less oil; b.p. 135° (4 mm.), $n^{20}D$ 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.), $n^{20}D$ 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°.

(1) J. L. E. Erickson and J. M. Dechary, THIS JOURNAL, **74**, 2644 (1952).

(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

BY MATTHEW E. DULLAGHAN, LOUIS J. OWEN AND F. F. NORD

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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

(1) W. J. King and F. F. Nord, *J. Org. Chem.*, **13**, 635 (1948).

(2) L. M. Long and H. D. Troutman, THIS JOURNAL, **71**, 2469 (1949); **71**, 2473 (1949); H. Keskin, C. D. Mason and F. F. Nord, *J. Org. Chem.*, **16**, 1333 (1951).

(3) L. J. Rinkes, *Rec. trav. chim.*, **51**, 1134 (1932).

the formation of the N-(5-nitro-2-thenyl)-piperidine picrate.

The 5-nitro-2-thenyl bromide was transformed to its hexamethylenetetramine salt and this salt in turn, hydrolyzed to the aldehyde both by steam distillation and also by refluxing it in 50% ethanol. Since neither method of hydrolysis gave an appreciable yield of the aldehyde, an alternative method of preparation was investigated. 5-Nitro-2-thenyl bromide was then oxidized to 5-nitro-2-thenaldehyde with selenium dioxide.[4] The product from the selenium dioxide oxidation was an oil which, after washing with water, gave a negative halogen test with alcoholic silver nitrate. Since attempted crystallization from such solvents as water and a variety of organic solvents were of no avail, the aldehyde was isolated in the form of its semicarbazone in a yield of 50%.

Experimental[5]

5-Nitro-2-thenyl Bromide.—2-Methyl-5-nitrothiophene (33 g., 0.23 mole), dissolved in 100 ml. of carbon tetrachloride, was treated with 27.38 g. of N-bromosuccinimide and 0.25 g. of benzoyl peroxide. There was no reaction on mixing and only after two to three hours of reflux did the reaction take on a reddish tinge. The mixture was then refluxed for 24 hours to ensure completion of the reaction. It was now cooled, filtered to remove the succinimide and distilled. It was then cooled, filtered to remove the succinimide and distilled. Unreacted 5-nitro-2-methylthiophene was removed at reduced pressure, b.p. 106° (6 mm.). Because of decomposition the 5-nitro-2-thenyl bromide was not distilled. Instead a portion was characterized as its piperidine picrate and the remainder converted to its hexamethylentetramine salt with a yield of 60%.

N-(5-Nitro-2-thenyl)-piperidine Picrate.—A portion of the above after re-solution in carbon tetrachloride was treated with an excess of piperidine dissolved in carbon tetrachloride. There was an immediate precipitation of piperidine hydrobromide. The solution was filtered and added to a saturated solution of picric acid in carbon tetrachloride. The picrate separated in yellow crystals, m.p. 193–194°.

Anal. Calcd. for $C_{16}H_{17}O_9N_5S$: N, 15.38. Found: N, 15.40.

Hydrolysis of Hexamethylenetetramine Salt.—(a).—The salt prepared as above was suspended in water and steam distilled. The distillate (2 liters) was extracted with ether, the ether removed and a small amount of a dark brown oil remained. This was converted to its 2,4-dinitrophenylhydrazone, m.p. 250° (dec.).

Anal. Calcd. for $C_{11}H_7O_6N_5S$: N, 20.77. Found: N, 20.70.

(b).—The hexamethylenetetramine salt was suspended in a solution of 50% ethanol and refluxed for two hours. The ethanol was removed and the residue chilled to induce crystallization. Since there was no separation of solid, the alcohol was removed and the residue extracted with ether. After drying and removal of the ether, a very small amount of brown solid remained. This was not further identifiable as the aldehyde.

Selenium Dioxide Oxidation.—5-Nitro-2-thenyl bromide (11.1 g., 0.05 mole) was dissolved in ethanol. Freshly prepared selenium dioxide (5.55 g., 0.05 mole) was added and the mixture kept at 140–150° (oil-bath) for two hours, during which time most of the solvent was allowed to distil off. After the reaction was completed, the residue was washed with water. Attempted crystallization from the usual organic solvents was unsuccessful and, consequently, the aldehyde was isolated as its semicarbazone, m.p. 223°, yield 50%.

Anal. Calcd. for $C_6H_6N_4O_3S \cdot H_2O$: N, 24.13. Found: N, 24.41.

(4) C. H. Fisher, THIS JOURNAL, **56**, 2056 (1934).

(5) Shortly before receipt of our proofs there appeared a Note by Emerson and Patrick (*ibid.*, **74**, 1356 (1952)) describing a different synthesis. The final data are in agreement with ours.

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CONTRIBUTION NO. 251 FROM THE DEPARTMENT OF ORGANIC CHEMISTRY AND ENZYMOLOGY FORDHAM UNIVERSITY, NEW YORK 58, N. Y.

Distribution of Hydroxyl Groups in Carboxymethyl Cellulose[1]

BY ELIZABETH DYER AND HARRY E. ARNOLD

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Prior to the completion of this work, there was only one report of the distribution of the free and substituted hydroxyl groups in carboxymethyl cellulose. Timell[2] determined glycol groups by periodate oxidation and stated that the tosylation–iodination method, used for other cellulose ethers,[3] was not applicable to this substance. In a recent extensive study of carboxymethyl cellulose, Rydholm[4] also used the periodate oxidation and stated that tosylation was tried without success.

In the present work both the tosylation–iodination procedure and the periodate method were used on two samples of carboxymethyl cellulose,[5] of a degree of substitution of 0.75 and 0.77. CMC 1 had been prepared by a slurry technique, and CMC 2 by dry mixing. The viscosity of a 2% aqueous solution was 4000 cps. and 500 cps. for CMC 1 and 2, respectively.

TABLE I

TOSYLATION OF CARBOXYMETHYL CELLULOSE AT 20°

CMC	Time, days	S,[a] %	Tosyloxy,[b] moles/g.u.[c]	Cl,[a] %	$-OCH_2COOH$,[c] mole/g.u.	$\eta_{rel.}$[d]
1	0	0	0	0.06	0.75	1.39
	0.25	7.01	0.68			
	0.50	7.95	.83			
	1.00	8.40	.91			
	2.00	8.70	.96	0.16	0.76	1.11
	3.00	9.01	1.02	.18	.78	1.04
	8.00	9.33	1.08	.33	.77	1.02
2	0	0	0	.07	.77	1.43
	0.25	6.99	0.68			
	0.50	7.66	.78			
	1.00	8.16	.87			
	2.00	8.62	.94	0.15	0.81	1.08
	3.00	8.90	1.01	.15	.77	1.06
	8.00	9.28	1.08	.33	.76	1.04

[a] Average value of at least two determinations done gravimetrically with the Parr bomb. [b] Calculations based on values of 0.75 and 0.77 for $-OCH_2COOH$ in tosylates of CMC 1 and 2, respectively. [c] Except for zero time, only small samples were available for analysis; hence the value at zero time, known with greater precision, was used in calculations. [d] Ratio of time of flow of solution and solvent in a Bingham viscometer at 25°, using a 0.2% solution of the compound in 0.25% aqueous sodium hydroxide. [e] G. u. means anhydroglucose unit.

(1) From the M.S. Thesis of Harry E. Arnold, September, 1950.

(2) T. Timell, *Svensk Papperstidn.*, **52**, 61 (1949).

(3) (a) J. F. Mahoney and C. B. Purves, THIS JOURNAL, **64**, 9, 15 (1942); (b) C. W. Tasker and C. B. Purves, *ibid.*, **71**, 1017, 1023 (1949); (c) T. Timell, *Svensk Papperstidn.*, **51**, 52 (1948).

(4) S. Rydholm, *ibid.*, **53**, 561 (1950).

(5) du Pont Sodium CMC, supplied through the courtesy of the Explosives Department of E. I. du Pont de Nemours and Company.