

moistened with caustic solution, the imprint gives an intense blue fluorescence in ultraviolet light, but shows no yellow-green fluorescence due to the photoeffect. It appears therefore that coumarin occurs only in the interior of the bean, while the outer skin contains only hydroxycoumarin.

### Organic Reductions by Sodium Aluminum Hydride

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The development of new procedures for preparing sodium aluminum hydride<sup>1</sup> made possible a preliminary study of the scope of organic reductions with this hydride. If one assumes that reductions take place through a mechanism involving a negative ion such as  $\text{AlH}_4^-$ ,<sup>2</sup> there should be little difference in the action of sodium aluminum hydride as compared with lithium aluminum hydride. The data in Table I indicate that reductions are similar for the two hydrides with aldehydes, ketones, carboxylic acids, esters, acid chlorides, alkyl halides, nitriles and the aryl and aliphatic nitro compounds. The yields in each example in Table I except for butanone-2 are within 10% of those reported for the reduction of the same compound with lithium aluminum hydride. The products were isolated and identified in the usual standard way.

TABLE I  
REDUCTIONS BY SODIUM ALUMINUM HYDRIDE

Compound reduced	Product	Yield, %
<i>n</i> -Heptaldehyde	<i>n</i> -Heptyl alcohol	79
Butanone-2	<i>s</i> -Butyl alcohol	64
Benzoic acid	Benzyl alcohol	81
Ethyl benzoate	Benzyl alcohol	91
Palmityl chloride	Cetyl alcohol	96
Acetanilide	<i>N</i> -Ethylaniline	63
1-Iodohexadecane	Hexadecane	85
Nitrobenzene	Azobenzene	78
Nitrobutane	1-Aminobutane	73
Cinnamaldehyde	Hydrocinnamyl alcohol	89
Cinnamaldehyde	Cinnamyl alcohol	85 <sup>a</sup>
Benzonitrile	Benzylamine	92
Benzonitrile	Benzaldehyde	70 <sup>a</sup>

<sup>a</sup> Inverse addition of the hydride to the organic compound. The benzaldehyde preparation was run at 0° and the cinnamyl alcohol preparation at room temperature.

The reductions of cinnamaldehyde and benzonitrile were undertaken to see if cinnamyl alcohol and benzaldehyde could be prepared by the normal reduction procedure in which the organic compound is added to the hydride. This was the procedure for all the reductions listed in Table I except those indicated by note *a*. As with lithium aluminum hydride,<sup>3</sup> it turned out that the unsaturated alcohol and the aldehyde could be obtained only by the inverse addition of sodium aluminum hydride to the organic compound. Thus sodium aluminum hydride was no milder a reagent than lithium aluminum hydride.

All the reactions were given ample time to be

(1) To be published by A. E. Finholt, G. D. Barbaras, G. K. Barbaras, G. Urry, T. Wartik and H. I. Schlesinger.

(2) L. W. Trevoy and W. G. Brown, *THIS JOURNAL*, **71**, 1675 (1949).

(3) F. A. Hochstein and W. G. Brown, *ibid.*, **70**, 3484 (1948).

completed. These studies, therefore, do not rule out the possibility that the rates of reduction of sodium and lithium aluminum hydride may be different. There is little doubt, however, that sodium aluminum hydride can be substituted effectively for lithium aluminum hydride in most organic reductions.

### Experimental

The same general experimental conditions were employed as those described for lithium aluminum hydride<sup>4</sup> except that diethyl ether could not be used as a solvent. All of the reductions except that of butanone-2 were run using a tetrahydrofuran solution of sodium aluminum hydride. With the ketone, the solvent was the dimethyl ether of triethylene glycol. One run (not reported in Table I) was made using a slurry of sodium aluminum hydride in diethyl ether. An 82% yield of benzyl alcohol was obtained by adding ethyl benzoate to the slurry.

**General Procedure.**—A stock solution of sodium aluminum hydride in tetrahydrofuran was prepared from aluminum hydride and sodium hydride.<sup>1</sup> The solution was standardized in the usual way by removing the solvent from an aliquot and hydrolyzing the solid; the strength of the solution was about 3% by weight. Commercial tetrahydrofuran was purified for all purposes by distillation from lithium aluminum hydride, taking care not to distill to dryness. The compound to be reduced usually was diluted with tetrahydrofuran. The tetrahydrofuran solution of sodium aluminum hydride was weighed into the reaction vessel; the system was swept with dry nitrogen gas, and the compound to be reduced was added dropwise to the sodium aluminum hydride solution. Stirring was maintained throughout the addition, the reaction period, and the decomposition of the excess hydrate with water. The reactions proceeded very smoothly and without undue liberation of heat. Periods allowed for the reaction varied from 2 to 17 hours. The excess sodium aluminum hydride was decomposed by addition of water; the intermediate complex was broken up by addition of either 10% sulfuric acid or 10% sodium hydroxide, sometimes with heating. One example will be given to illustrate the general procedure.

**The Reduction of Ethyl Benzoate.**—A solution of 25 g. (0.166 mole) of ethyl benzoate dissolved in 25 g. of tetrahydrofuran was added slowly to 250 g. of tetrahydrofuran containing 6.0 g. (0.111 mole) of sodium aluminum hydride. The mixture was stirred for 2.5 hours. After decomposition of excess hydride with water, 10% sodium hydroxide solution was added to break up the complex. The product was extracted from the reaction vessel with diethyl ether; this solution was dried over calcium sulfate, filtered, and distilled to remove ether and tetrahydrofuran. The product was fractionally distilled to give 16.4 g. (91%) of benzyl alcohol, b.p. 205–207°.

**Acknowledgment.**—The authors wish to thank the Office of Naval Research for financial support in this investigation.

(4) W. G. Brown, "Organic Reactions," Vol. VI, John Wiley & Sons, Inc., New York, N. Y., 1951, Chapter 10.

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### Thiophenetetracarboxylic Acids

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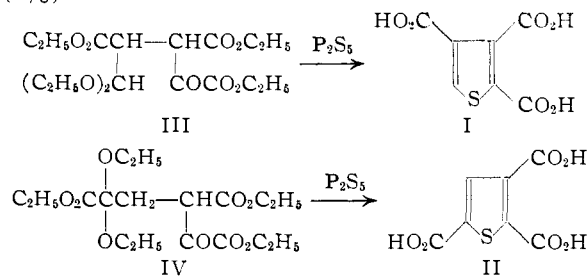
Recent communications<sup>1,2</sup> have described the preparation of 3,4-thiophenedicarboxylic acid. With the addition of this member to the series, all the mono- and dicarboxylic acids of thiophene and thiophenetetracarboxylic acid are known. The two tricarboxylic acids, 2,3,4-thiophenetetracarboxylic

(1) J. Sice, *J. Org. Chem.*, **18**, 70 (1954).

(2) E. C. Kornfeld and R. G. Jones, *ibid.*, **19**, 1671 (1954).

acid (I) and 2,3,5-thiophenetricarboxylic acid (II), appear not to have been synthesized previously. In connection with the preparation of other heterocyclic compounds in this Laboratory, intermediates have become available for the synthesis of I and II.

The acid I was obtained in 26% yield from diethyl  $\alpha$ -diethoxymethyl- $\alpha'$ -ethoxalylsuccinate (III)<sup>2</sup> and phosphorus pentasulfide. In like manner II was obtained from diethyl  $\alpha,\alpha$ -diethoxy- $\alpha'$ -ethoxalylglutarate (IV),<sup>3</sup> but the yield was very low (4%).



The acids I and II had solubility properties similar to the tricarboxylic acids of benzene, *i.e.*, they were highly soluble in ether and ethyl acetate as well as in water.

Messinger<sup>4</sup> has described an acid obtained by permanganate oxidation of a mixture of dimethylacetylthiophenes. The acid was not purified, but a trimethyl ester melting at 118° was prepared. Hartough<sup>5</sup> has assumed that this product was trimethyl 2,3,5-thiophenetricarboxylate. Its melting point, however, does not correspond with the melting point of either the trimethyl ester of I (87°) or the trimethyl ester of II (83°). It must be concluded, therefore, that Messinger probably did not have in hand a thiophenetricarboxylic acid.

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#### Experimental

**2,3,4-Thiophenetricarboxylic Acid.**—A mixture of 90 g. (0.25 mole) of crude diethyl  $\alpha$ -ethoxalyl- $\alpha'$ -diethoxymethylsuccinate<sup>2</sup> and 55 g. (0.25 mole) of phosphorus pentasulfide in 350 ml. of toluene was stirred and heated under reflux for two hours. After cooling, the dark toluene solution was decanted and washed successively with 500 ml. of ice-cold 2 *N* sodium hydroxide solution and two 250-ml. portions of water. Evaporation of the toluene solution by warming under reduced pressure left a dark liquid residue. This was distilled under reduced pressure until nothing more came over. There was much decomposition, and a large quantity of resin remained in the flask. The liquid that was collected over the range 130–200° (2–5 mm.) was redistilled to yield 28 g. of red brown liquid, b.p. 140–160° (0.2 mm.). This was saponified upon shaking and heating with a solution of 20 g. of sodium hydroxide in 50 ml. of water and 25 ml. of ethanol. The resulting semi-solid mixture was warmed under reduced pressure to remove alcohol. The residue was taken up in 200 ml. of water, and this solution was acidified with excess hydrochloric acid. After clarification with a little carbon to remove some tar that separated, the water solution was evaporated to dryness by heating under reduced pressure. Three 150-ml. portions of ether were used to extract the solid residue, and after evaporation of the ether solution, a sirup remained that slowly crystallized to a tan powder. This crude acid weighed 18.5 g.

(3) R. G. Jones, *THIS JOURNAL*, **77**, 4074 (1955).

(4) J. Messinger, *Ber.*, **18**, 2300 (1885).

(5) H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p. 399.

(34% yield). It was purified by recrystallization from 50 ml. of glacial acetic acid and obtained as a white powder, m.p. 247–249° (sublimed above 225°). The yield of pure acid was 14 g. (26%).

*Anal.* Calcd. for  $\text{C}_7\text{H}_4\text{O}_6\text{S}$ : C, 38.90; H, 1.87; S, 14.83. Found: C, 39.11; H, 1.92; S, 14.63.

The acid was readily soluble in water, ether, alcohol, ethyl acetate, etc., but insoluble in petroleum ether.

The trimethyl ester was obtained in 80% yield by esterification with methanol and sulfuric acid. It was purified by recrystallization from petroleum ether and by sublimation under reduced pressure; m.p. 87–87.5°.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{10}\text{O}_8\text{S}$ : C, 46.51; H, 3.90. Found: C, 46.86; H, 4.09.

**2,3,5-Thiophenetricarboxylic Acid.**—This was prepared in the same way as described above for the synthesis of the 2,3,4-isomer except that diethyl  $\alpha$ -ethoxalyl- $\alpha'$ -diethoxyglutarate<sup>3</sup> was used in place of diethyl  $\alpha$ -ethoxalyl- $\alpha'$ -diethoxymethylsuccinate. The yield of crude acid was about 10 g. (18%). It was purified with difficulty and with considerable loss by recrystallization from glacial acetic acid in which it appeared to be somewhat more soluble than the 2,3,4-isomer. It was readily soluble in water, ether or alcohol. The yield of pure acid, obtained as a white powder, was 2.3 g. (4%); m.p. 214–216°.

*Anal.* Calcd. for  $\text{C}_7\text{H}_4\text{O}_6\text{S}$ : C, 38.90; H, 1.87; S, 14.83. Found: C, 39.13; H, 1.97; S, 14.49.

Analytical sample was dried at 120°. When it was dried at 100° for two hours, unlike the 2,3,4-isomer, it still retained one-half mole of water.

The trimethyl ester melted at 82.5–83°.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{10}\text{O}_8\text{S}$ : C, 46.51; H, 3.90. Found: C, 46.80; H, 3.96.

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## Synthesis and Biological Properties of Diaryl-(trifluoromethyl)-carbinols

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Previous experiments<sup>1</sup> have shown that ethyl trichloroacetate fails to give with aromatic magnesium—or lithium—organic compounds the normal diaryl-(trichloromethyl)-carbinols (I); complicated dechlorination reactions take place instead. It seemed, therefore, desirable to study the analogous reaction of ethyl trifluoroacetate, as the C–F bond was likely to be more stable toward metalorganic compounds.<sup>2</sup> In addition, the reaction products II could be expected to have insecticidal properties.<sup>3</sup> The behavior of ethyl mono- and difluoroacetate toward Grignard compounds has remained unexplored, and ethyl trifluoroacetate has only been shown to react normally with methylmagnesium iodide and—partly—with ethylmagnesium bromide, when this investigation was begun.<sup>4–8</sup> Compound II (Ar =  $\text{C}_6\text{H}_5$ ), has, however, been ob-

(1) A. Kaluszyner and S. Reuter, *THIS JOURNAL*, **75**, 5126 (1953).

(2) For a comparison of the reactivity of C–Cl and C–F bonds, see J. Hine and D. E. Lee, *ibid.*, **74**, 3182 (1952).

(3) A survey of nuclear-fluorinated analogs of DDT has been given by R. Riemschneider and H. D. Otto, *Z. Naturforschung*, **9b**, 95 (1954). 1,1-Di-(*p*-chlorophenyl)-2,2,2-trifluoroethane has been described by S. Kirkwood and J. R. Dacey, *Can. J. Res.*, **24B**, 69 (1946); see S. Kirkwood and P. H. Phillips, *J. Pharmacol. Expt. Therap.*, **87**, 375 (1946).

(4) F. Swarts, *Bull. soc. chim. Belg.*, **36**, 191 (1927) (*C. A.*, **21**, 2659 (1927)).

(5) E. Grysckiewicz-Trochimowski, *Rec. trav. chim. Pays-Bas*, **66**, 427 (1947).

(6) K. N. Campbell, J. O. Knobloch and B. K. Campbell, *THIS JOURNAL*, **72**, 4380 (1950).