less oil; b.p. 135° (4 mm.), $n^{20}\text{D}$ 1.4514. *Anal.* Calcd. for $C_7H_{10}O_4N_2$: C, 45.16; H, 5.43; N, 15.05. Found: C, 45.21; H, 5.65; N, 15.31 (by the Micro-Chemical Laboratory of New York University).

Ethyl α-Nitroglutarate.—A solution of 1.15 g. (0.05 g. atom) of sodium in 75 ml. of *t*-butyl alcohol was added to a solution of 6.6 g. (0.05 mole) of ethyl nitroacetate and 5.5 g. (0.055 mole) of ethyl acrylate in 40 ml. of *t*-butyl alcohol. The mixture was refluxed for 90 minutes with stirring, and then was stirred overnight at room temperature, after which it was made acid to congo red with hydrochloric acid and most of the solvent was removed with the aid of an aspirator. The remaining solution was poured into four volumes of water and extracted by ether. The ether extract was washed twice with water, dried over anhydrous $MgSO_4$, and distilled. After a considerable amount of unreacted ethyl nitroacetate was distilled at 67° (3 mm.), ethyl α-nitroglutarate was obtained as a colorless oil, b.p. 128–129° (4 mm.), $n^{20}\text{D}$ 1.4410, yield 1.3 g. (11% based on starting material). *Anal.* Calcd. for $C_9H_{15}O_6N$: C, 46.35; H, 6.48; N, 6.01. Found: C, 46.47; H, 5.94; N, 6.09 (by the Micro-Chemical Laboratory of New York University).

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2,3-Dimethoxytriphenylmethane and Some of its Derivatives

BY J. L. E. ERICKSON AND J. M. DECHARY

During the investigation of the structure of the lactone resulting from the addition of diphenylketene to *o*-benzoquinone there were prepared 2,3-dimethoxytriphenylcarbinol and the new 2,3-dimethoxytriphenylchloromethane.[1] We now wish to report the preparation of 2,3-dimethoxytriphenylmethane and several other compounds of this series, none of which have been previously described.

The synthesis of 2,3-dimethoxytriphenylmethane was accomplished by formic acid reduction of the corresponding carbinol. Methyl 2,3-dimethoxytriphenylmethyl ether was obtained by treating the same carbinol with methanolic sulfuric acid. 2,3-Dimethoxytriphenylacetonitrile was prepared by heating 2,3-dimethoxytriphenylchloromethane with mercuric cyanide. Hydrolysis of the nitrile did not yield the corresponding 2,3-dimethoxytriphenylacetic acid,[1] a product obtained previously by the carbonation of 2,3-dimethoxytriphenylmethylsodium. Instead, it gave 2,3-dihydroxytriphenylacetic acid lactone.[1] Conventional methods used for the hydrolysis of nitriles had no effect, and when more vigorous methods were used, cleavage of the methoxyl groups as well as hydrolysis of the nitrile occurred to yield the lactone.

Experimental[2]

2,3-Dimethoxytriphenylmethane.—One gram of 2,3-dimethoxytriphenylcarbinol was boiled for 3.5 hours with 10 ml. of 88% formic acid.[3] After standing several days, the oily product solidified; it was then pulverized, washed thoroughly with water and dried to give 0.88 g. of crude material, which, when crystallized three times from alcohol, yielded glistening white rhombs, m.p. 84.5–85°.

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.68; H, 6.76.

Methyl 2,3-Dimethoxytriphenylmethyl Ether.—One gram of 2,3-dimethoxytriphenylcarbinol was dissolved in 10 ml. of boiling methanol; the solution was cooled, three drops of concentrated sulfuric acid was added, and the mixture warmed on the steam-bath for 20–30 minutes. When the solvent was removed by evaporation and the oily product was cooled, 0.96 g. of crude methyl ether separated. After three crystallizations from methanol, there were obtained glistening white hexagonal tablets, m.p. 119.5–120°.

Anal. Calcd. for $C_{22}H_{22}O_3$: C, 79.01; H, 6.63. Found: C, 79.00; H, 6.72.

2,3-Dimethoxytriphenylacetonitrile.—Into a 500-ml. round-bottomed flask, fitted with an air condenser and calcium chloride drying tube, were placed 20.0 g. (0.059 mole) of 2,3-dimethoxytriphenylchloromethane[1] and 18.8 g. (0.073 mole) of mercuric cyanide.[4] The mixture was heated at 150–170° for 1.5 hours in an oil-bath, then cooled, and the solid melt powdered and extracted with boiling benzene. The benzene solution was filtered, treated with low-boiling petroleum ether to precipitate oily impurities, and the filtered solution cooled. Upon standing, 4.5 g. (23%) of the crude nitrile crystallized. Recrystallization of the material from a small amount of glacial acetic acid (charcoal) yielded 2.3 g. of colorless leaflets, m.p. 157.5–158°.

Anal. Calcd. for $C_{22}H_{19}O_2N$: C, 80.21; H, 5.81; N, 4.25. Found: C, 79.51; H, 5.79; N, 4.13.

Simultaneous hydrolysis and demethylation of the nitrile was accomplished by boiling 120 mg. of the compound for 34 hours in a solution composed of 2 ml. of hydriodic acid (sp. gr. 1.70) and 5 ml. of glacial acetic acid. The cooled solution was treated with sufficient saturated sodium bisulfite solution to remove free iodine, and the fine white precipitate was collected, washed with a little water, and dried. There was thus obtained 110 mg. of 2,3-dihydroxytriphenylacetic acid lactone, m.p. 192.5–193°. After two crystallizations from a mixture of benzene and petroleum ether, the melting point was raised to 192.5–193.5°.

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[2] All melting points are uncorrected.

[3] H. Kauffmann and P. Pannwitz, *Ber.*, **45**, 766 (1912).

[4] E. Fischer and O. Fischer, *Ann.*, **194**, 260 (1878).

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5-Nitro-2-thenaldehyde

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In previous reports from this Laboratory we have enumerated several variously substituted 2-thenaldehydes which have been prepared by means of the one-step N-methylformanilide synthesis.[1] However, due to the failure of 2-nitrothiophene to form its corresponding aldehyde under the conditions of the reaction, it has been missing from our listing. With the advent of the synthesis of chloromycetin and its various aromatic and heterocyclic analogs,[2] the absence of this aldehyde has become more noticeable. With this in mind, we have attempted to prepare 5-nitro-2-thenaldehyde by another series of reactions.

Starting with 2-methyl-5-nitrothiophene[3] we have converted it to 5-nitro-2-thenyl bromide using N-bromosuccinimide in the presence of benzoyl peroxide. Since the 2-methyl-5-nitrothiophene is relatively inactive toward this reagent, at least two to three hours of reflux were necessary before there was a noticeable reaction. A maximum of 24 hours was required for the completion of the reaction. The 5-nitro-2-thenyl bromide was characterized by

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[3] I. J. Rinkes, *Rec. trav. chim.*, **51**, 1134 (1932).