C.A.

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The reaction of radical cleavage from completely asymmetric derivatives of tin. G. A. Razuvaev and V. Fetyukova (Gorki State Univ.). *Zhur. Obshchei Khim.* (J. Gen. Chem.) **21**, 1010-15(1951); cf. *Uchenye Zapiski Gor'kov. Gosudarst. Univ.* **15**, 91(1949); *C.A.*, **43**, 4579e.—Photochem. reactions of Et_2SnPh_2 with CCl_4, $CHCl_3$, and MeOH in all cases proceed through cleavage of the Ph radical which then reacts with the solvent yielding, resp., PhCl, C_6H_6, and C_6H_6 (these were identified after nitration). The reactions were run 110-40 hrs. In addn. to the above products, the $CHCl_3$ reaction mixt. also gave an insol. yellow solid and a mixt. of Et_4Sn and Et_2SnCl_2. Similarly, CCl_4 also gave an insol. solid, some Et_2SnCl_2 and C_2Cl_6, and a little Ph_3SnCl, m. 110°. MeOH gave some metallic Sn, CH_2O, and a Et_4Sn-Ph_2SnEt_2 mixt., as well as an insol. solid, possibly Et_2SnO. Reaction of the RMgX from 8.5 g. Mg and 44.3 g. $PhCH_2Cl$ with 20 g. Ph_2SnCl_2 gave 92% $Ph_2Sn(CH_2Ph)_2$, a yellow oil, d_{4}^{20} 1.271, which was subjected to irradiation in various solvents for 60-100 hrs. as above. In $CHCl_3$ there were formed C_6H_6, and $(PhCH_2)_2SnCl_2$, m. 163° (30%), but no bibenzyl could be isolated. In CCl_4 were formed C_6H_6, $(PhCH_2)_2SnCl_2$, and some unreacted starting material. $Ph_2Sn(CH_2Ph)_2$ (2.5 g.) in 10 ml. 0.86 N alc. HCl gave on concn. some C_6H_6 (isolated as 0.25 g. dinitro deriv.), and 80% $(PhCH_2)_2SnCl_2$, m. 163°. Heating $Ph_2Sn(CH_2Ph)_2$ (2 g.) with 0.92 g. succinimide to 170° gave 0.7 g. C_6H_6-MePh mixture; oxidation of the residue with $KMnO_4$ gave more C_6H_6 (isolated as 0.35 g. dinitro deriv.), 0.23 g. BzOH, and small amts. of $(PhCH_2)_2SnCl_2$ and Ph_2SnCl_2 (both isolated after treatment of the residues with alc. HCl). N-bromosuccinimide in the above reaction in $CHCl_3$ (refluxed 0.5 hr.) gave PhBr and succinimide, while the residue with alc. HCl gave some $(PhCH_2)_2SnCl_2$. G. M. K.

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RAZUVAEV, G. A.

USSR/Chemistry - Organomercury Compounds, Jun 51
Free Radicals

"Free Radicals in the Decomposition Reaction of Benzene Azotriphenyl Methane, Nitroso Acetanilide, and Benzene Azotrinitromethane in Solutions," G. A. Razuvaev, E. I. Fedotova, Gor'kiy State U

"Zhur Obshch Khim" Vol XXI, No 6, pp 1118-1122

Proved formation of phenyl radicals in decompn of benzene azotriphenyl methane in CCl_4 soln by fixation on metallic Hg. Phenyl mercurichloride is sepd from reaction mixt. Phenyl radicals formed in decompn attach themselves to diphenyl tin added to the mixt, forming hexaphenyl distannate. Upon

186T25

USSR/Chemistry - Organomercury Compounds, Jun 51
Free Radicals (Contd)

heating of CCl_4 soln of benzene azotrinitromethane in presence of diphenyl tin, the latter is phenylized to tetraphenyl tin. In decompn of benzene azotrinitromethane in various org solvents the usual products assocd with appearance of the phenyl radical, viz. diphenyl in benzene soln, benzene in ethyl cellosolve soln, chlorobenzene in CCl_4 soln, are not found. Nitrophenols are formed regardless of the solvent used.

186T25

RAZUVAEV, G. A.

USSR/Chemistry - Organomercury Compounds Jun 51

"Photoreactions of Organic Hg Compounds in Solutions," G. A. Razuvaev, Yu. A. Ol'dekop, Gor'kiy State U

"Zhur Obshch Khim" Vol XXI, No 6, pp 1122-1124

Photoreaction of diphenyl mercury with ethyl bromide, isopropyl bromide, and chlorex (bis-ϕ-chloroethyl ether) forms benzene and phenyl mercuribromide or chloride. Diphenyl mercury and chlorobenzene upon exposure to light form calomel. In photoreaction of diphenyl mercury with bromobenzene, phenyl mercuribromide is obtained, and p-bromodiphenyl is found in reaction products.

186T26

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The photoreaction of metalloörganic compounds of mercury in solution. VII. The reaction of diphenylmercury. G. A. Razuvaev and Yu. A. Ol'dekop. *J. Gen. Chem. U.S.S.R.* 21, 1225-6(1951)(Engl. translation).—See *C.A.* 46, 1479*f*. B. R.

RAZUVAYEV, G. A.

191T26

USSR/Chemistry - Organic Mercury Compounds Jul 51

"Interaction of Certain Organic Mercury Compounds With Succinimide," G. A. Razuvayev, Yu. A. Ol'dekop, N. S. Vyazankin

"Zhur Obshch Khim" Vol XXI, No 7, pp 1283-1287

Diphenyl, o-didolyl, diethyl, α-dinaphthyl, and β-dinaphthyl Hg all reacted with succinimide to form $RHgN(COCH_2)_2$ compds (prepd for 1st time), which are well-crystd colorless substances, sol in H_2O, interact with HCl and KI to form corresponding

191T26

USSR/Chemistry - Organic Mercury Compounds (Contd) Jul 51

RHg x Hal compds. With H_2S phenyl- and O-totylmercurysuccinimide form diphenyl- and O-ditolyl-Hg, resp, while α-naphthyl- and ethylmercurysuccinimide form sulfides $(RHg)_2S$. Dibenzyl Hg with succinimide yields dibenzyl and Hg.

191T26

CA

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The reaction of some organomercury compounds with succinimide. G. A. Razuvaev, Yu. A. Ol'dekop, and N. S. Vyazankin. *J. Gen. Chem. U.S.S.R.* 21, 1403-6(1951) (Engl. translation).—See C.A. 46, 1985h. B. R.

G. A. RAZUVAYEV

Nov 51

USSR/Chemistry - Organic Antimony and Mercury Compounds **Nov 51**

"Photoreactions of Iodoorganic Compounds," G. A. Razuvayev, M. A. Shubenko, Gor'kiy State U

"Zhur Obshch Khim" Vol XXI, No 11, pp 1974-1979

Conducted following photoreactions: Bz_2Hg and Me_2Hg with C_6H_6I and Bz_2Hg with MeI in MeOH and C_6H_6 solns; Et_2Hg with C_6H_6I, and Ph_2Hg and Ph_3Sb with MeI in MeOH solns; Ph_3Sb with C_6H_6I in MeOH, C_6H_6, and $CHCl_3$, solns. Described respective reaction products. Proposes mechanism of all

194T45

USSR/Chemistry - Organic Antimony and Mercury Compounds (Contd) Nov 51

reactions, based on photolysis of org I compds into at I and free radical; studies their behavior further.

194T45

RAZUVAYEV G. A.

PA 194T67

USSR/Chemistry - Organic Mercury
Compounds

Dec 51

"Photoreactions of Mercury-Organic Compounds in Solutions. VIII. Reactions in Mixtures of Solvents," G. A. Razuvayev, Yu. A. Ol'dekop, Gor'kiy State U

"Zhur Obshch Khim" Vol XXI, No 12, pp 2197-2199

Investigated photoreactions of Ph_2Hg with following mixts: CCl_4-MeOH, CCl_4-ethylcellosolve, $CCl_3 \cdot CCl_3$-MeOH, CCl_2CCl_2-MeOH, and EtBr-MeOH. Found that radicals formed by photolysis react in

194T67

USSR/Chemistry - Organic Mercury
Compounds (Contd)

Dec 51

following manner: PhHg radical takes halogen from halogen-contg component of mixt, forming PhHgHal, while Ph radical adds H.

194T67

RAZUVAYEV, G.A.

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Reactions of carbon tetrachloride with alcohols. G. A. Razuvaev and N. S. Vasil'evskaya (State Univ., Gorki). *Doklady Akad. Nauk S.S.S.R.* 80, 69-72(1951).—In studies of photoreactions of metalloörg. compds. in mixts. of 2 solvents, one of which contains halogen and the other does not, an interesting reaction was discovered which resulted in the following: each R or R_2Hg radical reacted by splitting off an atom of H from the nonhalogen solvent, but the RHg radical reacted with the halogen-contg. solvent with the formation of RHgX. Thus, $HgPh_2$ in MeOH soln. with CCl_4 on exposure to ultraviolet light gave C_6H_6, PhHgCl, HCHO, and C_2Cl_6. When $HgPh_2$ in MeOH was exposed to ultraviolet light, C_6H_6 and HCHO were formed. With CCl_4, $HgPh_2$ reacted similarly on exposure with formation of PhHgCl, PhCl, and C_2Cl_6 while upon heating the reaction was not observed. It appears probable that radicals are formed in the thermal reaction of $HgPh_2$ with MeOH, which can react with CCl_4. $HgPh_2$ (2.0 g.) in 15 cc. MeOH were heated in a sealed tube with 15 cc. CCl_4 at 200-10° for 20 hrs. The reaction mixt. after heating sepd. into 2 layers, water-sol. combustion gases which were condensed to liquid upon cooling, and 1.1 g. Hg in bottom of tube. The top H_2O layer contained HCHO and the nonaq. layer contained $CHCl_3$, C_6H_6, and CCl_4. A soln. of 1 g. $HgCl_2$ in 10 cc. CCl_4 and 17 cc. MeOH was similarly processed and the products of reaction were CH_3Cl, H_2O and Me_2O, HgCl (0.85 g.), HCHO (2.44 g.), $CH_2(OMe)_2$, CH_2Cl, and HCl (0.2 g.). Later tests indicated that the reaction between MeOH and CCl_4 proceeded without Hg compds. by merely warming the components. $2\ CCl_4 + MeOH \rightarrow 2\ CHCl_3 + 2\ HCl + HCHO$, then $MeOH + HCl \rightarrow H_2O + MeCl$, and $HCHO + 2\ MeOH \xrightarrow{HCl} CH_2(OMe)_2 + H_2O$. A series of reactions also occurred in the presence of Hg compds. HgCl reacted with CCl_4 to form $HgCl_2$ and C_2Cl_6. Alcs. (Me, Et, $PhCH_2$) were dehydrated upon heating with $HgCl_2$ with the formation of esters, and the reaction went more smoothly with large amts. of $HgCl_2$ and at increased temps. As shown in the tests, EtOH and $PhCH_2OH$ also gave esters upon heating with $HgCl_2$. $PhCH_2OH$ with CCl_4 gave $PhCH_2Cl$, dibenzyl ester, PhCHO, $CHCl_3$ and water, as well as considerable quantities of resinous products. It is possible that in the reactions with alcs. the CCl_3 radical was formed, which split off H from the alc. A mixt. of MeOH (20 cc.) with CCl_4 (20 cc.) on 14-day exposure to a Hg quartz lamp gave laminated mixts. The lower layer gradually enlarged and finally remained const. (14 cc.). The photoreaction

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GA. RAZUVAEV 2/2 6

produced much HCl. The reaction mixt. was processed with H_2O, the H_2O soln. contained 0.32 g. HCHO and 2.19 g. HCl; the nonaq. layer consisted of a soln. of 2.4 g. C_2Cl_6 in CCl_4. The thermal reaction and photoreaction are sharply distinguished. In the photoreaction the process also includes the reaction: MeOH + 2 Cl. → HCHO + 2 HCl. MeCl is not formed, but large quantities of HCl are formed; the same difference occurs in the behavior of the CCl_3 radical in the thermal process, as the reaction proceeds by removal of the H from the alc., but in the photoreaction dimerization takes place. The difference in the reactions with temp. change is marked for other radicals such as Me or Et. At lower temps. the dimerization reaction prevails but at higher temps. the reaction of the radicals with other mols. and reactions of disproportionation prevail. In the thermal reaction the radical CCl_3 partially dimerizes to C_2Cl_6, which can in turn react with MeOH. $CHCl_3$ is not found in the reaction products when MeOH is warmed with C_2Cl_6 in a sealed tube at 200–20°. HCHO, MeCl, and $CCl_2:CCl_2$ are obtained; therefore the reaction is: C_2Cl_6 + MeOH → $(Cl_2C)_2$ + 2 HCl + HCHO. F. S. Boig

RAZUVAYEV, G. A.

Chem Abs
v.48 25 Jan 54

Organic Chem

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N-Phenylmercurisuccinimide. G. A. Razuvaev and N. S. Vyazankin. *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik* 2, 136-7(1952).—Heating 3.6 g. Ph_2Hg and 2 g. succinimide to 135-40°, with continuous distn. of C_6H_6 yields a residue of 90.4% PhHgR (R = succinimido), m. 192-3° (from H_2O). Similarly are obtained: *Et analog*, 87%, m. 121°; *o-tolyl analog*, 84%, m. 178°; *1-naphthyl analog*, 63%, m. 183°; *2-naphthyl analog*, 57%, m. 220-2°; *N-phenylmercuriacetamide*, 93%, m. 167-8°; *p-tolyl analog*, 35%, m. 243-4°; *1-naphthyl analog*, 25%, m. 199-201°; and *N-phenylmercuridiacetamide*, 30%, m. 152-3°.

G. M. Kosolapoff

RAZUVAYEV, G. A.

USSR/Chemistry - Polymerization; Jul/Aug 52
Peroxides

"New Polymerization Initiators," G. A. Razuvayev, Yu. A. Ol'dekop, Ye. I. Fedotova, Gor'kiy U

"Uspekh Khim" Vol XXI, No 4, pp 379-421

Reviews foreign work on the subject (101 references). Among USSR contributions to this field (4 references), mentions investigation which established that hydroperoxides of tertiary alcs are extremely effective in promoting emulsion polymerization of 1,3 butadiene; comparison of rates of decompn of tertiary alc hydroperoxides

216T22

at various temps in alpha-methylstyrene; study of the effect of these peroxides on polymerization of styrene in the liquid phase; initial work by A.A. Berlin, A.A. Moiseyev, and F.Kh. Abel' on the use of azonitriles and azocarboxylic acid esters as polymerization initiators /the reference on this is apparently to a 1948 USSR patent application7.

216T22

USSR/Chemistry - Organic Mercury Compounds Mar 52

"Photoreactions of Organic Mercury Compounds in Solutions. X. Reactions of Dimethyl Mercury," G. A. Razuvayev, Yu. A. Ol'dekop, Z. N. Manchinova, Gor'kiy State U

"Zhur Obshch Khim" Vol XXII, No 3, pp 480-483

Dimethyl mercury (I), in photolysis, splits into the radicals $CH_3\cdot$ and CH_3Hg; the reaction proceeds as in the case of aryl mercury compds. When exposed to ultraviolet rays, I reacts with CH_3OH to form CH_4, Hg, and CHCHO. In photoreaction with

209T45

USSR/Chemistry - Organic Mercury Compounds (Contd) Mar 52

$CHCl_3$, it yields methyl mercurichloride, CH_4, and hexachloroethane. In soln of CH_3I when exposed to light, it forms methylmercuriiodide and CH_4. In CCl_4, upon exposure to light, it reacts to form methylmercurichloride, CH_3Cl and hexachloroethane. During photoreaction in soln of CH_3OH and CCl_4, it forms the radicals $CH_3Hg\cdot$ and $CH_3\cdot$ which react with various components of the soln. The former yields methylmercurichloride in reaction with CCl_4, the latter forms CH_4 in reaction with the CH_3OH.

209T45

RAZUVAYEV, G. A.

RAZUVAYEV, G. A.

USSR/Chemistry - Organic Mercury
Compounds

Mar 52

"Reactions of Diphenyl Mercury With Metal Chlorides, in Which No Stable Metalloorganic Compounds Are Formed," G. A. Razuvayev, M. C. Fedotov, Chair of Org Chem, Gor'kiy State U

"Zhur Obshch Khim" Vol XXII, No 3, pp 484-489

Diphenyl mercury in ethyl cellosolve or dioxane soln, when heated with cobalt chloride or iron chloride, yields phenyl mercurichloride and benzene as a result of the reaction between the phenyl radical and the solvent. With the same solvents,

209T46

USSR/Chemistry - Organic Mercury
Compounds (Contd)

Mar 52

upon heating with cupric chloride, it forms phenylmercurichloride, chlorobenzene, and cuprous chloride. On heating in morpholine soln with $FeCl_3$, $CuCl_2$, or $CoCl_2$, C_6H_6 is formed and metallic Hg separates. The reaction proceeds on account of reducing processes which take place upon heating of complex metallic chloride salts with morpholine.

209T46

RAZUVAYEV, G.A.

USSR/Chemistry - Organic Mercury Compounds Apr 52

"The Reaction of Mercury-Organic Compounds With Fatty Acid Amines," G. A. Razuvayev, N. S. Vyazankin

"Zhurn Obshch Khim" Vol XXII, No 4, pp 640-643

The reaction of acetamide and diacetamide with mercury-organic compds was investigated. Diaryl mercury derivs react with acetamide and diacetamide, splitting off one radical in the form of a hydrocarbon and forming arylmercuriacetamide or arylmercuridiacetamide. Diethyl mercury did not react with acetamide or diacetamide upon heating.

224T42

RAZUVAYEV, G. A.

PA 235T16

USSR/Chemistry - Mercury Organic Compounds 21 Jul 52

"The Reaction Between Symmetrical Organo-Mercury Compounds and Iodine," G.A. Razuvayev, A.B. Savitskiy, Gor'kiy State

"Dok Ak Nauk SSSR" Vol 85, No 3, pp 575-578

In order to learn the effect of neg charges at radicals attached to metals on the reactions which the compds in question undergo, the reaction between sym organo-mercury compds and iodine was studied. The kinetics were worked out and it was concluded that the reaction differs in

235T16

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nature from that with hydrogen halide acids. Increasing the neg charge of the radical leads to a change in the mechanism of the reaction and a quant change in the kinetic parameters. Presented by Acad A.N. Nesmeyanov 16 May 52.

235T16

(CA 47 no.19: 9911 '53)

RAZUVAYEV, G. A.

PA 227T14

USSR/Chemistry - Organometallic Compounds 1 Aug 52

"Free Radical Reactions of $M[B(C_6H_5)_4]$," G.A. Razuvayev, T.G. Brilkina, Gor'kiy State U

"Dok Ak Nauk SSSR" Vol 85, No 4, pp 815-818

Reactions of complexes of the type $M[B(C_6H_5)_4]$ where M = Be, Mg, Cd, Zn, Sn^{II} are analogous to those of onium compds. Despite the presence of phenyl radicals at the anions in one case and at the cations in the other case, both groups of compds react under formation of free radicals. Presented by Acad G.G. Urazov 2 Jun 52.

227T14

KAZUVAYEV, G.A.

5

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Photoreactions of organometallic compounds of mercury in solutions. XIII. Photoreactions of diethylmercury. G. A. Razuvaev and Yu. A. Ol'dekop (State Univ., Gorki). ~~Sbornik Statei Obshchei~~ Khim. 2, 981-3(1953); cf. C.A. 49, 912e.—Ultraviolet irradiation of 2 g. Et_2Hg in 20 ml. MeOH 40 hrs. gave 96% Hg, C_2H_6, and CH_2O. In iso-PrPh the products were 48% Hg and a little $(CPhMe_2)_2$, m. 113°. In $CHCl_3$ the products were 41% Hg, C_2Cl_6, 49% EtHgCl, m. 194°, and gases contg. 14% C_2H_4; in C_6H_6, 81% Hg and gases contg. 33% unsatd. hydrocarbons; in MeI, 57% EtHgI, m. 184°, some HgI_2, Hg, and gases contg. 10% unsatd. hydrocarbons. The results indicate radical cleavage of Et_2Hg into Et and EtHg radicals. G. M. K.

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[illegible] Vol II, [illegible]

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RAZUVAYEV, G.A.; MORYGANOV, B.N.

Thermal decomposition of benzoyl peroxide in a mixture of solvents.
Soob.o nauch.rab.chl.VKHO no.4:52-53 '53. (MIRA 10:10)
(Benzoyl peroxide) (Thermochemistry)

RAZUVAYEV, G. A.

Chem Abs V48
1-25-54
General & Physical
Chemistry

Chem
②
3

Free-radical reactions of carbon tetrachloride. G. A. Razuvaev and N. S. Vasilelskaya. *Uspekhi Khim.* 22, 36-61 (1953).—A review with 105 references on the properties and reactions of the CCl_3 radical. G. M. Kosolapoff

Chem Abs
V. 48 25 Jan 54

Organic Chem

Chem

✓ Reactions of arylmercuric hydroxides. G. A. Razuvaev and G. G. Petukhov (Gorki State Univ.). *Zhur. Obshchei Khim.* 23, 37-41(1953).—Irradiation of PhHg radicals leads to decompn. via Ph_2Hg. Photochem. decompn. of ArHgOH was studied in quartz tubes with the following results. PhHgOH (3 g.) in Ethyl Cellosolve (I) in 3 hrs. of irradiation gave 0.13 g. Ph_2Hg and 0.1 g. Hg; 20 hr. irradiation of a more dil. soln. gave the same products and a little Ph_2. *o*-MeC_6H_4HgOH in I in 18 hrs. gave 82.6% MePh, 87% Hg, and some AcH; the *p*-analog in 22 hrs. gave 76.1% MePh, 96.1% Hg, and some AcH. 2,4,6-$Me_3C_6H_2HgOH$ in I gave in 10 hrs. 75.4% mesitylene, 92.1% Hg, and some AcH. *p*-$Me_2NC_6H_4HgOH$ in I in 12 hrs. gave 65% Me_2NPh, 92.4% Hg, and some AcH. *o*-MeC_6H_4HgOH in C_6H_6 in 60 hrs. gave 65% *o*-MeC_6H_4Ph, 91.4% Hg, and some H_2O; the *p*-analog in 100 hrs. gave 84.7% *p*-MeC_6H_4Ph, 80.2% Hg, and some H_2O. 2,4,6-$Me_3C_6H_2HgOH$ in $CHCl_3$ in 70 hrs. gave 77.3% mesitylene, 23.4% $HgCl_2$, 74.1% $(HgCl)_2$, and some C_2Cl_6; similar reaction in CCl_4 in 60 hrs. gave 32.8% mesitylene, 14.2% $HgCl_2$, 34.8% $(HgCl)_2$, and C_2Cl_6 along with an organomercury compd. of unknown nature. PhHgOH irradiated 80 hrs. in PhI-C_6H_6 gave 80.1% PhHgI, some Ph_2, and H_2O; in C_6H_6-I the products were Ph_2, Hg, and AcH, while substitution of iso-PrOH for I gave Me_2CO instead of AcH; in C_6H_6-CCl_4 the products were PhHgCl, $PhCCl_3$, $HgCl_2$, $(HgCl)_2$, and C_2Cl_6. Heating PhHgOH in MeOH 70 hrs. to 180-5° gave 73.6% Hg, 24.9% Ph_2Hg, and traces of C_6H_6 and H_2CO; in 24 hrs. at 200° 88.2% Hg, 12.4% Ph_2Hg, and higher than above yields of C_6H_6 and H_2CO were obtained

G. M. Kosolapoff

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1-27-54

RAZUVAYEV, G.A.

Chemical Abst.
Vol. 48 No. 6
Mar. 25, 1954
Organic Chemistry

Free radicals in reactions of decomposition of benzylaminodiazobenzene in solvents. G. A. Razuvaev, E. I. Fedotova, and A. G. Ovchinnikova (Gorki State Univ.). *Zhur. Obshchei Khim.* 23, 435-8(1953).—Heating 6.6 g. $PhCH_2NHN:NPh$ (I) in 25 ml. CCl_4 and 50 g. Hg with stirring 7 hrs. (when N evolution ceased) gave C_2Cl_6 7, BzH 34.3, $PhCH_2NH_2$ 15, and $PhCH_2NHPh$ 19.6%; a tarry residue yielded 15.7% PhHgCl. Heating 2.5 g. I in 20 ml. $HOCH_2CH_2OEt$ on a steam bath, finally on a metal bath until N evolution ceased, gave BzH 31.5, $PhCH_2NH_2$ 10, $PhCH_2NHPh$ 20%, and some AcH, but no C_6H_6 was detected. Hence 2 processes occur simultaneously: a radical cleavage forming Ph and $PhCH_2NH$ radicals, and an intramol. reaction, which forms $PhCH_2NHPh$, with loss of N. G. M. Kosolapoff

RAZUVAEV, G. A.

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Reaction of diphenylmercury with carbon tetrachloride. G. A. Razuvaev and Yu. A. Ol'dekop. *Zhur. Obshchei Khim.* 23, 587-9(1953); cf. Whitmore and Thurman, *C.A.* 23, 2955.—Ph_2Hg heated in a sealed tube with CCl_4 20-42 hrs. to 230-70° gives formation of PhHgCl (max. yield 51.2% 78.4% after 23 hrs. at 230°), HgCl (max. yield 73.1% after 27 hrs.-after 20 hrs. at 270°), $HgCl_2$ (max. yield 73.1% after 27 hrs. at 260°), and $PhCCl_3$ (isolated as BzOH, max. yield being attained in 42 hrs. at 230°). At 270° and in prolonged runs, almost complete dearylation of Hg takes place and HgCl and $HgCl_2$ are formed. G. M. Kosolapoff

RAZUVAYEV, G. A.

Chemical Abstracts
May 25, 1954
Organic Chemistry

(3)

Reaction of acyl peroxides with metallic mercury. G. A. Razuvaev, Yu. A. Ol'dekop, and L. N. Grobov. *Zhur. Obshchei Khim.* 23, 580–03(1953).—Identification of alkyl radicals in the liquid phase was accomplished by fixation of Hg. In the thermal decompn. of Ac_2O_2 in C_6H_6 in the presence of metallic Hg there was obtained 64.7% MeHgOAc. A similar reaction with Bz_2O_2 gave 31.5% PhHgOBz. Thermal decompn. of Ac_2O_2 in CCl_4 in the presence of Hg gave HgCl and HgOAc, along with products of chlorination of Hg by CCl_4 initiated by the peroxide; C_2Cl_6 was the org. product isolated. Bz_2O_2 under these conditions gave HgOBz. G. M. Kosolapoff

RAZUVAYEV, G. A.

(4) 9

Thermal decomposition of benzoyl peroxide in a mixture of solvents: benzene and nitrobenzene, and nitrobenzene and carbon tetrachloride. G. A. Razuvaev, B. N. Moryganov, and V. A. Stepushkina (State Univ., Gorki). *Zhur. Obshchei Khim.* 23, 1379-81(1953).—In the thermal decompn. of Bz_2O_2, the Ph radicals react with both C_6H_6 and $PhNO_2$, the former being the preferred reaction. In this system after refluxing on a steam bath there are formed 1.48 moles CO_2, 0.07 mole mixed nitrobiphenyls (*p*-isomer isolated), an appreciable amt. of BzOH, some Ph_2 (about 0.09 mole), an appreciable amt. of tar. In $PhNO_2$-CCl_4, the preferred reaction is with the CCl_4, yielding C_2Cl_6, 0.31 mole PhCl, 0.06 mole nitrobiphenyls, 0.84 mole BzOH, 0.07 mole phthalic acid, and 0.88 mole CO_2. G. M. Kosolapoff

RAZUVAYEV, G. A.

Reaction of carbon tetrachloride with ethyl alcohol. G. A. Razuvaev and Yu. A. Sorokin (Gor'kii State Univ.). *Zhur. Obshchei Khim.* 23, 1510-22(1953).—Heating CCl_4 with EtOH 25 hrs. to 200° in a sealed tube gave a little AcH, EtCl, $CHCl_3$, and HCl, along with Et_2O, paraldehyde, and other substances. The photochem. reaction of CCl_4 with EtOH (520 hrs. with quartz-lamp irradiation) gave 78.6% HCl, a high yield of AcH, and C_2Cl_6. The latter is not an intermediate in the thermal reaction of CCl_4 with EtOH, since heating C_2Cl_6 with EtOH 24 hrs. at 220° gave EtCl, some AcH, Et_2O, and C_2Cl_4, along with tarry materials. G. M. Kosolapoff

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RAZUVAYEV, G. A.

3/4

USSR

✓Some reactions of α-methylmercurinaphthalene. G. A.
Razuvaev and Z. I. Bugaeva. *Uchenye Zapiski Gor'kov.*
Univ. 1953, No. 24, 143-5; *Referat. Zhur., Khim.* 1954,
No. 28811.—The reactions of 1-MeHgC$_{10}$H$_7$ (I) with CHCl$_3$
(II) and *N*-bromosuccinimide (III) were studied. The 1st
reaction proceeded homolytically upon irradiation with
ultraviolet light, the naphthyl radical being split off. The
radicals thus formed reacted with II giving MeHgCl (IV)
and C$_{10}$H$_8$ (V). "Symmetrization" of I takes place simul-
taneously yielding Me$_2$Hg (VI) and (1-C$_{10}$H$_7$)$_2$Hg (VII).
The reaction between I and III proceeds by an ionic mech-
anism forming bromonaphthalene (VIII) and (CH$_2$CO)$_2$-
NHgMe (IX). I (2.5 g.) and 20 ml. of II were irradiated by
an Hg lamp for 18 hrs. By steam distn. were removed V,
m. 80°, IV, m. 142° (27.0% yield), and VI, m. 154°. IV was
detd. by transforming it into MeHgI and VI into MeHgBr.
From the distn. residue was sepd. 66.0% VII, m. 239°. To
1.0 g. of III in 20 ml. of II was added 3.0 g. I in 10 ml. of II.
By steam distn. was sepd. VIII; picrate, m. 134°. After
evapn. of residue was obtained IX, m. 128°, yield 100%.
By the action of HI it formed MeHgI. M. Hosch

RAZUVAYEV, G.A.; OL'DEKOP, Yu.A.; GROBOV, L.N.

New method of synthesis of organomercury compounds. Doklady Akad. Nauk
S.S.S.R. 88, 77-8 '53. (MLRA 6:1)
(CA 48 no.1:142 '54)

1. Gorki State Univ.

RAZUVAYEV, G.A.; PETUKHOV, G.P.; REKASHEVA, A.F.; MIKLUKHIN, G.P.; VOL'FKO-
VICH, S.I., akademik.

Use of deuterium in the study of photochemical reactions in the liquid phase of metalorganic compounds. Dokl.AN SSSR 90 no.4:569-572 Je '53.
(MLRA 6:5)

1. Akademiya Nauk SSSR (for Vol'fkovich). 2. Institut fizicheskoy khimii im. L.V. Pisarzhevskogo Akademii nauk Ukrainskoy SSR (exc. Vol'fkovich). 3. Gor'kovskiy gosudarstvennyy universitet (for all exc. Vol'fkovich).
(Organometallic compounds) (Deuterium)

The photo reactions of phenylmercury and diphenylmercury do not proceed alike, although these compds are homologs. The reaction of the first apparently takes place in a reaction "knot" consisting of one molecule of the hydroxide and one molecule of the other reagent. Conversely, diphenyl-mercury reacts by an open-radical mechanism. Exptl proof of the transfer of the chain by free radicals with the regeneration of the reacting radical was obtained. The above work was done using methyl and ethyl alcs containing deuterium in the hydroxyl group. Presented by Acad S.I.Vol'fkovich 9 Mar 53. 254T95

RAZUVAYEV, G. A.

Chemical Abst.
Vol. 48 No. 6
Mar. 25, 1954
Inorganic Chemistry

Free-radical reactions of complexes $M(BR_4)$. G. A. Razuvaev and T. G. Brilkina (Gorki State Univ.). *Doklady Akad. Nauk S.S.S.R.* 91, 861-4(1953); cf. *C.A.* 47, 3744*d*.—Reaction of $Li(BPh_4).2LiBr$ with Hg in $CHCl_3$ yields some PhHgCl. Thus, $M(BR_4)$ reacts with Hg, forming a free radical R. Addn. of an equiv. of $1\text{-}C_{10}H_7Li$ with Ph_3B in Et_2O gives $Li[BPh_3C_{10}H_7]$ as a viscous oil; treatment with NH_4Cl or KCl gives the NH_4 or the K analog, colorless solid. To eliminate the LiBr contamination the technique of prepn. of pure RLi was employed for the necessary intermediates (cf. Talalaeva and Kocheshkov, *C.A.* 45, 10191*i*), and the resulting pure Li derivs. were treated with the boranes in Et_2O to give cryst. $Li[BPh_3C_6H_4Me\text{-}p]$ and $Li[B(C_{10}H_7\text{-}1)_2Ph]$. Treatment of these with Hg in $CHCl_3$ again gave free radicals derived from the BR_4 fragment, with predominant cleavage of $1\text{-}C_{10}H_7$ rather than of Ph group, and predominant cleavage of $p\text{-}MeC_6H_4$ rather than Ph. The results parallel those obtained in thermal decompn. of $NH_4(BAr_4)$ complexes; thus $NH_4[BPh_3C_{10}H_7\text{-}1]$ gives $C_{10}H_8$ and $NH_3.BPh_3$; $NH_4[BPh_3C_6H_4Me\text{-}p]$ gives MePh and $NH_3.BPh_3$; $NH_4[B(C_{10}H_7\text{-}1)_2Ph]$ gives 2 $C_{10}H_8$ and no C_6H_6, with probable intermediate formation of unstable $NH_3.B(C_{10}H_7)_2Ph$.

G. M. Kosolapoff

RAZUVAYEV, G. A.

5008

2

Chem

Triggering the reaction between carbon tetrachloride and isopropyl alcohol with benzoyl peroxide. G. A. Razuvaev and B. N. Moryganov. *Soobshcheniya Nauch. Rabot. Chlenov-Vsesoyuz. Nauch.-Issledovatel. Obshchestva im. Mendeleeva* 1954, No. 1, 4-6; *Referat. Zhur., Khim.* 1955, No. 3453.—Thermal decompn. of Bz_2O_2 (I) in a mixt. of CCl_4 and iso-PrOH gives HCl, Me_2CO, and $CHCl_3$ in quantities exceeding 30-20 times the original quantity of I. The yield of these products increases as the concn. of I decreases. It is suggested that I triggers a chain reaction between CCl_4 and iso-PrOH in accordance with $R\cdot + CCl_4 \rightarrow RCl + CCl_3\cdot$; $Me_2CHOH + CCl_3\cdot \rightarrow Me_2C(OH)\cdot + CHCl_3$; $Me_2C(OH)\cdot + CCl_4 \rightarrow Me_2C(OH)Cl + CCl_3\cdot$ and $Me_2C(OH)Cl \rightarrow HCl + Me_2CO$, where R is the primary radical formed on decompn. of I. It is also possible that the radical $Me_2C(OH)\cdot$ is formed by giving up H to $PhCOO\cdot$ radicals.

Mordecai Hoseh

RAZUVAYEV, G.A.

USSR/Chemistry - Photoreaction

Card 1/1 Pub. 151 - 14/38

Authors : Razuvaev, G. A.; Ol'dekop Yu. A.; and Latyaeva, V. N.

Title : Photoreaction of organometallic mercury compounds in solutions. Part 14.- Photoreaction of beta-mercuribispropionic acid and its dimethyl ether

Periodical : Zhur. ob. khim. 24/2, 260-262, Feb 1954

Abstract : The photoreaction (exposure to ultraviolet light) of beta-mercuribispropionic acid in solutions of methanol and monoethyl ether of ethylene glycol was investigated. The photoreaction was concluded with the separation of the mercury and formation of propionic and adipic acids. The separation of the hydrogen from the solvent by the carboxyethyl radicals was found to be instrumental in the formation of the propionic acid and the formation of adipic acid is due to the dimerization reaction of above mentioned radicals. Aldehydes were discovered in both cases. Four references: 3-USSR and 1-German (1907-1952).

Institution : State University, Gorkiy

Submitted : June 19, 1953

RAZUVAYEV, G.A.

USSR/Chemistry - Reaction processes

Card 1/1 Pub. 151 - 15/38

Authors : Razuvayev, G. A.; Moryganov, B. N.; Dlin, E. P.; and Ol'dekop, Yu. A.

Title : Reaction of acyl peroxides with metals and metal chlorides (Sn and Sb).

Periodical : Zhur. ob. khim. 24/2, 262-265, Feb 1954

Abstract : The reaction between benzoyl peroxide and $SnCl_2$, $SbCl_3$, metallic Sn as well as the reaction between acetyl peroxide and Sb were investigated. The reactions were carried out in benzene, dichloroethane and acetic anhydride solutions. The products derived from these reactions are listed. Four references: 3-USSR and 1-USA (1927-1953).

Institution : State University, Gorkiy

Submitted : June 19, 1953

RAZUVAYEV, G.A.

62

Complex compounds of type $M(BAr_4)$. G. A. Razuvaev and T. G. Brilkina (State Univ., Gorki). *Zhur. Obshchei Khim.* 24, 1415-21(1954); cf. *C.A.* 48, 3180*f*.—Addn. of 30 ml. 0.3*N* MeLi in Et_2O under N_2 to 2.4 g. Ph_3B in Et_2O gave after evapn. a cryst. residue of $Li[BPh_3Me]$, which decomposes on exposure to air; soln. in H_2O yields some Ph_2 and gives a basic soln.; fresh aq. solns. gave no ppts. with K or NH_4 salts, but on prolonged standing ppts. formed; thus $NH_4[BPh_4]$ was obtained. Symmetrization of the complex accounts for formation of this substance. Similarly, 5.54 g. $(1\text{-}C_{10}H_7)_3B.2C_6H_6$ in Et_2O and 1.15*N* EtLi in C_6H_6 (9 ml.) gave a ppt., which after vacuum drying yielded an air-unstable $Li[B(C_{10}H_7)_3Et]$. Aq. soln. of this treated with KCl or NH_4Cl gave after several hrs. a ppt. of the corresponding K or NH_4 salt; only $NH_4[B(C_{10}H_7)_4]$ was analyzed. Heating 5 g. KBPh with 80 ml. $EtOCH_2CH_2OH$ and 20 ml. H_2O 5-7 hrs., followed by steam distn. of C_6H_6 gave AcH and PhOH, along with crude diphenylboric acid. Similar reaction of NH_4BPh_4 gave a loss of 1 Ph group (as C_6H_6) in 2 hrs.; the aq. residue contained PhOH and diphenylboric acid. Heating NH_4BPh_4 with dry MeOH in sealed tube 5 hrs. at 100° gave 60% NH_3, 100% loss of 1 Ph group (C_6H_6) and Ph_3BNH_3, m. 212-14° (38% yield); the aq. soln. contained PhOH. Refluxing 3 g. $KB(C_{10}H_7)Ph_3$ in $EtOCH_2CH_2OH$ 2 hrs. gave a basic soln. which yielded $C_{10}H_8$ and PhOH. Heating 3 g. $NH_4B(C_{10}H_7)Ph_3$ with 75 ml. $EtOCH_2CH_2OH$ and 25 ml. H_2O 8 hrs. at reflux gave 1 g. $C_{10}H_8$ and 1.1 g. Ph_3BNH_3, along with some PhOH. Similar reaction of $KBPh_3(C_6H_4Me\text{-}p)$ gave 96% MePh and some PhOH. Similar reaction of $KB(C_{10}H_7)_3Ph$ gave in 4 hrs. a loss of 2 $C_{10}H_7$ groups as $C_{10}H_8$, along with phenylboric acid. To 3.5 g. $KBPh_4$ in dry MeOH 8 ml. 1.25*M* Br_2 in MeOH was added; diln. with H_2O gave 1.5 g. PhBr, 1 g. Ph_2, 1 g. phenylboric acid. Similar reaction of $LiBPh_3\text{-}C_6H_4Me\text{-}p$ with Br_2 in aq. soln. gave $p\text{-}BrC_6H_4Me$ (80%) and diphenylboric acid. Illumination of 3.5 g. $KBPh_4$ in $CHCl_3$ 100 hrs. gave some C_6H_6, Ph_2 and PhOH. To 4 g. $KBPh_4$ in dry Me_2CO 7.3 g. dry $FeCl_3$ was added. The mixt. heated 0.5 hr. gave on diln. 64% C_6H_6 (based on loss of 1 Ph group), 1.3 g. Ph_2 and phenylboric acid; the soln. gave tests for ferric and ferrous ions. G. M. Kosolapoff

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RAZUVAYEV, G.A.

USSR/Chemistry

Card 1/1 Pub. 151 - 41/42

Authors : Razuvayev, G. A.

Title : Remarks on the report by A. A. Bol'shakova entitled, "Reaction of Methyl-Alpha-naphthyl Mercury and Methylphenyl Mercury with Organic Acids".

Periodical : Zhur. ob. khim. 24/9, 1693-1694, Sep 1954

Abstract : Brief discussion on the report by A. A. Bol'shakova regarding the mechanism of reaction of methyl-alpha-naphthyl mercury and methylphenyl mercury with organic acids, is presented. Six references: 3-USA; 2-USSR and 1-German (1943-1954).

Institution : ...

Submitted : April 24, 1954

Razuvayev, G.A.

USSR/Chemistry - Photo-decomposition

Card 1/1 Pub. 151 - 13/37

Authors : Razuvayev, G. A., and Osanova, N. A.

Title : Photo-decomposition of pentachloroethane

Periodical : Zhur. ob. khim. 24/10, 1771-1775, Oct 1954

Abstract : The results obtained by exposing pentachloroethane to the effects of ultraviolet ray radiation are described. The complete reaction scheme, beginning with the separation of the elementary Cl-atom from the pentachloroethane, and the formation of tetrachloroethyl-radicals, which are finally dimerized into octachlorobutane, is explained. The separated Cl chlorinates the basic pentachloroethane and the formed octachlorobutane up to the ion- and decachlorobutane. Eleven references: 7-USA; 2-USSR and 2-German (1940-1953).

Institution : State University, Gorkiy

Submitted : February 10, 1954

RAZUVAYEV, G.A.

USSR/ Chemistry - Physical chemistry

Card 1/1 : Pub. 22 - 28/49

Authors : Razuvaev, G. A.; Ol'dekop, Yu. A.; and Mayer, N. A.

Title : Decomposition of mercuric salts of organic acids initiated by free radicals

Periodical : Dok. AN SSSR 98/4, 613-616, Oct. 1, 1954

Abstract : The reaction of acetyl peroxide with Hg was investigated to determine the decomposition characteristics of mercuric salts of organic acids when promoted by free radicals. It was found that the above peroxide reaction can be used as a suitable method for the synthesis of methyl-mercury compounds and alkyl-mercury derivatives. Six references: 5-USA and 1-USSR (1921-1953). Graphs.

Institution : ...

Presented by : Academician N. N. Semenov, May 22, 1954

RAZUVAYEV, G.-A.

5

1

Reactions of free radicals in liquid phase. Reactivity of hydroxy acyl radicals and of polychloromethyl and -ethyl radicals. G. A. Razuvaev. *Voprosy Khim. Kinetiki, Kataliza i Reaktsionnoi Sposobnosti, Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1955, 700-7.—The radical reaction of Bz_2O_2 in $PhNO_2$, CCl_4, MeOH, iso-PrOH, C_6H_6-Hg, C_6H_6-Cu, C_6H_6-Sn, and their combinations was examd. In $PhNO_2$-C_6H_6 there are formed Ph_2, $PhC_6H_4NO_2$, and CO_2. In $PhNO_2$-CCl_4 there formed PhCl, CO_2, and $CCl_3C_6H_4NO_2$. In MeOH-C_6H_6 there formed BzOH and CH_2O, as well as Ph_2 and BzOMe. In iso-PrOH there formed BzOH and Me_2CO. HCl and $CHCl_3$ are formed also in iso-PrOH-CCl_4, along with C_2Cl_6. In C_6H_6-Hg there formed $(BzHg)_2$, PhHgOBz, and CO_2; Ac_2O_2 or Bz_2O_2 react with mercuric salts yielding products explainable by radical chain mechanism. Reaction of Bz_2O_2 with Cu or Sn also proceeds similarly, yielding cuprous or stannic benzoate. Reaction with Hg in CCl_4 gave no CO_2 and yielded CCl_3 and PhHg radicals, as shown by formation of PhHgCl. Thus the order of reactivity with peroxides is descending: alcs., Hg, Cu, Sn, CCl_4, C_6H_6, $PhNO_2$. A convenient identification of transient radicals lies in their fixation on Hg; thus Ac_2O_2 in C_6H_6 in contact with Hg gave a detectable odor of alkyl-Hg derivs. $(m\text{-}O_2NC_6H_4CO_2)_2$ reacted with Hg on heating without loss of CO_2, yielding R_2Hg_2. Hydroquinone or alcs. suppress the reaction of acyl peroxides with Hg. Heating EtOH with CCl_4 to 210-20° does not produce C_2Cl_6, but yields C_2Cl_4, HCl, and AcH. Irradiation of C_2HCl_5 with ultraviolet gave C_2Cl_6, C_4Cl_{10}, and butane derivs. Ac_2O_2 heated with AcOH gave CO_2, succinic acid, C_2H_6, and other products.

G. M. Kosolapoff

RAZUVAYEV, G.A.

6

New method of synthesis of alkyl compounds of mercury from mercury salts of organic acids. G. A. Razuvaev, Yu. A. Ol'dekop, and N. A. Maier (State Univ., Gorki). *Zhur. Obshchei Khim.* 25, 697–705; *J. Gen. Chem. U.S.S.R.* 25, 665–71(1955)(Engl. translation).—Reaction of Hg salts of aliphatic acids in the presence of peroxides is used as a new method of synthesis of aliphatic organomercury compds. The reaction has a chain mechanism. To 90 g. Ac_2O and 2 g. NaOH was added with cooling 18–20 g. 30% H_2O_2 and the mixt. stirred 1 hr. with continued cooling contained no AcO_2H nor unreacted H_2O_2; the concn. of Ac_2O_2 was 0.16–0.18 g./ml. and the soln. (I) could be kept for several days. Heating 15 g. $(AcOHg)_2$, 18 ml. I, and 150 ml. C_6H_6 7.5 hrs. at reflux, filtering off and washing of the ppt. with H_2O, and treatment of the aq. ext. with KI gave 49% *MeHgI*, m. 145°. Refluxing 8 g. $(AcOHg)_2$, 3 g. Bz_2O_2, and 60 ml. C_6H_6 11.5 hrs., evapn. of the org. soln. and steam distn. of the residue in the presence of satd. aq. $CaCl_2$ gave 28% PhHgCl, some Ph_2, and BzOH. Refluxing 40 g. $Hg(OAc)_2$, 25 ml. I (contg. 3.8 g. Ac_2O_2), and 70 ml. C_6H_6 9 hrs., sepg. from a little Hg, extg. with H_2O, and adding KI to the aq. ext. gave 89.5% MeHgI; kinetic curves for this set of reactants are shown with different proportions of reactants. When the reaction was run in AcOH a 99% yield of MeHgI was obtained and the reaction rate was 25 times greater than in C_6H_6; the propagation coeff. of the chain reaction was estd. at near unity. In dil. AcOH only traces of MeHgI were formed under similar conditions. Refluxing 15 g. $Hg(OAc)_2$, 2.5 g. 1-hydroxycyclohexyl 1-hydroperoxide diacetate, and 150 ml. C_6H_6 7 hrs. gave 5.5 g. pptd. Hg salts and 40.4% MeHgI (after usual treatment), as well as unidentified yellow oil. The reaction run in AcOH-Ac_2O gave a little $(AcOHg)_2$ and 78.3% MeHgCl. Refluxing $Hg(OAc)_2$ with Bz_2O_2 in C_6H_6 12 hrs. gave pptd. Hg salts, 54% MeHgI (calcd. on Hg), 41.7% PhHgCl (calcd. on Bz_2O_2), some Ph_2, and BzOH. Refluxing 7.2 g. $Hg(OBz)_2$, 2 g. Bz_2O_2, and 60 ml. C_6H_6 12 hrs. gave 2.1 g. starting material with some Hg while the filtrate, after distn., treatment with $CaCl_2$ and steam distn. gave 2.9 g. Hg_2Cl_2 and some PhHgCl, along with Ph_2 and BzOH. $Hg(O_2CEt)_2$ (15 g.), 2 g. Bz_2O_2, and 60 ml. C_6H_6 refluxed 12 hrs. gave a ppt. of 0.8 g. $(EtCO_2Hg)_2$, while the filtrate extd. with H_2O and the ext. treated with KI gave 34% EtHgI and some Hg_2Cl_2 and PhHgCl; some BzOH was also formed.

G. M. Kosolapoff

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RAZUVAYEV, G.A.; ETLIS, V.S.

Condensation of benzene with certain symmetric chloroethers.
Zhur.ob.khim. 25 no.9:1711-1713 S '55. (MIRA 9:2)

1.Molotovskiy gosudarstvennyy universitet.
(Benzene) (Ethers)

RAZUVAYEV, G.A.

7

3

Radical reactions of pentaphenylphosphorus (pentaphenylphosphorane). Determination of structure of pentaphenylphosphorus by means of deuterium. G. A. Razuvaev, G. G. Petukhov, and N. A. Osanova (State Univ., Gorki). *Doklady Akad. Nauk S.S.S.R.* 104, 733-6(1955); cf. preceding abstr.—It was shown that the cleavage of Ph radicals from Ph_5P occurs with equal facility from polar and equatorial locations; thus all 5 Ph groups are energetically equally bound to the P atom in spite of their geometric inequality around the P atom in the form of a trigonal bipyramid. This result is different from exchange reaction rates of differently located Cl atoms in PCl_5 (cf. Gerding and Hautgraaf, *C.A.* 49, 5064*h* and Downs and Johnson, *C.A.* 48, 4901*b*). Ph_4PI and C_6D_5Li, or PhLi and $Ph_3C_6D_5PI$, yielded D-labeled Ph_5P, or $Ph_4C_6D_5P$. If ArLi adds to the Ph_4P cation at the polar location, the product should be labeled only in the polar location by the 1st method, while the 2nd synthesis should give a 1:1 mixt. of polar-equatorial labeling. If the Ph anion adds at the equatorial position, the 1st synthesis should give only the equatorial labeling, while the 2nd method should give a 1:1 mixt. of polar and equatorial labelings. The labeled Ph_5P was subjected to cleavage of 1 or 2 Ph radicals by reaction with $CHCl_3$, EtOH and C_6H_6, after which the D-content of the fragments was detd. The reaction with $CHCl_3$ was shown to proceed with equal facility from polar or equatorial positions of Ph_5P. Reaction with EtOH is complicated by capture of H from HO of the alc. by resulting Ph radicals, yielding again D distribution indicative of equal facility of loss of Ph radicals from all 5 positions. Reaction with C_6H_6 was also complex; unlabeled Ph_5P in C_6D_6 gave much D-labeled Ph_2 (18%); no exchange of Ph radicals took place between the solvent and reagent. Equal facility of loss of Ph for all 5 locations was again shown.

G. M. Kosolapoff

RAZUVAYEV, G.A

6

Reaction of photodecarboxylation of salts of mercury. G. A. Razuvaev and Yu. A. Ol'dekop (State Univ., Gorki). *Doklady Akad. Nauk S.S.S.R.* 105, 738-40(1955).—Ultraviolet irradiation of $Hg(OAc)_2$ in AcOH 10 hrs. gave 10% Hg; treatment of the residue with H_2O and NaI gave 71% MeHgI. Similarly $Hg(O_2CEt)_2$ gave in 4 hrs. 55% Hg and 40% EtHgI. Irradiation of $Hg(OAc)_2$ in dry MeOH 9 hrs. gave 47% HgOAc, some CH_2O, and a trace of MeHgI after aq. treatment with NaI. $Hg(OAc)_2$ in $HOCH_2CH_2OEt$ 6 hrs. gave 94% Hg, 3.7% HgOAc, and some AcH. $Hg(OAc)_2$ in C_6H_6 8 hrs. gave 94% Hg and 2.6% MeHgI after aq. NaI treatment. Thus the reaction proceeds by radical cleavage of the acyl groups from Hg. G. M. K.

2

RAZUVAYEV, G. A.

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8000

Chem

Exchange reactions during thermo- and photodissociation of organometallic compounds. G. A. Razuvaev, G. G. Petukhov, M. A. Shubenko, and V. A. Voitovich (State Univ., Gorki). *Ukrain. Khim. Zhur.* 22, 46–7(1956)(in Russian).—The following results were obtained for reactions involving the H exchange between the solvent and the products of the decompn. of organometallic compds. [expt. no., starting compd., solvent, D content in solvent (γ), isolated product, and D content in product (γ) given]: *1*, Ph_2Hg (I), C_6D_6 (II), 3800, Ph_2, 542; *2*, PhHgOH, II, 250, Ph_2, 120; *3*, Ph_3P, II, 3200, Ph_2, 295; *4*, $(PhCH_2)Hg$, C_6D_5Me, 1808, $(PhCH_2)_2$, 12; *5*, $PhCH_2I$, C_6D_5Me, 781, $(PhCH_2)_2$, 167; *6*, I + Na, II, 912, BzOH, 338; *7*, I + Na, II, 3200, BzOH, 2668; *8*, $(PhCH_2)_2Hg$ + Na, C_6D_5Me, 1218, $PhCH_2CO_2H$, 424; *9*, PhMgBr, II, 993, BzOH, 70; *10*, PhBr + Na, II, 3200, Ph_2, 38; *11*, PhBr + Na, II, 3200, Ph_2, 294; *12*, $PhCH_2Br$ + Na, C_6D_5Me, 418, $(PhCH_2)_2$, 58. In expts. *1*, *2*, *4*, and *5*, a sample (5 g.) of the starting compd. in 15 ml. solvent in a quartz test tube was irradiated with ultraviolet lamp (PRK-2). Sample *5*, in addn., contained 3 g. freshly pptd. Cu. In expt. *3*, the reactants were kept at 80°. In expts. *6*, *7*, and *8*, carried out in N, 3–4 g. Na and later an excess of Dry Ice were added to a sample (5 g.) of the organometallic compd. To the soln. of PhMgBr (expt. *9*) in 15 ml. C_6D_6 was added an excess of Dry Ice. The mixt. of PhBr (15 g.) in 8 g. solvent (expt. *10*) contained 3 g. Na. In expt. *11* to 8 g. C_6D_6 contg. 3 g. Na was added dropwise 15 g. PhBr and in the analogous expt. *12*, 10 g. C_6D_5Me and 3 g. Na was slowly mixed with 16 g. $PhCH_2Br$. In every instance a 2-hr. reaction time was sufficient to reach an equil. The av. error was ±15γ. A. P. Kotloby

USSR/Organic Chemistry - Theoretical and General Questions on Organic Chemistry, E-1

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 769

Author: Razuvayev, G. A., Stupen, A. B., and Minsker, K. S.

Institution: None

Title: Oxidizing Action of Some Acyl Peroxides

Original Periodical: Zh. obshch. khimii, 1956, Vol 26, No 2, 473-474

Abstract: The oxidizing action of benzoyl peroxide (I), acetyl benzoyl peroxide (II), and acetylated and benzoylated derivatives of type III and IV has been investigated with reference to the evolution of I_2 from KI. A marked difference was found in the oxidation rate of I and II (3-5 minutes) and III and IV (20-100 hours). A mathematical expression is given for the oxidation rate of III and IV: $V = x/(a-bx)$, where V is the milliliters of 0.1 N $Na_2S_2O_3$ used in the titration, x is the time of titration from the start of the reaction in minutes, and a and b are constants which have different values for III and IV (for III at 22° $a = 49.2$, $b = 0.0857$). The rate of the initiating reaction is

Card 1/2

Card 2/2

RAZUVAYEV, G.A.

3

Condensation of cyclohexanone with ammonia. G. A.
Razuvaev, E. N. Zil'berman, and S. V. Svetozarskii. *Zhur.*
Obshchei Khim. 26, 601-4(1956).—Shaking 490 g. cyclo-
hexanone, 40 g. $CaCl_2$, 10 g. NH_4Cl, and 110 g. NH_3 in an
autoclave 2 hrs. at 35-40° gave after washing with H_2O
94.5% *2,4-dipentamethylene-5,6-tetramethylene-2,3,4,5-tetra-*
hydropyrimidine (I), m. 52°; a 70% yield was obtained
if gaseous NH_3 was passed into the above reaction mixt. 7
hrs. The product is fairly stable in air and cannot be distd.
Hydrolysis with 10.9% H_2SO_4 gave 78% cyclohexanone,
$(NH_4)_2SO_4$, and 66% *2-(1-aminocyclohexyl)cyclohexanone*
sulfate, m. 108°, which with NaOH gave *2-(1-cyclohexen-1-*
yl)cyclohexanone (II), b_5 124°, d_{20} 1.002, n_D^{20} 1.5054. Treat-
ment of the above sulfate with 15% NH_4OH gave 86.5% 2-
(1-aminocyclohexyl)cyclohexanone, yellow liquid, undistil-
lable without decompn., d_{20} 1.0280, n_D^{20} 1.5058. II treated
with a stream of NH_3 16 hrs., followed by removal of ex-
cess NH_3 and refluxing 0.5 hr. with enough H_2SO_4 to acidify
the mixt., gave NH_3 in an amt. agreeing with formation of I.
Passage of NH_3 16 hrs. into cyclohexanone gave 24% I.
While II reacted with gaseous NH_3, aq. treatment destroyed
the expected aminocyclohexyl analog. G. M. Kosolapoff

Chem

USSR/Chemistry of High-Molecular Substances, F

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 1148

Author: Minsker, K. S., Shevlyakov, A. S., and Razuvayev, G. A.

Institution: None

Title: The Part Played by Oxygen in the Initial Stage of the Polymerization of Vinyl Chloride

Original Periodical: Zh. obshch. khimii, 1956, Vol 26, No 4, 1082-1087

Abstract: During the polymerization of vinyl chloride (I), both pure and in the presence of initiators (benzoyl peroxide (II), azoisobutyl cyanide, acetylbenzoyl peroxide, 2,2-azo-bis-n-isobutylpropyl cyanide, methylamino-bis-diazo-p-anisole, and methylamino-bis-diazobenzene), an induction period is observed, the duration of which depends on the amount of O_2 present, as well as on the nature and concentration of the initiator. In pure I the induction period is considerably longer than in the presence of initiators. During the induction period the formation of peroxides has been established iodometrically. In the

Card 1/2

RAZUVAYEV, G.A.

USSR/Organic Chemistry - Synthetic Organic Chemistry E-2

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 4463

Author : Razuvayev, G.A., D'yachkovskaya, O.S.
Title : Reaction of Tetrasubstituted Silanes with Carbon Tetrachloride.

Orig Pub : Zh. obshch. khimii, 1956, 26, No 4, 1107-1110

Abstract : Photoreaction of CCl_4 with $(C_2H_5)_4Si$ (160 hours, 35-40°) proceeds over chlorination without removal of radical, and the formation of $CH_3CHClSi(C_2H_5)_3$. If in lieu of irradiation with ultraviolet light the reaction is initiated with acetyl peroxide at the temperature of boiling of CCl_4, there is formed a mixture of alpha- and beta-chlorethyl-triethylsilanes, HCl, C_2Cl_6 and $CHCl_3$. Benzoyl peroxide does not initiate this reaction. On action of ultraviolet radiations on a mixture of alpha- and beta-chlorethyl-triethylsilanes, it is essentially the beta-isomer that undergoes decomposition.

Card 1/2

RAZUVAYEV, G.A.; OL'DEKOP, Yu.A.; LATYAYEVA, V.N.

Reactions of asymmetric acyl peroxides with mercury. Zhur.ob.
khim. 26 no.4:1110-1113 Ap '56. (MLRA 9:8)
(Peroxides) (Mercury organic compounds)

Razuvayev, G.A.

RAZUVAYEV, G.A.; OL'DEKOP, Yu.A.; SOROKIN, Yu.A.; TVERDOVA, V.M.

Free radical reactions of lead tetraacetate. Zhur.ob.khim. 26
no.6:1683-1685 Je '56. (MIRA 11:1)

1.Gor'kovskiy gosudarstvennyy universitet.
(Lead acetates) (Chemical reaction)

RAZUVAYEV, G.A.; PETUKHOV, G.G.; KALININA, R.V.

The catalytic decomposition of phenylmercury hydroxide in solvents.
Zhur.ob.khim. 26 no.6:1685-1687 Je '56. (MIRA 11:1)

1.Gor'kovskiy gosudarstvennyy universitet.
(Catalysis) (Mercury hydroxides)

Razuvayev, G. A.

E-1

USSR/Organic Chemistry. Theoretical and General
Questions of Organic Chemistry.

Abs Jour : Ref Zhur - Khimiya, No. 8, 1957, 26660.

Author : Kolpovskaya, G.A.; Moryganov, B.N.; Razuvayev, G.A.; Shushunov, V.A.

Inst :

Title : Chain Reaction of Carbon Tetrachloride with Isopropyl Alcohol Initiated by Acetylized and Benzoylated 1-Oxychclohexanone Hydroperoxides.

Orig Pub : Zh. obshch. khimii, 1956, 26, No. 7, 1981 - 1986.

Abstract : Acetylized (I) and benzoylated 1-oxycyclohexane hydroperoxide (II) starts a reaction between CCl_4 and isopropanol at 40 to 50°. The basic resulting products are HCl, $CHCl_3$ and acetone (III). The influence of the concentration of I and II on the initiation

Card 1/2

~~RAZUVAYEV, G. A.~~

RAZUYAYEV, G, A.

2

Chem

Reactions of acetyl benzoyl peroxide with alcohols and acetic acid. G. A. Razuvaev and V. N. Latyaeva (State Univ., Gorki). *Zhur. Obshchei Khim.* 26, 1986-91(1956).—Reactions of BzO_2Ac with MeOH, EtOH, iso-PrOH, and BuOH were examd. These proceed at reflux with dehydrogenation of the alcs. forming mixts. of AcOH and BzOH on one hand, and of BzOH, CH_4, and CO_2, on the other hand. The rate of reaction declines in the order: iso-Pr, Et, Me, *tert*-Am. Diphenylpicryl hydrazide inhibits the reaction which evolves CH_4 and CO_2. BzO_2Ac with AcOH at 90° yields CH_4, CO_2, BzOMe, $(CH_2CO_2H)_2$, C_6H_6, Ph_2, and *o*-phthalic acid, along with probably the isomers of homophthalic acids. Alkali with BzO_2Ac in EtOH forms Bz_2O_2, AcOH, and AcO_2H. Kinetic curves of the reaction with alcs. and BzO_2Ac are shown in the 40-60° range.

G. M. Kosolapoff

Razuvayev, G.A.

E-1

USSR/Organic Chemistry. Theoretical and General Questions of Organic Chemistry.

Abs Jour : Ref Zhur - Khimiya, No. 8, 1957, 26661.

Author : Razuvayev, G.A.; Moryganov, B.N., Kronman, A.G.

Inst :

Title : Reaction Between Hexachloroethane and Isopropyl Alcohol Initiated by Benzoyl Peroxide.

Orig Pub : Zh. obshch. khimii, 1956, 26, No. 8, 2224 - 2228.

Abstract : When hexachloroethane (I) is boiled with isopropanol (II) in presence of benzoyl peroxide (III), the reaction proceeds according to the radical chain mechanism: initiation: III $\longrightarrow 2C_6H_5COO^\circ \longrightarrow C_6H_5^\circ + CO_2$; beginning of the chain: $C_6H_5COO^\circ + II \rightarrow C_6H_5COOH +$

Card 1/

E-1

USSR/Organic Chemistry. Theoretical and General
Questions of Organic Chemistry.

Abs Jour : Ref Zhur - Khimiya, No. 8, 1957, 26661.

$CH_3C^\circ(OH)CH_3$(A); $C_6H_5^\circ + II \rightarrow C_6H_6 + A$; chain: $A + I \rightarrow (CH_3)_2\overset{\circ}{C} - O - H - Cl - \overset{\circ}{C}Cl_2CCl_3 \rightarrow$ chain transmission: $CH_3COCH_2 + HCl + CCl_3CCl_2^\circ$; $Cl^\circ CCl_3CCl_2^\circ + II \rightarrow A +$ $CCl_3CCl_2^\circ \rightarrow CCl_2 = CCl_2 + Cl^\circ$ break of chain: CCl_3CCl_2H; $Cl^\circ + II \rightarrow A + HCl$; $2A \rightarrow CH_3COCH_3 + II$. CO_2, HCl, acetone, benzene, pentachlorophthalic and benzoic acids and pentachloroethane were found among the reaction products. The circumstance indicating the chain mechanism of the reaction is that if it is carried out with 1 mol of II and 0.125 mol of I in presence of 0.0124 mol of III, 24.1 mols of HCl and 16.7 mols of CH_3COCH_3 will be received per mol of III, while 0.0021 mol of III will produce 73.3 mols of HCl and 37 mols of acetone under the same conditions. The length ν of the

Card 2/3

E-1

USSR/Organic Chemistry. Theoretical and General
Questions of Organic Chemistry.

Abs Jour : Ref Zhur - Khimiya, No. 8, 1957, 26661.

chain computed by the equation $\nu = (\Delta C_{HCl}/\Delta t) : (\Delta C_{III}/\Delta t)$, where ΔC_{HCl} is the gain in HCl during the time Δt, ΔC_{III} is the loss of III during the time Δt, increases with the decrease of III concentration, because at the concentration of $III = 3.6 \times 10^{-2}$ M, ν 7, and at the concentration $= 1.2 \times 10^{-2}$ M, $\nu = 18$.

Card 3/3

RAZUVAYEV, G.A.

Chem

Sulfonation of diphenylmethane. V. S. Etlis and G. A. Razuvaev. *Doklady Akad. Nauk S.S.S.R.* 111, 842-4 (1956).—Sulfonation of Ph_2CH_2 with 60% oleum in the cold yields the 4,4'-disulfonic acid and a small amt. of a colored product; a fresh portion of oleum at 150-60° converts the disulfonic acid to a colored substance whose $PhNH_2$ salt forms needles; the colored material is benzhydrol-*o*-sulfone-4,4'-disulfonic acid (I), also formed by heating diphenylmethane-*o*-sulfone with concd. H_2SO_4 until SO_3 fumes form. Oxidation of diphenylmethane-*o*-sulfone with $Pb(OAc)_4$ gives the *unsulfonated analog* of I (absorption spectra of both shown). When the oxidation is run with CrO_3, the product is not a dye. Mixed isomers of *o*- and *p*-dichloro substituted diphenylmethanes, from PhCl reaction with $O(CH_2Cl)_2$ and $AlCl_3$, were treated with 20% oleum yielding an insoluble substance, m. 166-7°, which is I with two Cl atoms in *m*-positions with respect to SO_2; this is yellow in alk. EtOH and colorless in acidic soln. The lack of sulfonation in this case is caused by the location of the Cl groups. All the above analogs of I are indicators with color change at pH 11.5-12.5. The *$PhNH_2$ salt* of I forms a *tetrahydrate*, which, in basic soln. in contact with air, changes its yellow color to green and passes to yellow; its HO group cannot be alkylated or benzoylated, and it does not react with CH_2N_2. The material readily couples with diazonium salts, yielding a dye with indicator properties, yellow in neutral or acid soln., red in alk. Thus I is regarded as a new form of a chromophoric group. G. M. Kosolapoff

RAZUVAYEV, G. A

6

7

Chem

Photoreactions of organochromium compounds. G. A.
Razuvaev, Yu. A. Sorokin, and G. A. Domrachev (N. I.
Lobachevskii State Univ., Gorki). Doklady Akad. Nauk
S.S.S.R. 111, 1264-6(1956); cf. C.A. 43, 4578e; Zeiss,
Yale Sci. Mag. 29, 14(1955).—Treatment of PhMgBr from
150 g. PhBr with an Et_2O suspension of 40 g. $CrCl_3$ at $-10°$
and on the following day with ice-H_2SO_4 gave orange 0.54 g.
$Ph_4CrOH.4H_2O$ (I) and 0.38 g. orange $Ph_4CrI.2CHCl_3$ (II)
(cf. Hein, et al., C.A. 16, 1405; 22, 2373). Ultraviolet
irradiation of I in $CHCl_3$ resulted in color change to green,
yielding 79.3% Ph_2 and a residue which after steam distn.
gave PhOH, no C_6H_6 being detected. Similarly, the reaction
run in MeOH also gave Ph_2 and PhOH. Irradiation of II
in $CHCl_3$ 30 hrs. gave a mixt., pink-violet in color (iodine
color), yielding Ph_2 (100%) and no detectable C_6H_6. Thus
II contained the 4 rings in the form of 2 biphenylyl structures
and not a chain. The structure of I was probably similar to
that of II, the 5th Ph group forming a phenolate anion.
Thus, the Zeiss structure of I and II with a "sandwich" struc-
ture of 2 biphenylyl groups in which one Ph of each of such
groups was linked to the central Cr atom appeared to be con-
firmed further. G. M. Kosolapoff

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MT

Razuvayev, G. A.

478

AUTHORS: Razuvayev, G. A., and Ol'dekop, Yu. A.

TITLE: Reactions of Acyl Peroxides with Mercury (Reaktsii Atsil'nykh perekisey so rtut'yu)

PERIODICAL: Zhurnal Obshchey Khimii, 1957, Vol. 27, No. 1, pp. 196-199 (U.S.S.R.)

ABSTRACT: The investigation of the reaction of acyl peroxides with Hg in various media was expanded to include in addition to benzoyl and acetyl peroxides also chloroacetyl and m-nitrobenzoyl peroxides which during decomposition offer more stable RCO_2 radicals. The solvents used in the reactions and their properties are described. It was found that acetyl peroxide reacts with Hg in a benzene medium at normal temperature without separation of CO_2 forming mercurous acetate. Chloroacetyl peroxide reacts in a similar manner; the fixation of the chloroacetyoxy-radical on Hg was observed during the mixing of the benzene solution with the Hg at normal temperature. The reaction tendency in boiling benzene remained unchanged; only the rate of reaction increased sharply. The product of this reaction was identified as mercurous chloroacetate. It became evident that the introduction of Cl sharply stabilizes the RCO_2 radical. The very same effect was demonstrated by a nitro-group on the stability of the $O_2NC_6H_4CO_2$ radical as compared with $C_6H_5CO_2$ radicals. A

Card 1/2

RAZUVAYEV, G. A.

7

Radical reactions of pentaphenylphosphorus. IV. Reaction of pentaphenylphosphorus with methyl iodide. Mechanism of radical reactions of pentaphenylphosphorus studied by means of diphenylpicrylhydrazine and diphenylpicrylhydrazyl. G. A. Razuvaev, N. A. Osanova, and I. A. Shlyapnikova (State Univ., Gorki). *Zhur. Obshchei Khim.* 27, 1400-9(1957); cf. *C.A.* 51, 1875b.—Ph_5P reacts with MeI by a radical route. Thus, 10 g. Ph_5P and 44 g. MeI after 20 hrs. at 90° in a sealed tube gave 0.1 ml. C_2H_6, 0.2 ml. CH_4, 0.19 g. Ph_2, 0.7 g. Ph_4PI, and C_6H_6, MePh, and PhI. The radical nature of the reaction was confirmed by variation of color of solns. of Ph_5P in C_6H_6, pyridine, MeOH, MeI, $CHCl_3$, or AcOH in the presence of 2,4,6-$(O_2N)_3C_6H_2NHNPh_2$ (Ia) (orange changing to the violet color of the free radical of 2,4,6-$(O_2N)_3C_6H_2NNPh_2$ (I) in the presence of free radical sources). The ionic nature of the reaction of Ph_5P with AcOH was confirmed by similar means. The reaction with $CHCl_3$ was followed colorimetrically and a kinetic curve is shown. The reaction in pyridine appears to proceed intramolecularly. I was prepd. as follows: 0.6 g. Ia in 9 ml. pure $CHCl_3$ was shaken with 7 g. PbO_2 and 0.5 g. dry Na_2SO_4 1 hr.; evapn. of the filtrate gave violet prisms of I. Ph_5P with C_6H_6 in the presence of Hg failed to fix any radicals on Hg. Free radical formation was found in reactions with alcs., MeI, C_6H_6, and $CHCl_3$, but none in pyridine. G. M. Kosolapoff

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Distr: 4E4j/4E3d/4E2c(j)

RAZUVAYEV, G.A.

79-11-39/56

AUTHORS: Etlis, V. S., Razuvayev, G. A.

TITLE: Synthesis and Properties of Some Derivatives of Thioxanthene-5-Dioxide, With Indicator Character (Polucheniye i svoystva nekotorykh proizvodnykh tioksanten - 5-dioksida, obladayushchikh indikatornymi svoystvami).

PERIODICAL: Zhurnal Obshchey Khimii, 1957, Nr 11, pp. 3092-3097 (USSR)

ABSTRACT: It was of interest to realize the synthesis of the otherwise little investigated derivatives of thioxanthene-5-dioxide with a good yield, by means of sulfonation of some aromatic compounds. At first diphenylamine was treated with 66% fuming sulfuric acid. After neutralization of the excese acid the alkaline solution took on an intensive orange yellow color. This fact incited the authors to investigate the nature of the coloring matter with indicator character produced in sulfonation. By the action of fuming sulfuric acid upon diphenylamine and its derivatives during strong cooling the oxidation of the methylene group and simultaneously the sulfonation in the position 4,4'takes place. A coloring product in a small quantity already forms on this occasion. When the resulting 4,4'-disulfonic acid

Card 1/2

Synthesis and Properties of Some Derivatives of Thioxanthene-5-Dioxide, With Indicator Character

79-11-39/56

of benzhydrol is treated with further quantities of fuming sulfuric acid at 150-160°C a coloring matter with high yield is obtained. 1,1-diphenylethane, triphenylmethane and 2,2 diphenylpropane were treated in the same manner. Coloring matters were also found in the first two compounds. On the basis of these tests it must be assumed that at least one hydrogen atom at the methylene group, where the oxidation takes place on sulfonation, is necessary for the formation of coloring matter (see formula). The following compounds were synthesized and their properties investigated: 3,7-dichlorothioxanthenol-5-dioxide and 3,7-dichloro-10-methylthioxanthenol-5-dioxide. The indicator properties of the derivatives of thioxanthenol-5-dioxide were determined and the structure of the coloring matter of these compounds was suggested. There are 2 figures, and 17 references, 2 of which are Slavic.

SUBMITTED: October 20, 1956

AVAILABLE: Library of Congress

Card 2/2 1. Thioxanthene-5-dioxide-Derivatives-Synthesis.

RAZUVAYEV, G. A.

Reaction kinetics of isopropyl alcohol with carbon tetrachloride initiated with benzoyl [illegible]oxide. V. A. Shushunov, G. A. Razuvaev, B. N. Moryganov, and M. K. Safonova (Inst. Chem., State Univ., Gorki). *Zhur. Fiz. Khim.* 31, 1203-9(1957).—The kinetic laws of Bz_2O_2 decompn. in a mixt. of iso-PrOH and CCl_4, and the reaction between iso-PrOH and CCl_4 initiated by Bz_2O_2 were studied by sealing 15 ml. of the mixts. of the reacting liquids in 20-ml. ampuls. After a predetd. time the mixt. was placed into a separatory funnel contg. H_2O, and the HCl in the water layer, and Bz_2O_2 in the upper layer, which consisted of a mixt. of org. substances, were detd. The reaction rate between iso-PrOH and CCl_4 was about 20 times as fast in the presence of 2.83×10^{-3} to 7×10^{-3} mol. Bz_2O_2/l. as in its absence, and the reaction rate of Bz_2O_2 decompn. was of the 1st order within these concn. limits. Bz_2O_2 in low concns. played no significant role in the reaction between the alc. and CCl_4. Me_2O, HCl, BzOH, CO_2, C_2Cl_6, and very small amts. of iso-PrOBz and trichlorotoluic acid were found in the reaction products. The av. chain length of the products formed (φ) was related to the initial Bz_2O_2 concn. (C_0) by the expression $\varphi\sqrt{C_0}$ = const. The initial Bz_2O_2 decompn., when present in a low concn. in the iso-PrOH-CCl_4 mixt., played no significant role in the formation of HCl. W. M. Sternberg

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Distr: 4E4j/4E3d

РАЗУВАЕВ, Г. А.

20-6-30/59

AUTHOR RAZUVAYEV, G.A., SOROKIN, YU A., DOMRACHEV, G.A., PETUKHOV, G.G., TSVETKOV, YU. D, MOLIN, YU.N.

TITLE On the structure of organochromic compounds. (O stroyenii khromorganicheskikh soyedineniy.- Russian)

PERIODICAL Doklady Akademii Nauk SSSR 1957, Vol 113, Nr 6, pp 1293-1294 (U.S.S.R.)

ABSTRACT In a paper recently published by Fischer the synthesis of neutral dibenzolchromium and its salts is described and a report is made concerning some further aromatic derivatives of the chromium-(0). This author assumes that the latter compound has an A-structure analogous to ferrocaen. Recently a series of reports was published in which the separation from the reaction products of C_6H_4MgBr and also of the dibenzolchromium with waterless chlorinechromium beside "pentaphenylchromhydroxide" and "tetra" as well as "triphenylchromiodides" is described by Hein. According to a bold, but not precisely proved assumption of Zeiss, the polyphenyl derivatives of chromium have a common bis-aren-structure. If it is assumed that in the chromium iodides (π-benzol, π-diphenyl) and di-(π-diphenyl)-chromium the diphenylgroups are covalently connected, 10 % of D should be expected in the diphenyl separated after the

CARD 1/3

On the structure of organochromic compounds. 20-6-30/59

reaction with $LiAlD_4$. If, however they have a B-structure (illustration 1) diphenyl would contain no deuterium. The composition and the yield of the organic products of the light dispersion of the organochromic compounds in the chloroform agree well with the B-structures. It is known that the compounds of the B-series are paramagnetic and have the magnetic moment = 1.7 of the Bohrs magneton. This corresponds to the existence of a not coupled electron in their molecule. Therefore, the photographing of the spectra of the paramagnetic electron-resonance of such compounds was interesting in order to obtain data about the localisation of the free electron. The absorption spectrum of the aqueous solution of one of these substances (III) is shown by illustration 2. The existence of a superfine structure and the qualitative analysis of the intensity distribution shows that the not coupled electron is in interaction with the hydrogen nuclei of the aromatic rings. (2 illustrations, 1 Slavic reference.)

ASSOCIATION: Scientific Research Institute for Chemistry at the Gorkij State University "N.I. LOBACHEVSKIY".
MOSCOW PHYSICAL'TECHNICAL INSTITUTE.
Institute for Chemical Physics of the Academy of Science of the U.S.S.R.

CARD 2/3

20-6-30/59

On the structure of organochromic compounds.

PRESENTED BY: N.N. SEMENOV, Member of the Academy.
SUBMITTED: 4.3. 1957
AVAILABLE: Library of Congress.

CARD 3/3

RAZUVAYEV G.A. 20-1-32/54

AUTHOR TSETKOV Yu.D., VOYEVODSKIY V.V., RAZUVAYEV G.A.,
SOROKIN Yu.V., DOMRACHEV G.A.

TITLE Electron Spin Resonance in Some Sandwich Type Chromaromatic Compounds.
(Elektronnyy paramagnitnyy rezonans v nekotorykh khromaromaticheskikh soyedineniyakh sandvichevogo stroyeniya -Russian)

PERIODICAL Doklady Akad.Nauk SSSR, 1957, Vol 115, Nr 1, pp 118- 121 (U.S.S.R.)

ABSTRACT In recent times increased interest was devoted to the study of the mentioned compounds of the ferrocene type, ($Fe(C_5H_5)2$), the ferrocene ion and analogous molecules with aromatic addenda. In spite of a great number of papers on this subject, there hitherto exists no general theory which might explain the present data on the "sandwich" structure of these molecules. Their formation and steadiness cannot be fully explained by the generally accepted conception of valence. The data obtained indicate that in the majority of compounds of this type the linage of addenda with the complex-forming atoms is of a covalent character. This is especially indicated by magnetic measurements. According to the latter these materials are either diamagnetic or they possess a magnetic momentum which correspond s to one, two or at most three non-paired electrons. The ion salts of these metals of such compounds by the method of electronic paramagnetic resonance (called EPR in the following) have hitherto been described in publications. The present paper gives measurements of the EPR spectra of the following compounds: $Cr(C_6H_6)_2J$ (I), $Cr(C_6H_5)2J$ (II) and $Cr(C_6H_5 - C_6H_5 - C_6H_5)_2OC_6H_5$ (III). The static magnetic susceptibility

Card 1/3

20-1-32/54

Electron Spin Resonance in Some Sandwich Type Chromaromatic Compounds.

of these materials corresponds to a single- non-coupled electron.The presence of a hydrogen-overrefined structure of the absorption line in solutions of the materials II and III can be explained in two ways. 1.The non-coupled electron and the positive charge of the complex are located on the chromium atom. The estimation made on the basis of this assumption shows that the density of the non-coupled 3d-electron on the positions of the hydrogen atoms of the aromatic rings is sufficient to effect an "overrefined" cleavage of the EPR spectrum.2.The non-coupled electron and the positive charge are located on the aromatic addenda of the complex.The overrefined structure is in this case due to the interaction of the non-paired π-electron of the aromatic ring with the hydrogen atoms of this ring.The extent of cleavage, the number of components and the ratio of their intensities are in this case dependent on the distribution of electron density on the addenda molecule.The following facts speak in favor of the first assumption: a) presence of the anisotropy of the g-factor in the materials I and II, b) the value of the g-factor is less than that of a free electron.The true picture of density distribution of the non-coupled electron is probably a superposition of the two extemum cases mentioned above.
(2 illustrations, 2 Slavic references.)

Card 2/3

20-1-32/54

Electron Spin Resonance in Some Sandwich Type Chromaromatic Compounds.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR, Gor'kovskiy gosudarstvennyy universitet

PRESENTED BY NESMEYANOV, A. N., Academician, April 19, 1957

SUBMITTED 13.4.1957

AVAILABLE Library of Congress

Card 3/3

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SOV/81-59-5-15249

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5.3700(B)

Translation from: Referativnyy zhurnal, Khimiya, 1959, Nr 5, p 167 (USSR)

AUTHORS: Razuvayev, G.A., Brilkina, T.G.

TITLE: An Investigation of Free-Radical Reactions of the M[BR_4] Complexes

PERIODICAL: Uch. zap. Gor'kovsk. un-ta, 1958, pp 169 - 173

ABSTRACT: It is shown that when Li[$B(C_6H_5)_4$]2LiBr (I) interacts with Hg in $CHCl_3$, C_6H_5HgCl is formed, which proves that the M[$B(C_6H_5)_4$]-type complex compounds are capable of reacting with Hg with the formation of only one free radical from the elementorganic anion. NH_4[$B(C_6H_5)_3C_{10}H_7$] (II) and K[$B(C_6H_5)_3C_{10}H_7$] (III), when reacting with Hg in $CHCl_3$ form α-dinaphthyl mercury, which, in addition to the absence of phenyl derivatives of mercury, points to the primary break of the naphthyl radicals from the complex anions studied. The thermal decomposition of II at 120 - 130°C causes the formation of naphthalene and triphenyl boron ammoniate, i.e., the mechanism of the thermal decomposition of the anion also takes place with the separation of one naphthyl radical from the

Card 1/2

80615

SOV/81-59-5-15249

An Investigation of Free-Radical Reactions of the $M[BR_4]$ Complexes

complex. II and III are obtained by their precipitation from the aqueous solution of $Li[B(C_6H_5)_3C_{10}H_7]$, which is synthesized similarly to I (G. Wittig and others. Liebigs Ann. Chem., 1949, Vol 563, p 110), with the addition of NH_4Cl or KCl, respectively.

V.A.

Card 2/2

66006

SOV/81-59-8-28424

5.3700(B)

Translation from: Referativnyy zhurnal. Khimiya, 1959, Nr 8, p 405 (USSR)

AUTHORS: Razuvayev, G.A., Ol'dekop, Yu.A.

TITLE: The Decarboxylizing Reaction of Organic Mercury Salts

PERIODICAL: Tr. po khimii i khim. tekhnolog., 1958, Nr 1, pp 178 - 181

ABSTRACT: The possibility has been studied of initiating a chain reaction of decarboxylizing mercury salts of organic acids with RCO_2· radicals formed in the thermal decomposition of peroxides or in the photolysis of mercury salts. In the heating of a solution of 0.047 mole of Hg acetate (I) in glacious CH_3COOH with 0.01 mole of μ-nitrobenzoyl peroxide (II) the separation of CO_2 and the formation of 0.032 mole of $CH_3HgOCOCH_3$ (III) was observed. The reaction proceeded in the following order: $(CH_3CO_2)_2Hg + O_2NC_6H_4COO\cdot \rightarrow$ $\rightarrow [(CH_3CO_2)_2HgO_2CC_6H_4NO_2] \rightarrow CH_3COOHgOCOC_6H_4NO_2 + CH_3CO_2\cdot \rightarrow CH_3HgOCOCH_3 +$ $+ CO_2 + CH_3CO_2\cdot$. II was taken for preventing the decarboxylizing of the R-COO· radicals, the stability of which increases along the series $R = CH_3$, C_6H_5, $NO_2C_6H_4$. The nitrobenzoate group in $CH_3COOHgOCOC_6H_4NO_2$ is not decarboxylized. In a C_6H_6 medium the same reaction proceeds with difficulty and the yield of III is ~7%. A 6-hour ultraviolet irradiation of a

Card 1/2

The Decarboxylizing Reaction of Organic Mercury Salts

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SOV/81-59-8-28424

boiling solution of 0.01 mole of $(C_6H_5COO)_2Hg$ (IV) in benzene causes a process which
leads to the formation of $(C_6H_5CO_2)_2Hg_2$, Hg, phenylmercury benzoate, diphenyl,
C_6H_5COOH and CO_2. During irradiation of IV the formation of $C_6H_5HgOCOC_6H_5$ is not
observed in boiling CH_3OH, $C_6H_5CO_2$· - radicals react only with CH_3OH according to the
equation: $IV + CH_3OH \rightarrow 2C_6H_5COOH + Hg + H_2CO$. An analogous photoreaction of IV in
a medium of boiling ethylcellosolve is conjugated with the partial decarboxylizing of
the $C_6H_5CO_2$·-radical (formation of C_6H_6).

4

O. Chernitsov

Card 2/2

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A006/A001

Translation from: Referativnyy zhurnal, Khimiya, 1960, No. 17, p. 63, # 68688

AUTHORS: Razuvayev, G.A., Bobinova, L.M., Etlis, V.S.

TITLE: Titanium Compounds as Catalysts of Olefin Polymerization. Information II

PERIODICAL: Tr. po khimii i khim. tekhnol. 1958, No. 3, pp. 659-663

TEXT: It is shown that the $TiCl_4 + Ti(iso\text{-}OC_3H_7)_4$ system is an effective catalyst for propylene polymerization, the molar ratio of $TiCl_4$ to $Ti(iso\text{-}OC_3H_7)_4$ being 3 - 6, and a liquid polymer is formed consisting of unsaturated hydrocarbons with a branched chain. The following titano-organic compounds are synthesized: $iso\text{-}C_3H_7OTiCl_3$; $sec\text{-}C_4H_9OTiCl_3$; $cyclo\text{-}C_6H_{11}OTiCl_3$. It is established that these compounds decompose rapidly during storage resulting in the formation of titanium oxychloride which is an active catalyst in the polymerization of olefins (propylene, isobutylene, styrene).

The authors' summary

Translator's note: This is the full translation of the original Russian abstract.

Card 1/1

X

SOV/81-59-8-27394

Translation from: Referativnyy zhurnal. Khimiya, 1959, Nr 8, p 213 (USSR)

AUTHORS: Razuvayev, G.A., Vasilsyskaya, N.S.

TITLE: The Reaction of Carbon Tetrachloride With Cyclohexanol

PERIODICAL: Uch. zap. Gor'kovsk. un-ta, 1958, Nr 32, pp 175 - 178

ABSTRACT: The heating of cyclohexanol (I) with an equal amount of CCl_4 in a sealed ampoule (30 - 35 hours at 200 - 210°C) is accompanied by dehydrogenation, leading to $CHCl_3$ and cyclohexanone. Simultaneously with the dehydrogenation the dehydration of I to cyclohexane takes place. As a result of secondary processes, cyclohexyl chloride and a mixture of dicyclohexyl chloride isomers are formed. The latter is polluted apparently by a small quantity of cyclohexenylcyclohexyl chloride.

L. Kheyfits

Card 1/1

AUTHORS: Razuvayev, G. A., Minsker, K. S. 79-28-4-30/60

TITLE: Polymeric Chlorovinylperoxide (Polimernaya perekis' khloristogo vinila)

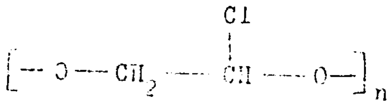
PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 4, pp. 983-991 (USSR)

ABSTRACT:

In the present paper the authors have separated the polymeric chlorovinylperoxide compounds and determined their structure. Moreover they have investigated their properties, their reactivity as well as their influence on the quality and properties of the polymer. Because of the instability of these compounds and because of the difficulty of obtaining a sufficient quantity (all operations were carried out with some dozens of milligrams separately produced for each experiment) it was not possible to separate the precipitated chlorovinylperoxide. It can be assumed that during the oxidation of the chlorovinyl the development of the polymeric peroxide takes place at the expense of the copolymerization process of the chlorovinyl with oxygen. The formula for the ideal 1 : 1 copolymer of the oxygen and of the chlorovinyl must be

Card 1/4

Polymeric Chlorovinylperoxide 79-28-4-30/60



$$\left[-O-CH_2-\overset{Cl}{\overset{|}{C}H}-O-\right]_n$$

It is easy to compute that in the weighed portion of the polyperoxide 33,86 % of oxygen and 37,59 % of chlorine must be contained. Ratio % O/% Cl = 0,903. As the polymeric chlorovinylperoxide was neither purified nor recrystallized, it can be assumed that the respective compound probably has a 1 : 1 structure with regular alternation of the bonds ($-CH_2CHClOO-$). The infrared spectrum of chlorovinylperoxide in the carbon tetrachloride solution showed an intense and wide adsorption band at 883 cm^{-1} of the indispensable O-O- bond, which is characterized for peroxide compounds, as well as a strong adsorption band at 1080 cm^{-1}, which can have developed because of the presence of -C-O-O- groups. The extraordinary mobility of the chlorine atoms in chlorovinylperoxide must be emphasized. During the hydrolysis chlorine already at low temperatures splits off from the polymeric molecule (Figure 1). Experiments with the inition of the polymerization of different monomers with polymeric chloro-

Card 2/4

79-28-4-30/60

Polymeric Chlorovinylperoxide

vinylperoxide have shown that they cause the polymerization of styrene, vinylidene chloride, chlorovinyl, butylacrylate and methacrylic acid. The facts that were obtained during the investigation of the properties of the polyvinylic chloride in the initiation by polymeric chlorovinylperoxide imply the presence of a peculiar block polymer. One part of the latter has a polyperoxide structure and the other has the structure of a real polymer. Thus during the polymerization of the chlorovinyl, the molecular oxygen has apart from an intense inhibiting effect also a negative effect on the quality of the developing polymer. This polymer has a lower decomposition temperature and a lower molecular weight than a polymer produced by ordinary initiators. The diminution of pH in the reaction medium during the suspended polymerization of the chlorovinyl can be conditioned by the presence of the molecular oxygen-owing to the hydrolysis of the polymeric peroxides, developing during the induction period.

Card 3/4

Polymeric Chlorovinylperoxide 79-28-4-30/60

The authors credit A.I. Finkel'shteyn with having made the spectroscopic analysis of the polymeric peroxide. There are 2 figures, 2 tables, and 23 references, 11 of which are Soviet.

SUBMITTED: December 15, 1957

Card 4/4

AUTHORS: Etlis, V. S., Razuvayev, G. A. 79-28-5-20/69

TITLE: Synthesis and Properties of Some Aryl Derivatives of Thioxanthenol-5-Dioxide Having Indicator Properties (Polucheniye i svoystva nekotorykh aril'nykh proizvodnykh tioksantenol-5-dioksida, obladayushchikh indikatornymi svoystvami)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 5, pp. 1225 - 1227 (USSR)

ABSTRACT: As was already reported by the authors (Reference 1) they obtained in the sulfonation of some aromatic compounds of the $Ar_2CH - R'$ -type (where R' = H, alkyl or aryl), on certain conditions, derivatives of thioxanthenol-5-dioxide, which have indicator properties. It was of interest to investigate the influence of various aryl substituents on the color of the compounds obtained in sulfonation as well as to investigate their applicability as indicators in acidimetric determinations. For this purpose the sulfonation process of 4-benzyl diphenyl, α-benzyl naphthalene and α,α'-dinaphthyl methane was investigated. This process was carried out with 25 - 40% oleum at high

Card 1/3

79-28-5-20/69

Synthesis and Properties of Some Aryl Derivatives of Thioxanthenol-5-Dioxide Having Indicator Properties

temperature. The final products were sulfoacids which have indicator properties similar to those described earlier (Reference 1). In neutral and acidous media these compounds remained colorless and only colored intensely on the addition of alkali. Also the color of the one or the other compound depends on the nature of the substituent, which can be seen from the absorption curves in the visible spectrum of alkaline solutions of the mentioned compounds in the picture. The synthetized compounds are easely oxidized by potassium permanganate and on this occasion lose their capability of changing the color in alkaline media. They can be used in the filtration as indicators. The absolute error in the titration of various organic compounds on the average amounts to ± 0,3%. Starting from their properties and from the analysis their structure can be given by the formulae (I - III). A simple synthesis of α,α'-dinaphthyl methane of naphthalene, and of the α,α"-dichlorodimethyl ether

Card 2/3

79-28-5-20/69

Synthesis and Properties of Some Aryl Derivatives of Thioxanthenol-5-Dioxide Having Indicator Properties

nitrobenzene in the presence of $AlCl_3$ were elaborated. There are 1 figure and 5 references, 3 of which are Soviet.

SUBMITTED: June 8, 1957

Card 3/3

AUTHORS: Razuvayev, G. A., Bobinova, L. M., Etlis, V. S. SOV/ 79-28-6-43/63

TITLE: Organozinc Compounds, Catalysts for the Polymerization of Propylene (Tsinkorganicheskiye soyedineniya-katalizatory polimerizatsii propilena)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6, pp. 1623 - 1626 (USSR)

ABSTRACT: The authors regarded it necessary to investigate the catalytic activity of organozinc compounds (diethyl-, dipropyl- and diphenyl zinc) for the polymerization of propylene. Diethylzinc with an addition of titanium chloride proved to be an active catalyst. In the presence of diethylzinc and tin tetrachloride (or sodium isopropylate) propylene does not polymerize. The influence of the reaction temperature on the polymerization of propylene, of the reaction duration, the composition of the catalyst (molar ratio between $Zn(C_2H_5)_2$ and $TiCl_4$ (furtheron denoted by C) and of the solvent were investigated. It was found that the best yield of polypropylene was obtained at 110-120° (Tab 1). After a longer duration of the polymerization (from 3 to 5 hours)

Card 1/3

the yield increased only little (Tab 1). The composition of the catalyst has a strong effect on the yield and the quality of the polymer. The best yield was obtained at the equimolecular ratio between $Zn(C_2H_5)_2$ and $TiCl_4$, however, in this case the polymer was obtained as an oil of varying viscosity. At C=3 a solid propylene was obtained (yield = 30%, melting point= 150-158°, molecular weight = 10000-18000). On a further increase of C its yield decreased considerably (Tab 2). Heptane and isooctane were used as solvents for the polymerization, the first mentioned supplying somewhat smaller yields (Tab 3). The substitution of zincdiethyl by zinc dipropyl and zincdiphenyl changed only little the activity of the catalyst in the polymerization of propylene. Thus the character of the radial exerts only little influence on the catalytic activity of the organozinc compound. The authors investigated the influence of the component molecular ratio on the yield and quality of the polymer in the case of the catalysts $Zn(C_3H_7)_2 + TiCl_4$ and $Zn(C_6H_5)_2 + TiCl_4$. There are 5 tables and

Organozinc Compounds, Catalysts for the Polymerization SOV/79-28-6-43/63
of Propylene

7 references, 4 of which are Soviet.

SUBMITTED: May 23, 1957

1. Propenes--Polymerization

Card 3/3

AUTHORS: Razuvayev, G. A., Latyayeva, V. N. SOV/79-28-8-48/66

TITLE: Reactions of the Acyl Peroxides With Metals (Reaktsii atsil'nykh perekisey s metallami)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 8, pp. 2233 - 2239 (USSR)

ABSTRACT: The authors were interested in investigating more closely the influence of different metals on the decomposition of symmetrical and unsymmetrical acyl peroxides in solutions. Special attention was paid to the reactions of the radioactive hydrogen atom which gives up its electron pair in alcohols. For this purpose decomposition reactions of benzoyl peroxide were carried out in methyl, ethyl, and isopropyl alcohols, and in chloroform, CCl_4 and C_6H_6 in the presence of metallic Na, Zn, Cu, Fe, Ni, Ag and Pt and at room temperature. A few reactions with phenacyl, phenacylbenzoyl, and p-nitrobenzoyl peroxide were also carried out. The experiments with benzoyl peroxide showed that in benzene and alcohol solutions and in the presence of Na (2% amalgam) and Zn, salts of benzoic acid form quantitatively, but no salts form from the mercury

Card 1/3

Reactions of the Acyl Peroxides With Metals SOV/79-28-8-48/66

in the sodium amalgam. In the presence of Ni and Fe in alcohol only some of the benzoyl radicals become anions. Free benzoic acid and aldehydes were found in the reaction products in addition to the salts. The mechanism of the described reaction are probably thus: in one case the peroxide accepts two electrons from the metal and forms benzoate anions: $(C_6H_5CO_2)_2+Zn \longrightarrow 2C_6H_5COO^-+Zn^{2+}$. In the other case the electron transfer occurs with the formation of a benzoate anion and a benzoyl-oxy radical (see the second reaction diagram). The latter reacts with the solvent, the alcohol. In the case of acetylbenzoyl peroxide similar results were obtained, i.e., acetate and benzoate in the presence of Na, Hg, and Zn reacted in benzene in the same manner as in the alcohol solution; in the presence of Ni, Cu, and Ag acetates of the metals and free benzoic acid were found. In chloro-organic solvents chlorides of the metals were observed to form initially. In the presence of platinum a hydrogenation of the peroxide with the alcohol hydrogen occurred. The table indicates the reactions of the acyl peroxides with the metals. There are 1 figure, 1 table, and 11 refer-

Card 2/3

ences, 7 of which are Soviet.

ASSOCIATION: Gor'kovskiy gosudarstvennyy universitet (**Gor'kiy State University**)

SUBMITTED: July 8, 1957

SOV/79-28-7-21/64

AUTHORS: Spasskaya, I. F., Etlis, V. S.,
Razuvayev, G. A.

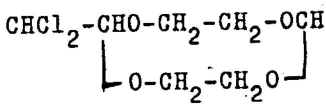
TITLE: The Chlorination of Ethylene Glycol (Khlorirovaniye etilenglikolya)

PERIODICAL: Zhurnal obshchey khimii, Vol 28, Nr 7,
pp 1827 - 1831 (USSR)

ABSTRACT: Contrary to the chlorination of monovalent alcohols only few publications are known on that of bivalent and especially of ethylene glycols. The authors were interested in a detailed investigation of this reaction. The chlorination of ethylene glycol takes place sufficiently rapid only in ultraviolet light at room temperature, with a great amount of heat being developed (maximum up to 127°) with a pronounced absorption of chlorine, and the initial weight increasing by 70 - 80%. The final product consists of 27% β-chloro-ethyldichloro acetate, of 15% of a cyclic acetal not described in papers (A), 12% H_2O, 11% of dichloro acetaldehyde, 11 % chloroethylene hydrine, 6% dichloromethyl-1,3-dioxolane and of an admixture of oxalic and dichloroacetic acids. The cyclic acetal corresponds to the formula

Card 1/3

The Chlorination of Ethylene Glycol SOV/79-28-7-21/64



$CHCl_2-CHO-CH_2-CH_2-OCHCHCl_2$, $O-CH_2-CH_2O$ (A).

This structure was proved by cleavage with concentrated hydrochloric acid under the formation of dichloro acetaldehyde and chloroethylene hydrine. The chlorination only with a previous addition of $SbCl_3$ yielded about the same composition of the mixture, however, without the acetal of the ethylene glycol and without the $CHCl_2CHO$. Prior to the separation of the mixture it had to be liberated from the disturbing hydrogen chloride. In order to explain the nature of the high-boiling products it was of interest to subject the main product of the ultraviolet treatment, the β-chloro-ethyl dichloro acetate, to the conversion with chlorine. The chlorination experiments in the ultraviolet range yielded α-, β-, β', β"-tetrachloro-ethyl ester of trichloro acetic acid. Thus, in the case of the above mentioned chlorination reaction in the ultraviolet range, or with a catalyst, the oxidation and chlorination processes, i. e., the formation of ester and acetal, take place at the same time.

Card 2/3

The Chlorination of Ethylene Glycol SOV/79-28-7-21/64

There are 1 table and 10 references, 1 of which is Soviet.

SUBMITTED: May 31, 1957

1. Ethylene glycol--Chlorination 2. Ultraviolet waves--Chemical effects

Card 3/3

AUTHORS: Spasskaya, I. F., Etlis, V. S., Razuvayev, G. A. SOV/79-28-11-22/55

TITLE: Chlorination of Olefin Chlorohydrins (Khlorirovaniye khlorgidrinov olefinov)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 11, pp 3004 - 3008 (USSR)

ABSTRACT: The reaction of chlorine with olefin chlorohydrins is little investigated. There are no reports on the chlorination of the propylene chlorohydrin. The aim of this paper was the chlorination of the ethylene and propylene chlorohydrin. The chlorination of ethylene chlorohydrin was carried out under ultraviolet irradiation at $30-40^{0}$, $60-70^{0}$, $90-100^{0}$: At $30-40^{0}$ in the presence of 1% water, at $50-60^{0}$ in the presence of marble, and at $70-80^{0}$ in the presence of 0.5% acetyl cyclohexane sulfonyl peroxide. The compounds (I), (II), (III), (IV), and (V) were separated from the products of the chlorination. The data on the composition of the formed mixtures are mentioned in table 1. As the β-chloro-ethyl dichloro

Card 1/2

Chlorination of Olefin Chlorohydrins SOV/79-28-11-22/55

acetate was found in all experiments in the company of dichloro acetaldehyde of dichloro acetyl chloride, it must be assumed that on the action of chlorine on (I)an oxidation and chlorination take place easily, accompanied by secondary formations of the acetal and ether. The free chloro acetaldehyde could not be separated, its formation is, however, beyond any doubt, due to the acetal (V) separated in most experiments. Thus, the reaction of chlorine with ethylene hydrin could be explained by means of the reactions mentioned in the scheme. In the chlorination of propylene chlorohydrin under ultraviolet irradiation at 30-100° a mixture of chlorine ketones is formed, from which the 1,1,3-trichloro acetone is separated - and was also identified as such. There are 2 tables and 12 references, 4 of which are Soviet.

SUBMITTED: September 30, 1957

Card 2/2

AUTHORS: Razuvayev, G. A., Petukhov, G. G., Artem'yev, A. G. 20-118-5-31/59

TITLE: Reactions of the Exchange of Radicals in Presence of $AlCl_3$
(Reaktsii obmena radikalov v prisutstvii $AlCl_3$)

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 118, Nr 5, pp. 960-963 (USSR)

ABSTRACT: The authors proved that the exchange of radicals of organo-metallic compounds with the "solvent" takes place in reactions of the radical as well as in ionic reactions (reference 1). In the present paper the authors wanted to examine the possibility of the progress of the exchange of cations $R^+ + R^{*}D \rightleftarrows R^{*+} + RD$ (1), by using deuterium-containing "solvents" and $AlCl_3$. The use of this last catalyst was chiefly investigated in reactions of one acid type (reference 3). Exchange reactions which take place with the participation of carbonium ions were investigated by means of deuterium in reactions between aliphatic hydrocarbons and H_2SO_4 (references 4, 5). For the investigation

Card 1/4

Reactions of the Exchange of Radicals in Presence of $AlCl_3$ 20-118-5-31/59

of the exchange of cations haloid and aromatic hydrocarbons were used. The chosen substances show as exchange systems a double interaction with $AlCl_3$: the haloid compounds show carbonium ions in presence of $AlCl_3$, as is well known (references 6, 7). Here the exchange can take place according to the equation (1). Aromatic hydrocarbons form a π-complex with $AlCl_3$ in which they are subjected to a strong protonization (reference 8). The exchange can take place according to the reaction of the acid type. Table 1 shows that chlorobenzene-deuteriobenzene as well as cyclohexyl-deuteriocyclohexanechloride carry through the exchange in presence of $AlCl_3$ until the state of equilibrium. The exchange takes place in these systems according to the equation (1) with the participation of the phenylcarbo-cation and the cyclohexylcarbo-cation. It is possible that the deuterolysis of the deuteriobenzene favors the reaction of the hydrogen exchange. This condition, however, is not necessary. Contrary to these systems the hydrogen exchange between toluene and deuteriobenzene (table 1, experiments number 1o, 11) only takes place according to the equation (2) (acid type). The particles that take part in the exchange

Card 2/4

are a proton and a deuteron. The exchange process can also be represented as a reaction of electrophilic substitution. By 2 isotopic markings (deuteriotoluene and radiobenzene 1-6 C^{14}) it was proved that besides the exchange of hydrogen there is also an intramolecular migration of the CH_3 group of toluene towards the benzene nucleus. There is practically no exchange between deuteriobenzene and cyclohexane and between cyclohexane and deuteriocyclohexane (table 1, experiments number 12-15). This partly confirms the correctness of the conclusions drawn above. There is no exchange of hydrogen if one of the components forms no π-complex with $AlCl_3$ (cyclohexane) or if the formation of such a complex is not accompanied by a protonization. In chloronitrobenzene and bromoanisole the influence of the substituents on the exchange was to be investigated. In spite of the expectations it was proved here that only a limited exchange occurs between p-chloronitrobenzene and deuterionitrobenzene, and between o-bromoanisole and deuterioanisole (table 1, experiments 6-9). These results do not quite agree with the fact as stated above that the radicals located at the oxygen

Reactions of the Exchange of Radicals in Presence of $AlCl_3$ 20-118-5-31/59

atom are stable (reference 11). Finally the experimental methodology is given. The results of the analysis are included in the tables 1 and 2. There are 2 tables and 11 references, all of which are Soviet.

ASSOCIATION:	Gor'kovskiy gosudarstvennyy universitet (Gor'kiy State University)
PRESENTED:	October 23, 1957, by V. N. Kondrat'yev, Member, Academy of Sciences USSR
SUBMITTED:	July 17, 1957

Card 4/4

AUTHORS: Razuvayev, G. A., Corresponding Member, Academy of Sciences, USSR, Bobinova, L. M., Etlis, V. S.

SOV/20-122-4-22/57

TITLE: Production and Properties of Several Trichloro-Titane-Alkoxy Compounds With Secondary and Tertiary Alkyl Groups (Polucheniye i svoystva nekotorykh trikhlortitanalkoksi-soyedineniy s vtorichnymi i tretichnymi alkil'nymi gruppami)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 4, pp 618 - 620 (USSR)

ABSTRACT: Some authors believe the titane organic compounds to be the initiators of the polymerization of the olefines; therefore, they have been carefully considered recently as possible intermediate products of the reaction of trialkylaluminum with titane tetrachloride (Refs 1 - 3). In the present paper some titane compounds of the type $TiCl_3OR$ were synthetized and investigated. In this connection R denotes the secondary or tertiary group. Since in the synthesis, according to reference 6 an insufficient pure compound was obtained, the authors used isopropyl alcohol and an excess of $TiCl_4$ in a petroleum ether solution (boiling point 60 -

Card 1/4

Production and Properties of Several Trichloro-Titane-Alkoxy Compounds With Secondary and Tertiary Alkyl Groups

SOV/20-122-4-22/57

70^{0}) for the synthesis of i-$C_3H_7OTiCl_3$ at approximately 0^{0}. Crystals of the pure titane-trichloro-isopropylate were precipitated from the filtrate after a part of the solvent had been distilled off and cooled down. Secondary $C_4H_9OTiCl_3$ and $C_6H_{11}OTiCl_3$ (hitherto not described) were produced in a similar way, but by distilling off under vacuum in order to reduce the decomposition of the said compounds (Table 1). The latter are, however, unstable in contrast to similar compounds with primary groups. In the case of decomposition, gaseous products escape and titane oxychloride is produced. The following compounds were furthermore identified in the case of isolation of liquid products under vacuum: hydrogen chloride, alkylchloride, i-C_3H_7Cl from the secondary $C_4H_9OTiCl_3$ and $C_6H_{11}OTiCl_3$. Furthermore, polymerization products of the olefines were closely adsorbed on the surface of the oxychloride. Table 2 shows a balance of this decomposition. Table 3 gives the physical-chemical properties of the decomposition products. From the isolated products it may be assumed that the

Card 2/4

Production and Properties of Several Trichloro-Titane-Alkoxy Compounds With Secondary and Tertiary Alkyl Groups

SOV/20-122-4-22/57

primary decomposition process of the mentioned compounds is the formation of the titane oxychloride and of the radicals. The latter might then yield one olefine and HCl or an alkylchloride. Finally the authors were able to prove that the titane oxychloride effectively catalyzes the reaction of the hydrochlorination of propylene, isobutylene, and cyclohexene. Alkylchlorides with good yields are formed in this case. No inverse reaction (dehydrochlorination of alkylchlorides) takes place in the case of decomposition of the titane organic initial compounds. On the strength of the above-mentioned results a decomposition scheme is suggested. Further ranges of application are finally given along with exemplifications. There are 3 tables, and 7 references, 2 of which are Soviet.

SUBMITTED: June 17, 1958

Card 3/4

Production and Properties of Several Trichloro-Titane-Alkoxy Compounds With Secondary and Tertiary Alkyl Groups

SOV/20-122-4-22/57

Card 4/4