that a practical electrolytic method for periodate oxidations might be developed wherein the periodate would be continuously regenerated *in situ*. Thus, only a fraction of the theoretical amount of periodic acid required for the oxidation would be needed. We report here the application of such a method to the oxidation of corn starch to oxystarch by known procedures for the electrolytic oxidation of iodic to periodic acid.[1,2]

The product is nearly identical with the oxystarch we prepared by the method of Purves.[3] Oxystarch was also prepared by oxidation with periodic acid as described by Jackson and Hudson.[4] Data on the preparation and characterization of the products by the three methods are given in Table I. Comparison of the dialdehyde content of the oxystarches made by the non-electrolytic methods substantiates Purves' contention that oxidation is selective only below 20° and at *p*H 2–5.[3c] The data for the electrolytic oxystarches prepared at 40–45° indicate that these restrictions do not apply to the electrolytic oxidation.

TABLE I

ANALYSES OF PERIODATE OXYSTARCHES[a]

Oxystarch	Temperature of oxidation, °C.	Yield, %	$[\alpha]^{25}\text{D}$ (*c* 2, water)	Dialdehyde,[b] %	Dicarboxyl,[c] %	Yield brucine D-erythronate, %
Electrolytic	40–45	89	+17°	89		77
	40–45	91	+19°	89	0.2	
	20–25	85	+38°	81		45
Purves	12–25		+14°	89	.03	
	12–25	98	+15°	89		85
Jackson and Hudson	25	97	+ 9°	68	.1	

[a] All values on dry basis. [b] Estimated by oxime formation using Method A described by E. K. Gladding and C. B. Purves, *Paper Trade J.*, 116, 150 (1943). [c] Based on calcium acetate method described by E. C. Yackel and W. O. Kenyon, THIS JOURNAL, **64**, 121 (1942).

Jackson and Hudson[5] characterized their oxystarch and oxycellulose by hydrolyzing with $0.1N$ acid and identifying the D-erythrose present by oxidation with bromine to D-erythronic acid, isolated as the brucine salt. They obtained 22 and 15% yields from oxystarch and oxycellulose, respectively. These low yields were attributed in part to destruction of the material during hydrolysis and to incomplete degradation of the polymer. In substantiation of this, Pacsu[6] isolated the 2,4-dinitrophenylhydrazone of glyoxylic acid from periodate oxycellulose in 75% yield when bromine oxidation preceded hydrolysis in *N* acid. Accordingly, oxystarches prepared electrolytically and by Purves' method were oxidized by bromine and brucine D-erythronate isolated after hydrolysis (Table I).

Experimental

Electrolytic Oxidation.—The cell consisted of a battery jar (150 mm. in diameter by 150 mm. high) which contained a Coors' porous cup (90 mm. in diameter by 145 mm. high) as the anode compartment. The cathode was several turns of $^{1}/_{4}$-in. o.d. lead tubing which served as a cooling coil. The anode of lead dioxide was prepared by oxidizing the lower 60 mm. of a 175-mm. by 25-mm. by 2-mm. lead strip, freshly roughened with a steel brush, in *N* sulfuric acid at 1.5 amperes for 30 minutes. The coated anode was then washed in water for 30 minutes.

The corn starch was prepared by extraction with methanol, drying over concentrated sulfuric acid, and equilibrating to room humidity after grinding to pass 60 mesh. Its moisture content and that of the oxystarches were determined by drying for eight hours in an Abderhalden dryer at 100°.

The anolyte was made up of 30.0 g. of corn starch, dry basis, and 10.0 g. of iodic acid (0.31 mole per anhydroglucose unit) in 300 ml. of water. The catholyte was 1200 ml. of 2% sulfuric acid which was sufficient to put the catholyte level several centimeters above that of the anolyte to diminish electroendosmosis and diffusion. The anolyte was well stirred as 3.0 amperes (0.12 ampere per sq. cm.) at 7–8 volts was passed for 8 hours 15 minutes (250% of theory).[7] The occasional addition of octyl alcohol to the anolyte was necessary to inhibit foaming.

At the end of the electrolysis, the anolyte was poured into a beaker and stirred one hour at which time all the periodic acid had reacted. The oxystarch was collected by filtration on a Buchner funnel, resuspended three times in 400 ml. of water in a Waring Blendor, twice in 400 ml. of acetone and then dried over concentrated sulfuric acid *in vacuo*. It was ground to pass 60 mesh and equilibrated to room humidity.

Bromine Oxidation and Isolation of Brucine D-Erythronate.[8]—A suspension of 9.8 g. of oxystarch, dry basis, was dissolved by heating on a steam-bath for two hours in 350 ml. of water. After the solution was filtered and diluted to 500 ml., 10 ml. of bromine was added, and the solution was then stored in the dark. Two days later, 4.5 ml. of bromine was added. The solution was allowed to stand two more days; the excess bromine was removed by aeration; and 50 ml. of 12 *N* hydrochloric acid was added. The solution was diluted to 600 ml. (1 *N* in hydrochloric acid) and heated for five hours on a steam-bath. The acids present were neutralized with barium hydroxide solution and an excess added to precipitate basic barium glyoxylate. The basic salt was removed by filtration after several days at 5°, and the excess barium hydroxide neutralized with carbon dioxide to precipitate barium carbonate. The procedure after this point followed that of Jackson and Hudson.[5]

The product resulting from this treatment was free-flowing and had the gross granular characteristics of the original corn starch. It showed no color with iodine and no birefringence.

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[3] (a) D. H. Grangaard, J. H. Michell and C. B. Purves, THIS JOURNAL, **61**, 1290 (1939); (b) J. H. Michell and C. B. Purves, *ibid.*, **64**, 585 (1942); (c) D. H. Grangaard, E. K. Gladding and C. B. Purves, *Paper Trade J.*, **115**, 75 (1942).

[4] E. L. Jackson and C. S. Hudson, THIS JOURNAL, **59**, 2049 (1937).

[5] E. L. Jackson and C. S. Hudson, *ibid.*, **60**, 989 (1938).

[6] E. Pacsu, *Textile Research J.*, **15**, 359 (1945).

[7] This is a current efficiency of 40%. Willard and Ralston, ref. (2), obtain similar values for the oxidation of iodic to periodic acid.

[8] We are indebted to Dr. Allene Jeanes for suggestions relating to this procedure (unpublished work of Allene Jeanes and C. S. Hudson).

[9] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

2-Phenyl-2-*p*-chlorophenyl-4-methylmorpholine

BY HENRY GILMAN AND CALVIN C. WANSER

RECEIVED MAY 12, 1952

In a previous communication[1] the synthesis of several 2-substituted-4-methylmorpholines as possible antihistaminic agents was reported. Among the compounds prepared was 2,2-diphenyl-4-methylmorpholine, a cyclic analog of Benadryl. In view of the marked antihistaminic activity of certain 1-(*p*-halobenzhydryl)-4-methylpiperazines,[2,3] of

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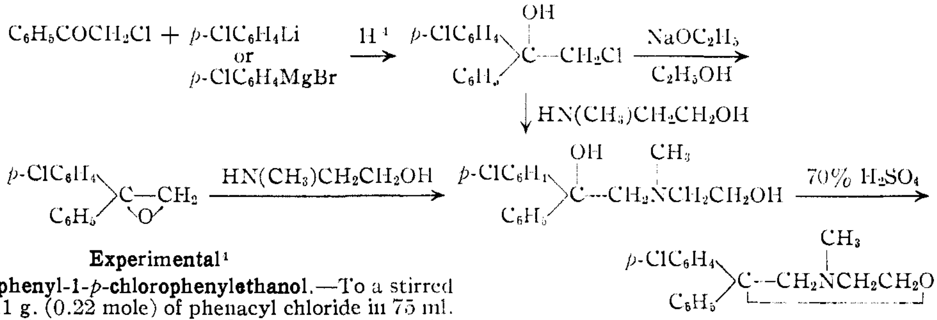
[1] H. Gilman and C. C. Wanser, THIS JOURNAL, **73**, 4030 (1951).

[2] K. E. Hamlin, A. W. Weston, F. E. Fischer and R. J. Michaels, Jr., *ibid.*, **71**, 2731 (1949).

[3] R. Baltzly, S. DuBreuil, W. S. Ide and E. Lorz, *J. Org. Chem.*, **14**, 775 (1949).

which 1-(*p*-chlorobenzhydryl)-4-methylpiperazine was the most active, it was considered desirable to prepare 2-phenyl-2-*p*-chlorophenyl-4-methylmorpholine. The synthesis of this compound was effected by the following sequence of reactions



Experimental[4]

2-Chloro-1-phenyl-1-*p*-chlorophenylethanol.—To a stirred solution of 34.1 g. (0.22 mole) of phenacyl chloride in 75 ml. of anhydrous ether cooled to −70° was added dropwise 0.22 mole of *p*-chlorophenyllithium[5] under an atmosphere of nitrogen. The reaction mixture was stirred for one hour at −70° after completion of the addition. Color Test I[6] was positive and the mixture was hydrolyzed with a solution of ammonium chloride at −20°. The ether layer was separated and the aqueous layer extracted with ether. The combined extracts were washed with water and dried over anhydrous sodium sulfate. After removal of the solvent, the unreacted phenacyl chloride was distilled under reduced pressure and then 23.5 g. (85%) of the product, b.p. 182–186° (0.2–0.3 mm.), was collected. The yellowish viscous liquid solidified on seeding, m.p. 59–60.5°. An analytical sample melted at 62–63°.

Anal. Calcd. for $C_{14}H_{12}Cl_2O$: Cl, 26.59. Found: Cl, 26.52.

The compound was also prepared in 52% yield by the addition of *p*-chlorophenylmagnesium bromide to phenacyl chloride. The method used was in essential accordance with that of Pepper and Kulka[7] for the preparation of 2-chloro-1,1-bis-(*p*-chlorophenyl)-ethanol.

1-Phenyl-1-*p*-chlorophenylethylene Oxide.—The epoxide was synthesized by the procedure of Klages and Kessler[8] for the preparation of 1,1-diphenylethylene oxide using 1.2 g. (0.05 g. atom) of sodium dissolved in 30 ml. of absolute ethanol and 13.4 g. (0.05 mole) of 2-chloro-1-phenyl-1-*p*-chlorophenylethanol in 30 ml. of the same solvent. There was obtained 7.5 g. (65%) of the product, b.p. 160–167° (0.1 mm.), n^{20}_{D} 1.5978, d^{20}_{20} 1.2322. Calcd. MR_D: 63.96. Found MR_D: 63.87.

Anal. Calcd. for $C_{14}H_{11}ClO$: Cl, 15.40. Found: Cl, 15.41.

β-Phenyl-β-*p*-chlorophenyl-N-methyldiethanolamine.—Six and seven-tenths grams (0.025 mole) of 2-chloro-1-phenyl-1-*p*-chlorophenylethanol and 5.6 g. (0.075 mole) of methylethanolamine[9] were heated on the steam-bath overnight. The product was taken up in ether, washed with water, and dried over anhydrous sodium sulfate. Removal of the solvent left a residue which solidified on seeding. Crystallization of the solid from a mixture of petroleum ether (b.p. 60–70°) and absolute ethanol gave 5.9 g. (78%) of white crystals, m.p. 96–97°.

Anal. Calcd. for $C_{17}H_{20}ClNO_2$: Cl, 11.62. Found: Cl, 11.81.

β-Phenyl-β-*p*-chlorophenyl-N-methyldiethanolamine was also synthesized in 83% crude yield through the reaction of 1-phenyl-1-*p*-chlorophenylethylene oxide with methylethanolamine, the procedure being the same as that for the preparation of β,β-diphenyl-N-methyldiethanolamine.[1]

2-Phenyl-2-*p*-chlorophenyl-4-methylmorpholine.—The reaction was carried out according to the method for the preparation of 2,2-diphenyl-4-methylmorpholine.[1] Three and six-tenths grams (0.012 mole) of β-phenyl-β-*p*-chlorophenyl-N-methyldiethanolamine and 4 ml. of 70% sulfuric acid were used. The yield of product was 2.3 g. (66%), m.p. 95°. One recrystallization from 95% ethanol gave 2.1 g. of the pure material, m.p. 96–97°.

Anal. Calcd. for $C_{17}H_{18}ClNO$: Cl, 12.34. Found: Cl, 12.49.

Acknowledgment.—The authors are grateful to Burt Hofferth for assistance, and to Parke, Davis and Co. for arranging for the tests.

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(4) All melting points and boiling points are uncorrected. Analyses for chlorine were carried out by an initial Parr fusion followed by a Volhard titration.

(5) H. Gilman, W. Langham and F. W. Moore, THIS JOURNAL, **62**, 2327 (1940).

(6) H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

(7) J. M. Pepper and M. Kulka, *ibid.*, **72**, 1417 (1950).

(8) A. Klages and J. Kessler, *Ber.*, **39**, 1753 (1906).

(9) Generously supplied by the Carbide and Carbon Chemical Corporation, New York, N. Y.

Solvent Effects in the Conversion of Nitriles to Perhydro-*s*-triazines[1]

BY WILLIAM D. EMMONS, HENRY A. ROLEWICZ, WILLIAM N. CANNON AND ROBERT M. ROSS

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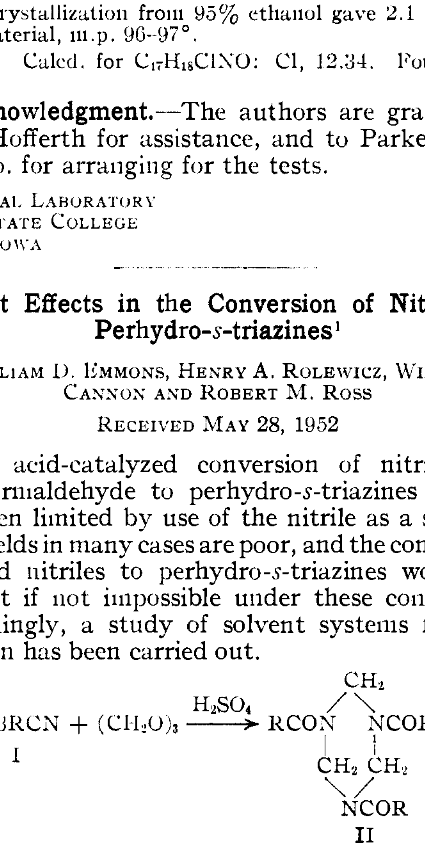
The acid-catalyzed conversion of nitriles (I) and formaldehyde to perhydro-*s*-triazines (II),[2–4] has been limited by use of the nitrile as a solvent. The yields in many cases are poor, and the conversion of solid nitriles to perhydro-*s*-triazines would be difficult if not impossible under these conditions. Accordingly, a study of solvent systems for this reaction has been carried out.



Propionitrile, acrylonitrile and benzonitrile were chosen as model compounds. The data obtained with the better solvents are summarized in Table I. As a class, the chlorinated solvents appear to be particularly good for the reaction. The reported yields of perhydro-*s*-triazines from propionitrile, acrylonitrile and benzonitrile are 47, 52 and 38%, respectively.[2,5] Significant increases in yield are therefore possible with carbon tetrachloride. Furthermore, perhydro-*s*-triazines as a

(1) This work was carried out under Army Ordnance Contract W-01-021-ORD-334.

(2) M. A. Gradsten and M. W. Pollock, THIS JOURNAL, **70**, 3079 (1948).

(3) C. C. Price and I. V. Krishnamurti, *ibid.*, **72**, 5334 (1950).

(4) R. Wegler and A. Ballauf, *Ber.*, **81**, 527 (1948).

(5) T. L. Gresham and T. R. Steadman, THIS JOURNAL, **71**, 1872 (1949).