G-OL DFARB

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Inst. Organic
Chem. im.
N. D. Zelinskogo
ASUSSR

Synthesis and transformations of some di-2-thienylmethane derivatives. Ya. L. Gol'dfarb and M. L. Kirmalova CH (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1955, 570-3; *Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci.* 1955, 509-11(Engl. translation).—5-(2-Hydroxyethyl)-2-thenylthiophene (3.5 g.) in Et_2O treated at -5° with 0.03 mole BuLi in Et_2O, then with Dry Ice in Et_2O and H_2O, and the aq. layer acidified gave 32% *5-(2-hydroxyethyl)-2-(5-carboxy-2-thenyl)thiophene*, m. 110.5-11° (from 50% EtOH), while the org. layer gave 48% starting material. The acid heated with Raney Ni in aq. Na_2CO_3 1.5 hrs. at 90° gave 94% $HO(CH_2)_{11}CO_2H$, m. 83-3.5° (from EtOAc-petr. ether). Di-2-thienylmethane (1.8 g.), 3 g. $MeO_2CCH_2CH_2COCl$, and 20 ml. C_6H_6 at 0° treated with 5.2 g. $SnCl_4$ in C_6H_6 and, after 4 hrs. at room temp., with aq. HCl, steam distd. and thoroughly extd. with hot H_2O yielded 47.5% CH_2R_2 [*R = 5-(3-carboxy-1-oxopropyl)-2-thienyl*] (I), m. 205-7° (from EtOH), which, refluxed with 100% $N_2H_4.H_2O$ in $O(CH_2CH_2OH)_2$ 15 min., treated with KOH, and refluxed 1.5 hrs. gave 70% $CH_2R'_2$ [*R' = 5-(3-carboxypropyl)-2-thienyl*], m. 119-19.7° (from H_2O); this with Raney Ni as above gave a low yield of $(CH_2)_{11}(CO_2H)_2$, m. 118-18.7°.

G. M. Kosolapoff

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GOL'DFARB, Ya.L., professor.

Recognition of common organic solvents. Khim. v shkole 10 no.1:44-50 Ja-F '55. (MLRA 8:4)
(Solvents)

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R000515620019-2"

Gol'dfarb, Ya. L.

G

CH

Action of ethylene oxide on 2-aminopyridine and on N-alkyl-2-pyridonimines. Ya. L. Gol'dfarb and M. A. Pryanishnikova (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Zhur. Obshchei Khim.* 25, 1003–11(1955).—Keeping 26.7 g. 2-aminopyridine in 15 ml. dry MeOH with 13 g. ethylene oxide 4 days gave 30% *N-(2-hydroxyethyl)-2-pyridonimine*, b_1 168–70° (crude), m. 127–8° (from EtOH); *HCl salt*, m. 146–7.5°. No reaction took place in dioxane, but in aq. dioxane the yield of the hydroxyethyl deriv. reached 25% in 2.5 days. A very low yield of this was formed in dry Me_2CO. Mixing 5.5 g. *N*-methyl-2-pyridonimine (I) with 2.7 g. CH_2:CHCN and, after subsidence of initial reaction, heating the mixt. in sealed tube 3 hrs. at 100° gave 3.7 g. *N-methyl-2-pyridone (2-cyanoethyl)imide*, b_1 169–70°, which solidified on standing; this rapidly absorbed CO_2 and H_2O from the atm. Heating 9.8 g. BzH with 10 g. I in 21.2 g. dry HCO_2H 6 hrs. to 150° and finally to 170° gave 4.4 g. *N-methyl-2-pyridone benzylimide*, b_1 194–5°; *picrate*, m. 123.5°. Heating 10 g. *N*-(2-hydroxyethyl)-2-pyridonimine with 7.7 g. BzH and 16 g. dry HCO_2H 10 hrs. gave 0.4 g. starting material and 3 g. *N-(2-hydroxyethyl)-2-pyridone benzylimine* (II), b_1 [illegible]; *picrate*, m. 115–15.5° (from EtOH). Heating *N*-(2-hydroxyethyl)-2-pyridonimine with $PhCH_2Cl$ in EtOH at room temp. gave HCl salt of II. Ethylene oxide and *N*-benzyl-2-pyridonimine in MeOH gave in several days at room temp. about 60% *N-benzyl-2-pyridone (2-hydroxyethyl)imide*, b_1 18[illegible]–90° (crude); *HCl salt*, m. 169–72°; *picrate*, m. 171.5–3.5°. Similar reaction of I gave in 4 days some 25% *N-methyl-2-pyridone (2-hydroxyethyl)imide*, b_1 145–6.5°; *picrate*, m. 110–10[illegible]; *HCl salt*, m. 147–9°. Almost no reaction occurred in dry dioxane, while in moist dioxane a fair yield of the above product formed. Hydrolysis of the product with 25% NaOH 4 hrs. gave *N*-methyl-2-pyridone and $HOCH_2CH_2NH_2$. Fractionation of higher fractions of the reaction products of 2-aminopyridine with ethylene oxide gave a low yield of *N-(2-hydroxyethyl)-2-pyridone (2-hydroxyethyl)imide*, m. 71–2°; *HCl salt*, m. [illegible]; *picrate*, m. 119–20.5°. This formed from the action of ethylene oxide on *N*-(2-hydroxyethyl)-2-pyridonimine in moist Me_2CO in 1 month at room temp.; the yield was about 10%, the product being isolated by distn., $b_{0.5}$ 170–82°. Hydrolysis of this material with 10% NaOH gave after 5 hrs. $HOCH_2CH_2NH_2$ and *N*-(2-hydroxyethyl)-2-pyridone.

G. M. Kosolapoff

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APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R000515620019-2

Gol'dfarb, Ya. L.

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CH

Synthesis and transformations of some derivatives of di-2-thienylmethane. Ya. L. Gol'dfarb and M. L. Kirmalova (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Zhur. Obshchei Khim.* 25, [illegible] (1955); *J. Gen. Chem. U.S.S.R.* 25, 1331-4 (1955) (Engl. translation); cf. preceding abstr.—Di-2-thienylmethane (I) (5.4 g.) in Et_2O treated at −5° with 0.03 mole BuLi in Et_2O, stirred 20 min., then treated with 0.05 mole ethylene oxide, and the resulting ppt. decompd. with EtOH and acidified H_2O yielded 13.1% *bis[5-(2-hydroxyethyl)-2-thienyl]methane* (II), m. 59-1° (*bis(phenylurethan)*, m. 140.5-1°), and 73.6% *5-(2-hydroxyethyl)di-2-thienylmethane*, b_1 158-60° (*phenylurethan*, m. 73.5-4°); 2 equivs. BuLi gave 77% and 12.5%, resp., of these products. Hydrogenolysis by refluxing in EtOH with Raney Ni gave 81% *$HO(CH_2)_{11}OH$*, m. 76°, and 76% *undecyl alc.*, b_5 118-21°, resp. Carbonation of the Li deriv. of I gave *5-carboxydi-2-thienylmethane*, m. [illegible]-3°, hydrogenolyzed with Raney Ni to [illegible] acid; [illegible] I gave a *mixt.* [illegible] and on reduction some [illegible] 185-95°. Thiophene with 1 mole BuLi and ethylene oxide as above gave 78% 2-(2-hydroxyethyl)thiophene (III), [illegible] 102°, n_D^{20} 1.5416 (*phenylurethan*, [illegible]) [illegible] of *2,5-bis(2-hydroxyethyl)thiophene*, [illegible] (*bis(phenyl-urethan)*), m. 151.5-5°. III [illegible] treated at [illegible] with [illegible] g. cooled H_2SO_4 and 25 ml. H_2O, [illegible] formalin, and shaken 5 [illegible] which, washed and taken up [illegible] yielded [illegible] product of an oil, b_1 255°, solidifying on standing; the phenylurethan, m. 140.5°, formed from the [illegible], was identical with that formed from II [illegible] G. M. Kosolapoff

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GOL'DFARB, YA. L.

USSR/ Chemistry - Organic Chemistry

Card 1/1 Pub. 22 - 16/54

Authors : Gol'dfarb, Ya. L., and Fabrichnyy, B. P.

Title : Synthesis of aliphatic amino-acids from thiophene derivatives

Periodical : Dok. AN SSSR 100/3, 461-464, Jan 21, 1955

Abstract : Experimental data are presented regarding the synthesis of alpha-amino acid with a normal carbon atom chain from thiophene derivatives. It was found that by applying a certain principle of cleaving the bifunctional thiophene derivatives it would be possible to obtain also other amino-acids with branched chain and other arrangements of the carboxyl and amino groups. Eight references: 4 USA, 1 French, 2 German and 1 USSR (1886-1954).

Institution : Academy of Sciences USSR, The N. D. Zelinskiy Institute of Organic Chemistry

Presented by: Academician B. A. Kazanskiy, September 10, 1954

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APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R000515620019-2"

Gol'dfarb, Ya. L.

HUNGARY / General Problems - Methodology. History. Scientific Institutions and Conferences. Teaching. Problems of Bibliography and Scientific Documentation. -1

Abs Jour : Referat Zhur - Khimiya, No 6, 25 March 1957, 18078

Author : Gol'dfarb Ya. L. and Smorgonskiy, L. M.
Inst : --
Title : Problems and Exercises in Chemistry. For Middle School. 3rd Edition.

Orig Pub : Kiiv Uzh [illegible] d "Radyans'ka Shkola", 1956, [illegible], 2 rubles.

Abstract : No abstract.

Card 1/1

GOL'DFARB, Ya. L.

APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R000515620019-2

Destructive hydrogenation of 2-methylthiophene at high hydrogen pressure. N. G. [illegible], V. V. [illegible] and Ya. L. Gol'dfarb (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1956, 207-9; *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1956, 210-12 (Engl. translation). —Hydrogenation of 2-methylthiophene (I) 4 hrs. at 300°, 1070 atm. H (for method cf. *C.A.* 40, 8155) gave [illegible]% of the original S as gases, mainly H_2S. Fractionation of the liquid material gave some pentane, no thiophene or tetrahydrothiophene, and an appreciable amt. of 2-methyltetrahydrothiophene. At a slightly lower pressure, there were isolated pentane and mixed compds. contg. S; these were not identified. The above reactions were run at 400°, indicating that destructive hydrogenation of I occurs more readily than that of MePh. G. M. Kosolapoff

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GOLDFARB-Y.L.

3 chem

708

✓A study of the hydrogen bond in α-aminonicotine by the method of comparison of infrared absorption spectra. Ya. L. Gol'dfarb, M. S. Kondakova, and L. S. Shiraein (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1956, 336-9; cf. C.A. 45, 15034.—The presence of H bond of intramol. type was shown in α-aminonicotine by the infrared band in the cryst. solid at 3325 cm.$^{-1}$, while in CCl_4 soln. this is 3290 cm.$^{-1}$ The bond is ruptured or disturbed by the addn. of HX or MeI. The HCl salts of α-aminonicotine and α'-aminonicotine have similar spectra. The hydrogen bond exists between the 2 N atoms and must lie in the plane of pyrrolidine and pyridine rings. G. M. K.

Inst. Organic Chem.
im. N.D. Zelinskogo
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L. Ya. Karpova

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Gol'dfarb, Ya. L.

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Individual composition of compounds of thiophene series contained in the gaseous products of thermal decomposition of Kashpirsk shales. Ya. L. Gol'dfarb, G. I. Gorushkina, and B. P. Fedorov (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1956, 340-51; *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1956, 327-35 (Engl. translation).—The main part of the light fraction of the Kashpirsk gasoline is composed of C_6H_6, MePh, *m*-xylene, thiophene, 2-methylthiophene, 2,5-dimethylthiophene, and 2-methyl-5-ethylthiophene. The sepns. were performed by fractionation and chromatography on SiO_2. Thiophene was isolated by treatment of the appropriate fraction with AcCl and $SnCl_4$ yielding 2-acetylthiophene. 2-Methylthiophene was identified as the 5-acetyl deriv. by treatment of appropriate fraction with Ac_2O and H_3PO_4 (d. 1.02) 3 hrs. at 100-10°. Dimethylthiophene was isolated as the 3-acetyl deriv. (obtained by treatment with AcCl-$SnCl_4$), while the 2-methyl-5-ethylthiophene was isolated as the mercuric acetate deriv., decompg. 249-50°, which was duplicated from authentic 2-methyl-5-ethylthiophene prepd. by reduction of 2-methyl-5-acetylthiophene with $N_2H_4.H_2O$ in $(CH_2OH)_2$ followed by heating the hydrazone with KOH to 1[illegible]; this with $Hg(OAc)_2$ in 67% AcOH gave *3,4-bis(acetoxymercuri)-2-methyl-5-ethylthiophene*, fusing with darkening 249-50°. Treatment of 12.6 g. 2-methyl-5-ethylthiophene with 36.7 g. Br in CS_2 over 1.5 hrs. gave 44.5% *3,4-dibromo-2-methyl-5-ethylthiophene*, $b_{1.5}$ 110-11°, n_D^{20} 1.[illegible]; this with 30% H_2O_2 gave *3,4-dibromo-2-methyl-5-ethylthiophene sulfone*, m. 81-2° (from MeOH); the same derivs. were similarly formed from the appropriate fraction of the gasoline.

G. M. Kosolapoff

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GOL'dFARB, YA. L.

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Chem

Chloromethylation of 2,5-dimethylthiophene. [illegible] Gol'dfarb and M. S. Kondakova (N. D. Zelinskii [illegible] Org. Chem., Moscow). [illegible] Otd. Khim. Nauk 1956, [illegible]-503.—Passage of a rapid stream of HCl into 10 g. 2,5-dimethylthiophene (I), 60 ml. concd. HCl, and 14 ml. 37% formalin with ice-cooling 1 hr. gave after extn. with C_6H_6 [illegible] g. 2,5-dimethyl-3-thenyl chloride (II), b_{10} 90-118°, 3.4 g. 3,4-bis(chloromethyl) deriv. (III) of I, b_4 138-45°, m. 67-8° (from benzene), and a small amt. of $C_{14}H_{18}Cl_2S_2$, m. 172-3°, identical with the product of chloromethylation of bis(2,5-dimethyl-3-thienyl)methane. II with NaOAc and AcOH in 4 hrs. at 60° gave the corresponding acetate, b_8 126-8°, n_D^{20} 1.5135, which kept 2 days in abs. EtOH contg. a little Na gave 2.1 g. of the corresponding alc., b_8 112-13°, n_D^{20} 1.5433 (phenylurethan, m. 70-0.5°). Paraformaldehyde (15 g.) and 150 ml. concd. HCl were satd. with HCl, after which 27.5 g. I was added maintaining the HCl stream; after 1.5 hrs. the mixt. was dild. with ice and extd. with C_6H_6 yielding 14.9 g. III, b_4 [illegible]-42°, m. 5-8.5°; this reacts with $AgNO_3$ yielding AgCl. Hydrolysis of the acetoxy deriv. formed with NaOAc gave the [illegible]hydroxymethyl analog, which shaken with HCl readily reverted to III. I (10 g.) in 11.4 g. $ClCH_2OCH_3$ and 30 ml. AcOH was kept 0.5 hr. at 0°, then 3 hrs. at 23°, yielding after aq. treatment 7.5 g. material, b_4 90-100°, and a little material, m. 66.5-7.0°. Keeping 4.6 g. II, 4 g. I, 35 ml. CS_2, and 0.3 g. $AlCl_3$ 4 hrs. with stirring, followed by standing overnight gave a substance, m. 74-5°, identical with that formed from condensation of I with II in the presence of $AlCl_3$. To ice-cooled 2 g. I and 1.65 g. 3-hydroxymethyl

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Gol'dfarb, Ya.L., + Kondakova, M.S.

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deriv. of I was added 30 ml. 1:1 AcOH-concd. H_2SO_4; after 2 days at room temp. there was isolated 0.3 g. substance, m. 170-3°, identical with the above. A small amt. of product, m. 48°, was also isolated; this was identical with the condensation product of I with II. To 6.1 g. I and 7.3 g. II in CS_2 was added 0.2 g. $AlCl_3$, stirred 3 hrs., treated with 0.3 g. $AlCl_3$, kept overnight, heated 0.5 hr. at 40-50° and treated with ice, gave 2.8 g. product, m. 160-8°, b. 191-207°, which after distn., m. 174-5°, and was identified as *2,5-dimethyl-3,4-bis(2,5-dimethyl-3-thenyl)thiophene*, [illegible]; in addn. there was formed 3.4 g. product, b. 180°, m. 4[illegible]-5.5°, $C_{13}H_{16}S_2$, *bis(2,5-dimethyl-3-thienyl)methane*. To 11.[illegible] g. I,

5 g. concd. HCl and 10 g. $ZnCl_2$ with ice cooling was added during 15 min. 4.5 g. 37% formalin; after stirring 40 min. the mixt. was heated 3 hrs. to 60°; usual treatment gave 3.1 g. substance, m. 170-2.5°, b. 205-15°, identical with the dimer described above; the mother liquor gave 3.8 g. $C_{13}H_{16}S_2$, b. 134-5°, m. 48°, identical with the product of condensation of I with II. To 5.6 g. I and 11 g. $PhCH_2OH$ in 10 ml. AcOH was added with ice-cooling 25 g. AcOH and 25 g. concd. H_2SO_4; after 3 days at room temp. the mixt. gave a series of fractions from which was isolated 2.1 g. product, m. 68-9°, identified as *2,5-dimethyl-3,4-dibenzylthiophene*. This was readily obtained in 3 g. yield (1.9 g. pure) when 5 g. III in C_6H_6 was treated with 0.2 g. $AlCl_3$, followed by 10 ml. C_6H_6 and kept several hrs. at room temp. Into 14 ml. 38% formalin and 45 ml. concd. HCl was passed a strong stream of HCl, followed by 10 g. 2,5-diethylthiophene added at 30°; after 2 hrs., the usual treatment gave 10.9 g. crude or 8 g. pure *3,4-bis(chloromethyl)-2,5-diethylthiophene*, m. 63-4°, b. 138-48°. Into 40 g. 37 formalin and 20 ml. concd. HCl and

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Gol'dfarb, Ya. L. & Kondakova, M. S.

100 ml. AcOH was passed HCl, after which [illegible] the mixt. was treated over 1 hr. with 25.[illegible] g. 2,5-di-tert-butylthiophene at 0–5°; after 1 hr. at 10–[illegible]°, 1 hr. at room temp., and cooling, the mixt. was treated with ice, yielding [illegible] *bis(chloromethyl)-2,5-di-tert-butylthiophene*, m. 66–6.5° (from AcOH), which was the only pure substance isolated. Into 50 g. $SnCl_4$ in 100 ml. AcOH was passed HCl until [illegible] formed; this was filtered and treated gradually with 10 g. III; on the following day the mixt. was treated with H_2O, yielding 4.4 g. [illegible], b. [illegible] 70–8°, n[illegible] 1.520[illegible]. The substance, m. 47–8°, obtained from chloromethylation of [illegible] with formalin-HCl-$ZnCl_2$ (3 g.) was taken up in 40 ml. AcOH, treated with cooling with 8 g. [illegible](CH_2)[illegible], heated 2 hrs. at 80° and cooled, yielding 4 g. compd., [illegible], m. 7[illegible]–8° (from heptane). [illegible], m. 68–3[illegible], was reduced with $N_2H_4.H_2O$ in diethylene glycol in the presence of KOH 3 hrs. at 195°, yielding a substance, m. 47.5°, b. 172°, identical with the above described. *2,5-Di-tert-butylthiophene-3-carboxylic acid*, m. 1[illegible]17°; its acyl chloride, m. 103–5°, was used for [illegible] of the above ketone, m. 49.5–50°. The consts. of these substances do not agree with those reported by Buu-Hoï, *et al.* (C.A. 43, 4668d). The product, m. 73°, of chloromethylation of I described by Buu-Hoï, *et al.* (*loc. cit.*), could not be obtained by the present authors. G. M. Kosolapoff

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GOLDFARB, A.C.

Sulfonation of tri-butyl derivatives of thiophene. Ya. L. Gol'dfarb, I. V. Antik, and P. A. Konstantinov (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1956 [illegible] — Sulfonation of [illegible] [illegible] [illegible] but not from 2- [illegible] [illegible] probably [illegible] although [illegible] is not [illegible] [illegible] and [illegible] pyridine [illegible] in [illegible] 14 hrs. followed by treatment with 20 ml. H_2O gave [illegible] of a pyridine complex which was decomposed [illegible]

98 g [illegible] in 900 ml. [illegible] was added at [illegible] in 1.5 hrs. [illegible]

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[illegible]

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USSR/Organic Chemistry. Synthetic Organic Chemistry.

Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19183

Author : Gol'dfarb Y. L., Kirmalova M. L.
Inst : ---------
Title : About Di-2- thienylcarbinole.

Orig Pub: Izv. AN SSSR, Otd. Khim. N., 1956, No 6, 745-747

Abstract: Di-2-(thienyl)-carbinol (I) and its ether $[(C_4H_3S)_2\,CH]_2O$ (II) is synthesized. To 5.6 g. thiophenylaldehyde-2 (III) in 10 cc anhydrous ether is added while stirring at (0°) a solution of 2-thienylmagnesiumbromide (IV) (from 8.2 g. of 2-bromothiophene and 1.2g. Mg), in ether, the precipitate is decomposed with 14 cc dil. HCl (1:1), and from the ether solution is obtained 1.4 g. II, m.p. 81.5-82.5° (from ligroin and alcohol). To the solution IV(from 12.6 g. 2-bromothiophene and 1.9 g. Mg) in ether is added 8.4 g. III in 20 cc ether (~0°, N_2), left standing for 20

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Gol'dfarb, Ya. L.

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Synthesis of alcohols of aliphatic series from [illegible] **and its homologs.** Ya. L. Gol'dfarb and [illegible] Acad. Sci. [illegible] nov (N. D. Zelinskii [illegible] Acad. Sci. [illegible] Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1956, 862-9.—To 41.0 g. PhNMeCHO and 40.5 g. $POCl_3$ at 25° was added 42 g. 2-butylthiophene at 25-35° and the mixt. stirred 3 hrs.; on the following day it was treated with ice and extd. with Et_2O yielding 80% *5-butyl-2-thiophenecarboxaldehyde*, b_{13} 143-6°, n_D^{20} 1.5490, d_{20} 1.0667; *oxime*, m. [illegible] To 30.4 g. 5-methyl-2-thiophenecarbonyl chloride in [illegible] g. thiophene and 20 ml. C_6H_6 was added at 0° 21.4 ml. $SnCl_4$ and after stirring 1 hr. at room temp. the mixt. was treated with 10% HCl yielding 83% *5-methyl-2,2'-dithienyl ketone* (I), b_4 185-6°, m. 48.5-50° (from 70% EtOH); *oxime*, m. 98-9°. I (12.2 g.), 12 ml. 85% $N_2H_4.H_2O$, and 70 ml. $(CH_2CH_2OH)_2$ were treated at 50-60° with 12 g. KOH and the mixt. heated 4 hrs. until gas evolution ceased; after distn. with superheated steam and extn. of the distillate with Et_2O there was obtained 8.7 g. *5-methyl-2,2'-dithienylmethane* (II), b_4 116-17°, n_D^{20} 1.6015, d_{20} 1.1810. II (6.4 g.), 8.4 g. PhNMeCHO, and 9.4 g. $POCl_3$ gave 44% *5-(5-methyl-2-thenyl)-2-thiophenecarboxaldehyde* (III), b_4 118-8°, [illegible] 1.6218, d_{20} 1.2260; *oxime*, m. 110.5-21°. 2-*tert*-Butylthiophene (21 g.), 20.3 g. PhNMeCHO, and 2[illegible] g. $POCl_3$ gave 91% *5-tert-butyl-2-thiophenecarboxaldehyde*, b_{13} [illegible] n_D^{20} 1.5[illegible]41; *semicarbazone*, m. 215-16°. 2,5-Di-*tert*-butylthiophene (42 g.), 40.[illegible] g. PhNMeCHO, and 40 g. $POCl_3$ at 55-60° gave 40% *2,5-di-tert-butyl-3-thiophenecarboxaldehyde* [illegible]

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APPROVED FOR RELEASE: Thursday, September 26, 2002 CIA-RDP86-00513R000515620019-2"

Gol'dfarb, Ya.L., Konstantinov, P.A.

hyde, b_{10} 144-5.5°, n_D^{20} 1.5308, d_{20} 1.0130; oxime, m. 13[illegible]-. 2-Methyl-5-*tert*-butylthiophene gave *3-methyl-5-tert-*[illegible] *3(or 4)-thiophenecarboxaldehyde*, b_{10} 96-7°, n_D^{20} 1.55[illegible], d_{20} 1.0553; *semicarbazone*, m. 216.5-17°. To 11 g. 5-butyl-[illegible] thiophenecarboxaldehyde and 700 ml. 95% EtOH was added at 60° 60 g. Raney Ni and the mixt. stirred under [illegible] 1 hr., yielding after filtration, distn. of EtOH, diln. with H_2O, and extn. with $CHCl_3$ 60% *1-nonanol*, b_{17} 137-8°, [illegible] 1.4335, d_{20} 0.8304 (*phenylurethan*, m. 59.5-60°). 1-[illegible] *decanol*, b_{12} 111-13°, n_D^{20} 1.4135, [illegible] 1.4012, d_{20} [illegible] (*1-naphthylurethan*, m. 57-8°). III gave 54% [illegible] b_{11} 130-1°, n_D^{20} 1.4400, d_{20} 0.83[illegible] (*phenylurethan*, m. [illegible]). In 4 hrs. 5-*tert*-butyl-2-thiophenecarboxaldehyde gave [illegible] 50% *6,6-dimethylheptanol*, b_{11} 86-8°; n_D^{20} 1.4430, d_{20} 0.[illegible] 2,5-Di-*tert*-butyl-3-thiophenecarboxaldehyde gave 48% [illegible] *dimethyl-2-neopentylhexanol*, b_{11} 125-6°, n_D^{20} 1.44[illegible], d_{20} 0.84705 (*naphthylurethan*, m. 110.5-12°). The reaction product of 5.5 g. 2-methyl-5-*tert*-butyl-3(or 4)thiophenecarboxaldehyde with 55 g. Raney Ni in EtOH was a compd. $C_{10}H_{22}O$, b_{11} 92-3°, n_D^{20} 1.4350, d_{20} 0.8381 (*phenylurethan*, m. 62-3°), provisionally identified as *5,5-dimethyl-3-ethylhexanol*. 2,5-Di-*tert*-butyl-3-acetylthiophene could not be completely desulfurized after even prolonged reaction with [illegible].

O. M. Kosolapoff

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GOL'DFARB, YA. L.

Action of water on 3,4-bis(chloromethyl)-2,5-dimethyl-
thiophene. Ya. L. Gol'dfarb and I. S. Kon[illegible]ova
(N. D. Zelinskii Inst. Org. Chem., Moscow). Izvest.
Akad. Nauk S.S.S.R. Otdel. Khim. Nauk 1954, 1208-11.—
Heating 6 g. 3,4-bis(chloromethyl)-2,5-dimethylthiophene
with 120 ml. H_2O 1.25 hrs. at 70-80° gave 2 g. [illegible] 6,7-
bis(2,5-dimethyl-3,4-thienomethyl)[illegible] (I), m. 154-5.5°
(from Me_2CO). The substance has a dipole moment in
C_6H_6 of 1.42 D. The aq. filtrate from the product contained
CH_2O. I (2.3 g.), 30 ml. C_6H_6, 0.5 g. $SOCl_2$, and 2 drops
$SnCl_4$ heated 5 hrs. on a steam bath, then treated with H_2O
gave 1.9 g. bis(4-chloromethyl-2,5-dimethyl-3-thienyl)methane,
m. 171-2°, which heated with H_2O at 60° gave I. Heating
3,4-bis(chloromethyl)-2,5-tert-butylthiophene (II) with H_2O
gave a low yield of the bis(hydroxymethyl) analog, m.
162.5°, and a larger amt. of 2,5-di-tert-butyl-3,4-dimethylene-
oxythiophene (III), m. 220-1°; the above glycol in pure
state, m. 166-7°. II heated with AcONa-AcOH 4.5 hrs.
gave 3,4-bis(acetoxymethyl)-2,5-di-tert-butylthiophene, m. 135-
5.5°, which with EtONa-EtOH saponif. to the above
glycol, m. 166-7°. III heated in C_6H_6 with $SOCl_2$ and
$SnCl_4$ 3 hrs. gave II. Heating 3,4-bis(chloromethyl)-2,5-
diethylthiophene with H_2O 1.5 hrs. at 60-5° gave a low
yield of apparently 2,5-diethyl-3,4-(dimethyleneoxy)thiophene,
m. 119°. Heating 5.0 g. 2,5-dimethylthiophene, 10 ml.
concd. HCl, 10 ml. H_2O and 10 ml. 37% formalin 1 hr. at
75° gave 1.5 g. $C_{10}H_{14}O_2S$, m. 16-8.5°, which does not contain
active H and appears to be $CH_2.O.CH_2.O.CHCH_2.C_4H_4S$
CMe:C, and 0.9 g. I.

G. M. Kosolapoff

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Gol'dfarb, Ya. L.

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Synthesis of amino dicarboxylic acids of aliphatic series from thiophene. Ya. L. Gol'dfarb, B. P. Fabrichnyi, and I. F. Shalavina (N. D. Zelinskii Inst. Org. Chem., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1956, 1270-8; cf. *C.A.* 49, 8244*b*.—Hydrogenolysis (cf. above ref. for technique) of 2,5-$[HO_2CCH(NH_2)](HO_2CCH_2CH_2CH_2)C_4H_2S$ gave 83% *α-aminosebacic acid*, decomp. 230-4°; *p-tosylate*, m. 94-5°; *HCl salt*, m. 156-8°. The starting material decomp. 191° (*p-tosylate*, m. 1?2-3°). Similarly, 2,5-$[HO_2CCH(NH_2)](HO_2CCH_2CH_2CH_2CH_2)C_4H_2S$ decomp. 175° (*p-tosylate*, m. 127-8°); on hydrogenolysis it gave *α-amino-1,9-nonanedicarboxylic acid*, decomp. 220-8°; *HCl salt*, m. 149-51°. Acylation by the usual method of 2-$(EtO_2CCH_2CH_2CH_2)C_4H_3S$ with $ClCO(CH_2)_2CO_2Me$ in C_6H_6 with $SnCl_4$ catalyst gave 93% *2,5-$[MeO_2C(CH_2)_2CO][EtO_2C(CH_2)_3]C_4H_2S$*, which after alk. sapon. to the dicarboxylic acid (93% yield), was converted to the oxime in 95% yield and hydrogenated over Raney Ni in 5% NH_4OH by stirring with the catalyst at 70-80° to *δ-aminosebacic acid* (I) mixed with its *lactam*, $HO_2C(CH_2)_3CH.CH_2.CH_2.CH_2.CO.NH$, m. 140-1.5°, the latter being obtained pure after repptn. from NaOH with AcOH; the lactam refluxed in either pure state or mixed with the open chain form with concd. HCl readily gave I.HCl, m. 148-5°, which with NH_4OH gave free I, m. 189.5-90° (*p-tosylate*, m. 114-15°).

G. M. Kosolapoff

Chem

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GOLDFARB, YA. L.

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Structure of compounds formed from thiophene and 2-methylthiophene under conditions of chloromethylation in the presence of zinc chloride. Ya. L. Gol'dfarb and [illegible] L. D[illegible] (N. D. Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1956, 1381-9; cf. Blicke and Burckhalter, C.A. 36, 2351°.—The product $C_{14}H_{12}S_3$ formed among others in chloromethylation of thiophene was shown to be 2,5-di(2-thenyl)thiophene (I). To 108 g. $ZnCl_2$ in 82 ml. concd. HCl at −7° was added 100.8 g. thiophene followed by 75 g. 37% formalin over 1.5 hrs., the mixt. stirred 1 hr., treated with H_2O, extd. with Et_2O, and the ext. washed with $NaHCO_3$ giving 86.3 g. di-2-thienylmethane (II), b. 131-3°, m. 44.5-6.5°, and 11% I, b. 184-7°, m. 57.5-8.5°. Similarly 2-methylthiophene gave 61.4% bis(5-methyl-2-thienyl)methane, m. 38.5-9.5°. Heating 5.82 g. di(2-thienyl) ketone in 55 ml. $O(CH_2CH_2OH)_2$ with 4.8 ml. 90% $N_2H_4.H_2O$ to 135°, cooling, adding 6 g. KOH, refluxing 1 hr., removing excess N_2H_4 and H_2O, refluxing the residue 3 hrs., dilg. with H_2O, and extg. with Et_2O gave 81% crude di-2-thienylmethane, b. 133-3.5°, m. 46-7.5° (from EtOH-petr. ether). Similarly, di(5-methyl-2-thienyl) ketone gave 63% di(5-methyl-2-thienyl)methane, b. 128.5-31°, m. 38.5-9.5°. Similarly, 2-(2-thenyl)-5-(2-thenoyl)thiophene gave 50.5% 2,5-di(2-thenyl)thiophene, b. 182-5°, m. 57.5-8° (from BuOH), shown to be identical with I. To 41.8 g. HCONMePh and 85.92 g. $POCl_3$ was added over 1 hr. 33.4 g. II in 40 ml. MePh at 25-35°; after 1 hr. the mass left overnight, then treated with ice H_2O and extd. with Et_2O and MePh, and the ext. after washing yielding a series of fractions including 8 g. II and 63% [illegible]

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Gol'dfarb, Ya.L.; Danyushevskiy, Y.L.

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carboxaldehyde, b[illegible] m. [illegible] (after prolonged storage) (from MeOH); semicarbazone, m. 202°; oxime, m. 93.5-5°. To 13.0 g. II and 10.3 g. 2-thiophenecarbonyl chloride in 100 ml. C_6H_6 was added at 0° over 0.5 hr. 18.3 g. $SnCl_4$, after 1 hr. at room temp. the mixt. stirred 3 hrs. with 100 ml. 10% HCl, the residual tar treated with fresh aq. HCl and C_6H_6, and the org. layer distd. giving II and 13% *5-(2-thenyl)-2-(thenoyl)thiophene* (III), b_2 232-5°, m. 104.5-5.5°. Refluxing 10.6 g. 5-(2-thenyl)thiophene-2-carboxaldehyde in 700 ml. EtOH with 100 g. Raney Ni 3.5 hrs. and allowing this to stand 16 hrs. gave, after removal of EtOH, addn. of H_2O, and extn. with $CHCl_3$, 30.4% pure n-$C_{10}H_{21}OH$, b_{11-5} 115-7°, n_D^{20} 1.4389, d 0.8320 (phenylurethan, m. 58.5-9.5°). Similar treatment of I gave 59.2% n-tetradecane, b_{10} 114-18°, n_D^{20} 1.4310, along with solid high mol. wt. hydrocarbon, b_3 185-200°. To 8.38 g. I was added at 5° in 3 hrs. 260 ml. 0.33N $KBrO_3$ and after 3 hrs. the mass extd. with C_6H_6 yielding 40% *$C_{13}H_{10}Br_2S_2$*, m. 59-60°, apparently a *dibromo deriv.* of I. Similarly, III after reduction with N_2H_4 as described above and bromination, as above, also gave the same product, m. 58-9°. To 8.4 g. 5-methyl-2-thiophenecarbonyl chloride and 5.72 g. 2-methylthiophene in C_6H_6 was added at −2° over 40 min. 6.8 ml. $SnCl_4$ in C_6H_6, yielding after 1 hr. stirring and an aq. HCl treatment 88% *bis(5-methyl-2-thienyl) ketone*, b_3 212-14°, m. [illegible]9° (from MeOH). To 22 g. II in Et_2O was added at [illegible]° over 40 min. 153 ml. 0.65 N BuLi in Et_2O and after 10 min. treated over 70 min. with 14.2 g. thenyl chloride in Et_2O and after 16 hrs. at room temp. and refluxing 6 hrs. the mass treated with H_2O yielding a range of fractions from which was obtained some unreacted II and 47% I, b_3 188-9°, m. 37.2-8.2° (from BuOH-Me_2CO).

G. M. Kosolapoff

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GOLDFARB, Ya. L.

Chem

Synthesis of amino acids of aliphatic series from thiophene derivatives. I. Synthesis of α-amino acids. Ya. L. Gol'dfarb, B. P. Fabrichnyi, and I. F. Shalavina (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Zhur. Obshchei Khim.* 26, 2595–602(1956).—To 17.2 g. KCN in 30 ml. H_2O was added 15.5 g. NH_4Cl in 40 ml. H_2O and 32.0 g. 5-methylthiophene-2-carboxaldehyde in 130 ml. MeOH and 40 ml. concd. NH_4OH; after shaking 4 hrs. the mixt., contg. a dark oil, was dild. with H_2O, extd. with C_6H_6, the org. layer washed with H_2O and 1:1 HCl, H_2O, $NaHCO_3$, and H_2O. Distn. gave 2.2 g. unreacted aldehyde. The aq. HCl ext. was refluxed 4 hrs. and concd. *in vacuo* (some unreacted aldehyde was recovered) and the residue after treatment with C was evapd. yielding *dl-α-amino(5-methyl-2-thienyl)acetic acid HCl salt* and NH_4Cl; this treated with aq. $Cu(OAc)_2$ gave 19.2% Cu salt, which treated with H_2S, filtered and evapd. gave 41.8% *free amino acid* (I), decomp. 199–200° (from dil. EtOH); *HCl salt*, m. 182–3°; *p-toluenesulfonyl deriv.*, decomp. 176–7°. Similarly, 5-ethylthiophene-2-carboxaldehyde gave *dl-α-amino(5-ethyl-2-thienyl)acetic acid* (II), decomp. 213°; *p-toluenesulfonyl deriv.*, m. 172–3°. Thiophene-2-carboxaldehyde gave *dl-α-amino-2-thienylacetic acid* (III), decomp. 233–4° (*p-toluenesulfonyl deriv.*, m. 159–60°). Reduction of 2-thienylglyoxalic acid oxime with Sn-HCl gave a low yield of *dl-α-amino-2-thienylacetic acid*, identical with the above. 2,5-Dimethyl-3-thiophenecarboxaldehyde gave *dl-α-amino(2,5-dimethyl-3-thienyl)acetic acid* (IV), decomp. 203–4° (*p*-toluenesulfonyl deriv., decomp. 172–3°). 5-*tert*-Butyl-2-thiophenecarboxaldehyde gave *dl-α-amino(5-tert-butyl-2-thienyl)acetic acid*

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Gol'dfarb, Ya. L., Fabrichnyi, B.P.

decomp. 180-7° (*p-toluenesulfonyl deriv.*, m. [illegible]); a by-product was *5-tert-butyl-3-[illegible]* HCl salt, m. 229-30°; *picrate*, m. 185-6°. Refluxing 2 g. I with 0.7 g. Na_2CO_3 in 100 ml. H_2O with 9 g. Raney Ni 1 hr. gave after the usual purification through the Cu salt, 63% *dl-α-aminoenanthic acid*, decomp. 270-80°; benzoyl deriv., m. 13[illegible]-4°. II gave 41% *dl-α-aminocaprylic acid*, decomp. 220-1° (*benzoyl deriv.*, m. 126-8°). III gave 60% *dl-α-aminocaproic acid*, decomp. 275-7° (*benzoyl deriv.*, m. 132°). IV gave 51% *dl-α-amino-β-ethylcaproic acid*, decomp. 244-6° (*p-toluenesulfonyl deriv.*, m. 106.5-7°). Oxime of α-thienylglyoxalic acid (cf. Gol'dfarb and Fabrichnyi, C.A. 49, 8244*b*) (3 g.) in 50 ml. H_2O with 1.3 g. Na_2CO_3 and 20 ml. concd. NH_4OH was stirred with 15 g. Raney Ni at 70-5° 2 hrs. yielding after the usual treatment through the Cu salt, 50% *dl-α-aminocaproic acid*, decomp. 273-4°; *benzoyl deriv.*, m. 132°, identical with above described specimen.

G. M. Kosolapoff

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Synthesis and transformations of some derivatives of di-2-thienylmethane. III. Bromo derivatives of di-2-thienylmethane. Ya. L. Gol'dfarb and M. L. Kirmalova (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Zhur. Obshchei Khim.* 26, 3400-14(1956); cf. C.A. 50, 6432h.—To 17.1 g. *di-2-thienylmethane* (I) in 100 ml. C_6H_6 was added 75 ml. concd. HCl followed by 528 ml. 0.6*N* KBr-KBrO$_3$ soln. at 2°; after stirring 1 hr. at room temp. the org. layer was sepd., washed with aq. NaOH and evapd., yielding 72% *di(5-bromo-2-thienyl)methane* (II), m. 59-9.5° (48% yield of pure product, from EtOH), which darkens in light. Similar reaction of 9 g. I in C_6H_6 with 67 ml. concd. HCl and 210 ml. 0.5*N* KBr-KBrO$_3$ gave 44% di-Br *deriv.* of I, b_2 146-7°, b_1 128°, n_D^{20} 1.6330, d_{20} 1.540, along with 23.4% above dibromide. To 3 g. ZnCl$_2$ in 9 ml. concd. HCl was added 5 g. 2-bromothiophene followed at −7° by 2 ml. 37% formalin with stirring 1.5 hrs., yielding on extn. with Et$_2$O, and evapn. of the ext. 1.1 g. II. Heating 6.8 g. Br deriv. of I, 1.85 g. Mg activated with iodine, 2 ml. EtBr and 70 ml. Et$_2$O 0.5 hr. and treating with Dry Ice gave on usual working-up 71% *di-2-thienylmethane-5-carboxylic acid*, m. 105-6°. Similar reaction with II gave 84% *di(5-carboxy-2-thienyl)methane*, decomp. about 230° (from AcOH); *di-Me ester*, m. 74-4.5° (from heptane). II (6.8 g.) treated with 100 ml. BuLi soln. in Et$_2$O (25 g./l.) at −10°, stirred 20 min. at −2°, and 5 ml. ethylene oxide added in Et$_2$O, gave after treatment with EtOH and dil. acid 2.15 g. *di[5-(2-hydroxyethyl)-2-thienyl]methane*, m. 140-40.5° (from EtOH); working up the residues gave a total 78% yield. Refluxing

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Ya. L. Goldfarb and M.L. Kirmalova

10 g. II with 5.6 g. *N*-bromosuccinimide and 0.1 g. Bz_2O_2 in CCl_4 3.5 hrs. gave after filtration and evapn. of the filtrate (washed with 10% Na_2CO_3), an oil which treated with hot EtOH crystd., yielding a less-sol. in Me_2CO portion of 3 g. *1,1,2,2-tetrakis(5-bromo-2-thienyl)ethane*, m. 140.5-41°, and a 1-g. portion of more sol. *N-[di(5-bromo-2-thienyl)methyl]succinimide*, m. 111-11.5°. Bromination of 5 g. I with 4 g. *N*-bromosuccinimide as above in presence of 0.35 g. Bz_2O_2 in chilled $CHCl_3$ gave 68% 5-Br deriv. of I and 1.1 g. II.

G. M. Kosolapoff

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Gol'dfarb, Ya. L.

Chem

Synthesis of tertiary amines of aliphatic series from thiophene derivatives. Ya. L. Gol'dfarb and M. B. Ibragimova. *Proc. Acad. Sci. U.S.S.R., Sect. Chem.* 106, 71-4 (1956)(Engl. translation).—See C.A. 50, 13882c.

B. M. R.

GOL'DFARB, Ya.L.; IBRAGIMOVA, M.B.

Synthesis of aliphatic tertiary amines from thiophene derivatives. Dokl.AN SSSR 106 no.3:469-472 Ja '56. (MLRA 9:6)

1.Institut organicheskoy khimii imeni N.D.Zelinskogo Akademii nauk SSSR. Predstavleno akademikom A.A.Balandinym.
(Amines) (Thiophene)

GOL'DFARB, Ya.L.; FABRICHNYY, B.P.; SHALAVINA, I.F.

New general method of preparing aliphatic aminoacids. Dokl. AN SSSR 109 no.2:305-308 Jl '56. (MLRA 9:10)

1. Institut organicheskoy khimii imeni N.D. Zelinskogo Akademii nauk SSSR. Predstavleno akademikom A.A. Balandinym.
(Amino acids)

GOL'DFARB, Yakov Lazarevich, prof.; SMORGONSKIY, Leonid Mikhaylovich,
prof. [deceased]; POZDNYAKOVA, N.I., red.; MAKHOVA, N.N., tekhn.red.

[Problems and exercises in chemistry for secondary schools]
Zadachi i uprazhneniia po khimii dlia srednei shkoly. Izd.18.,
perer. Moskva, Gos.uchebno-pedagog.izd-vo M-va prosv.RSFSR,
1957. 142 p. (MIRA 12:4)
(Chemistry--Problems, ezercises, etc.)

62-1-15/21

AUTHORS: Gol'dfarb, Ya. L., and Konstantinov, P. A.

TITLE: The Structure of Products Obtained from the Acylation and Formylation of 2-Methyl-5-Tertiary Butyl Thiophene and 2,5-Di-Tri-butyl Thiophene (O stroyenii produktov atsilirovaniya i formilirovaniya 2-metil-5-tret.butiltiofena i 2,5-di-tret.butiltiofena).

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, 1957, No. 1, pp. 112-117 (U.S.S.R.)

ABSTRACT: Experiments showed that formylation, acetylation and also bromination of 2-methyl-5-tertiary butyl thiophene force the new substitute into position 3. During the acetylation of 2,5-di-tri-butyl thiophene in the presence of stannicchloride, the migration of the tertiary butyl group has not been observed. The possibility of obtaining thiophencarboxylic acids, substituted in alpha position with alkyl radicals (methyl, tertiary butyl) by simultaneous reaction of iodine

Card 1/2

GOL'DFARB, Ya.L.; KONSTANTINOV, P.A.

Action of Raney-nickel catalyst on ethers of the thiophene series. Izv.AN SSSR.Otd.khim.nauk no.2:217-223 F '57. (MLRA 10:4)

1. Institut organicheskoy khimii im. N.D.Zelinskogo Akademii nauk SSSR.

(Thiophene) (Catalysts)

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GOL'DFARB, YA. L.

No. 4

Synthesis and transformations of some derivatives of di-2-thienylmethane. IV. Acylation of di-2-thienylmethane with [illegible] and their hydrogenolysis. Ya. L. Gol'dfarb and M. L. Kirmalova (N. D. Zelinskii Inst. Org. Chem., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1957, 479-84; cf. C.A. 51, 9571h.—Addn. over 1 hr. of 6 g. $MeO_2CCH_2CH_2COCl$ in C_6H_6 and 7.4 g. $SnCl_4$ in C_6H_6 to 7.1 g. di-2-thienylmethane (I) in 2:1 C_6H_6-ligroine at −14° gave after quenching in dil. HCl 71% *Me 3-[5-(2-thenyl)-2-thenoyl]propionate* (II), b. [illegible], m. 34°, and 10.8% *di-Me 2,2'-methylenebis[β-(5-thenoyl)]propionate* (III), m. 88-9.5° (from EtOH). The use of 2 moles RCOCl added at once gave much of the latter substance and 30% of the former. Acylation of 18.6 g. I as above with 9.07 g. $MeO_2CCH_2CH_2CH_2COCl$ gave 61.8% *Me γ-[5-(2-thenyl)-2-thenoyl]butyrate* (IV), b. [illegible], m. 59.5-60°, and 12.1% *di-Me 2,2'-methylenebis[γ-(5-thenoyl)butyrate]* (V), b. [illegible] 305°, m. 77-8°; the use of a larger proportion of RCOCl lowered the yield of the former and raised that of the latter product. Refluxing II with 10% K_2CO_3 1 hr. gave 100% corresponding *free acid*, m. [illegible]. III similarly gave 100% corresponding *free acid*, m. [illegible]. Refluxing II with $N_2H_4.H_2O$ in $O(CH_2CH_2OH)_2$ 1.5 hr., adding concd. KOH, and refluxing 30 min. longer gave, after final heating to 310° 1.5 hrs., 54.5% *γ-[5-(2-thenyl)-2-thienyl]butyric acid*, m. 48°; IV similarly gave 65% *δ-[5-(2-thenyl)-2-thienyl]valeric acid*, m. 51°; V gave 83% *2,2'-methylenebis[δ-(5-thienyl)valeric acid]*, m. 121.5-2°. Heating these in 10% Na_2CO_3 with Raney Ni in H_2O 2 hrs. at 90° gave, resp., [illegible] tridecanoic acid, 72.7% myristic acid, and 61.4% 1,19-nonadecanedioic acid. G. M. Kosolapoff

GOL'DFARB, Ya.L.; TAYTS, S.Z.; BELEN'KIY, L.I.

A new method for the synthesis of macrocyclic compounds. Preparation of alicyclic compounds from thiophene derivatives. Izv. AN SSSR Otd. khim. nauk no.10:1262-1265 O '57. (MIRA 11:3)

1.Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.
(Alicyclic compounds) (Thiophene)

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Gol'farb, Ya. L.

Formic acid thiolo[illegible]. Ya. L. Gol'dfarb and [illegible]. [illegible] U.S.S.R. 109,[illegible], Apr. 30, 1957. Esters of HCOSH are obtained by the action of Ac_2O and $(HCO)_2O$ on mercaptans.

M. Hosch

GOL'DFARB, Ya.L. (Moskva); BELEN'KIY, L.I. (Moskva).

Transannular effect in macrocyclic compounds. Usp. khim. 26 no.3: 362-387 My '57. (MLRA 10:

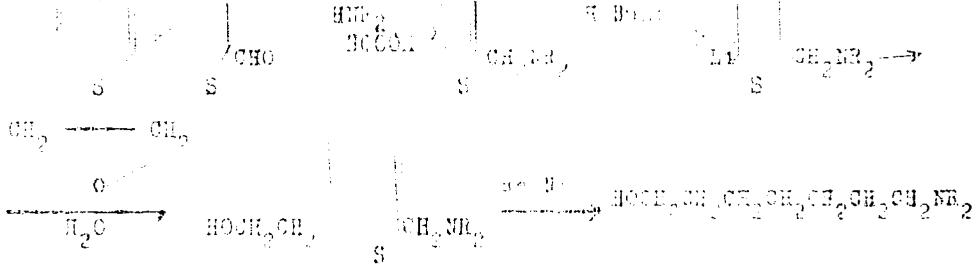
(Macromolecular compounds)

AUTHOR GOL'DFARB, Ya. L., IBRAGIMOVA, [illegible] B. PA - 3153

TITLE Production of Aliphatic Dialkylaminoalcohols From Thiophene Derivates.
(Sintez alifaticheskikh dialkilaminospirtov iz proizvodnykh tiofena. Russian)

PERIODICAL Doklady Akademii Nauk SSSR, 1957, [illegible] (U.S.S.R.)
Received 6/1957 Reviewed 7/1957

ABSTRACT A method was worked for the production of dialkylaminoalcohols according to the following scheme:



As however the coordination of lithium alkyls might take place both in the sulphur- and in the nitrogen atom (according to the opinion of H. Gilman Organic Reactions, N.Y. London, 8, 1954, p. 258) the synthesis of one of the aminoalcohols obtained by the authors was carried out according to another scheme. It was found that the aminoalcohols

Card 1/2

AUTHORS: Gol'dfarb, Ya. L., Fabrichnyy, B. P., Shalavina, I.F., 62-1-17/29

TITLE: On the Synthesis of the B-(2-thienyl) Alanine (O sinteze B-(2-tiyenil) alanina)

PERIODICAL: Izvestiya AN SSSR, Otdeleniye Khimicheskikh Nauk, 1958
Nr 1, pp. 98 - 100 (USSR)

ABSTRACT: The data published of late prove that B-(2-tienyl) alanine has an extensive biological activity. In connection here with a series of papers was published which delt with the synthesis of the B-(2-tienyl) alanine. Crowe and Nord (reference 4) obtained this aminoacid by exploiting the reaction of the 2-thiophenaldehyde with rodanine. However, the experimental results of the synthesis which was based only on the use of rodanine were less satisfactory. For this reason it seemed expedient to the authors of this paper to investigate the possibility of the synthesis of the B-(2-tienyl) alanine according to the method of Sasaki. The experiments carried out by the authors showed that the method of the synthesis of B-(2-tienyl) alanine with the aid of diketopiperazine is comparatively simple: in any case it is more useful than the hitherto published methods. There are 8 references.

Card 1/2

On the Synthesis of the β-(2-thienyl) Alanine 62-1-17/29

ASSOCIATION: Institute of Organic Chemistry imeni N. D. Zelinskiy AS USSR (Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR)

SUBMITTED: July 12, 1957

AVAILABLE: Library of Congress

1. β -(2-Tienyl) alanine--Synthesis 2. Alanines--Synthesis

Card 2/2

AUTHORS: Kondakova, L. S., [illegible], Ya.L. 62-5-16/27

TITLE: Synthesis of Some Bifunctional Derivatives of 2,5-Dimethylthiophen (Sintez nekotorykh bifunktsional'nykh proizvodnykh 2,5-dimetiltiofena)

PERIODICAL: Izvestiya Akademii Nauk SSSR Otdeleniye Khimicheskikh Nauk, Nr 5, pp. [illegible] - [illegible] (USSR)

ABSTRACT: Rather substantial quantities of 2,5-dimethylthiophen (Reference 1) are found in sulfurous compounds which are formed due to the decomposition (heat-decomposition) of Kashpir-slate. It was of interest to investigate the possibility of synthetization of simple bifunctional derivatives. 3,4-bis-(methyl-chloride)-2,5-dimethylthiophen was used for obtaining a synthesis of the bifunctional derivatives of 2,5-dimethylthiophen. 3,4-bis-(acetoxymethyl)-2,5-dimethylthiophen, 3,4-bis(oxymethyl)-2,5-dimethylthiophen, 3,4-bis-(cyanomethyl)-2,5-dimethylthiophen, 3,4-bis-(ethoxymethyl)-2,5-dimethylthiophen, 3,4-bis-(carboxymethyl)-2,5-dimethylthiophen (see formulae II to VI) were obtained by the action of corresponding reagents on 3,4-bis-(methyl-chloride)-2,5-dimethylthiophen. No symmetric

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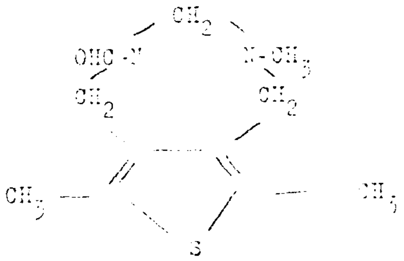
Synthesis of Some Bifunctional Derivatives of 2,5-Dimethylthiophen

62-5[illegible]-3-16/27

diamine, but 3-amino-methyl-4-methyl aminomethyl-2,5-dimethyl-thiophen was obtained by means of the hydrolysis of hexamin-salt (formed from 3,4-bis-(methyl-chloride)-2,5-dimethylthiophene and hexamethylene-tetramine). A compound of the structure $C_{11}H_{16}N_2OS$ corresponding to the formula



is formed as secondary product with the formation of diamine. There are 2 figures and 11 references, 2 of which are Soviet.

Card 2/3

Synthesis of Some Bifunctional Derivatives of 2,5-Dimethylthiophen

12-[illegible]-5-10/27

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute for Organic Chemistry imeni N. D. Zelinskiy AS USSR)

SUBMITTED: December 10, 1956

1. Cyclic compounds--Synthesis

Card 3/3

AUTHORS: Gol'dfarb, Ya. L., Zvorykina, V. K. SOV/62-58-6-[illegible]

TITLE: Investigation of the N-Oxides of Some Heterocyclic Bases (Izucheniye N-okisey nekotorykh geterotsiklicheskikh osnovaniy) Communication I. On the Production and Properties of Nicotine Oxides (Soobshcheniye 1. O poluchenii i svoystvakh N-okisey nikotina)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 6, pp 718-7[illegible] (USSR)

ABSTRACT: Three types of oxides can be produced from nicotine: Pl-N-oxide, Py-N-oxide, Py,Pl-N-dioxide. Most papers on nicotine oxidation deal with the compounds of the first type. The authors begin by mentioning the papers by Pinner and Wolfenstein (Vol'fenshteyn) (Ref 1), Auerbach (Auerbakh) and Wolfenstein (Ref 2), Weil (Veyl') (Ref 3), Heinz (Khayns) and Eisner (Eyzner) (Ref 4) and other authors. The present paper deals with the investigation of the reaction of the oxidation of nicotine H_2O_2, on which occasion all three N-oxides were obtained in form of crystals. Of these, nicotine-Pl-Py-dioxide and nicotine-Py-N-oxide have as yet not been described in

Card 1/2

Investigation of the N-Oxides of Some Heterocyclic Bases. Communication I. On the Production and Properties of Nicotine Oxides

SOV/62-58-6-15/37

published works. Pl-Py-dioxide was obtained as a crystal hydrate (with 2 water molecules and a water-free base) as monopicrate, dichlorohydrate and mercury complex. For the Py-monoxide of nicotine a crystal base, dichlorohydrate, dipicrate, and a mercury derivative were obtained. For nicotine-Pl-N-oxide, which had already been obtained by Pinner (under the name of "Oxynicotine") the authors obtained a hitherto not described chlorohydrate; the water-free base was separated. There are 11 references, 1 of which is Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy AS, USSR)

SUBMITTED: December 13, 1956

1. Nicotine oxides--Production [illegible]

Card 2/2

AUTHORS: Zvorykina, V. K., Alashev, F. D., Gol'dfarb, Ya. L. 62-58-6-29/37

TITLE: The Production of N-Oxides of N-Methylanabasine (Polucheniye N-okisey N-metilanabazina)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 6, pp. 788 - 790 (USSR)

ABSTRACT: Continuing the investigation of the N-oxides of bi-tertiary cyclic bases (Refs 1,2), the authors carried out the oxidation (by means of hydrogen peroxide) of N-methylanabasine. Bases of the N-oxides of N-methylanabasine which had hitherto not been described in published works, viz. N,N'-dioxide, Py-N-oxide, and Pi-N-oxide, as well as the picrates and hydrochlorides of these oxides were obtained. The structure of the N-oxides of N-methylanabasine was determined by reduction by means of zinc and hydrochloric acid in N-methylanabasine (and was identified as a di-picrate). There are 4 references, 2 of which are Soviet.

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The Production of N-Oxides of N-Methylanabasine 62-58-6-29/37

ASSOCIATION: Institut organicheskoy khimii im. N.D.Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N.D.Zelinskiy, AS USSR)

SUBMITTED: January 29, 1958

1. Nitrogen oxides--Production 2. Cyclic compounds--Oxidation

Card 2/2

[illegible]

[illegible] and [illegible]

[illegible]

[illegible] are [illegible] more [illegible] -amin [illegible] and [illegible]

AUTHORS: Gol'dfarb, Ya. L., Kiseleva, V. V. SOV/62-58-7-22/26

TITLE: On the Py-N-Methyl-α-Metanicotone (O Py-N-metil-α-metanikotone) The Action of Benzoyl Chloride on N-Methyl-α-Nicotone (Deystviye benzoilkhlorida na N-metil-α-nikoton)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 7, pp 903 - 905 (USSR)

ABSTRACT: After a number of investigations of various nicotine derivatives and of metanicotine it was found that they have a smaller toxicity than nicotine and that they maintain some useful properties (in a pharmacological respect). In the present paper the authors describe which way the compound 1-methyl-3 [4'-methyl benzoyl amino butenyl-(1')]-pyridone- (2) was produced by the cleavage of the pyrrolidine ring of the N-methyl-α-nicotone by means of benzoyl chloride. By the saponification of this compound Py-N-methyl-α'-metanicotine could be synthesized. There are 9 references, 4 of which are Soviet.

Card 1/2

SOV/62-58-7-22/26

On the Py-N-Methyl-α-Metanicotone. The Action of Benzoyl Chloride on N-Methyl-α-Nicotone

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy, AS USSR)

SUBMITTED: February 28, 1958

GOL'DFARB, YA. L.

79-1-[illegible]/[illegible]

AUTHORS: Gol'dfarb, Ya. L., Fabrichnyy, B. I., Shalavina, I. F.

TITLE: The Synthesis of Amino Acids of the Aliphatic Series From Thiophene Derivatives (Sintez aminokislot alifaticheskogo ryada iz proizvodnykh tiofena) II. The Synthesis of β-Amino Acids (II. Sintez β-aminokislot)

PERIODICAL: Zhurnal Obshchey Khimii, [illegible] Vol. [illegible] Nr [illegible], pp. 21[illegible] (USSR)

ABSTRACT: In recent years new data were published in periodicals on the investigation of β-amino acids and their biologically active compounds, of whom earlier little was known. Thiophene as initial product (references [illegible] and [illegible]) plays an important part. The way from thiophene aldehydes to amino acids is illustrated by the formulae (I), (II) and (III). The second stage of this process consists of the condensation of the aldehyde, which can easily be produced, with malonic acid and ammonia to β-amino acid according to V. M. Rodionov. The final stage is brought about by the reducing desulphurization with the aid of nickel. The

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[illegible]

The Synthesis of Amino Acids of the Aliphatic Series From Thiophene Derivatives. II. The Synthesis of β-Amino Acids

given synthesis of β-amino acids contains all possibilities which were characterized by the authors in papers devoted to the methods of synthesis of amino acids of another type. From the above-mentioned scheme follows that the acid of a ramified structure must form when ever the substituent or the aldehyde group are in positions 3 and 4, or when the substituent in position 5 has a ramified structure. Thus the following compounds were obtained from the corresponding 2-thiophene-aldehydes according to Rodionov's method: β-(2-thienyl)-β-aminopropionic-, β-(5-methyl-2-thienyl)-β-aminopropionic-, β-(5-ethyl-2-thienyl)-β-aminopropionic and β-(5-tert-butyl-2-thienyl)-β-aminopropionic acid. By the hydrogenolysis of these amino acids of the thiophene series the authors synthesized β-amino-n-heptyl-, β-amino-n-capronic, β-amino-n-pelargonic acid. By hydrogenolysis of the acetyl derivatives of β-(5-ethyl-2-thienyl)-β-aminopropionic and β-(5-tert-butyl-2-thienyl)-β-aminopropionic acid the acetyl derivatives of β-amino-n-pelargonic and θ,θ-dimethyl-β-amino-n-pelargonic acid respectively are obtained. By saponification of the acetyl derivative of θ,θ-dimethyl-β-aminopelargonic acid [illegible]-1-45/63

The Synthesis of Amino Acids of the Aliphatic Series From Thiophene Derivatives. II. The Synthesis of β-Amino Acids

with hydrochloric acid the hydrochloride of β,β-dimethyl-β-aminopropionic acid was obtained; by neutralization free amino acid was liberated. There are 1[illegible] references, 10 of which are Slavic.

ASSOCIATION: Institute for Organic Chemistry AN USSR
(Institut organicheskoy khimii Akademii nauk SSSR)

SUBMITTED: December 15, 1956

AVAILABLE: Library of Congress

Card 3/3

1. Chemistry 2. Amino acids--Synthesis 3. Aliphatic compounds
4. Thiophene

FABRICHNYY, B.P.; SHALAVINA, I.F.; GOL'DFARB, Ya.L.

Synthesis of aliphatic amino acids from thiphene derivatives. Part 3: Synthesis of ω-amino acids. Zhur.ob.khim. 28 no.9: 2520-2530 S '58. (MIRA 11:11)

1. Institut organicheskoy khimii AN SSSR.
(Amino acids)

GOL'DFARB Ya. L.

О СОСТАВЕ СОЕДИНЕНИЙ РЯДА БЕНЗОЛА И ТИОФЕНА В ЛЕГКИХ ФРАКЦИЯХ СМОЛЫ ТЕРМИЧЕСКОГО РАЗЛОЖЕНИЯ СРЕДНЕВОЛЖСКИХ СЛАНЦЕВ САВЕЛЬЕВСКОГО МЕСТОРОЖДЕНИЯ

Б. П. Федоров, Я. Л. Гольдфарб, Г. И. Горушкина

VIII Mendeleyev Congress for General and Applied Chemistry ##
Section of Chemistry and Chemical Technology of Fuels,
publ. by Acad. Sci. USSR, Moscow 1959

abstracts of reports scheduled to be presented at above mentioned congress,
Moscow, 15 March 1959.

5(3)

AUTHORS: Gol'dfarb, Ya. L., Konstantinov, [illegible] SOV/62-59-1-[illegible]

TITLE: On the Effect of Raney Nickel on Ketones and Acetals of the Thiophene Series (O deystvii nikelya Reneya na ketony i atsetali ryada tiofena)

PERIODICAL: Izvestiya Akademii nauk SSSR. [illegible], 1959, Nr 1, pp 121 - [illegible] (USSR)

ABSTRACT: In the present paper the authors [illegible] exercised by the structure of [illegible] compounds of the thiophene series [illegible] the reduction of the carbonyl group during hydrogenolysis in the presence of Raney Nickel as a catalyst. The authors tried to explain the possibility of using the factors mentioned for the maintenance of this function in hydrogenolysis. Observation of hydrogenolysis of [illegible] but [illegible] (I) under various conditions have shown that: 1) the [illegible] decrease during treatment with skeleton nickel within a range of 80 to -10° favors a higher yield of [illegible] (II) and accordingly decreases the yield of [illegible] (III); 2) Prolongation of hydrogenolysis from 1 to [illegible] hours [illegible]

Card 1/3

On the Effect of Raney Nickel on Ketones and Acetals of [illegible]
the Thiophene Series

changes considerably the yield of the [illegible]
of acetic acid to the original mixture [illegible]
the alkali collected by nickel [illegible]
erably the ratio oct[illegible]nol. The n-butyl-tertiary-
butylketone is formed during the [illegible] desulfurization
of tert-butyl-2-thienyl ketone [illegible]
according to [illegible] and Billica. Under [illegible] conditions,
a mixture of aliphatic [illegible] and secondary [illegible]
produced by ketones of the n-but[illegible]
of the fact that Raney nickel [illegible]
bonds between carbon atoms and others [illegible]
predict its effect on acetals. It [illegible] that [illegible]
acetals of aliphatic aldehydes are [illegible] by [illegible]
[illegible]olysis of acetals. This may serve [illegible]
in such cases where the synthesis of the [illegible]
methods is [illegible] limited. [illegible]
are Soviet.

Card 2/3

On the Effect of Raney Nickel on Ketones and Alcohols of the Thiophene Series SOV/62-[illegible]

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: April 17, 1957

Card 3/3

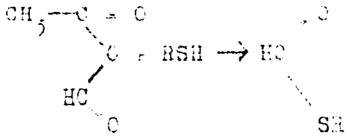
5 (3)

AUTHORS: Gol'dfarb, Ya. L., Kura[illegible]ova Ye. S. SOV/62-59-6-24/36

TITLE: On Some Esters of Thiolformic Acid (O nekotorykh efirakh tiolmuravinoy kisloty)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 6, pp 1102 - 1105 (USSR)

ABSTRACT: The thiolesters are widely used in different industrial branches as intermediate products (Refs 1-11). The present investigation was concerned with a detailed investigation of the thiolformic acid esters which are of interest for these intermediates and up till now scarcely described in publications. Thiolformic acid was produced by formylation of the sulfohydrile group of the compound RSH by use of an anhydride combination of formic and acetic acid.



(R = $C_6H_5CH_2$; $n-C_4H_9$; C_2H_5)

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The anhydride forming reacts with its formylradical with hydro-

On Some Esters of Thiolformic Acid SOV/62-59-6-24/36

xyl containing compounds (Refs 14-17). On the basis of an example, formylation of benzylmercaptan was carried out for the purpose of avoiding a decomposition of the anhydride compound, the reaction temperature was chosen in so low a range that no separation of carbondioxide could take place. The benzylester of the thiolformic acid (I) was obtained. The buthylester of the thiolformic acid was under quite similar conditions also produced from buthyl- and ethylmercaptan with the anhydride combination. Furthermore, it was shown that the trithiolformic acid, by passing an intermediate stage, forms the esters of the thiolformic acid. (I) reacted in the presence of hydrochloric acid with benzylmercaptan under formation of the ester of the orthotrithiolformic acid. The esters of the thiolformic acid proved to serve as N-formylating agents. By the action of (I) upon α-aminopyridine formyl-α-aminopyridine was obtained; by reacting with all thiolformates described here with phenylhydrazine β-formylphenylhydrazine is formed. There are 20 references, 2 of which are Soviet.

Card 2/3

On Some Esters of Thiolformic Acid SOV/62-59-6-24/36

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: September 11, 1957

5 (3)

AUTHORS: Gol'dfarb, Ya. L., Fabrichnyy, B. P., SOV/79-29-3-30/61
Shalavina, I. F.

TITLE: Synthesis of the Aliphatic Amino Acids From the Thiophene Derivatives (Sintez alifaticheskikh aminokislot iz proizvodnykh tiofena). IV. 5-Acyl-(2-thienyl)-alkanic Acids as Initial Products for the Synthesis of the Aliphatic Amino Acids (IV. 5-Atsil(2-tiyenil)-alkanovyye kisloty kak iskhodnyye veshchestva dlya polucheniya alifaticheskikh aminokislot)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 3, pp 891-897 (USSR)

ABSTRACT: There are comparatively little data available on the highest aliphatic amino acids of the structure $RCH(NH_2)(CH_2)_nCOOH$, where R = alkyl, although they are interesting as polycondensation objects (Ref 1) or as derivatives for physiological investigations (Ref 2). Their general method of synthesis is so far unknown; for the synthesis of some of these amino acids natural products were used; thus, for instance, the 10-amino-undecanic acid (Refs 1,2) was obtained from

Synthesis of the Aliphatic Amino Acids From the Thiophene Derivatives. IV. 5-Acyl-(2-thienyl)-alkanic Acids as Initial Products for the Synthesis of the Aliphatic Amino Acids SOV/79-29-3-30/61

undecylenic acid which is formed on the pyrogenetic cleavage of castor oil. The method previously suggested by the authors which is based on the reductive desulfurization (hydrogenolysis) of the oximino and amino acids of the thiophene series (Refs 5-8) yields aliphatic amino acids of any kind. The thiophene-keto acids previously used by the authors permit only the synthesis of such amino acids in which the carbon atom, as carrier of the amino group, is combined with an alkyl which contains not less than 4 carbons. This restriction was partly removed with the oximes of the aldehyde acids as initial products (Ref 9). In the present paper the synthesis of the highest amino acids of the mentioned type from the oximes of the keto acid (II) according to the given scheme is described. In this way the highest aliphatic amino acids can be synthesized which have the amino group in the required position to the carboxyl and an alkyl radical at the carbon atom combined with the amino group, with the necessary number of carbon atoms. The experimental part gives details on the carrying out of the reaction scheme mentioned. By the

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Synthesis of the Aliphatic Amino Acids From the Thiophene Derivatives. IV. 5-Acyl-(2-thienyl)-alkanic Acids as Initial Products for the Synthesis of the Aliphatic Amino Acids SOV/79-29-3-30/61

hydrogenolysis of the oximes which were obtained from the thiophene keto acids the following acids were synthesized by means of the skeleton-nickel catalyst: The 10-amino undecanic, 11-aminolauric, 9-amino undecanic, and 11-amino tridecanic acid. There are 3 tables and 8 references, 6 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: January 20, 1958

Card 3/3

5(3)

AUTHORS: Gol dfarb, Ya. L., Kirmalova, M. L. SOV/79-29-3-[illegible]

TITLE: Synthesis and Transformation of Some Di-(2-Thienyl)Methane Derivatives (Sintez i prevrashcheniya nekotorykh proizvodnykh di-(2-tiyenil)metana). V. On the Effect of n-Butyl Lithium on the 5-Methyl- and 5,5'-Dimethyl-2,2'-Dithienylmethane (V. O deystvii n.-butillitiya na 5-metil- i 5,5'-dimetil-2,2'-dityienilmetan)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 3, pp 897-904 (USSR)

ABSTRACT: Considering the results described by several chemists on the mechanism of metallization by means of lithium alkyls of those compounds which possess a hetero atom (Refs 1-4) it was of interest for the authors to investigate the effect of n. butyl lithium on the α-mono- and in particular on the α, α'-dialkyl-substituted compounds of dithienyl methane. According to the concepts expressed in the references 5, 6 and 7 it could be assumed that in these cases the metallization rate of the lithium alkyls into the nucleus should be bound to decrease abruptly since the α-hydrogen atoms are substituted and the nucleus is deactivated with respect to the nucleophilic substitution by alkyl groups. For this reason the

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Synthesis and Transformation of Some
Di-(2-Thienyl)Methane Derivatives. V. On the Effect of n.-Butyl Lithium
on the 5-Methyl- and 5,5'-Dimethyl-2,2'-Dithienylmethane

SOV/79-29-3-31/61

5,5'-dimethyl-2,2'-dithienyl methane (II) should be bound to yield, predominantly or exclusively, a metallization product (in the methylene group) and, in the case of compound (III), a formation of the organometallic compounds (IV) and (V) could be expected. It can be seen from the reaction results mentioned that these assumptions were only partly correct. In the reaction of the n.-butyl lithium with 5-methyl-2,2'dithienyl methane this compound was found to yield a product of the single metallization in the thiophene ring. By the action of ethylene oxide or of carboxylic acid upon the lithium derivative of 5-methyl-2,2'-dithienyl methane the corresponding alcohol and the corresponding acid were formed which were converted by the reductive desulfurization into the dodecyl alcohol and the undecanic acid. The metallization of the 5,5'-dimethyl-2,2'-dithienyl methane with subsequent action of carboxylic acid did not yield the theoretically expected product.

Card 2/3

Synthesis and Transformation of Some Di-(2-Thienyl)Methane Derivatives. V. On the Effect of n.-Butyl Lithium on the 5-Methyl- and 5,5'-Dimethyl-2,2'-Dithienylmethane

SOV/79-29-3-31/61

but only an acid of unknown structure. There are 20 references, 4 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: January 13, 1958

Card 3/3

5(3)

AUTHORS: Gol'dfarb, Ya. L., Zalik, M. A., Kirmalova, M. L. SOV/79-29-6-57/72

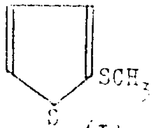
TITLE: Synthesis and Some Conversions of Sulfides of the Thiophen Series (Sintez i nekotoryye prevrashcheniya sul'fidov ryada tiofena)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 6, pp 2034-2042 (USSR)

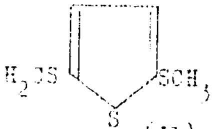
ABSTRACT: As far as the authors are informed only two alkyl thienyl sulfides i.e. methyl-2-thienyl sulfide (Refs 7-9) and ethyl-2-thienyl sulfide (Ref 8) have been described up to present. The yield of the accessible synthesis of 2-thienyl magnesium iodide, sulfur and methyl iodide (Ref 9) is 50-60 %. A more convenient way of synthesis of sulfides of the above mentioned type yielding up to 80 %, is described in the experimental part. It uses lithium derivatives of thiophen or its homologues which react with sulfur, like the organic magnesium compounds, the preparation of 2-halogen thiophen however, is unnecessary and this is essential. In this way methyl-2-thienyl sulfide, ethyl-2-thienyl sulfide, methyl-(5-methyl-2-thienyl) sulfide, and ethyl-(5-ethyl-2-thienyl) sulfide were obtained. The conversion of thiophen with two mol n.-buthyl lithium and

Card 1/3

further with sulfur and methyl iodide leads in addition to methyl-2-thienyl sulfide (I) also to 2,5-bis-(methyl mercapto) thiophen (II).



(I)



(II)

Acetylation of alkyl thienyl sulfides in the presence of tin chloride and ortho-phosphoric acid was analyzed. It was proved that the acetyl group enters into the ortho-position in relation to the sulfide group, if both α-positions in thiophen are occupied and into position 5 in alkyl-2-thienyl sulfides. For the synthesis of compounds of the aliphatic series of the corresponding 3-substituted compounds of thiophen the method of hydrogenolysis is most convenient because it protects the α-positions of the thiophen nucleus with activating alkyl mercapto groups. The synthesized compounds are listed in both

Synthesis and Some Conversions of Sulfides of the Thiophen Series SOV/79-29-6-57/72

tables. There are 2 tables and 21 referances, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: June 2, 1958

Card 3/3

APPROVED FOR RELEASE: Thursday, September 26, 2002

SOV/80-32-2-32/56

AUTHORS: Angert, L.G., Gol'dfarb, Ya.L., Gorushkina, G.I., Zenchenko, A.I., Kuz'minskiy, A.S., Fedorov, B.P.

TITLE: Syntheses of Some Thiophene Derivatives and the Study of Their Behavior as Ingredients of Resins (Accelerators and Antioxidants) ((Sintezy nekotorykh proizvodnykh tiofena i izucheniye ikh povedeniya v kachestve ingrediyentov rezin (uskoriteley i antioksidantov))

PERIODICAL: Zhurnal prikladnoy khimii, 1959, Vol XXXII, Nr 2, pp 408-416 (USSR)

ABSTRACT: A total of 15 compounds of the thiophene series were investigated as ingredients of resin mixtures. They all contained the azomethine group $XC_4H_2SCH = NRY$ where X is hydrogen or CH_3 -, R an aliphatic or aromatic radical, Y a substituting group. Secondary amines were prepared by heating thenyl dichloride with amines in a solution of benzene or toluene. The products of this reaction, their melting and boiling points, analyses and yields are given in Table 2. These compounds inhibit the oxidation of rubber. The inhibiting action is due to the nature of the ortho- and paragroups in the benzene ring. As a control sample rubber containing phenyl-β-naphthylamine was used in the experiments. The thenyl group $C_4H_3SCH_2$- has nearly the same inhibiting influence

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SOV/80-32-2-32/56

Syntheses of Some Thiophene Derivatives and the Study of Their Behavior as Ingredients of Resins (Accelerators and Antioxidants)

as the phenyl group. The most pronounced effect have the inhibitors 5-methyl-2-thenylidene-n-aminophenol, 2-thenyl-β--naphthylamine, etc. The synthetized compounds were tested also as vulcanization accelerators on the rubbers SKB, SKS-30, SKN-26 and NK. Most effective were 2-mercapto-4-(2'-thienyl)--thiazole and di-2-thenylideneethylenediamine. The thenylidene group had a greater effect on vulcanization acceleration than the benzene ring.

There are 5 tables, 1 graph and 20 references, 10 of which are Soviet, 3 American, 3 English, 2 German, and 2 French.

SUBMITTED: May 13, 1957

Card 2/2

5 (3).

AUTHORS: Gol'dfarb, Ya. L., Polonskaya, M. M., SOV/20-126-1-23/62
Fabrichnyy, B. P., Shalavina, I. F.

TITLE: Reductive Acetylation of Thiophene Series Nitrocompounds in the Presence of Skeleton Nickel (Vosstanovitel'noye atsetilirovaniye nitrosoyedineniy ryada tiofena v prisutstvii skeletnogo nikelya)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 1, pp 86 - 89 (USSR)

ABSTRACT: The first and the third author proved earlier (Ref 1) that δ-amino-valeric acid is produced with a small yield by the effect of skeleton nickel (Ni_{sk}) on the 5-nitro-2-thiophene-carboxylic acid (I). On the strength of reference 2 the authors tried to increase this yield by the application of acetic acid anhydride as medium. However, they succeeded only in isolating the acetyl-amino acid (II) from the reaction mixture. The recognition that this acid produces (III) in the case of the effect of Ni_{sk} in the aqueous medium (Ref 3) led to the conclusion that the acetic acid anhydride deactivates Ni_{sk}. This conclusion was confirmed in the case of two other examples. Thus the react-

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Reductive Acetylation of Thiophene Series Nitro-compounds in the Presence of Skeleton Nickel SOV/20-126-4-23/62

ion of Ni_{sk} with thiophene-nitroderivatives remains under the mentioned conditions in the production stage of an acetyl amino compound. That is to say, the result of the process is a reductive acetylation. Although the effect of the solvent upon the reducing properties of Ni_{sk} in the case of the hydrogenation of the thiophene derivatives has already been published (Ref 4) the authors could not find data concerning the capacity of the acetic acid of suppressing the desulfurizing function of Ni_{sk} in such cases. The authors found contradictions in the publications concerning the properties of the 5-acetyl-amino-2-thiophene-carboxylic acid (II) (Refs 6-11) when they identified the latter. Since the melting point 230-232° of the acetyl-amino acid (with a II-structure as is assumed) produced by the authors did not agree with that of the publications (272°) they determined the position of the acetyl-amino group in the nucleus. Thus the structure II was confirmed. On the strength of these data the authors doubted whether the experi-

Reductive Acetylation of Thiophene Series Nitro- compounds in the Presence of Skeleton Nickel

SOV/20-126-1-23/62

mental results of reference 8 were right. The authors then repeated the experiment of reference 8 and obtained acid potassium tartarate with a melting point 273-274°. The authors assume that Campaigne and Archer (Ref 8) erroneously regarded this acid salt as the acetyl-amino acid (II). There are 18 references, 3 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

PRESENTED: February 25, 1959, by B. A. Kazanskiy, Academician

SUBMITTED: February 16, 1959

Card 3/3

5(2, 3) SOV/20-128-3-28/58

AUTHORS: Gol'dfarb, Ya. L., Vol'kenshteyn, Yu. B.

TITLE: Action of Bromine on 2-Acetothienone in the Presence of Excessive Aluminum Chloride

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 3, pp 536-539 (USSR)

ABSTRACT: In the bromination of acetophenone, the bromine does not enter - as otherwise with ketones - into a side chain but into the ring, in metaposition to the carbonyl group (Ref 1). This happens in the presence of 2.5-3 moles of anhydrous $AlCl_3$ without a solvent. Apparently, this method can also be used for a similar halogenation of other aromatic carbonyl compounds. The role of $AlCl_3$ is probably the blocking of the acyl group by formation of a resistant complex with dimeric cyclic structure. Both from a practical and a theoretical point of view, it was interesting to investigate - by the example of the substance mentioned in the title - this peculiar blocking of the side chain; under usual conditions, this substance can only be halogenated in the side chain

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SOV/20-123-3-28/58

Action of Bromine on 2-Acetothienone in the Presence of Excessive Aluminum Chloride

(Refs 3, 4). Publication data speak of an α-orienting action of the sulphur atom stronger than the action of meta-orientation (Ref 5). The bromination mentioned in the title yielded a 4-bromo-2-acetothienone (I) not described in publications. 4,5-dibromo-2-acetothienone, the structure of which was confirmed by reference 10, was formed as a by-product. The structure of the bromine-substituted ketone I was confirmed by 2 methods (see Diagram), namely by oxidation or by reduction. The bromination method described above, and the mostly high yields, offer new possibilities of synthesizing the poorly accessible 2,4-substituted thiophenes. Detailed data on the introduction of a 2nd acyl group into the 2-acetothienone, as well as on its chloromethylation by the method of reference I, will be published later. There are 11 references.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR
(Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

Card 2/3

GOL'DFARB, Ya.L.; KISELEVA, V.V.

Products of the hydrogenation of 1-methyl-5-[4'-methyl-1'-amino-butenyl]-2-pyridone. Izv. AN SSSR.Otd. khim. nauk no.12:2208-2214 D '60. (MIRA 13:12)

1. Institut organicheskoy khimii im.N.D.Zelinskogo AN SSSR. (Pyridone)

GOL'DFARB, Ya.L.; VOL'KENSHTEYN, Yu.B.

Composition of a mixture of products from the chloromethylation of 2-acetothienone in the presence of excess aluminum chloride, and synthesis of 4- and 5-formyl- and 4- and 5-hydroxymethyl-2-acetothienones. Izv. AN SSSR.Otd. khim. nauk no.12:2238-2240 D '60. (MIRA 13:12)

1. Institut organicheskoy khimii AN SSSR.
(Ketones)

69634

S/074/60/029/04/02/005
B008/B014

5.4130
5.3100

AUTHORS: Gol'dfarb, Ya. L., Belen'kiy, L. I.

TITLE: Stress and Reactivity of Monocyclic Systems

PERIODICAL: Uspekhi khimii, 1960, Vol. 29, No. 4, pp. 470-507

TEXT: This is a survey of the most interesting papers published in recent years on stress theory. First, the authors give a brief summary of the development of the basic assumptions of this theory in the forties (Refs. 4-18). Details of the development of the stress theory are contained in Refs. 1-3. On the basis of the latest results (Refs. 19-30) it may be assumed that cyclic systems exhibit also the so-called conformation stress in addition to the classical angular or Baeyer stress. In an actually existing molecule the two stresses are usually present at the same time and are interdependent. With the help of physical and chemical methods it is only possible to determine the total stress of the cyclic system. It is merely an assumption that the Baeyer angular stress predominates in smaller rings and the conformation stress in five-membered and medium rings. It is frequently possible to determine the stress by studying several

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Stress and Reactivity of Monocyclic Systems

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B008/B014

physical properties. The stress becomes particularly manifest in exact measurements of the combustion heat (Table 1: combustion heat of cycloparaffins). The physical properties of the following cyclic systems are discussed: cyclopentane and cyclohexane (Refs. 29, 41-51, Fig. 2); cis-cycloolefins (Refs. 47, 54-57; Table 2); cyclobutane (Refs. 58, 59); cyclopropane (Refs. 60-67). The data obtained for cycloalkanes are applicable to the simplest heterocyclic compounds. The stress of a heterocyclic compound having oxygen or sulfur in its ring is, however, always lower than that of a cycloalkane with an equally large ring (Refs. 34, 68-72, Table 3). The combustion heats of the simplest oxygen-containing heterocycles are given in table 4 and need no explanation (Refs. 73, 74). Microwave- (Ref. 75) and oscillation spectra (Ref. 76) indicate that the trimethyl oxide has a plane structure. Concerning the combustion heats of nitrogen-containing heterocycles there are data available only on ethylenimine (Ref. 77), piperidine (Ref. 78), and pyrrolidine (Ref. 189). The conformation stress manifests itself in cyclic compounds with conjugate double bonds in a very peculiar manner (Fig. 3). The absence of coplanarity raises the energy content and reduces and even eliminates the properties of a conjugate system (Refs. 28, 79-85). When discussing various types of stress and the influence exerted by stresses on the reactivity of cyclic compounds, the authors make use

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Stress and Reactivity of Monocyclic Systems

S/074/60/029/04/02/005
B008/B014

of Brown's concept of the F- and B-stresses (Refs. 86-89) as well as of the I-stress (Refs. 93,94)(Table 5). Numerous examples show that the ratio of the reaction rates of various rings follows the theory of I-stresses. This holds not only for the addition to carbonyl groups and according to S_N1, but also for radical reactions and reactions of the type S_N2. It may be assumed that the reaction rate is differently influenced by the size of the ring, depending on the type of reaction (Table 6). Next, some examples are given which demonstrate the effect of I-stress on the reaction rate (Refs. 95-136, Tables 7-15, Figs. 4 and 5). As the I-stress is only one of the factors influencing the relative reaction rate of cyclic compounds, it is also necessary to take account of steric and polar factors (Tables 16 and 17). The authors give several examples which contradict the theory of I-stress (Tables 18-20). The last part of the present article deals with the formation and opening of rings and with the relationship between these processes and stress (Refs. 8,28,132, 177-185). The tendency toward ring closure is a complicated function of the following functions: distance between the reacting groups and the entropy loss which is connected with the fixation of the ring; Baeyer- and Pitzer stress as well as the compression of the van der Waals radii. Two reactions compete with each

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[illegible] 69634

Stress and Reactivity of Monocyclic Systems

S/074/60/029/04/02/005
B008/3014

other in the cyclization: the intramolecular - ring closure - and the intermolecular - polycondensation or polymerization As the height of the activation barrier of any chemical reaction is determined by the change in the so-called thermodynamic activation potential, it is possible to speak of enthalpy- and entropy barriers. The synthesis of larger, unstressed rings (13 and more members) is predominated by the entropy barrier, whereas the enthalpy barrier predominates in the case of smaller, stressed rings. Though there is no relation between the stress and the formation rate of rings, the latter are usually closed more easily if unstressed rings are formed, or if the chain has an adequate shape. The development of an adequate chain shape depends on the reaction mechanism. Ring closure is promoted by the existence of substituents (Table 21). Some thermodynamic and kinetic problems of the polymerization of cyclic compounds were dealt with in the paper mentioned in Ref. 155 (Fig. 6). It should be emphasized that the fact that this process is possible from the thermodynamic point of view does not warrant its practical realizibility The polymerization of numerous heterocyclic compounds may be regarded as an equilibrium process. The character of the products obtained depends on the conditions of reaction. Though many examples seem to prove a parallelism between the stress of rings and their polymerizability, such a relationship does not always exist. Thus, it is

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Stress and Reactivity of Monocyclic Systems

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B008/B014

not possible to determine the state of stress of a cyclic compound from its polymerizability. The following Soviet authors are mentioned in this article: N.A. Domnin, P.V. Zubov, M.Ye. Dyatkina, Ya.K. Syrkin, G.G. Gustavson, A.Ye. Chichibabin, V.V. Markovnikov, N.Ya. Dem'yanov, and N.A. Menshutkin. There are 6 figures, 21 tables, and 190 references, 36 of which are Soviet.

ASSOCIATION: In-t organicheskoy khimii im. N.D. Zelinskogo (Institute of Organic Chemistry imeni N.D. Zelinskiy)

Card 5/5

5.3610

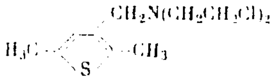
77359
SOV/79-30-1-20/78

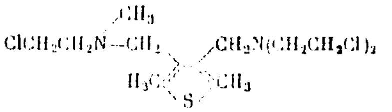
AUTHORS: Gol'dfarb, Ya. L., Kondakova, M. S.

TITLE: Synthesis of Some (β -Chloroethyl)amine Derivatives of Thiophene

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 1, pp 102-107 (USSR)

ABSTRACT: Several anticancerous compounds, β-chloroethylamino derivatives of thiophene, were synthesized from 3-chloromethyl- and 3,4-bis(chloromethyl)-2,5-dimethylthiophene. Reaction of chloromethylated thiophenes with β, β'-dichlorodiethylamine yielded compounds I, mp 171-172°, II, mp 183-185°, and III, mp 176-178°.

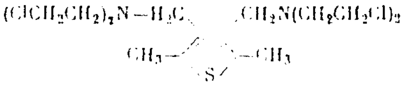

(I)

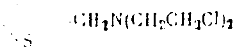

(II)

Card 1/5

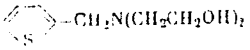
Synthesis of Some (β-Chloroethyl)amine Derivatives of Thiophene

77359
SOV/79-30-1-20/78


(III)

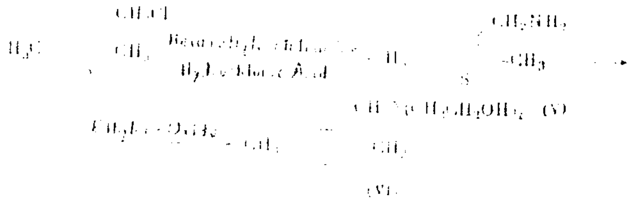

(IV)

In order to find the effect of the displacement of di-(β-chloroethyl)aminomethyl group in thiophene ring from α to β position on physiological properties of compound IV, yield 23.6%, mp 102-103°, the latter was synthesized from compound VIII, bp 186-190° (7 mm), n_D^{20} 1.5497.

 ,
(VIII)

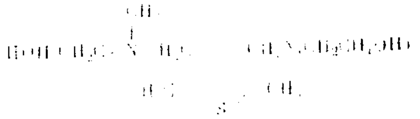
Synthesis of [illegible] ([illegible]
Derivatives of [illegible]

[illegible] -dimethylthio- [illegible] (mm). [illegible] in the following scheme:



Th [illegible] ([illegible]), [illegible] -2,5-dimethylthiophene.

Synthesis of Some (β-[illegible]
Derivatives of Thiop[illegible] [illegible]-30-1-20/[illegible]



(V)

[illegible]-amin[illegible] (V). [illegible], bp 10[illegible] (1 mm), [illegible] prepared from quaternary salt, obtained from hexamethylenetetramine and 2,5-dimethyl-3-thenyl chloride, alcohol, and concentrated HCl by heating on a water bath for 6 hr. All prepared compounds were tested for toxicity and anticancerous activity by P'an Ch'i-[illegible] at the Institute of Experimental Pathology and C[illegible] of the Academy of Medical Sciences [illegible] USSR. [illegible] compounds are comparatively toxic, [illegible] di(β-chloroethyl) amine [illegible] and are not very effective [illegible], participated in this work. [illegible] P'an Ch'i-[illegible] for testing the prepared compounds. There are 1[illegible] references.

Card 4/5

Synthesis of Some (β-Chloroethyl)amine [illegible]
Derivatives of Thiophene

[illegible]
SOV/79-30-1-20/78

7 Soviet, 7 U.S., 1 U.K., 1 Czechoslovakian. The 5 most recent U.S. references are: Wilson, E., Tishler, M., J. Am. Chem. Soc., 73, [illegible] (1951); Jones, R., Jr., Price, Ch. C., Sen, A. K., J. Org. Ch., 22, 783 (1957); Campaigne, E., Thomas, R. L., J. Am. Chem. Soc., 77, [illegible] (1955); Wissler, R. W., [illegible], L. F., Soules, K. H., et al., Arch. Pathol., [illegible], [illegible] (1956); Rabinovitz, M., Olson, M. E., Greenberg, D. M., J. Biol. Ch., 210, 837 (1954).

ASSOCIATION: Institute of Organic Chemistry of the Academy of Sciences, USSR (Institut organicheskoy khimii Akademii nauk SSSR)

SUBMITTED: November 20, 1958

Card 5/5

[illegible]

AUTHORS: [illegible], L., [illegible]

TITLE: [illegible]

PERIODICAL: [illegible]

ABSTRACT: [illegible] in the presence of [illegible] two-component mixtures of benzene [illegible]. The order of [illegible] > [illegible] > [illegible] > [illegible] > [illegible] > [illegible] > [illegible] > [illegible] > [illegible]

Card 1/2

[illegible]
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[illegible]

SUBMITTED: [illegible]

Card [illegible]

5.3(0)

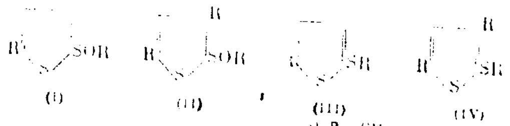
78361
SOV/79-30-3-35/69

AUTHORS: Gol'dfarb, Ya. L., Kalik, M. A., Kirmalova, M. L.

TITLE: Synthesis and Conversions of Sulfides in Thiophene Series. III. Preparation and Cleavage of Sulfoxides

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 3, Pp [illegible] (USSR)

ABSTRACT: A number of compounds of (I) and (II) types were obtained for the first time by the oxidation of the corresponding sulfides (III and IV) with 30% H_2O_2 in glacial acetic acid at room temperature.



(I) (II) (III) (IV)

a) R = CH_3,
b) R = C_6H_5.

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Synthesis and Conversions of Sulfides in Thiophene Series. III. Preparation and Cleavage of Sulfoxides

78301
SOV/79-30-3-55/69

Synthesis of compounds of types (I) and (II) was undertaken in order to study the bond cleavage between the alkylmercapto group and thiophene ring in (I) and (II) by the action of n-butyllithium at low temperature. Sulfoxides of type (III) were synthesized by authors previously (ZhOKh, 29, 2034, 1959). Compounds of type (IV) were obtained for the first time by the reduction of 2-ethylmercapto-5-ethyl-3-acetothienone and 2-methylmercapto-5-methyl-3-thiophene aldehyde (V) according to the Kishner method (modified by Huang-Minlon, J. Am. Chem. Soc., 71, 3301, 1949). (V) was obtained from methyl 5-methyl-2-thienyl sulfide by the action of N-methylformanilide in the presence of phosphoryl chloride. Structure of (V) is proved by its conversion, under the conditions of Cannizzaro reaction, into (VI). Oxidation of (V) with potassium permanganate yields (VII). (IVa) can be also obtained by the action of n-butyllithium on (VIII), followed by treatment with dimethyl sulfate.

Card 2/6

Synthesis and Conversions of Sulfides in Thiophene Series. III. Preparation and Cleavage of Sulfoxides

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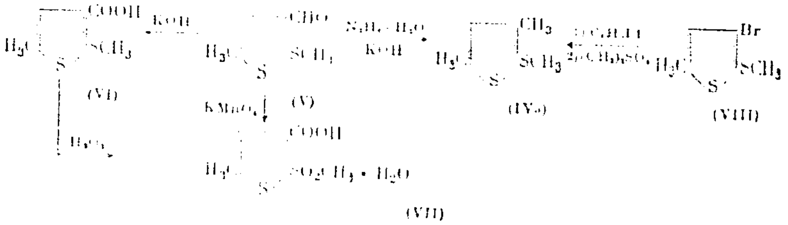
SOV/79-30-3-55/69

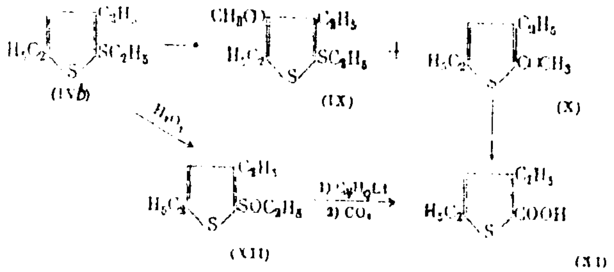


A mixture of (IX) and (X) was obtained by acetylation of (IVb) with acetyl chloride.

Card 3/5

Synthesis and Conversions of Sulfides in Thiophene Series. III. Preparation and Cleavage of Sulfoxides

78[illegible]1
SOV/79-30-3-55/69



Structure of (X) was proved by oxidation to (XI), which can also be obtained from (XII). It was found that the other sulfur atom of alkyl alkylthienyl sulfoxides is eliminated by the action of n-butyllithium at low temperatures. The thiophene ring remains unchanged. The following compounds are listed. 2-Methylmercapto-[illegible]-methyl-[illegible]-thiophenealdehyde (V), obtained (71.2%) as described above, bp [illegible] ([illegible] mm), n_D^{20} 1.[illegible]291.

Card 4/6

Synthesis [illegible]
Thiophene Series [illegible]
Cleavage of [illegible]

SOV/[illegible]

[illegible] by oxidation of (V), mp 101°. [illegible]-methyl-3-thiophenecarboxylic acid [illegible] was obtained from (V) by the action of KOH. [illegible] Methyl 3,5-dimethyl-2-thienyl sulfide [illegible] was obtained [illegible] as mentioned above, [illegible] bp [illegible] Ethyl 3,5-diethyl-2-thienyl [illegible] was obtained [illegible] from 2-ethylmercapto-[illegible]thiophene, bp 121-123° (10 mm), [illegible] n_D [illegible] 3,5-Diethyl-2-thiophenecarboxylic acid was obtained by oxidation of (X), mp 84-85.5°. Ethyl [illegible]-thienyl sulfoxide (IF) was obtained (75%) by [illegible] 3-methyl-2-thienyl sulfide, bp [illegible] n_D [illegible] 5636. Methyl 3-methyl-2-thienyl sulfoxide [illegible] was obtained (72%) by oxidation [illegible]-2-thienyl sulfide, n_D^{20} 1.5652. Methyl 3,5-dimethyl-2-thienyl sulfoxide (IIa), obtained [illegible] n_D [illegible] There are 1[illegible] references, [illegible] Soviet. The [illegible] most recent U.S [illegible] Dietrich, J. Org.

S/080/60/033/005/008/008

AUTHORS Kuz'minskiy, A.S., Gol'dfarb, Ya.L., Fedorov, B.P., Zenchenko, A.I., Kogerman, A.P., Gorushkina, G.I., Angert, L.G.

TITLE: The Synthesis of Some Thiophene Derivatives and the Study of Their Behavior as Rubber Ingredients (Accelerants and Antioxidants) Communication 2.

PERIODICAL Zhurnal prikladnoy khimii, 1960, Vol 33, No 5, pp 1182 - 1187

TEXT: Some azomethines of the thiophene series are accelerants of the vulcanization process [Ref 1], some of them being also antiseptics [Ref 2] which is important for the cable industry. The most suitable azomethines are those containing hydroxyl groups. Other substances of this type were synthesized, therefore, which differed only in the position of the hydroxyl groups. The following substances were synthesized: bis-[2-thenylidene]-hydrazine, bis-[5-methyl-2-thenylidene]-hydrazine, bis-[2-thenylidene]-μ-phenylenediamine, 5'-methyl-2'-thenylidene-6-amino-2-mercaptobenzothiazole, 5-methyl-2-thenylidene-o-aminophenol and 2'-oxybenzylidene-2-thenylamine, as well as two new sulfides [β-oxyethyl]-2-thenylsulfide and 2-thenyl-[n-oxyphenyl]-sulfide. The two sulfides mentioned and 2'-thenylidene-o-

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The Synthesis of Some Thiophene Derivatives and the Study of Their Behavior as Rubber Ingredients (Accelerants and Antioxidants) Communication 2.

amino-2-mercaptobenzothiazole and 6-amino-2-mercaptobenzothiazole are accelerants, but their efficiency is less than that of mercaptobenzothiazole It was evident that the hydroxyl group positively affects the accelerating action of the compounds, if it is located in the para-state of the benzene ring. The introduction of molecules of mercaptobenzothiazole of the amino-group into the benzene ring decreases the efficiency of the compound. A further complication of the molecule decreases the efficiency still more. The cause of these phenomena is not known at the present time. The principal role in the accelerating action of the compounds considered is played by the hydroxyl group.
There are 4 tables and 5 references 2 Soviet, 2 English and 1 German

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TITLE: Reducing Desulfurization of Some Diamines of the Thiophene Series

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 5, pp 1102-1105 (USSR)

TEXT: The authors wished to extend the reducing desulfurization method to the di-tertiary amines of the thiophene series. Thus, higher alkylene diamines can be obtained, which, in turn, could be utilized to synthetize the bis-ammonium salts with a potential curare-like effect. As compared to decamethonium, the halogen alkylates of the diamines IV and IVa would form a new type of such compounds. They are ramified in the center of the chain. Such ramifications exert an influence on the activity of some substances with a curare-like effect (Ref 4). The authors used 2,2-bis(2-thienyl)-butane which is easily formed from thiophene and methyl ethyl ketone as the starting material. By chloromethylation, the bis-chloro-methyl derivative (I) was obtained. This derivative was used in the "raw" state, since it decomposes to a considerable degree when subjected to vacuum distillation. When hexamethylene tetramine is reacted with I, the corresponding salt, and from this, the diamine II is obtained in the ordinary way. Hydrogenolysis with Raney nickel yielded only mixtures distillable in a too broad range. Therefore, skeleton cobalt was used by the authors, although it is

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