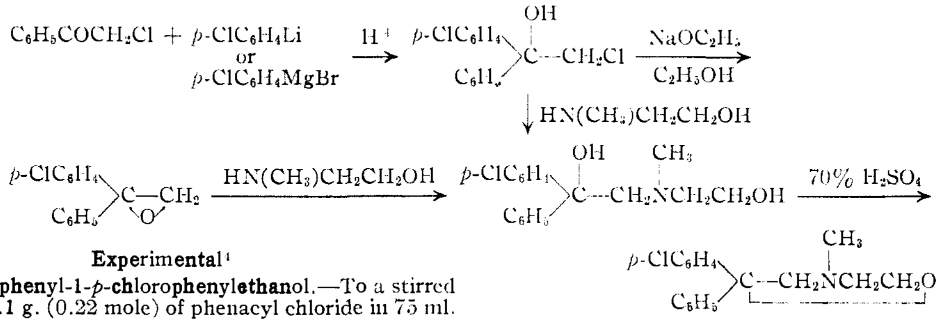
which 1-(*p*-chlorobenzhydryl)-4-methylpiperazine was the most active, it was considered desirable to prepare 2-phenyl-2-*p*-chlorophenyl-4-methylmorpholine. The synthesis of this compound was effected by the following sequence of reactions



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 1[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.

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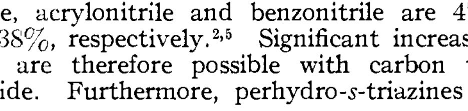
The acid-catalyzed conversion of nitriles (I) and formaldehyde to perhydro-*s*-triazines (II),[2–4] has been limited by use of the nitrile as a solvent. The yields in many cases are poor, and the conversion of solid nitriles to perhydro-*s*-triazines would be difficult if not impossible under these conditions.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

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[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).

TABLE I

FORMATION OF PERHYDRO-*s*-TRIAZINES IN VARIOUS SOLVENTS

Solvent	Temp., °C.	Perhydro-*s*-triazine yield, % Propionitrile	Acrylonitrile	Benzonitrile
Carbon tetrachloride	77	86	89	95
Carbon disulfide	46	66	64	8
Chlorobenzene	100	64	37	78
Nitromethane	102	64	21	79
Trichloroethylene	87	63	38	56
Methyl chloroform	74	53	9	56
Ethylene dichloride	84	45	69	73
s-Tetrachloroethane	100	42	76	81

class are insoluble in this solvent and precipitate from solution as they are formed. Consequently, the quality of the crude perhydro-*s*-triazine obtained with carbon tetrachloride has been in every case superior to that obtained under any other conditions. It is interesting to note that Gresham and Steadman[5] reported that commercial acrylonitrile was a superior reactant for perhydro-*s*-triazine formation, while we have observed that freshly distilled acrylonitrile gives much better and more reproducible yields in carbon tetrachloride. Carbon disulfide is also of considerable interest since with this solvent the reaction may be carried out at relatively low temperatures and under mild conditions. Solvents in which the perhydro-*s*-triazines were obtained in low yield were nitrobenzene, dioxane, chloroacetic acid, trichloroacetic acid, and acetic acid. In ethyl acetate, formic acid and ethyl ether, no perhydrotriazine was isolated.

In order to test further the excellence of carbon tetrachloride as a solvent for this reaction, *p*-chlorobenzonitrile and *p*-methoxybenzonitrile (both solids) were converted to the previously unknown perhydro-*s*-triazines in yields of 88 and 98%, respectively. Vinylacetonitrile failed to react in carbon tetrachloride, probably due to the fact that it is relatively insoluble in this solvent.

Experimental[6,7]

Typical procedures for the experiments summarized in Table I are given below. Formaldehyde was introduced in every case as *s*-trioxane, and the experimental conditions were standardized insofar as was conveniently possible. The products were identified by infrared spectra and by melting point and mixed melting point where applicable. The procedures for preparation of tris-*p*-chlorobenzoylperhydro-*s*-triazine and tris-*p*-methoxybenzoylperhydro-*s*-triazine are also described.

1,3,5-Triacrylylperhydro-*s*-triazine.—A solution of 13.2 g. of freshly distilled acrylonitrile, 0.65 g. of sulfuric acid and 50 ml. of dry carbon tetrachloride was brought to reflux. A solution of 13.3 g. of acrylonitrile and 15.0 g. of *s*-trioxane in 50 ml. of carbon tetrachloride was then added dropwise with stirring over a 15-minute period. A white solid separated out before addition was complete. The mixture was then stirred one hour under reflux. After cooling to room temperature, the white amorphous solid was collected on a filter and washed with carbon tetrachloride, yield 37.0 g. (89%). The product did not melt before polymerization but its infrared spectrum was identical to that previously reported.[2]

1,3,5-Tripropionylperhydro-*s*-triazine.—To a boiling solution of 5.5 g. of propionitrile, 0.20 g. of sulfuric acid and 20 ml. of carbon disulfide was added over a 10-minute period 5.5 g. of propionitrile and 6.0 g. of *s*-trioxane in 20 ml. of carbon disulfide. The solution was stirred under reflux for two hours and then cooled to room temperature. The product was washed with carbon tetrachloride and 11.3 g. (66%) of white crystalline material was obtained. After recrystallization from ethyl acetate the perhydro-*s*-triazine melted at 170–173°. A melting point of 169–171° has been reported.[2] The infrared spectrum was identical to that reported in the literature.[2]

1,3,5-Tris-*p*-chlorobenzoylperhydro-*s*-triazine.—*p*-Chlorobenzonitrile (17.2 g.) was dissolved in 50 ml. of carbon tetrachloride containing 0.65 g. of sulfuric acid. To this solution under reflux was added with stirring over a 20-minute period 17.2 g. of *p*-chlorobenzonitrile and 7.5 g. of *s*-trioxane in 50 ml. of carbon tetrachloride. The resulting mixture was boiled for 75 minutes. No product separated out during this period. The solution was then cooled to −15° and 40.8 g. (98% yield) of light yellow solid separated, m.p. 208–213°. The product was recrystallized from a mixture of carbon tetrachloride and ether. After recrystallization, the melting point increased to 216–217°. The infrared spectrum of the compound was in agreement with the proposed structure and showed an amide carbonyl band at 1652 cm.$^{-1}$.

Anal. Calcd. for $C_{24}H_{20}N_3O_3Cl_3$: C, 57.29; H, 3.61; N, 8.35. Found: C, 57.74; H, 3.88; N, 8.16.

1,3,5-Tris-*p*-methoxybenzoylperhydro-*s*-triazine.—To 20 ml. of carbon tetrachloride was added 6.7 g. of *p*-methoxybenzonitrile and 0.20 g. of sulfuric acid. A solution of 6.6 g. of *p*-methoxybenzonitrile and 3.0 g. of trioxane in 20 ml. of carbon tetrachloride was added to this hot mixture over a 15-minute period. The solution was heated under reflux for one additional hour and was then cooled to −15°. The white crystalline material was collected on a funnel and washed with carbon tetrachloride; yield 14.3 g. (87%). The material was recrystallized from ethyl acetate, m.p. 216–217°. Infrared examination of the compound showed a typical spectrum for a 1,3,5-triacylperhydro-*s*-triazine with a carbonyl frequency at 1656–1659 cm.$^{-1}$.

Anal. Calcd. for $C_{27}H_{27}N_3O_6$: C, 66.20; H, 5.55; N, 8.59. Found: C, 65.95; H, 5.74; N, 8.61.

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[6] All melting points are uncorrected.

[7] We are indebted to Dr. Keith S. McCallum for infrared interpretations and to Mr. Al Kennedy for microcombustion data.

The Extent of Dimerization of Sulfur Monoxide[1]

BY ERSEL A. EVANS, ALLEN B. SCOTT AND JOHN L. HUSTON

RECEIVED MAY 19, 1952

Since the first reported preparation of a "monoxide" of sulfur by Schenk[2] a considerable body of controversial literature has been published[3] regarding the formula of the molecule in the vapor state. Kondrat'ev and Kondrat'eva[4,5] concluded that within a few seconds after sulfur monoxide was formed during the oxidation of H_2S, it exists entirely in the form of the dimer, S_2O_2, at room temperature. On the other hand, Schenk[6] found the molecular weight of the monoxide from the condensed electrical discharge through SO_2 to be about 70; from data of Kondrat'ev he also calculated[3] the molecular weight to be 45.3 for monoxide from the discharge; further he noted a volume decrease of about 25% when the gas was condensed with liquid air and decomposed to sulfur and SO_2 by warming.

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[1] Published with the approval of the Oregon State College Monograph Committee, Research Paper No. 207, Department of Chemistry, School of Science.

[2] P. W. Schenk, *Z. anorg. allgem. Chem.*, **211**, 150 (1933).

[3] See P. W. Schenk, *Chem. Z.*, **67**, 273 (1943), for an extensive bibliography.

[4] V. Kondrat'ev and E. Kondrat'eva, *J. Phys. Chem. U. S. S. R.*, **21**, 1251 (1948).

[5] E. Kondrat'eva and V. Kondrat'ev, *ibid.*, **14**, 1528 (1940).

[6] P. W. Schenk, *Z. anorg. allgem. Chem.*, **248**, 297 (1941).