references: 2-USSR; 1-Belgian; 1-French and 1-German (1902-1954).

Institution : ...

Submitted : March 19, 1954

Titov, A.I.

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Mechanism of catalytic nitration of aromatic compounds in the presence of salts of mercury. III. New directions of the reaction in nitration of toluene. A. I. Titov and A. N. Baryshnikova. *J. Gen. Chem. U.S.S.R.* ~~24, 686~~-8(1954) (Engl. translation).—See *C.A.* 49, 14050a. B. M. R.

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Titov, A. I.

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Mechanism of catalytic nitration of aromatic compounds in the presence of salts of mercury. III. New directions of the reaction in nitration of toluene. A. I. Titov and A. N. Baryshnikova. *Zhur. Obshchei Khim.* 24, 2040-4(1954); cf. *C.A.* 43, 6585e.—MePh (40 ml.), 100 ml. HNO_3 (d. 1.32), 10 g. $Hg(NO_3)_2$, and 2 g. $NaNO_2$ kept 10 days in a closed flask, 10 g. $Hg(NO_3)_2$ and 40 ml. HNO_3 (d. 1.5) added and the mixt. cooled and filtered after 15 more days, yielded 1.3 g. p-$O_2NC_6H_4CO_2H$, 1.3 g. isomeric tolyldiazonium salts (detd. by titration with 2-$C_{10}H_7OH$), 1.84 g. trinitro-*m*-cresol, m. 90-100°, and 2.4 g. mixed nitrocresols. The org. layer heated with Et_2NH gave 0.31 g. $PhCH_2NEt_2$ (picrate, m. 122°) and mixed nitrotoluenes, contg. 62% *p*-isomer. Heating 50 ml. MePh, 200 ml. HNO_3 (d. 1.1), and 40 g. $Hg(NO_3)_2$ 50 hrs. at 50-60° in a stream of NO gave 3.3 g. mixed nitrocresols contg. 0.73 g. trinitro-*m*-cresol and some dinitro-*m*-cresol, m. 83°, from which was isolated dinitro-*p*-cresol, m. 80-2°, and some mixed nitrotoluenes. MePh (20 ml.), 100 ml. HNO_3 (d. 1.1), 20 g. $Hg(NO_3)_2$, and 0.2 g. trioxymethylene in 10 hrs. at 100° gave 2.19 g. trinitro-*m*-cresol, 0.15 g. dinitro-*o*-cresol, 0.8 g. mixed nitrocresols, 2.3 g. mixed nitrotoluenes, and 7.0 g. Hg salts. Heating 1 g. p-$O_2NC_6H_4CO_2CH_2Ph$, 5 ml. $PhNO_2$, and 3 ml. Et_2NH 8 hrs. on a steam bath gave 0.12 g. p-$O_2NC_6H_4CO_2H$, 0.15 g. $PhCH_2NEt_2$, and 0.73 g. unreacted ester. A similar alkylation was observed with $BzOCH_2Ph$. G. M. Kosolapoff

Titov, A. I.

USSR/Chemistry - Addition reactions

Card 1/1 Pub. 22 - 26/47

Authors : Titov, A. I., and Maklyayev, F. L.

Title : Conjugated addition reactions of halides to olefins

Periodical : Dok. AN SSSR 98/5, 795-798, Oct 11, 1954

Abstract : The mechanism of conjugated addition reactions, especially in the case of the addition of halides to olefins of an ionic or radical nature, is explained. Using the method of conjugated reactions - simultaneous introduction of halides and olefin into appropriate acids - the authors realized the synthesis of Beta-chloro- and beta bromoalkyl esters of different acids. The addition products, obtained from halide-olefin conjugated reaction, are described. The application of the conjugated reaction idea to other types of additions, with multiple bonds, was recommended. Five references: 2-USSR; 2-USA and 1-German (1925-1947).

Institution : ...

Presented by : Academician I. L. Knunyants, May 27, 1954