However, this method possesses a number of disadvantages which considerably complicate the technology of the production of Thio-TEPA and make it more expensive. These include:

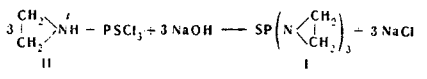
a) the necessity for using anhydrous ethyleneimine (its dehydration is an extremely laborious and unproductive process);

b) the necessity for using as hydrogen chloride acceptor the expensive and scarce triethylamine, which possesses a very unpleasant smell and also requires additional dehydration;

c) the necessity of carrying out the filtration of the reaction mixture from the precipitate of triethylamine hydrochloride which is associated with losses of valuable product and solvent.

We have developed a simple and convenient method for obtaining I. It is based on the performance in a two-phase system of the reaction of aqueous ethyleneimine and alkali (for example, NaOH) with a solution of phosphorothioic trichloride in carbon tetrachloride, chloroform, dichloroethane, or another suitable solvent.

The reaction takes place according to the equation:



The process is carried out by adding the solution of phosphorothioic trichloride in an organic solvent to a stirred mixture of the same solvent and an aqueous solution of ethyleneimine and NaOH at a temperature of from −10 to +5° C.

Compound I is separated from the organic layer by distilling off the solvent in a low vacuum and is purified by recrystallization. Its yield amounts to 62–68% of theoretical.

The proposed method has been carried out on the experimental scale in the pilot plant of the Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR.

Phosphorothioic triethylenetriamide (I). With stirring, a solution of 16.9 g (0.1 mole) of $SPCl_3$ in 25 ml of CCl_4 was added dropwise to a mixture of 50 ml of carbon tetrachloride and a solution of 13.5 g of 97–98% ethyleneimine (0.305 mole) and 13.2 g (0.33 mole) of NaOH in 50 ml of water cooled to from −10 to 0° C. After this, the reaction mixture was stirred at room temperature for another hour and at 35–40° C for 2 hr. The lower layer was separated off, dried with anhydrous magnesium sulfate (this operation is not essential but leads to a purer product), and the solvent was distilled off in a water-pump vacuum. The residue was recrystallized from petroleum ether. The yield of I with mp 52° C was 11.7–12.8 g (61.8–67.6%).

When the reactants are mixed at −10° C, the yield of I amounts to 60–67%, and at 0° C it amount to 57–61%.

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Institute of Organic Synthesis
AS Latvian SSR, Riga

PAPERS DEPOSITED IN VINITI [All-Union Institute for Scientific and Technical Information]*; NOTES

SYNTHESIS AND REACTIONS OF FURAN DERIVATIVES

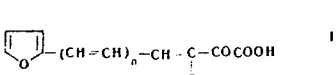
VII. Unsaturated α-Oxocarboxylic Acids of the Furan Series and Their Derivatives

N. O. Saldabol

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 3, p. 571, 1969

UDC 547.725.07:543.422.6

The condensation of furfural and 3-(2-furyl)acrolein with pyruvic and α-oxoglutaric acids in 3 N NaOH has given the Na salts of acids from which by the action of hydrochloric acid 2-furfurylidenepyruvic acid (I), [3-(2-furyl)allylidene]pyruvic acid (II) and β-(2-furfuryl-idene)-α-oxoglutaric acid (III), respectively, have been isolated. Compound I is also formed by the condensation of furfural with oxaloacetic acid (yield 52%). The molar ratios of aldehyde pyruvic acid NaOH = 1 : 1 : 1.25; in the case of dibasic acids, the amount of NaOH was increased.



I n = 0, R = H. II n = 1, R = H.
III n = 0, R = CH_2COOH

The following information is listed: compound, empirical formula, yield of the Na salt, %, yield of the acids, %, mp, °C, [λ_{max}, nm (log ε)]: I, $C_8H_6O_4$, 96, 52, 109–112, [239, 332 (3.40, 4.54) H_2O]: II, $C_{10}H_8O_4$, 66, 52, 126–128 [225, 360 (3.83, 4.30) ethanol]; III, $C_{10}H_8O_6 \cdot 1/2(H_2O)$, –, 86, 78–80 [238, 330 (3.25, 4.48) H_2O]. III · · $1/2(H_2O)$, is converted on drying over $CaCl_2$ into III, mp 114–116° C. Mp of the Na salt of II 320° C. Derivatives of compounds I–III at the

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carbonyl group were prepared (mp, °C): semicarbazone of I (169–171), II (176, decomp.), III (177–179); thiosemicarbazones of I (169–171), II (178–181), III (168–169); 2,4-dinitrophenylhydrazone of I (208–209), 4-phenylsemicarbazone of I (187–188), 4-phenylthiosemicarbazone of I (164–166), guanylhydrazone of I · HNO_3 (114–120), guanylhydrazone of I · HCl (218–220), guanylhydrazone of I (~330, decomp.). The UV spectra of the semicarbazones and thiosemicarbazones are given.

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SYNTHESIS AND REACTIONS OF FURAN DERIVATIVES

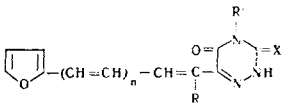
VIII. Derivatives of 6-Azauracil from Unsaturated α-Oxocarboxylic Acids of the Furan Series

N. O. Saldabol

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 3, pp. 571–572, 1969

UDC 547.725.873.07:543.422.6

Derivatives of 6-azauracil (**I–VI**) have been prepared by the cyclization of semicarbazones and thiosemicarbazones of 2-furfurylidenepyruvic acid, β-(2-furfurylidene)-α-oxoglutaric acid, and [3-(2-furyl)allylidene]pyruvic acid. The cyclization was carried out by heating the substances with an aqueous solution of NaOH for 5 min and the products were precipitated by acidification with hydrochloric or acetic acid; yields 87–99%. Compound **VII** was obtained with a yield of 24% by boiling 2-furfurylidenepyruvic acid and 4-phenylthiosemicarbazide in ethanol for 3 hr. The products were purified by recrystallization from CH_3COOH (**I, VII**), aqueous dimethylformamide (**II, III**), aqueous dioxane (**IV**), or ethanol (**V, VI**).



The following information is listed: compound, n, R, R', X, empirical formula, mp, °C (decomp.), [λ_{max}, nm (log ε)]: **I**, o, H, H, O, $C_9H_7N_3O_3$, 285–286, [275, 325 (4.51, 4.05)]; **II**, o, H, H, S, $C_9H_7N_3O_2S$, 267–269, [253, 310, 365 (3.79, 4.18, 4.30)]; **III**, 1, H, H, O, $C_{11}H_9N_3O_3$, 280; [355 (4.44)]; **IV**, 1, H, H, S, $C_{11}H_9N_3O_2S$, 250, [277, 397 (4.00, 4.31)]; **V**, o, CH_2COOH, H, O, $C_{11}H_9N_3O_5$, 260, [221, 317 (3.85, 4.29)]; **VI**, o, CH_2COOH, H, S, $C_{11}H_9N_3O_4S$, 260–261, [220, 260, 299, 370 (3.81, 3.65, 3.90, 4.07)]; **VII**, o, H, C_6H_5, S, $C_{15}H_{11}N_3O_2S$, 264–265, [241, 309, 389 (3.48, 3.94, 4.13)]. The UV spectra were recorded for **III** and **IV** in 2 vol. % dimethylformamide and 98 vol. % ethanol solution and for **I, II,** and **V–VII** in ethanol.

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AS Latvian SSR, Riga

DERIVATIVES OF sym-OCTAHYDROACRIDINE

VI. Synthesis from 9-Chloro-sym-octahydroacridine N-Oxide

G. A. Klimov and M. N. Tilichenko

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 3, p. 572, 1969

UDC 547.835.07

The paper describes some reactions of 9-chloro-sym-octahydroacridine N-oxide (**I**). It is shown that under the action of acetic anhydride **I** undergoes a rearrangement and forms the acetate of 9-chloro-sym-octahydroacridin-4-ol (**II**), giving 9-chloro-sym-octahydroacridin-4-ol (**III**) on hydrolysis. On treatment with thionyl chloride at room temperature, **III** gives 4,9-dichloro-sym-octahydroacridine, and on