Anal. Calcd. for $C_{12}H_{21}N_7$: C, 54.73; H, 8.04. Found: C, 54.38; H, 8.12.

When the reaction was carried out with only two moles of diethylamine in ether at room temperature and worked up after 24 hr., the substitution was limited to one chlorine atom, resulting in **6-chloro-2-diazomethyl-4-diethylamino-*s*-triazine (XX)**. Yellow prisms (4.5 g., 79%) were obtained from ligroin, m.p. 52.5°. *Anal.* Calcd. for $C_8H_{11}ClN_6$: C, 42.39; H, 4.89; Cl, 15.64; N, 37.08. Found: C, 42.23; H, 4.93; Cl, 14.91; N, 37.07.

4,6-Bis-ethyleneimino-2-diazomethyl-*s*-triazine (XXII) was obtained in 52% yield by reaction of II with ethyleneimine (two moles) and triethylamine (two moles) in boiling ether in an analogous manner. Recrystallization from ligroin (b.p. 60–70°) yielded a yellow powder, which decomposed at 108° without melting.

Anal. Calcd. for $C_8H_9N_7$: C, 47.28; H, 4.47. Found: C, 47.32; H, 4.52.

Conversion of the Diazomethyl-*s*-triazines into the Dihalogenomethyl-*s*-triazines.—The finely powdered diazo compound (II resp. XIII) was suspended in carbon tetrachloride containing one mole of the required halogen and kept at room temperature with stirring for 24 hr. If the halogen had not yet reacted completely, the reaction mixture was then refluxed for 2–3 hr., filtered from solid by-products and the solvent removed by distillation. The residue was fractionated twice under vacuum. In the case of the di-iodo derivative XXIV, which decomposes on heating, the crude product was recrystallized from ligroin. Data of the individual compounds are compiled in Table I.

Reaction of the 2-Diazomethyl-*s*-triazines with Acids.—The diazomethyltriazines II and XIII were dissolved in ether and an excess of hydrogen chloride passed in, followed by refluxing for 3 hr. After filtering off the insoluble hydrochlorides and evaporating the ether, the products XXVII and XXVIII were isolated by vacuum distillation or recrystallization from ligroin. The amount of the insoluble hydrochlorides could be considerably increased if the treatment with hydrochloric acid was extended for two days. For example, from 12.6 g. of 2-diazomethyl-4,6-dimethoxy-*s*-triazine (XIII) in 1500 ml. of pure anhydrous ether, we obtained 10.1 g. of the crude hydrochloride of **2-chloromethyl-4,6-dihydroxy-*s*-triazine (XXIX)** (found: N, 21.12, 21.25; Cl, 36.02, 36.13). From the mother liquor another crop (0.6 g.) of XXIX deposited after standing overnight (for analysis *cf.* Table II).

XXIX was characterized by coupling it in alkaline solution with β-naphthol in 90% yield to the **4,6-dihydroxy-2-[2′-naphthoxymethyl]-*s*-triazine**. After recrystallization from acetic acid, glistening leaflets were obtained, m.p. 300° dec.

Anal. Calcd. for $C_{14}H_{11}N_3O_3$: C, 62.45; H, 4.11; N, 15.61. Found: C, 62.45, 62.36; H, 4.08, 4.16; N, 15.56, 15.62.

The conversion of XIII into the carbinol XXX occurred spontaneously with evolution of heat when 4.75 g. of XIII was suspended in 50 ml. of water and 0.6 g. of concd. sulfuric acid was added. After all had gone into solution, the carbinol was extracted five times with ether, the combined ethereal extracts evaporated and the solid residue recrystallized from ligroin. The diazomethyltriazines in general reacted much more easily with organic acids in the presence of a small amount of water. Thus the conversion of XIII into the acetate XXXI was best effected with 90% acetic acid. The spontaneous reaction was completed by refluxing for 10 minutes. After diluting with much water and neutralizing with sodium bicarbonate, XXXI was extracted with ether. The residue remaining after evaporation of the ether was recrystallized from ligroin. The reaction of XIII and XXI with the aromatic acids was carried out in xylene with an excess of the acid and addition of about 1% of water. After refluxing for 3–4 hr., the reaction mixture was diluted with ether and the excess acid extracted with sodium bicarbonate solution. The solvents were then removed by distillation, the last of the xylene being removed under vacuum. The residue was recrystallized from ligroin, in the case of XXXIII preferably by seeding. Physical and analytical data for the above compounds are compiled in Table II.

2-Chloromethyl-4,6-diamino-*s*-triazine (XXXIV).—A saturated solution of ammonia in ethanol (25 ml.) was added dropwise at 0° to a solution of 3.2 g. of 2-chloromethyl-4,6-dichloro-*s*-triazine (XXVII) in 3 ml. of anhydrous ether. The yellowish precipitate was collected and recrystallized twice from 20 ml. of water with addition of charcoal to give white needles (1.7 g., 66%). The substance XXXIV darkened above 220° but did not melt up to 330°.

Anal. Calcd. for $C_4H_6ClN_5$: C, 30.11; H, 3.79; Cl, 22.21; N, 43.89. Found: C, 30.81; H, 3.83; Cl, 21.84; N, 43.37.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

Oxetanes. VI.[1] Reductive Cleavage and Substituent Effects[2]

BY SCOTT SEARLES, JR., KENNETH A. POLLART AND EUGENE F. LUTZ

RECEIVED AUGUST 3, 1956

Reductive cleavage of ten oxetanes, having two or fewer alkyl substituents, has been carried out with lithium aluminum hydride and that of 2-phenyloxetane, with lithium borohydride. A single alcohol product was formed in each case, cleavage of unsymmetrical oxetanes occurring between the oxygen atom and the least substituted α-carbon atom. The ease of cleavage was found to be much affected by substitution, particularly *gem*-dialkyl substitution at position 3, which caused marked deactivation. These substituent effects are discussed. The preparations of 2-phenyloxetane and 3-methyloxetane are described for the first time.

Reductive cleavage of the oxetane (trimethylene oxide) ring would be of obvious value in establishing the structure of new oxetanes, as well as in certain synthetic applications. Reductive cleavage of 1,2-epoxides has been very widely and successfully used,[3,4] and its extension to oxetanes was suggested by the fairly high degree of reactivity observed for trimethylene oxide in Grignard reactions and in other reactions.[1]

The smooth cleavage of trimethylene oxide with lithium aluminum hydride, forming *n*-propyl alcohol, was reported in a preliminary fashion several

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[1] (1) Earlier papers considered to be in this series are: (a) S. Searles, THIS JOURNAL, **73**, 124 (1951); (b) 4515 (1951); (c) S. Searles and C. F. Butler, *ibid.*, **76**, 56 (1954); (d) S. Searles, *ibid.*, 2313 (1954); S. Searles and V. P. Gregory, *ibid.*, 2789 (1954).

[2] (2) Portions of the dissertations presented by K. A. P. (1956) and to be presented by E. F. L. in partial fulfillment of the requirement for the degree Doctor of Philosophy in Chemistry at Kansas State College.

[3] (3) Lithium aluminum hydride reductions are reviewed by W. B Brown in Adams' "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 476.

[4] (4) M. S. Newman, G. Underwood and M. Renoll, THIS JOURNAL, **71**, 3362 (1949).

years ago,[5] but recently other workers have reported that certain tri- and tetrasubstituted oxetanes were not cleaved by this reagent.[6,7] It may be of interest that in this Laboratory reductive cleavage of the oxetane ring with lithium aluminum hydride has been accomplished with all the oxetanes studied in connection with a general program of investigation on these compounds, but none of these possessed more than two alkyl or aryl substituents. The results with eleven representative compounds are presented in Table I.

TABLE I

LITHIUM ALUMINUM HYDRIDE REDUCTION OF OXETANES

Substituents	Products	Conditions[a] and yields		
		E, 3	T, 7	Other
None	1-Propanol	45%	65%	
2-Methyl	2-Butanol	32	60	
2-Ethyl	3-Pentanol	31		56 (T,14)
2-Phenyl	1-Phenyl-1-propanol	36	70	73 (E,20)
2,2-Dimethyl	2-Methyl-2-butanol			55 (T,13)
2,2-Diethyl	3-Ethyl-3-pentanol		42	
3-Methyl	2-Methyl-1-propanol		66	
3,3-Dimethyl	2,2-Dimethyl-1-propanol	<5		32 (T,20)
3,3-Diethyl	2-Ethyl-2-methyl-1-butanol			43 (T,40)
2,3-Dimethyl	3-Methyl-2-butanol			58 (T,26)
3-Ethyl-2-propyl	3-Methyl-4-heptanol			72 (T,37)

[a] The solvent used is designated as follows: E for ethyl ether and T for tetrahydrofuran; the number following indicates the number of hours the reaction mixture was refluxed.

In each case the reaction proceeded smoothly to form a single product,[8] an alcohol. The direction of cleavage of unsymmetrical oxetanes was always between the oxygen atom and the least substituted adjacent carbon atom. This is, of course, in accord with the displacement-type mechanism previously observed with this reagent.[3,9]

Even with 2-phenyloxetane only this type of cleavage was observed, which is interesting because its analog, styrene oxide, apparently gives a small amount of 2-phenylethanol along with the "normal" product, 1-phenylethanol. The amount of the former is increased to 26% when lithium borohydride is the reagent, presumably due to its lower nucleophilic character and steric requirements.[10] The reaction of 2-phenyloxetane with this reagent was much slower than with lithium aluminum hydride, and again only the "normal" product, 1-phenyl-1-propanol, was obtained. No hydrocinnamyl alcohol could be detected by distillation or infrared spectrum. This would seem to indicate that the oxetane ring is not inclined to become polarized in the transition state for such reductive cleavage, so that the reaction has to go by a direct displacement process.

The lithium aluminum hydride reactions were generally carried out under one or both sets of standard conditions, except with the less reactive oxetanes, where longer reaction times were necessary to get enough product to purify and identify. Incompleteness of reaction was certainly the main cause of low yield, and starting oxetane was generally recovered to some extent. The apparent lack of side reactions suggested that this reductive cleavage might serve as a useful tool for deducing the effect of substituents on the reactivity of the oxetane ring. Since the yields were determined by product isolation involving distillation, differences of 5% are probably not significant.

Viewed in this way, the data in Table I indicate that a methyl or ethyl group at position 2 decreases the reactivity of the oxetane ring somewhat, but at position 3 it does not have much effect. This may be ascribed to the steric factor, reducing the number of reactive sites from two to one. Electronic factors apparently are influential, also. It will be noted that 2-phenyloxetane seems slightly more reactive than 2-alkyloxetanes and the 2,2-dialkyloxetanes somewhat less so, even though the reaction does not occur at the substituted carbon atom. Possibly these differences reflect differences in the stability of the oxetane ring caused by the presence of electron-withdrawing or electron-repelling groups on the electronically deficient carbon atoms of the oxetane ring.[11]

The low degree of reactivity associated with dialkyl substitution at position 3 seems particularly interesting. This position, of course, has no analogy in the ethylene oxides. Since the previously reported attempts at reductive cleavage of substituted oxetanes involved compounds with two substituents at 3 and at least one at 2,[6,7] it is not surprising that difficulty was experienced in that work.

The cause of the strong deactivation associated with 3,3-dialkyl substitution may be due to at least two factors: the Thorpe–Ingold effect and the relatively low basicity of such oxetanes. The former considers that the mutual repulsion of bulky groups attached to a small-ring carbon atom tends to diminish the distortion of the internal bond angle.[12] The *gem*-dialkyl structure might well stabilize the oxetane ring as a whole more when at 3 than at 2 because of the probably smaller internal bond angle at 3.[13] Another result of the Thorpe–Ingold effect would be to modify the strain at position 2, *gem*-dialkyl substitution at 3 decreasing it but at 2 increasing it. This, too, agrees with the observation of the greater reactivity of the 2,2-dialkyloxetanes over the 3,3-dialkyloxetanes.

The effect of *gem*-disubstitution on the basicity of the ring oxygen would seem to affect the ease of cleavage in a somewhat parallel manner. At position 2, disubstitution enhances the basicity, while at 3 it diminishes the basicity.[14] Higher basicity, of course, strengthens the coördination with lith-

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[5] S. Searles, 118th Meeting of the American Chemical Society, September 3, 1950 (Abstracts, p. 5N, though they give no details of this work, which was reported orally).

[6] G. Buchi, G. G. Inman and E. S. Lipinsky, THIS JOURNAL, **76**, 4327 (1954).

[7] W. S. Allen, S. Bernstein, M. Heller and R. Littel, *ibid.*, **77**, 4784 (1955).

[8] An exception was the reduction of 1-phenyloxetane, which gave some polymeric material also. The latter appeared to arise from dehydration of 1-phenyl-1-propanol and polymerization during the distillation, since similar polymer was obtained on distillation of the pure alcohol.

[9] L. W. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949).

[10] R. Fuchs and C. A. VanderWerf, *ibid.*, **76**, 1631 (1954).

[11] H. S. Gutowsky, R. L. Rutledge, M. Tamres and S. Searles, *ibid.*, **76**, 4242 (1954).

[12] J. W. Baker, "Tautomerism," Rutledge, London, 1934, p. 179. A test of this explanation is being carried out at present and will be reported on later.

[13] H. de V. Robles, *Rec. trav. chim.*, **59**, 184 (1940).

[14] S. Searles and M. Tamres, THIS JOURNAL, **73**, 3704 (1951), and unpublished results by the same authors on hydrogen bonding ability of other oxetanes.

ium ion during the reaction, resulting in a stronger "pull" on the oxygen to aid the displacement process.

Reductive cleavage by catalytic hydrogenation over either Adams platinum or Raney nickel catalyst appears unpromising, as with trimethylene oxide there was little or no reduction. This is an interesting contrast to the reduction of 1,2-epoxides.[4] Sodium borohydride also was ineffective.

Several of the compounds studied here appear to be new to the literature. 2-Phenyloxetane, the first simple aryl-substituted oxetane reported, was prepared from β-chloropropiophenone by lithium aluminum hydride reduction, acetylation and treatment with hot alkali to effect ring closure. This method of converting a β-chloroketone to an oxetane was applied to the synthesis of 2-methyloxetane[15] and 2-ethyloxetane, but it was not successful in the synthesis of 2-(4-anisyl)-oxetane, due to the instability of the intermediate chloroalcohol. 3-Methyloxetane was prepared by addition of hydrogen bromide to methyl methacrylate, followed by lithium aluminum hydride reduction, acetylation and ring closure with hot caustic. The two 2,3-dialkyloxetanes were prepared from the corresponding glycols, as described in the following paper.[16] The infrared spectra of these oxetanes showed characteristic bands at 8.1 and 10.2 μ, similar to those which have been described previously.[17]

Experimental[18]

2-Ethyloxetane.—Addition of 25 g. of lithium aluminum hydride in 700 ml. of ether to 241 g. of 1-chloro-3-pentanone[19] in 500 ml. of ether, followed by the usual hydrolysis and isolation procedure, gave 174 g. (71%) of 1-chloro-3-pentanol, b.p. 82° (25 mm.), $n^{20}\mathrm{D}$ 1.4435 (reported[20] b.p. 77–77.5° (20 mm.), $n^{20}\mathrm{D}$ 1.448). This was dissolved in 200 ml. of chloroform containing 178 g. of pyridine, and 173 g. of acetyl chloride was added with cooling. After standing overnight the reaction mixture was washed with water, 5% hydrochloric acid and 5% sodium bicarbonate; it was then dried and distilled to yield 200 g. (96%) of 1-chloro-3-pentyl acetate, b.p. 82–84° (20 mm.), $n^{20}\mathrm{D}$ 1.4310 (reported[20] b.p. 81° (13 mm.), $n^{24}\mathrm{D}$ 1.431). This ester (100 g.) was added dropwise to the liquid mixture of 200 g. of potassium hydroxide, 200 g. of sodium hydroxide and 20 ml. of water at 150°, followed by raising the temperature to 170° and adding 50 ml. of water. The gaseous product was passed through a 30-cm. Vigreux column and condensed in a cold trap. After drying over potassium hydroxide pellets and distilling from sodium, 35.5 g. (60%) of 1-ethyloxetane was collected, b.p. 87° (730 mm.), $n^{20}\mathrm{D}$ 1.4040, d. 0.850 (reported[20] 88.5–89° (748 mm.), $n^{20}\mathrm{D}$ 1.4072).

2-Methyloxetane.—The procedure, starting with 4-chloro-2-butanone, was analogous to that above and very similar to a published description.[15] It was found that a shortening of the procedure can be accomplished by decomposing the lithium aluminum hydride reaction mixture with acetyl chloride (2 molar equivalents, warmed briefly after the addition), giving 4-chloro-1-butyl acetate, b.p. 67–70° (15 mm.), directly without a separate step for acetylation. The over-all yield of the ester is about the same, however. Ring closure with the hot caustic mixture gave 55% yield of 2-methyloxetane, b.p. 59°, $n^{20}\mathrm{D}$ 1.3913 (reported[15] b.p. 60–61°, $n^{20}\mathrm{D}$ 1.3894).

3-Methyloxetane.—Methyl 2-bromo-1-methylpropionate was prepared in 90% yield by adding dry hydrogen bromide to methyl methacrylate, as described by Price and Coyner.[21] To a solution of 125 g. of this ester in 300 ml. of ether was added a solution of 20 g. of lithium aluminum hydride in ether, and after the usual processing there was obtained 70.7 g. (67%) of 3-bromo-2-methyl-1-propanol, b.p. 81–82° (20 mm.), $n^{20}\mathrm{D}$ 1.4824, m.p. of 3,5-dinitrobenzoate 81° (recrystd. from alcohol).

Anal. Calcd. for C_4H_9OBr: Br, 52.2. Found: Br, 52.4.

Isobutyl alcohol (9 g.) was identified as a by-product of the reduction by means of the infrared spectrum and the m.p. of the 3,5-dinitrobenzoate (86°).

Addition of 102 g. of acetyl chloride to a cold, stirred solution of 133 g. of the bromohydrin in 104 g. of pyridine and 150 ml. of ether, followed by the usual isolation procedure, gave 157 g. (93% yield) of 3-bromo-2-methyl-1-propyl acetate, b.p. 90–91° (21 mm.), $n^{20}\mathrm{D}$ 1.4553.

Anal. Calcd. for $C_6H_{11}O_2Br$: C, 36.85; H, 5.64. Found: C, 37.15; H, 5.71.

Treatment of 151 g. of the bromo ester with caustic in the same manner as described for the preparation of 2-ethyloxetane gave 22.3 g. (43%) of 3-methyloxetane, b.p. 67°, $n^{20}\mathrm{D}$ 1.3956.

Anal. Calcd. for C_4H_8O: C, 66.6; H, 11.1. Found: C, 65.0; H, 11.1.[22]

2-Phenyloxetane.—β-Chloropropiophenone, m.p. 52°, was prepared in 93% yield by the method of Campbell, *et al.*,[23] except that the β-chloropropionyl chloride was added to the cold suspension of aluminum chloride in benzene, and the resulting mixture was simply allowed to stand 15 hr. with stirring. The catalytic reduction of this chloroketone, described by Case,[24] was found to be much inferior to lithium aluminum hydride reduction, carried out by means of inverse addition as described for 1-chloro-3-pentanol. The yield of 3-chloro-1-phenyl-1-propanol was 87%, b.p. 75° (0.03 mm.), $n^{20}\mathrm{D}$ 1.5412 (reported[23] b.p. 130–132° (8 mm.)). Dropwise addition of acetyl chloride (65 g.) to a cold solution of 93.7 g. of this chlorohydrin in 65 g. of pyridine and 100 ml. of dry ether, followed by processing as described above for 1-chloro-3-pentyl acetate, gave 95 g. (83%) of 3-chloro-1-phenyl-1-propyl acetate, b.p. 84–85° (0.1 mm.), $n^{20}\mathrm{D}$ 1.5121.

Anal. Calcd. for $C_{11}H_{13}O_2Cl$: Cl, 16.68. Found: Cl, 16.71.

3-Chloro-1-phenyl-1-propyl acetate (41 g., 0.193 mole) was added dropwise, at a rapid rate, to a solution of 252 g. of potassium hydroxide and 100 ml. of water at 130° with rapid stirring. After the addition of chloroester was complete, the oil-bath temperature was raised to 170° and steam passed into the reaction mixture until no more product steam distilled over. The distillate was extracted several times with ether, the combined organic layers washed with water and dried over anhydrous magnesium sulfate. After removal of the solvent, the product was distilled from sodium metal yielding 17.5 g. (70% yield) of 2-phenyloxetane, b.p. 52° (0.5 mm.), or 87–88° (8 mm.), $n^{20}\mathrm{D}$ 1.5288, d^{20}_4 1.023. Treatment of 3-chloro-1-phenyl-1-propanol with hot alkali directly gave 58% yield of pure 2-phenyloxetane.

Anal. Calcd. for $C_9H_{10}O$: C, 80.51; H, 7.46. Found: C, 80.80; H, 7.60.

2,2-Dimethyloxetane was prepared as described by Bennett and Philip,[25] b.p. 70° (742 mm.), $n^{20}\mathrm{D}$ 1.3907 (reported[24] b.p. 71 (750 mm.). The preparation and properties of 3,3-dimethyloxetane were as previously described.[26] **2,2-Diethyloxetane** was prepared by the method of Moureu and Barrett,[27] b.p. 124–126°, $n^{23}\mathrm{D}$ 1.4168 (reported[26] b.p. 129°, $n^{22}\mathrm{D}$ 1.4200). **3,3-Diethyloxetane** was

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(15) F. Sondheimer and R. B. Woodward, This Journal, **75**, 5438 (1953), have reported the synthesis of 2-methyloxetane by the same method, which had been independently used in this work earlier.

(16) S. Searles, K. A. Pollart and F. Block, *ibid.*, **79**, 952 (1957).

(17) G. M. Barrow and S. Searles, *ibid.*, **75**, 1175 (1953).

(18) All melting and boiling points are uncorrected. Microanalyses were performed by Weiler and Straus, Oxford, England.

(19) E. M. McMahon, *et al.*, This Journal, **70**, 2971 (1948).

(20) R. Lespieau. *Bull. soc. chim.*, [5] **7**, 254 (1940).

(21) C. C. Price and E. C. Coyner, This Journal, **62**, 1306 (1940).

(22) Combustion analysis of the more volatile oxetanes tends to give low carbon values as has been observed previously (ref. 25).

(23) K. N. Campbell, R. A. LaForge and B. K. Campbell, *J. Org. Chem.*, **14**, 346 (1949).

(24) F. H. Case, This Journal, **55**, 2927 (1933).

(25) G. M. Bennett and W. G. Philip, *J. Chem. Soc.*, 1938 (1928).

(26) S. Searles and M. J. Gortatowski, This Journal, **75**, 3030 (1953).

(27) C. Moureu and G. Barrett, *Bull. soc. chim.*. [4] **29**, 994 (1921).

TABLE II

IDENTIFICATION OF CLEAVAGE PRODUCTS

Compound	B.p., °C.	n^{20}D	Deriv.[a]	M.p., °C.	Lit.,[b] m.p., °C.
1-Propanol	93–94		DNB	74	74
2-Butanol	95–97	1.3958	DNB	71–72	76
3-Pentanol	112	1.4104	DNB	97	99
2-Methyl-1-propanol	106	1.3959	DNB	86	87
3-Methyl-2-butanol	108–110	1.3972	DNB	76	76[c]
3-Methyl-4-heptanol	82–84 (38 mm.)	1.4235	DNB	91–92	91.8[d]
2-Methyl-2-butanol	99–101	1.4020			
1-Phenyl-1-propanol	95° (7 mm.)	1.5255	NC	101	102[e,f]
2,2-Dimethyl-1-propanol	110–111 (m.p. 52°)		PC	113–114	112–113[g]
2-Ethyl-2-methyl-1-butanol	156.5		HTC	146–147	144–145[h]
3-Ethyl-3-pentanol	136–138	1.4265	A	170	173[i]

[a] DNB signifies 3,5-dinitrobenzoate; NC, N-(α-naphthylcarbamate); PC, N-phenylcarbamate; HTC, hydrogen tetrachlorophthalate; A, allophanate. [b] Except as otherwise noted, these are the literature values compiled by E. H. Huntress and R. S. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941. [c] R. L. Shriner, R. C. Fuson and D. Y. Curtin, "Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 280, although R. C. Huston and R. G. Brault, *J. Org. Chem.*, **15**, 1216 (1950), report 163° for this compound. [d] G. L. Dorough, *et al.*, THIS JOURNAL, **63**, 3109 (1941). [e] V. T. Bickel and H. E. French, *ibid.*, **48**, 749 (1926). [f] *p*-Nitrobenzoate also prepared, m.p. 56° (L. F. King, *ibid.*, **61**, 2386 (1939)), reported 56.5–57.5°). [g] F. C. Whitmore, *et al.*, *ibid.*, **60**, 2458 (1938). [h] R. V. Rice, G. L. Jenkins and W. C. Harden, *ibid.*, **59**, 2000 (1937). [i] M. A. Spielman, J. D. Barnes and W. J. Close, *ibid.*, **72**, 2521 (1950).

prepared from the corresponding bromoalcohol,[28] b.p. 138–140°, n^{20}D 1.4230. The preparation and properties of **2,3-dimethyloxetane and 3-ethyl-2-propyloxetane** are described in the following paper.[15]

Lithium Aluminum Hydride Reactions.—The following is a typical procedure used for the reactions in Table I. A solution of 15 g. (0.24 mole) of 2-methyloxetane in 50 ml. of ether was added to a solution of 4.0 g. (0.11 mole) of lithium aluminum hydride in 100 ml. of ether. After 3 hr. of refluxing, the mixture was hydrolyzed with 20% sodium carbonate solution and filtered. The filter cake was washed with four 50-ml. portions of ether. After drying over magnesium sulfate, the ether solutions were distilled through a 6-inch glass-helices packed column with a reflux head, to give 2 g. of recovered 2-methyloxetane and 4.6 g. (32%) of 2-butanol. The infrared spectrum of all fractions of the product was identical to that of authentic 2-butanol.

The products obtained from this and other reductive cleavages are described in Table II, but one case requires special comment. The 3-hr. reaction of 2-phenyloxetane in ether did not give complete reduction, and the product happens to boil only a few degrees higher than the starting oxetane. The composition of the several cuts from the fractional distillation was determined by comparison of the infrared spectra with those of the pure alcohol and oxetane. The recovery of oxetane in this case was 28%, but none was found after the reduction in tetrahydrofuran or in ether for 20 hr.

Lithium Borohydride Reaction.—A mixture of 13.4 g. of 2-phenyloxetane (0.10 mole), 1.1 g. of lithium borohydride (0.05 mole) and 100 ml. of anhydrous butyl ether was stirred at 120–125° for 44 hr. and was then processed in the same manner as the lithium aluminum hydride reduction products. The composition of the several cuts obtained by distillation was determined by comparison with the infrared spectra of the starting oxetane, 1-phenyl-1-propanol and 3-phenyl-1-propanol, showing it to contain 5.5 g. (43% yield) of 1-phenyl-1-propanol, 4.1 g. (29% recovery) of 2-phenyloxetane and no 3-phenyl-1-propanol. With ether as the solvent no reaction was detected after 54 hr. of refluxing.

Catalytic Reduction.—Trimethylene oxide (4.5 g.) was reduced with hydrogen (1600 p.s.i. initially) over Raney nickel[29] (2 g.) at 150° for 3 hr.; 60% of the theoretical pressure drop was observed. Distillation gave 1.1 g. (25%) of *n*-propyl alcohol, b.p. 93–94° (735 mm.), and 2.0 g. of a colorless liquid, b.p. 170° (735 mm.) to 150° (8 mm.), which may have been a mixture of trimethylene glycol, ditrimethylene glycol, etc., caused by traces of alkali impurity in the catalyst. No reduction was observed over platinum oxide at room temperature and 45 p.s.i.

Acknowledgment.—A research grant from the National Science Foundation supported most of this work and is gratefully acknowledged. We wish to acknowledge also the valuable assistance of Mr. James G. Gillespie, who carried out the described syntheses of 2-methyloxetane and 2-phenyloxetane and did preliminary work on the reductive cleavage of them in the course of senior research at Northwestern University in 1952.

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[28] R. G. Nickerson, Ph.D. Thesis, Northwestern University, 1955, p. 33.

[29] R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).