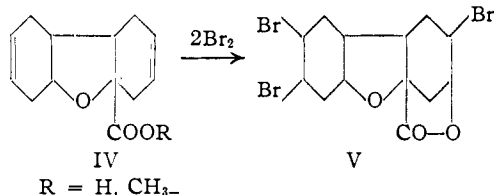


imino-ether formation involving the resulting hydroxy nitrile ester has not been demonstrated. We observed, however, that the saturated compound, 2,2-diethylvaleronitrile (obtained by hydrogenation of 2,2-diethyl-4-pentenitrile over Pd:CaCO₃, b.p. 84–86° (20 mm.)), when subjected to the same experimental conditions was recovered largely unchanged; only a small amount of the amide⁷ (crystallized from petroleum ether, m.p. 68–69.5°) was formed.

Craig³ demonstrated that similar cyclizations of α -disubstituted allylacetic acids or esters could be carried out by the use of bromine. We became aware of this possibility during a study of the reactions of 2,3,4,5-bis-(Δ^2 -butenylene)-tetrahydrofuroic acid (IV)⁸ (octahydrodibenzofuran-4a-carboxylic acid). When either the acid or its methyl ester was treated with an excess of bromine in chloroform at 0°, there was obtained a neutral, colorless crystalline product (needles from acetic acid, m.p. and mixed m.p. 228–230° dec.) which contained but three atoms of bromine. *Anal.* Calcd. for C₁₃H₁₈O₂Br₃: Br, 52.2. Found: Br, 51.8, 52.2. This we believed to be the tribromolactone (V).



More detailed study of the mechanism of the transformations involving allylic systems of this type may be expected to contribute to the knowledge of the structure of the compounds related to IV and V. It has been pointed out that such a study has been undertaken in another laboratory.⁹

(7) C. L. Carter and S. N. Slater, *J. Chem. Soc.*, 130 (1946).

(8) This structure was proposed by J. C. Hillyer, *et al.*, *Ind. Eng. Chem.*, **40**, 2216 (1948). An extensive series of compounds may be derived from the aldehyde formed by condensation of furfural with butadiene. We do not regard this structure as unequivocally established.

(9) See Craig, ref. 3, footnote 6.

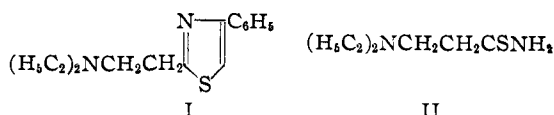
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β, β' -Di-(2-thiazolyl)-diethyl Sulfides

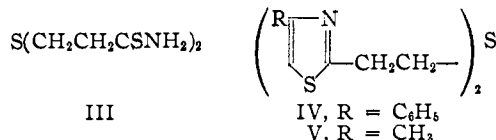
BY EDGAR A. STECK AND LYNN T. FLETCHER

RECEIVED APRIL 29, 1952

A recent publication of Dahlbom¹ prompts us to record observations of similar nature in attempts to prepare 2-(β -diethylaminoethyl)-4-phenylthiazole (I). It was found that the action of hydrogen sulfide on β -diethylaminopropionitrile had not produced the expected thioamide (II), but, rather, another substance, since (I) did not result from the reaction of the intermediate with phenacyl bromide. The intermediate, which we did not obtain in crystalline form, was indicated to be β, β' -thiodi-(propionthioamide) (III) through analyses of the compounds (IV) and (V) formed by reaction with phenacyl bromide and chloroacetone. Only the β, β' -di-(4-substituted-2-thiazolyl)-diethyl sulfide type could be isolated, and no further study was done. Dahlbom¹ has given the problem more detailed consideration.



(1) R. Dahlbom, *Acta Chem. Scand.*, **5**, 690 (1951).



Experimental

β, β' -Thiodi-(propionthioamide) (III).—A mixture of 139.0 g. (4.1 moles) of hydrogen sulfide, 180.9 g. (1.43 moles) of β -diethylaminopropionitrile and 700 cc. of absolute ethanol was shaken at 60° for 10 hours. The viscous, brownish residue which remained after removal of the low-boiling material weighed 150.0 g. (50.5% yield). Attempts to induce the thioamide to crystallize were unsuccessful.

β, β' -Di-(4-phenyl-2-thiazolyl)-diethyl Sulfide (IV).—A solution of 17.5 g. (0.08 mole) of crude (III) in 175 cc. of absolute ethanol was treated with 20.0 g. (0.1 mole) of phenacyl bromide and refluxed three hours. The cooled mixture gave a greenish-white solid (21.3 g., m.p. 192–193°) when a large volume of ether was added. The crude dihydrobromide was converted to the base (IV) with aqueous ammonia. After three crystallizations from hexane, 8.7 g. (43%) of pure (IV) resulted; m.p. 68.2–69.2° cor. (lit.¹ m.p. 68–69°).

Anal. Calcd. for C₂₂H₂₀N₂S₂: N, 6.86; S, 23.54; mol. wt., 408.6. Found:² N, 6.98; S, 23.48, 23.62; mol. wt., 420.

β, β' -Di-(4-methyl-2-thiazolyl)-diethyl Sulfide (V).—The reaction of 0.08 mole of crude (III) with 0.1 mole of chloroacetone in ethanol was run as indicated above. A crude yield of 11.0 g. of dihydrochloride of (V), m.p. 195–197°, resulted; two crystallizations from ethanol-hexane gave 7.4 g. (42%) of fine white needles, m.p. 215–216°. The base (V) was an oil.

Anal. Calcd. for C₁₂H₁₆N₂S₂·2HCl: N, 7.84; S, 26.91; Cl⁻, 19.84. Found:² N, 8.05; S, 26.97; Cl⁻, 19.91.

(2) Analyses by Mr. M. E. Auerbach and staff of the Analytical Laboratories of this Institute.

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Polarographic Behavior of 12-Ketosapogenins

BY CONSTANTINE RICCIUTI, C. O. WILLITS, M. E. WALL AND M. M. KRIDER

RECEIVED DECEMBER 19, 1951

Steroidal compounds containing α, β -unsaturated keto groups are polarographically reducible. Eisenbrand and Picher¹ and Sartori and Bianchi² found that steroids such as testosterone, progesterone, pregnenol-17-one-3 and desoxycorticosterone, are reducible at the dropping electrode in aqueous ethanol solutions and give waves which are proportional to concentration. The polarographic method was applicable only to the Δ^4 -unsaturated-3-ketosteroids, for their saturated analogs did not give polarographic waves. Wolfe, Hershberg and Fieser^{3,4} investigated Δ^1 -cholestenone and found that it was reducible. All of these reducible compounds contain an α, β -unsaturated keto group. They also extended the polarographic method to include 17-ketosteroids and 20-ketosteroids by reaction of these steroids with Girard Reagent T to form polarographically reducible Girard derivatives.

There have been no previous reports on the polarographic behavior of 12-ketosapogenins which

(1) J. Eisenbrand and H. Picher, *Z. physiol. Chem.*, **260**, 83 (1939).

(2) G. Sartori and E. Bianchi, *Gazz. chim. ital.*, **74**, 8 (1944).

(3) J. K. Wolfe, E. B. Hershberg and L. F. Fieser, *J. Biol. Chem.*, **136**, 653 (1940).

(4) J. K. Wolfe, E. B. Hershberg and L. F. Fieser, *ibid.*, **140**, 215 (1941).