

TABLE II

Compound	Yield. %	°C.	B. p.		n_D^{20}	Formula	Carbon %		Hydrogen %	
			mm.				Calcd.	Found	Calcd.	Found
Dimethyl-(2-hydroxyethylthio)-acetal ^a	68-72	90	0.63		1.4810	C ₆ H ₁₄ O ₃ S
IIIc	72	92-93	0.55		1.4654	C ₉ H ₂₀ O ₃ S	51.89	51.25	9.68	9.81
IIIId	74	95	0.3		1.4650	C ₁₀ H ₂₂ O ₃ S	54.02	53.50	9.97	9.58

^a The dimethyl chloroacetal was kindly supplied by the General Aniline and Film Corporation.

Preparation of 2-*n*-Butoxy-*p*-oxathiane.—A mixture of 20 g. (0.13 mole) of 2-ethoxy-*p*-oxathiane and 50 g. (0.67 mole) of *n*-butyl alcohol containing 3 drops of ethanolic hydrogen chloride was heated at the reflux temperature for five minutes. The mixture was allowed to cool and treated with 5 g. of anhydrous potassium carbonate. After standing for an hour the mixture was filtered and distilled under reduced pressure. 2-*n*-Butoxy-*p*-oxathiane, 16.6 g. (72%) was collected as a colorless liquid at 109° (13 mm.). This acetal has a sweet odor somewhat similar to butyl ether.

Anal. Calcd. for C₈H₁₆O₂S: C, 54.51; H, 9.15. Found: C, 54.76; H, 9.44.

2-*n*-Butoxy-6,6-dimethyl-*p*-oxathiane—This compound was obtained from 2-ethoxy-6,6-dimethyl-*p*-oxathiane in 73% yield by the same method used for the preparation of 2-*n*-butoxy-*p*-oxathiane, b. p. 119° (13 mm.), n_D^{20} 1.4700. This cyclic acetal possessed a faint fruity odor.

Anal. Calcd. for C₁₀H₂₀O₂S: C, 58.78; H, 9.87. Found: C, 58.70; H, 10.03.

2-Hydroxypropylmercaptan.—A cold solution of 135 g. of potassium hydroxide in 750 ml. of 95% ethanol was saturated with hydrogen sulfide and 209 g. (1.5 moles) of propylene bromohydrin was added over a period of one hour. During the entire process the mixture was stirred and a slow stream of hydrogen sulfide was introduced. The mixture was then stirred overnight, heated at the reflux temperature for one hour, cooled and made slightly acid with acetic acid. The salt was removed by filtration and the alcohol at the water-pump. When most of the ethanol was removed the residue set to a light yellow solid. This was diluted with 100 ml. of water and the organic layer was removed. The aqueous layer was saturated with sodium chloride and extracted with ether. The combined organic layer and ether extract was dried and dis-

tilled under reduced pressure. There was obtained 64 g. (46%) of 2-hydroxypropylmercaptan, b. p. 58-60° (17 mm.), n_D^{20} 1.4805. The product obtained by Sjoberg⁹ by the hydrolysis of acetyl- β -oxy-propylmercaptan boiled at 51° (12 mm.), n_D^{20} 1.4862.

2-Hydroxyisobutyl Mercaptan (V).—This compound was obtained in 46% yield from isobutylene α -chlorohydrin by the same method described for 2-hydroxypropylmercaptan, b. p. 64° (26 mm.), n_D^{20} 1.4768.

Anal. Calcd. for C₄H₁₀OS: C, 45.24; H, 9.49. Found: C, 45.05; H, 9.42.

Summary

It has been shown that simple δ -hydroxyacetals undergo an acid catalyzed cyclization to produce mixed cyclic acetals by the elimination of a mole of alcohol. This reaction has been shown to be general whether the δ -hydroxyl group is primary, secondary or tertiary. 2-Ethoxy-1,4-dioxane and a series of 2-ethoxy-*p*-oxathianes have been prepared by application of this reaction and it has been shown that the ethoxy group of these cyclic acetals can be replaced readily by other primary alkoxy groups, such as *n*-butoxy, by treatment with the corresponding primary alcohol under acidic conditions. Furthermore, evidence is presented which indicates that tertiary alcohols undergo appreciable alcohol exchange with acetals only when the reaction is intramolecular.

(9) Sjoberg, *Ber.*, **75B**, 13-29 (1942).

MINNEAPOLIS, MINN.

RECEIVED APRIL 30, 1947

[CONTRIBUTION FROM THE FLIGHT PROPULSION RESEARCH LABORATORY OF THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS]

The Synthesis and Purification of Ethers

BY WALTER T. OLSON, HAROLD F. HIPSHER, CHARLES M. BUSS, IRVING A. GOODMAN, ISAAC HART, JOHN H. LAMNECK, JR., AND LOUIS C. GIBBONS

As part of an investigation of possible components of aviation gasoline, this laboratory has prepared a series of 24 ethers of various types. Seven of these ethers are aliphatic in type, both alkyl and alkylene; three are of the methylcycloalkyl type; six of the ethers contain the simple phenoxy radical; and eight are alkyl ethers of alkyl-substituted phenyl radicals. Approximately 2-liter quantities of these ethers were prepared either by purification of commercially available materials or by synthesis and purification. In most cases it was necessary to remove traces of halogen from the crude product by treatment with sodium in liquid

ammonia or by azeotropic distillation. After treatment all materials were found to be halogen-free by the Beilstein test. With the exception of the solid, *t*-butyl *p*-*t*-butylphenyl ether, which was successively recrystallized, final purification of each ether was by fractional distillation through helix-packed, glass columns of 80 theoretical plates. All distillations were conducted under nitrogen to prevent oxidation; all but a few were at atmospheric pressure. The ethers were prepared to an estimated purity of 99.5 mole per cent. or better as evidenced by time-temperature freezing and melting curves that were determined

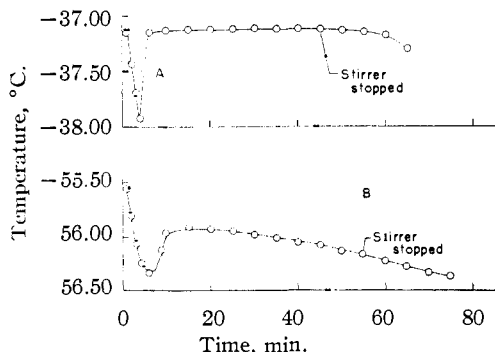


Fig. 1.—Time-temperature freezing curves for anisole (A), f. p. -37.11° , and methyl *m*-tolyl ether (B), f. p. -55.92° , typical examples of data obtained for 24 ethers.

by methods described by Rossini and co-workers.¹ Typical curves are shown in Fig. 1. The freezing points reported are the highest values obtained rather than extrapolated values. The physical constants tabulated in Table I were determined by methods previously described² and were measured immediately after final distillation in order to minimize error from peroxides that were found to form in the ethers upon exposure to air. It was noted that pure benzyl ethers formed peroxides extremely rapidly. A sample of benzyl methyl ether stored in a dark cabinet for six months was found to contain 2.6 equivalents of peroxidic oxygen per liter.

Experimental

Purification of Commercial Products.—Methyl, ethyl and isopropyl *t*-butyl ethers, methyl and ethyl phenyl ethers, and methyl *o*-, *m*- and *p*-tolyl ethers were obtained commercially and were first fractionally distilled in 10-gallon quantities through stainless steel, helix-packed columns of 40 theoretical plates. Finally, 5-liter samples comprising selected fractions were carefully refractionated through columns of 80 theoretical plates. When the distillation of isopropyl *t*-butyl ether was attempted in a stainless steel column, the ether partially decomposed to yield isobutene and isopropyl alcohol; fractional distillation of this ether in an all-glass helix-packed column of 80 theoretical plates was entirely satisfactory.

Eleven ethers were prepared by the familiar Williamson-type condensation between an alcohol and a halide by means of either sodium metal or a strong alkali. As mentioned previously approximately a 2-liter quantity of the final purified material was obtained in each case. The procedures listed below represent typical runs.

***t*-Butyl Methallyl Ether.**—In the synthesis of *t*-butyl methallyl ether, hitherto unreported in the literature, metallic sodium (2.02 kg., 88 g. atoms) was treated with an excess (40.0 kg., 540 moles) of *t*-butyl alcohol. Methallyl chloride (7.24 kg., 80 moles) was added to the heated, stirred mixture over a period of two hours. After refluxing and stirring for an additional eight hours, the mixture was cooled and diluted with water. The ether layer was separated, washed with successive portions of water, dried in an alumina-packed tower, and finally distilled. A yield of 3379 g. or 33% was obtained. Calculated for $C_8H_{16}O$: C, 74.93; H, 12.58. Found: C, 74.22; H, 12.74. These data were the only ones obtained in approximately ten attempts at analyzing this ether because of its

tendency to explode in the combustion tube even on slight heating.

Isopropyl Methallyl Ether.^{3,4}—Isopropyl alcohol (720 g., 12 moles) reacted with 82.8 g. (3.6 g. atoms) of sodium metal. Methallyl chloride (271.5 g., 3 moles) was added and refluxed for sixteen hours. For final purification the product was azeotropically distilled with ethyl alcohol to give 195 g. of the ether or 57%.

Methallyl Methyl Ether.^{3,4,5}—Into 1920 g. (60 moles) of methyl alcohol, 1460 g. (36.5 moles) of sodium hydroxide was added. Methallyl chloride (2715 g., 30 moles) was added to this mixture over a period of six hours with an additional reflux time of twelve hours. The product was azeotropically distilled with acetone for final purification. The yield was 1866 g. or 72.3%.

Dimethallyl Ether.^{4,6}—Methallyl chloride (1131 g., 12.5 moles) was added slowly to a mixture of 1800 g. (25 moles) of methallyl alcohol and 857 g. of 90% (13.8 moles) potassium hydroxide at reflux and held at reflux temperature for ten hours. The excess alcohol was removed by several extractions with water. The yield was 1023 g., 65% of theoretical.

Methallyl Phenyl Ether.⁷—A mixture of 940 g. (10 moles) of phenol, 1518 g. (11 moles) of potassium carbonate, 1006 g. (11 moles) of methallyl chloride, and 1250 ml. of acetone was refluxed for twenty-two hours. The product was distilled at 8–10 mm. The yield was 1040 g., 70%.

Phenyl *n*-Propyl Ether.—A mixture of 950 g. (10.1 moles) of phenol, 150 ml. of water and 640 g. (16 moles) of sodium hydroxide was heated to 70–90° while 1550 g. (12.6 moles) of *n*-propyl bromide was added over a period of four hours. Fractional distillation yielded 855 g., 63%.

Isopropyl Phenyl Ether.^{8—1} This ether was prepared in 54% yield by the method reported for phenyl *n*-propyl ether using isopropyl bromide. Propene was formed in a side reaction in this case. It was identified as 1,2-dibromopropane (b. p. 141–142, n_D^{20} 1.520).

2. Isopropyl phenyl ether was also prepared by adding 98 g. (1 mole) of concentrated sulfuric acid to a solution of 94.1 g. (1 mole) phenol in 120.2 g. (2 moles) of isopropyl alcohol. The yield in this case was 57 g., 42%.

Isopropyl *p*-Tolyl Ether.^{8,9}—A slurry of 864 g. (8 moles) of *p*-cresol and 352 g. (8.8 moles) of sodium hydroxide was made and heated to 110–120°. Isopropyl bromide, 1082.4 g. (8.8 moles), was added under the surface of the slurry over a period of four hours. The product was distilled at atmospheric pressure and yielded 923 g., 77% of theoretical.

Cyclopentyl Methyl Ether.¹⁰—Sodium metal (370 g., 16 g. atoms) was treated with methyl alcohol (2370 g., 74 moles). The excess alcohol was distilled off until the sodium methylate started to precipitate. The solution was cooled to 60° and 1254 g. (12 moles) of chlorocyclopentane¹¹ added and kept at 60° for hundred hours. On distillation 20% of the cyclopentyl chloride was recovered unchanged, 24% was found to have been converted to cyclopentyl methyl ether and 31% to cyclopentene, which distilled as an azeotrope with methyl alcohol (b. p. 37–38°). The yield of ether was 278 g., 29% of theoretical based on reacting cyclopentyl chloride.

(3) G. H. Coleman and G. V. Moore, U. S. Patent 2,148,437 (February 28, 1939).

(4) M. Tamele, C. J. Ott, K. E. Marple and G. Hearne, *Ind. Eng. Chem.*, **33**, 115–120 (1941).

(5) B. K. Merejkowsky, *Bull. soc. chim.*, **37**, 711–713 (1925).

(6) H. P. A. Groll and C. J. Ott, U. S. Patent 2,042,219 (May 26, 1936).

(7) Q. R. Bartz, R. F. Miller and Roger Adams, *THIS JOURNAL*, **57**, 371 (1935).

(8) J. B. Niederl and S. Natelson, *ibid.*, **53**, 1928 (1931).

(9) R. A. Smith, *ibid.*, **56**, 717 (1934).

(10) J. Loevenick, H. Utsch, P. Moldrickx and E. Schaeffer, *Ber.*, **62B**, 3088 (1929).

(11) J. Zalkind and I. Markov, *J. Applied Chem. U. S. S. R.*, **11**, part 1, 818 (1938).

(1) A. R. Glasgow, A. J. Streiff and F. D. Rossini, *J. Res. Natl. Bur. Standards*, **56**, 355 (1945).

(2) L. C. Gibbons, *et al.*, *THIS JOURNAL*, **68**, 1130 (1946).

TABLE I
 PHYSICAL CONSTANTS OF ETHERS

Ether	Freezing point, °C.	B. p., °C. at 760 mm.	Density, g./ml.	n_D^{20}	Molar refraction	
					Calcd.	Found
<i>t</i> -Butyl methyl	-108.65	55.1	0.7406	1.3690	26.93	26.85
<i>t</i> -Butyl ethyl	- 94.00	72.7	.7399	1.3755	31.55	31.65
<i>t</i> -Butyl isopropyl	- 88.07	87.6	.7414	1.3798	36.17	36.28
Methallyl methyl	-113.09	66.20	.7772	1.3943	26.47	26.53
Isopropyl methallyl	^b	103.88	.7742	1.4014	35.70	35.86
<i>t</i> -Butyl methallyl	- 84.61	120.51	.7841	1.4082	40.32	40.35
Dimethallyl	- 57.62	134.38	.8132	1.4285	39.85	39.96
	- 57.52 ^a					
Cyclopentyl methyl	-134.86	105.44	.8627	1.4206	29.39	29.42
	-134.75 ^a					
Cyclohexyl methyl	- 74.37	133.4	.8756	1.4346	33.97	34.00
Anisole	- 37.11	153.6	.9940	1.5172	32.69	32.91
Phenetole	- 29.47	169.9	.9651	1.5076	37.31	37.70
<i>n</i> -Propyl phenyl	- 27.09	189.3	.9474	1.5014	41.93	42.37
Isopropyl phenyl	- 33.05	176.8	.9406	1.4975	41.93	42.40
<i>t</i> -Butyl phenyl	- 18.31	61.8 ^c	.9247	1.4880	46.54	46.80
Methallyl phenyl	- 33.31	79.6 ^e	.9634	1.5157	46.08	46.43
		106.4 ^f				
Methyl <i>o</i> -tolyl	- 34.10 ^a	171.8	.9798	1.5178	37.31	37.77
Methyl <i>m</i> -tolyl	- 55.92	176.5	.9716	1.5137	37.31	37.83
Methyl <i>p</i> -tolyl	- 32.05	176.7	.9702	1.5123	37.31	37.80
Isopropyl <i>p</i> -tolyl	- 35.91 ^a	198.1	.9276	1.4957	46.54	47.28
<i>p</i> - <i>t</i> -Butylanisole	+ 19.14	223.2	.9383	1.5030	51.16	51.74
Benzyl methyl	- 52.63	170.5	.9634	1.5022	37.31	37.43
Benzyl isopropyl	- 67.19	83.0 ^g	.9214	1.4859	46.54	46.79
	- 67.07 ^a					
Cyclopropyl methyl	-119.08 ^a	44.73	.8100	1.3802	20.11	20.63
<i>t</i> -Butyl <i>p</i> - <i>t</i> -butylphenyl	68.7-69.0 ^d

^a Melting point. ^b Formed a glass; would not crystallize. ^c At 10 mm. ^d Melting point taken in capillary tube. ^e At 8 mm. ^f At 30 mm. ^g At 16 mm.

Benzyl Methyl Ether.¹²—Sodium hydroxide (6.9 kg., 172 moles) was mixed with 38 kg. (1190 moles) of methyl alcohol. Benzyl chloride (15.1 kg., 119 moles) was added at reflux temperature and refluxed nine to twelve hours. The product was distilled azeotropically with cyclohexanol (2400 g. of the ether with 750 g. of cyclohexanol). A 90% yield (10.7 moles, 13.1 kg.) was obtained.

Benzyl Isopropyl Ether.¹³—This ether was prepared similarly to benzyl methyl ether using 2400 g. (40 moles) of isopropyl alcohol, 400 g. (10 moles) of sodium hydroxide, and 1265 g. (10 moles) of benzyl chloride. The product was distilled at 16 mm. yielding 1267 g., 84.4%

***t*-Butyl *p*-*t*-Butylphenyl Ether.**—Ten moles of phenol (940 g.) were mixed with twenty moles of *t*-butyl alcohol (1480 g.) and 1310 g. of 73% sulfuric acid was added slowly. The mixture was placed on a steam-bath and stirred for one hour. During this time two layers separated. The bottom layer contained no ether and was discarded. The upper layer was washed twice with 5% sodium hydroxide solution and then with water. The product was dried and fractionated under vacuum to 123° at 8 mm. At this point the distillate began to solidify in the condenser, so the residue was withdrawn and crystallized from petroleum ether. On the third recrystallization, a colorless, crystalline product (m. p. 68.7-69.0° uncor.) was obtained. The yield was 1130 g. or 55%. *t*-Butyl *p*-*t*-butylphenyl ether was previously reported¹⁴ to have been prepared by the Williamson reaction from *p*-*t*-butylphenol and *t*-butyl chloride and was described as boiling at 255-260° at 740 mm.

(12) F. Sintenis, *Ann.*, **161**, 329 (1872).

(13) Senderens, *Compt. rend.*, **178**, 1412 (1924).

(14) Burkett and Brewster, *Trans. Kansas Acad. Sci.*, **46**, 133 (1943).

The ether was split with zinc chloride and 3,5-dinitrobenzoyl chloride and the resulting ester melted at 156.0-156.5° after the second recrystallization. The ester from *p*-*t*-butylphenol and 3,5-dinitrobenzoyl chloride melted at the same temperature and a mixed melting point was not depressed. The ether was also prepared from *p*-*t*-butylphenol, *t*-butyl alcohol and 73% sulfuric acid, and a mixed melting point with the two ethers gave no depression. The molecular weight determined by melting point depression of camphor was 202 (calcd. 206.3). Calcd. for C₁₄H₂₂O: C, 81.46; H, 10.75. Found: C, 81.12; H, 10.84.

***t*-Butyl Phenyl Ether.**—(1) Twenty moles (1880 g.) of phenol was dissolved in 20 moles (1580 g.) of *t*-butyl alcohol. After 300 g. of 80% sulfuric acid was added at less than 30°, the temperature was raised to 49-51° for one and one-half hours. The product was distilled at 10 mm. yielding 200 g. (6.7%).

(2) Using 100 g. of *p*-toluenesulfonic acid instead of sulfuric acid and heating to 55° for three hours, a yield of 5.3% was obtained.

Similar low yields were observed in attempts to prepare this ether by the Williamson reaction¹⁵ and the reaction of isobutene and phenol in the presence of sulfuric acid.¹⁶ Repeated efforts to increase the yield by higher temperatures, more concentrated sulfuric acid, larger amounts of condensing agent, and longer time of reaction resulted only in the formation of higher boiling compounds.

***p*-*t*-Butylanisole.**—A slurry was made of 750 g. (5.0 moles) of *p*-*t*-butylphenol and 400 g. (10.0 moles) of sodium hydroxide dissolved in 2 liters of water. Dimethyl sulfate (945 g., 7.5 moles) was stirred into this mixture while the

(15) R. A. Smith, *This Journal*, **55**, 3718 (1933).

(16) T. W. Evans and K. R. Edlund, *Ind. Eng. Chem.*, **28**, 1186 (1936).

temperature was maintained below 45° until the exothermic reaction stopped. Excess dimethyl sulfate was decomposed by heating to 90° for two hours. The upper layer of the reaction mixture was washed with water, dried, and fractionally distilled at reduced pressure to give a 60% yield of the ether. Calculated for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.37; H, 9.98.

Cyclohexyl Methyl Ether.¹⁷—Anisole (750 g., 7 moles) was hydrogenated in the presence of 75 g. of nickel-on-kieselguhr catalyst at 180° to give 600 g. of ether, 76%.

Cyclopropyl Methyl Ether.—Glycerol was brominated, in approximately 18 mole runs, to glycerol α,γ -dibromohydrin, in 60% yields, following the procedure of Braun.¹⁸ The dibromohydrin (10.8 moles, 2347.5 g.) was treated with 1449 g. (11.5 moles) of dimethyl sulfate according to Krantz and co-workers.¹⁹ A mixture of 212 g. (2 moles)

of sodium carbonate, 600 g. (4 moles) of sodium iodide, 390 g. (6 moles) of zinc dust, and 400 g. (6.7 moles) of acetamide was heated to 120–125° and 2 moles (464 g.) of the 1,3-dibromo-2-methoxypropane was added slowly, all according to Krantz and co-workers.¹⁹ A 50% yield (72 g.) of crude ether was obtained. It was found to contain approximately 13% propionaldehyde, presumably formed from unreacted dibromohydrin, which forms an azeotrope (b. p. 43°) with the cyclopropyl methyl ether. It was heated with sodium bisulfite solution and fractionally distilled over sodium hydroxide pellets.

Summary

The physical constants of 24 pure ethers of various types, together with a description of the preparative method for each ether, have been presented. The synthesis, purification, and physical constants of *t*-butyl methyl ether and *p*-*t*-butylanisole have been described for the first time.

CLEVELAND, OHIO

RECEIVED FEBRUARY 20, 1947

(17) E. M. van Duzee and Homer Adkins, *THIS JOURNAL*, **57**, 147 (1935).

(18) Braun, "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 308.

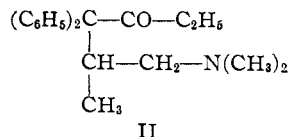
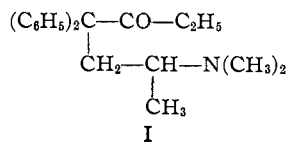
(19) J. C. Krantz, Jr., C. J. Carr, S. E. Forman and Wm. E. Evans, Jr., *J. Pharmacol.*, **69**, 207–220 (1940); J. C. Krantz, Jr., and N. L. Drake, U. S. Patent 2,330,979 (October 5, 1944).

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, MEDICAL RESEARCH DIVISION, SHARP AND DOHME, INC.]

The Reaction of 1-Dimethylamino-2-chloropropane with Diphenylacetonitrile. The Structure of Amidone

By EVERETT M. SCHULTZ, CHARLES M. ROBB AND JAMES M. SPRAGUE

In the United States Department of Commerce report¹ that first disclosed the new German analgesic drug, Amidone or No. 10820, in this country, it was noted that the method given by the German chemists for the synthesis would not be expected to lead to the structure I, which was assigned by the Germans, but rather to lead to the isomeric structure II. This uncertainty of the structure is further indicated by recent publications² in which the structure I is given for the compound but a chemical name for the structure II is used. In a recent note³ from this Laboratory, structure I was established for this drug. The present paper describes the details of this structure proof.



The reaction of diphenylacetonitrile with 1-dimethylamino-2-chloropropane either in the pres-

ence of sodamide according to the German procedure or in the presence of potassium *t*-butoxide led to a high yield of a semisolid product from which the isomeric nitriles III and IV were isolated in approximately equal amounts. The high-melting nitrile (IV, m. p. 90–91°) reacted smoothly with ethylmagnesium bromide to give Amidone (I). The low-melting nitrile (III, m. p. 66–67°) on treatment with the Grignard reagent did not give the Amidone isomer II but instead a dibasic product that appears to be the corresponding ketimine V. Although analytical data support the ketimine structure, the ordinary condition of hydrolysis failed to give the ketone.⁴

The structures of the isomeric nitriles, and hence the structure of Amidone, were established by decomposition of the quaternary bases derived from the methiodides of the nitriles by treatment with silver oxide. Two isomeric unsaturated nitriles,⁵ VI and VII were obtained. Although the analyses and molecular weights support the unsaturated nitrile structure, neither of these compounds exhibited typical unsaturation reactions. They did not absorb bromine in carbon tetrachloride solution and did not decolorize permanganate in neutral acetone solution except on long standing. No uptake of hydrogen was observed when methanolic solutions were shaken with hydrogen and

(1) Office of the Publication Board, Department of Commerce, Report No. PB-981, page 96-A.

(2) Scott and Chen, *J. Pharmacol.*, **87**, 63 (1946); Scott, Robbins and Chen, *Science*, **104**, 587 (1946); Scott, *et al.*, *Anesthesia and Analgesia*, **26**, 12, 18 (1947).

(3) Schultz, Robb and Sprague, *THIS JOURNAL*, **69**, 188 (1947).

(4) Easton, Gardner and Stevens, *ibid.*, **69**, 976 (1947).

(5) No attempt was made to locate definitely the position of the double bond in VII. The structure indicated seems probable. However, the isomeric structure, 2,2-diphenyl-4-pentenitrile, is not excluded.