carbanion solution rapidly added to a freshly prepared solution of benzyl chloride in pyridine, the addition being performed under the surface of the solution, in order to prevent exposure to the atmosphere. The individual reaction mixtures were worked up as above and analyzed by gas chromatography. The results are presented in Table II in the discussion.

C. Carbonation of pyridine solutions of fluorenyl anion was carried out by squirting the solution from a syringe directly onto a Dry Ice–ether slurry (very exothermic!). A solution of 0.01 mole each of fluorene and lithium aluminum hydride in 20 ml. of pyridine was kept overnight, then carbonated, and worked up in the usual manner yielding 0.34 g. (16%) of 9-fluorenecarboxylic acid, m.p. 218–222°, which was recrystallized from acetic acid, m.p. 230–231° (reported[17] 230–232°).

The metalations of triphenylmethane, followed by subsequent benzylation and carbonation of the carbanions, were carried out exactly as in parts A and C above, the maximum yield of 1,1,1,2-tetraphenylethane being about 18% and the amount of triphenylacetic acid reaching *ca.* 20%. Attempted metalations of 4-benzylbiphenyl and 1-benzylnaphthalene yielded colored solutions (purple and green, respectively) but alkylation products could not be obtained. Diphenylmethane gave a 1.4% yield of 1,1,2-triphenylethane when the bright orange carbanion solution was benzylated.

Generation of Triphenylmethide Ion from Reductive Cleavage of Benzpinacolone.—A solution of 1.59 g. (4.5 mmoles) of benzpinacolone and 0.30 g. lithium aluminum hydride (8 mmoles) in 20 ml. of pyridine was kept in a sealed Erlenmeyer flask for 1 hr. at room temperature, then treated with 2 ml. of benzyl chloride, whereupon the red color was completely bleached out. The reaction mixture was then hydrolyzed and the crude product chromatographed over alumina. Elution with 1:3 benzene–petroleum ether afforded 0.59 g. (53%) of triphenylmethane, m.p. 89–92° (after recrystallization from methanol), followed by 0.36 g. (24%) of 1,1,1,2-tetraphenylethane, m.p. 142.5–144° (from ethanol). Further elution with benzene-ethanol yielded 0.13 g. (8%) of benzpinacolyl alcohol.

Effect of Lithium *N*-Dihydropyridylaluminum Hydride on Carbanions.—When solutions of the reagent, prepared by aging pyridine solutions of lithium aluminum hydride,[8] were treated with freshly prepared pyridine solutions of the above carbanions which did not react appreciably with electrophiles, *instant* bleaching of the color was evident. The additions were performed in the nitrogen-flushed system by the hypodermic technique, being careful to inject the carbanion solutions below the surface of the other solution.

Metalation of Triphenylmethane, 4-Benzylbiphenyl, and 2-Benzylbiphenyl with *n*-Butyllithium.—Quantities (10 to 20 mmoles) of each of the three arenes were dissolved in 20–40 ml. of anhydrous ether and treated separately with a fivefold excess of *n*-butyllithium in ether. Each flask was flushed with nitrogen, tightly stoppered, and kept at room temperature for 18 hr. The colored solutions were carbonated by pouring onto Dry Ice–ether slurries, keeping exposure to the atmosphere as little as possible. Hydrolysis and work-up of each reaction mixture in the usual manner gave the following results, the data referring to crude acid before recrystallization: triphenylacetic acid, m.p. 240–265° (reported[18]: m.p. 265°), 71% yield; phenyl-*p*-xenylacetic acid, m.p. 132–136° (reported[19]: m.p. 141–142°), 41% yield; phenyl-*o*-xenylacetic acid, m.p. 161–169° (reported[20]: m.p. 171–173°), 25% yield.

Acknowledgment.—We gratefully acknowledge the generous support of this research by the National Science Foundation.

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(18) H. Gilman and R. V. Young, *J. Org. Chem.*, **1**, 315 (1936).

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Reduction of Glycidic Esters with Lithium Aluminum Hydride[1]

H. M. WALBORSKY AND C. COLOMBINI

Chemistry Department, Florida State University, Tallahassee, Florida

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A series of 2- and 3-substituted glycidic esters has been reduced with lithium aluminum hydride to yield mixtures of 1,2- and 1,3-glycols. The percentages of 1,2-glycol in the mixtures were determined by the periodic acid titration method. The effect of substituents on the ratio of 1,2- to 1,3-glycols produced is discussed.

There is an extensive literature on the reduction with lithium aluminum hydride of various functional groups in polyfunctional molecules.[2] However, the use of this reducing agent for the reduction of glycidic esters has received very little attention. It has been reported that ethyl 3,3-pentamethyleneglycidate and ethyl 3-trifluoromethylglycidate upon reduction with lithium aluminum hydride yield, respectively, 1-hydroxyethyl-1-cyclohexanol[3] and 4,4,4-trifluorobutan-1,3-diol.[4] In both cases a 1,3-glycol was produced although the substituents in the 3-position of the oxirane ring differed widely in both their steric and electronic effects. In order to gain some insight into the effects of various substituents on the course of the reduction of glycidic esters a series of 2- and 3-substituted glycidic esters was prepared and reduced with lithium aluminum hydride.

(1) This investigation was supported by a research grant (C-1461) from the National Cancer Institute of the National Institutes of Health, Public Health Service.

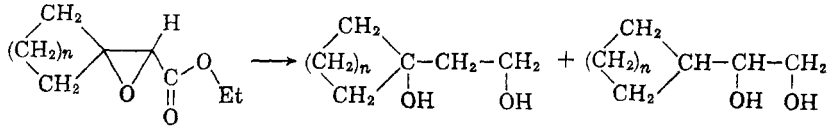
(2) For a comprehensive review of the literature through 1953 see N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Ind., New York, N. Y., 1956.

(3) J. D. Billimoria and N. F. Maclagan, *J. Chem. Soc.*, 3067 (1951); M. Mousseron, R. Jacquier, M. Mousseron-Canet, and R. Zagdoun, *Bull. soc. chim. France*, 5, **19**, 1042 (1952).

(4) H. M. Walborsky and M. E. Baum, *J. Am. Chem. Soc.*, **80**, 187 (1958).

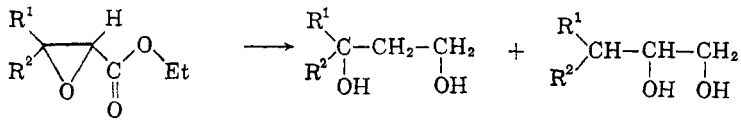
TABLE I

OXASPIRANES



Compound *n*	Glycol mixture B.p. T, °C. (mm.)	$n^{25}D$	Calcd. C	Calcd. H	Found C	Found H	Glycol, %	1,2-Glycol, %
1	120–121 (12)	1.4706	62.04	10.41	62.33	10.31	78	2
2	101–104 (3)	1.4792	64.58	10.84	64.31	11.12	73	26
3	109–112 (3)	1.4857	66.62	11.19	66.22	11.41	92	4
4	121–126 (3)	1.4923	68.31	11.47	68.08	11.58	79	27

TABLE II



Substituent R^1	Substituent R^2	Glycol mixture B.p. T, °C. (mm.)	$n^{25}D$	Calcd. C	Calcd. H	Found C	Found H	Glycol, %	1,2-Glycol, %
H	H	88–91 (15)	1.4260	47.35	10.60	47.02	10.49	56	92
CH_3	H	95–101 (12)	1.4385	53.30	11.21	53.12	11.27	73	49
CF_3	H	118 (34)[b]	...	50.19	4.80	50.31	4.53	33	0
CH_3	CH_3	97–99 (11)	1.4376	57.66	11.61	57.83	11.58	89	8
C_6H_5	H	115–120 (1)	1.5430	71.05	8.15	70.83	8.11	91	67
C_6H_5	CH_3[a]	120–122 (1)	1.5351	72.26	8.49	72.26	8.72	87	25
C_6H_5	C_6H_5	87–90[c]	...	87.92	7.06	87.62	7.16	85	12

[a] Stereochemistry was not established and is probably a mixture of *cis* and *trans* isomers. [b] Ref. 4. [c] M.p.

Results and Discussion

The glycidic esters were reduced by the addition of an ether solution of the ester to a 1 *M* solution of lithium aluminum hydride in ether at 0° to 4°. After hydrolysis of the reaction mixture the mixture of glycols was isolated by distillation with care being exercised to prevent fractionation of the isomeric glycols. Two samples were then removed. One sample was subjected to elemental analysis in order to establish that the mixture contained isomeric products and the other sample was titrated with periodic acid to determine the percentage of 1,2-glycol in the mixture. In a number of selected cases [1-hydroxyethyl-1-cyclohexanol (0%), 3-phenylpropan-1,3-diol (<2%), and 3-phenylbutan-1,3-diol (<2%)] it was demonstrated that under the conditions of our analytical procedure the 1,3-glycol did not react appreciably with periodic acid.

In the discussion to follow we have made the reasonable assumption that the ester group in the glycidic ester is reduced prior to the reduction of the epoxide.[5]

It can be seen from Table I that the 1,3-glycol is the major product formed which indicates that the attack by hydride is occurring predominantly at the 2-position of the oxirane ring. This is to be expected on the basis of steric effects since the 2-position is less hindered[5] to nucleophilic attack than is the 3-position.

The percentages of 1,2-glycol produced in these reductions is instructive. The four-membered (n = 1) and the six-membered ring (n = 3) oxaspiranes give rise to roughly the same percentages of 1,2-glycol as do the five-membered (n = 2) and the seven-membered (n = 4). Since the 1,2-glycol is produced by the attack of hydride at the ring carbon the amount produced is a reflection of the structural aspects of these ring systems. Since lithium aluminum hydride is a nucleophilic reagent one observes the same order of reactivity in these cases as with other nucleophilic substitution reactions such as for example, in the bimolecular attack of iodide ions on various alicyclic bromides.[6]

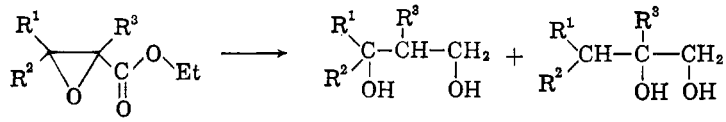
3-Alkyl and Aryl Substituted Glycidates.—Table II lists a series of glycidic esters which have both alkyl and aryl substituents in the 3-position. The results obtained from the reduction of these esters with lithium aluminum hydride again clearly indicate that steric effects are playing the major role in determining the course of ring opening.

As one changes R^1 from hydrogen to methyl the percentage of 1,2-glycol formed is almost reduced by 50% and when both R^1 and R^2 are methyl then the opening of the oxirane ring occurs almost exclusively at the 2-position. When phenyl substitu-

(5) See E. L. Eliel and M. N. Rerick, *J. Am. Chem. Soc.*, **82**, 1362 (1960) who discuss the difficulties encountered in the reduction of substituted epoxides.

(6) P. J. C. Fierens and P. Verschelden, *Bull. soc. chim. Belges*, **61**, 427 (1952); H. C. Brown, *Rec. Chem. Progr.* (Kresge-Hooker Sci. Lib.), **14**, 83 (1953).

TABLE III



Substituent			B.p.		Calcd.		Found		Glycol,	1,2-Glycol,
R^1	R^2	R^3	T, °C. (mm.)	$n^{25}D$	C	H	C	H	%	%
H	H	CH_3	97–100 (35)	1.4291	58.31	11.19	53.38	11.06	98	98
CH_3	H	CH_3	106–107 (30)	1.4182	57.66	11.62	57.49	11.54	80	95
CH_3	CH_3	CH_3	97–99 (11)	1.4376	60.10	11.77	60.70	11.94	90	88[a]
C_6H_5	H	CH_3[b]	113–116 (2)	1.5214	72.26	8.49	72.08	8.72	92	92
C_6H_5	CH_3	CH_3[b]	130–132 (2)	1.5300	73.30	8.95	73.16	8.94	82	11
$-(CH_2)_5-$		CH_3	106–110 (1)	...	68.31	11.47	68.40	11.30	89	49
$-(CH_2)_6-$		CH_3	104–112 (0.5)	...	69.72	11.70	68.80	11.83	91	87[a]

[a] Elemental analysis slightly off. [b] Stereochemistry not established and is probably a mixture.

ents are placed in the 3-position the picture becomes a bit more complex since not only steric but electronic effects may become important. Substituting a phenyl group for a hydrogen in the 3-position does not result in as much of a decrease of 1,2-glycol as substituting a methyl does. Although the phenyl group has a larger steric requirement than a methyl group the phenyl also exerts an electronic effect in that it delocalizes the partial position charge in the transition state.[7] This latter effect would tend to promote attack at the 3-position whereas the steric effect would be operating in an opposing manner. On this basis the amount of 1,2-glycol produced would be reasonable. This same rationalization can be applied to account for the results obtained from the reduction of ethyl 3,3-dimethylglycidate, ethyl 3-methyl-3-phenylglycidate, and ethyl 3,3-diphenylglycidate. The striking effect produced by placing a trifluoromethyl group in the 3-position of the oxirane ring has previously been noted and an explanation advanced.[4]

3-Substituted 1-Methylglycidates.—In the cases discussed up to this point, the oxirane ring has had one substituent in the 2-position ($COOC_2H_5$) and the substituents have been varied in the 3-position. It was of interest to determine what the effect would be on the ratio of isomeric glycols if one placed another substituent in the 2-position of the oxirane ring. A series of 3-substituted 2-methylglycidic esters was prepared and reduced with lithium aluminum hydride and the results are shown in Table III.

Again, as can be seen from Table III, the steric effects exert the most significant influence. Hydride attack occurs at the least substituted carbon atom of the oxirane ring so that in the case of ethyl 2-methylglycidate where the 2-position is disubstituted and the 3-position contains only hydrogen atoms the attack is almost exclusively at the 3-position. Similar results are obtained when the 2-position is disubstituted and the 3-position is monosubstituted as with ethyl 2,3-dimethylglycidate and ethyl 2-methyl-3-phenylglycidate. The high yield of 1,2-glycol obtained from the reduction of ethyl 2,3,3-trimethylglycidate and the corresponding low yield obtained from ethyl 3-phenyl-2,3-dimethylglycidate is anomalous since both compounds have the same degree of substitution. Actually, based on the electronic effect of the phenyl group one might have expected that ethyl 3-phenyl-2,3-dimethylglycidate would yield a larger proportion of 1,2-glycol than would ethyl 2,3,3-trimethylglycidate.

Finally, it should be noted that in the 3,3-hexamethylene and the 3,3-pentamethyleneglycidic esters there is a marked increase in the percentage of 1,2-glycol produced in these cases over that observed when the 2-position did not have the methyl substituent. Here again one also observes the effect of ring size[6] in that the 3,3-hexamethylene derivative yields a larger amount of 1,2-glycol than does the 3,3-pentamethylene derivative.

Experimental

Ethyl 3,3-trimethyleneglycidate,[8] ethyl 3,3-tetramethyleneglycidate,[9] ethyl 3,3-pentamethyleneglycidate,[9] ethyl 3,3-hexamethyleneglycidate,[9] ethyl glycidate,[10] ethyl 3-methylglycidate,[10] ethyl 3,3-dimethylglycidate,[9] ethyl 3-phenylglycidate,[9] ethyl 3-methyl-3-phenylglycidate,[9] ethyl 3,3-diphenylglycidate,[9] ethyl 2-methylglycidate,[10] ethyl 2,3-dimethylglycidate,[10] ethyl 2,3,3-trimethylglycidate,[11] ethyl 2-methyl-3-phenylglycidate,[12] ethyl 2-methyl-3-methyl-3-phenylglycidate,[11] ethyl 2-methyl-3,3-pentamethyleneglycidate,[9] and ethyl 2-methyl-3,3-hexamethyleneglycidate[13] were prepared according to literature procedures. All the glycidic esters gave negative Beilstein and ferric chloride tests.[14]

Lithium Aluminum Hydride Reduction.—The following procedure is typical of that used for all the reductions. A standard 1 *M* solution of lithium aluminum hydride in ether was prepared[15] and the necessary aliquots removed when needed. For every mole of glycidic ester to be reduced 1.5

(7) For an excellent discussion of electronic factors on the direction of ring opening in unsymmetrical epoxides see A. A. Feldstein and C. A. Vanderwerf, *J. Am. Chem. Soc.* **76**, 1626 (1954).

(8) G. Chiurdeglu, *et al.*, *Bull. soc. chim. Belges*, **65**, 664 (1956).

(9) W. S. Johnson, J. S. Belew, L. J. Chinn, and R. H. Hunt, *J. Am. Chem. Soc.*, **75**, 4995 (1953).

(10) W. D. Emmons and A. J. Pagano, *ibid.*, **77**, 89 (1955).

(11) G. Darzens, *Compt. rend.* **141**, 766 (1905).

(12) G. Darzens, *ibid.*, **142**, 214 (1960).

(13) Prepared by the usual procedure,[9] in 67% yield, b.p. 129–131° at 9 mm., $n^{23}D$ 1.4650 and gave a satisfactory elemental analysis.

(14) H. O. House, J. W. Blaker, and D. A. Madden, *J. Am. Chem. Soc.*, **80**, 6389 (1958).

(15) W. C. Brown, *Org. Reactions*, **6**, 484 (1951).

equivalents of lithium aluminum hydride was used. A 40% ether solution of the glycidic ester was added to the solution of lithium aluminum hydride while the flask was being cooled by an ice bath. After the addition of the ester was completed the ice bath was removed and stirring was continued for 6–7 hr. at room temperature. The reaction mixture was then hydrolyzed, extracted with ether and the ether extracts dried over anhydrous sodium sulfate. The solvent was removed and the residue distilled *in vacuo*. Samples from the distillate were removed for elemental analysis and periodic acid titration.

Analysis of the Glycols.—The glycols were analyzed by allowing aqueous (or water-dioxane) solutions to stand with excess periodic acid for 1 hr. and determining the excess periodic acid in the usual manner, using standard solutions of sodium arsenite and iodine, the titration mixtures being buffered with excess sodium bicarbonate.[16] The values obtained from titration of duplicate and triplicate samples of the glycol are reproducible to ±0.2 %. However, due to the errors introduced during the isolation of the glycols by the extraction and distillation procedures a confidence of only about ±10% can be placed on the percentages of 1,2-glycols reported in this work. For example, the results obtained by different workers in the reduction of ethyl-3-methylglycidate were 49% and 53%, respectively. In three different reductions of ethyl 3,3-pentamethyleneglycidate the percentages of 1,2-glycol were 3.4, 4.3, and 4.8%.

(16) K. G. Stone, "Determination of Organic Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 54.

The Reduction of Aromatic Nitro Compounds by Potassium Borohydride[1]

H. J. SHINE AND H. E. MALLORY

Department of Chemistry, Texas Technological College, Lubbock, Texas

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It has been found that some *m*- and *p*-substituted nitrobenzenes carrying a substituent with a positive value of the Hammett sigma constant are reduced in good yield by potassium borohydride to the azoxy compounds. Nitrobenzenes with negative sigma constants are not reduced.

Few examples are to be found in the literature of the reduction of nitro compounds by complex borohydrides, and it is generally reported[2–5] that nitro groups are reduced either with difficulty or not at all by borohydrides.

Brown[6,7] has shown that the nitro group in ethyl *p*-nitrobenzoate is resistant to reduction by sodium borohydride–metal halide mixtures when the temperature is kept moderate. On the other hand the azido group[4] and the nitroso group[8] have been reduced by sodium borohydride.

As part of a research program requiring the synthesis of aromatic hydrazo compounds we have investigated further the reaction of borohydrides with aromatic nitro compounds. We have found that some substituents render an aromatic nitro group inert to reduction by potassium borohydride, while with other substituents the corresponding azoxy compound is formed in excellent yield. Most of our results are given in Table I. It can be seen that the difference between inertness and reducibility in the nitro group depends on the electronic effect of the substituent. Groups with a positive value of sigma constant enhance reduction of the nitro group to the azoxy group while the reverse is true of substituents with negative values. This means that in the formation of the azoxy compound at least one of the nitro groups of the pair involved needs to be made susceptible to attack by borohydride (or hydride) ion. It is evident that this attack is inhibited by electron donation from substituent to nitro group nitrogen.

The only exception in Table I is *p*-nitrobenzoic acid in pyridine solution. However, it can be seen that in general reduction in pyridine is not at all as extensive as in ethanol. In the case of *p*-nitroacetanilide in ethanol hydrolysis by the added potassium hydroxide occurs.

Some of the compounds used did not give identifiable products. Thus, both *m*- and *p*-dinitrobenzene gave large amounts of red-brown solids, which were rather insoluble in organic solvents and which could not be recrystallized. These solids left a residue on ignition. *p*-Fluoronitrobenzene in ethanol gave *p*-nitrophenetole, but in pyridine gave small amounts of products with melting point ranges between 82° and 264°. No recognizable product could be obtained from *p*-nitrobenzonitrile in ethanol and *p*-iodonitrobenzene in pyridine.

In two instances our data differ from data in the literature. Gore and Wheeler[9] have reported the λ_{max} of 4,4′-diiodoazoxybenzene in ethanol as 295 mμ. We find λ_{max} 342 mμ, which fits the order expected. Apparently, Gore and Wheeler measured the λ_{max} of *p*-iodonitrobenzene, for which we obtained 293 mμ.

(1) From the M.S. degree thesis of H. E. Mallory, Texas Technological College, 1961. This work forms part of a program of research in hydrazoaromatic rearrangements. We are grateful for support by the Research Corporation and by the National Science Foundation (Grant No. NSF-G-14551).

(2) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, 1956, pp. 776, 777.

(3) J. H. Billman and A. C. Diesing, *J. Org. Chem.*, **22**, 1068 (1957).

(4) J. H. Boyer and S. E. Ellzey, Jr., *ibid.*, **23**, 127 (1958).

(5) E. Schenker, *Angew. Chem.*, **73**, 81 (1961).

(6) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 3164 (1955).

(7) H. C. Brown, E. J. Mead, and B. C. Subba Rao, *ibid.*, **77**, 6209 (1955).

(8) J. H. Boyer and S. E. Ellzey, Jr., *ibid.*, **82**, 2525 (1960).

(9) P. H. Gore and O. H. Wheeler, *ibid.*, **78**, 2160 (1956).