TABLE V

POLYMERIZATION OF 2-METHYL-1-PENTENE

Sample	Heptane,[a] g.	Al(i-Bu)$_3$, g.	TiCl$_4$, g.	Moles Al(i-Bu)$_3$[b] / moles TiCl$_4$	Monomer, g.	Time, hr.	Temp., °C.	Polymer wt., g.	Conversion, %
1	4	0.10	0.085	1.16	10	30	54	1	10
2	3.5	.10	.085	1.16	10	30	54	1.3	13
3	3.5	.10	.085	1.16	10	50	54	1	10

[a] A solvent ratio to monomer of 1.5 (wt. ratio) failed to produce polymer. [b] A catalyst ratio of 3.0 failed to produce polymer.

infrared analysis of carbon tetrachloride solutions of both 1,5-hexadiene and poly-1,5-hexadiene were made by comparing the absorption maxima of the C=C at 1650 cm.$^{-1}$ and the vinyl C–H at 920 cm.$^{-1}$. The analysis showed that the polymer contained from 5.6 to 8.6% of the monomer units which still retained one of the two double bonds. No attempt was made to dehydrogenate this polymer.

Anal. Calcd. for $(C_6H_{12})_n$: C, 87.72; H, 12.24. Found: C, 86.78; H, 12.16.

Poly-2,5-dimethyl-1,5-hexadiene (XIV, XV).—Table IV shows the results of the polymerization of 2,5-dimethyl-1,5-hexadiene. These polymers had melting points of 80–85° and a quantitative infrared analysis of carbon tetrachloride solutions of both 2,5-dimethyl-1,5-hexadiene and its polymer by comparison of the maxima for C=C and vinyl CH showed that from 3.4 to 12.8% of the monomer units retained one double bond during polymerization. No attempt was made to dehydrogenate this polymer.

Anal. Calcd. for $(C_8H_{14})_n$: C, 87.19; H, 12.81. Found: Sample 1: C, 87.43; H, 12.57. Sample 2: C, 87.13; H, 13.21.

Poly-2-methyl-1-pentene.—The results of polymerization of 2-methyl-1-pentene are shown in Table V. The oils obtained were combined and distilled under diminished pressure (150° (0.1 mm.)). The infrared spectrum of this hydrocarbon showed no unsaturation was present in the molecule.

Anal. Calcd. for $(C_6H_{12})_n$: C, 84.63; H, 14.37; mol. wt. (n = 5), 425.8. Found: C, 85.45; H, 14.13; mol. wt., 424.

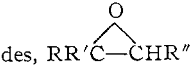
URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Mechanism of Halide Reductions with Lithium Aluminum Hydride. VI. Reduction of Certain Bromohydrins and Epoxides[1,2]

BY ERNEST L. ELIEL AND DAVID W. DELMONTE[3]

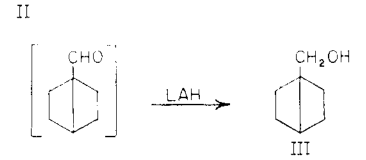
RECEIVED OCTOBER 24, 1957

Lithium aluminum hydride reduction of 1,1-diphenyl-2-bromoethanol yields 2,2-diphenylethanol, in addition to the expected 1,1-diphenylethanol. Similarly, reduction of 1,1,2-triphenyl-2-bromoethanol yields 1,2,2-triphenylethanol, and reduction of 1,1-diphenyl-2-(p-chlorophenyl)-2-bromoethanol yields 1-(p-chlorophenyl)-2,2-diphenylethanol. The "oxygen shift" observed in these reductions is explained on the basis of an epoxide intermediate. In accordance with this explanation, it has been found that lithium aluminum hydride reduction of unsymmetrically substituted epoxides,  $RR'\overset{O}{C\text{—}C}HR''$ *in the presence of aluminum halides* gives rise to the less highly substituted carbinols RR'CHCHOHR″, although similar reduction *in the absence of aluminum halides* gives the more highly substituted carbinols RR'COHCH$_2$R″. Tracer studies show that the reduction of styrene oxide and isobutylene oxide in the presence of aluminum halides involves the corresponding aldehydes (phenylacetaldehyde and isobutyraldehyde) as intermediates. The implications of these results on the mechanism of reduction of halohydrins in general are discussed.

In a previous publication[4] it has been shown through tracer studies that lithium aluminum hydride reduction of a halohydrin with tertiary halogen, such as 2-chloro-2-methyl-1-propanol (I), proceeds largely through a hydride shift

$$\underset{\text{I}}{(CH_3)_2CClCH_2OH} \xrightarrow[-HCl]{H^-} (CH_3)_2CHCHO \xrightarrow{LiAlD_4} (CH_3)_2CHCHDOH \quad \text{(i)}$$

It was the original aim of the present work to establish whether a corresponding *alkyl* shift would occur in the reduction of halohydrins of the type  $RR'COH\overset{|}{\underset{|}{C}}X$. Isolated instances of alkyl shifts of this kind in lithium aluminum hydride reductions are already on record; thus reduction of the bicyclic bromoketone II gives rise to the alcohol III[5]; in the treatment of *trans*-2-chlorocyclohexanol (IV) with lithium aluminum hydride under drastic conditions some cyclopentaldehyde (V) is ob-



---

[1] Presented before the Organic Division of the American Chemical Society at Miami, Fla., on April 11, 1957. For a preliminary communication of part of this work, see THIS JOURNAL, **78**, 3226 (1956); cf. also G. J. Park and R. Fuchs. *J. Org. Chem.*, **21**, 1513 (1956).

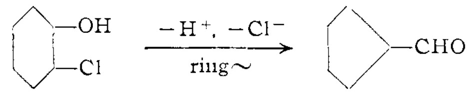
[2] Paper V, E. L. Eliel and J. T. Traxler, THIS JOURNAL, **78**, 4049 (1956).

[3] This paper is based on the Ph.D. dissertation of D. W. Delmonte, Shell Research Fellow, 1955–1956.

[4] E. L. Eliel and Th. J. Prosser, THIS JOURNAL, **78**, 4045 (1956).

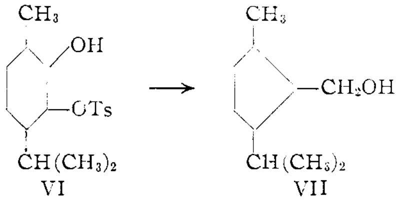
[5] A. C. Cope, E. S. Graham and D. J. Marshall, *ibid.*, **76**, 6159 (1954). These authors postulate rearrangement at the bromoketone stage, but, reasoning by analogy with the hydride shift in eqn. (i),[4] we prefer to assume that the ring contraction occurs at the bromohydrin stage.

tained[6]; and reduction of *cis*-2-hydroxymenthyl



IV V

tosylate (VI) yields 2-isopropyl-5-methylcyclopentylcarbinol (VII) among other products.[7]



VI VII

The compounds chosen for study in this work were 1,1-diphenyl-2-bromoethanol (VIII) and 1,1,2-triphenyl-2-bromoethanol (IX). It would have been preferable to study 1,1,2,2-tetraphenyl-2-bromoethanol (X), since previous work[2,4] had indicated that a *hydride* shift would occur only in halohydrins, such as I, in which the halogen is tertiary. However, attempts to synthesize compound X were unsuccessful.[8]

$(C_6H_5)_2COHCH_2Br$ VIII $\quad (C_6H_5)_2COHCHBrC_6H_5$ IX

$(C_6H_5)_2COHCBr(C_6H_5)_2$ X

The results of the reduction of compound VIII are summarized in Table I. Very little reduction occurred when a slight excess over the theoretically required amount of hydride (0.5 mole, *viz.*, 0.25 mole for the acidic hydrogen and 0.25 mole for reduction of the halogen) was employed. Even with the use of 1.5 moles of hydride, substantial amounts of bromohydrin remained unattacked and somewhat better reduction (though still not complete) was obtained with 2.4 moles of hydride which quantity was therefore used in all subsequent reductions of halohydrins.[9]

TABLE I

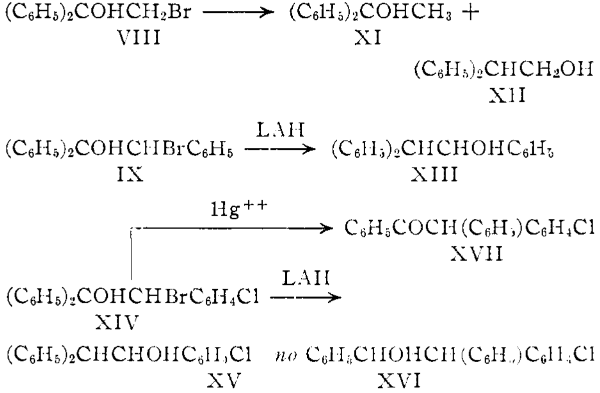
REDUCTION OF 1,1-DIPHENYL-2-BROMOETHANOL (VIII)

Mole ratio LAH/VIII	Reaction time, hr.	Recovered, VIII, %	1,1-Diphenylethanol (XI), %	2,2-Diphenylethanol (XII), %
0.6	10	70	[a]	[a]
1.5	10	24	[a]	[a]
2.4	10	8	49	19[b]
2.4	2	12	42	4.2[c]
2.4	2[d]	16[e]	33	5[f]

[a] Not analyzed. [b] Also obtained *ca.* 5% diphenylacetaldehyde and benzophenone. [c] Also obtained *ca.* 14% carbonyl compound, largely diphenylacetaldehyde. [d] Tartrate work-up, all other runs were worked up with acid. [e] As 1,1-diphenylethylene oxide. [f] Also obtained *ca.* 2.5% benzophenone.

No phenylbenzylcarbinol, the product to be expected from a phenyl shift in the bromohydrin VIII, was obtained; in fact comparison of the infrared spectrum of the crude reduction mixture with that of authentic phenylbenzylcarbinol indicated the latter substance to be absent. The major product of the reduction was the expected 1,1-diphenylethanol (XI). In addition, however, substantial amounts of diphenylacetaldehyde and the corresponding alcohol (XII) 2,2-diphenylethanol (XII) were formed. Formation of these compounds involves a shift of the oxygen function (see Fig. 1).

A similar oxygen shift was observed in the reduction of IX which yielded exclusively 1,2,2-triphenylethanol (XIII). This alcohol might alternatively have resulted from a phenyl shift, but this possibility was excluded when it was found that reduction of 1,1-diphenyl-2(*p*-chlorophenyl)-2-bromoethanol (XIV) yielded only 1-(*p*-chlorophenyl)-2,2-diphenylethanol (XV), the product of the oxygen shift, completely free of 1,2-diphenyl-2-(*p*-chlorophenyl)-ethanol (XVI), the expected product of a phenyl shift. Furthermore, it was shown that the absence of a phenyl shift in XIV is not due to any inherent difference in behavior between XIV and the corresponding chlorine-free compound IX, for in the presence of mercuric ion XIV does undergo a phenyl shift to give phenyl *p*-chlorobenzhydryl ketone (XVII).[10] These results are summarized in Fig. 1.



$$\underset{\text{VIII}}{(C_6H_5)_2COHCH_2Br} \xrightarrow{\text{LAH}} \underset{\text{XI}}{(C_6H_5)_2COHCH_3} + \underset{\text{XII}}{(C_6H_5)_2CHCH_2OH}$$

$$\underset{\text{IX}}{(C_6H_5)_2COHCHBrC_6H_5} \xrightarrow{\text{LAH}} \underset{\text{XIII}}{(C_6H_5)_2CHCHOHC_6H_5}$$

$$\underset{\text{XIV}}{(C_6H_5)_2COHCHBrC_6H_4Cl} \xrightarrow{\text{Hg}^{++}} \underset{\text{XVII}}{C_6H_5COCH(C_6H_5)C_6H_4Cl}$$

$$\underset{\text{XIV}}{(C_6H_5)_2COHCHBrC_6H_4Cl} \xrightarrow{\text{LAH}} \underset{\text{XV}}{(C_6H_5)_2CHCHOHC_6H_4Cl} \quad \textit{no} \quad \underset{\text{XVI}}{C_6H_5CHOHCH(C_6H_5)C_6H_4Cl}$$

Fig. 1.

The "oxygen shift" observed in the above reductions suggested almost compellingly that epoxides were intermediates in the reduction of the halohydrins VIII, IX and XIV to the rearranged alcohols XII, XIII and XV. Yet such a suggestion appeared at first sight unlikely, since it is well established[11] that reduction of an unsymmetrically substituted epoxide with lithium aluminum hydride gives rise to the more highly substituted carbinol, whereas compounds XII, XIII and XV are the less highly substituted of the two possible isomeric carbinols. Thus the reduction of triphenylethylene

---

(6) M. Mousseron, R. Jacquire, M. Mousseron-Canet and R. Zagdoun, *Bull. soc. chim. France*, 1043 (1952).

(7) P. R. Jefferies and B. Milligan, *Chemistry & Industry*, 487 (1956).

(8) D. Delmonte, unpublished results.

(9) The stoichiometry of the reduction of halohydrins with lithium aluminum hydride remains uncertain. Whereas J. E. Johnson, R. H. Blizzard and H. W. Carhart, THIS JOURNAL, **70**, 3664 (1948), found that it requires one *mole* of the hydride to reduce one mole of halide, R. E. Lutz, R. L. Wayland and H. G. France, *ibid.*, **72**, 5511 (1950), report ready removal of the aliphatic halogen in 1-(*p*-bromophenyl)-2-bromoethanol, p-$BrC_6H_4CHOHCH_2Br$ with a "molecular equivalent" of lithium aluminum hydride.

(10) A corresponding phenyl shift which occurs when IX is treated with mercuric ion has been demonstrated by labeling: C. J. Collins and W. A. Bonner, THIS JOURNAL, **75**, 5379 (1953).

(11) For examples see (a) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 646–673; (b) V. M. Micovic and M. L. Mihailovic, "Lithium Aluminum Hydride in Organic Chemistry," Belgrade, Yugoslavia, 1955, pp. 68–74.

TABLE II

PRODUCTS OF REDUCTION OF EPOXIDES $\mathrm{RR'\overset{O}{C—C}HR''}$ WITH LITHIUM ALUMINUM HYDRIDE

R	R'	R''	Yield, %	$RR'COHCH_2R''$ XX, %	RR'CHCHOHR'' XXI, %	Method of anal.[a]
CH_3	H	H	60	100	0	M, I
CH_3	CH_3	H	26	95–98[b]	2–5[b]	M, I
CH_3	CH_3	CH_3	*ca.* 25[c]	100	0	I
C_6H_5	H	H	82	90–95[b,d]	5–10[b]	M, I
C_6H_5	C_6H_5	H	92	100	0	I, Is
C_6H_5	C_6H_5	C_6H_5	12[e]	100	0	C

[a] M, mass spectrometry; I, infrared spectroscopy; Is, actual isolation of pure material; C, chromatographic separation and isolation. [b] The range given indicates the uncertainty of the analysis. [c] Also recovered epoxide.[12] [d] Previous reports[13] mention only this product (phenylmethylcarbinol). The presence of the isomeric 2-phenylethanol in the reaction product is likely but not absolutely certain. [e] Also 80% recovered epoxide.[12] No reduction at all occurred with 0.35 mole of $LiAlH_4$.

TABLE III

REDUCTION OF EPOXIDES $\mathrm{RR'\overset{O}{C—C}HR''}$ WITH LITHIUM ALUMINUM HYDRIDE IN THE PRESENCE OF HALIDE

R	R'	R''	LAH, moles	Halide,[a] moles	Yield, %	$RR'COHCH_2R''$ XX, %	RR'CHCHOHR'' XXI, %	Method of anal.[b]
CH_3	H	H	0.30	1.25	60	93	7	M
			.25	1.00	42[e]	81–84[d]	16–19[d]	M, I
CH_3	CH_3	H	.50	0.25	18[e]	70	30	M
			.25	1.00	55	5–7[d]	93–95[d]	M, I
CH_3	CH_3	CH_3	.28	1.00	32	0	100	I
C_6H_5	H	H	1.5	1.00[f]	80	72	28	M
			0.30	0.25	80	16	84	M
			.25	0.25	75	10	90	M
			.25	1.00	71	2–5[d,g]	95–98[d]	M, I
C_6H_5	C_6H_5	H	2.64	1.00[f]	72	16	84	I, C
			0.25	1.00	89	0	100	I, C
C_6H_5	C_6H_5	C_6H_5	2.64	1.00[f]	91	*ca.* 0	*ca.* 100	Is

[a] Halide is aluminum chloride unless otherwise indicated. [b] M, mass spectrometry; I, infrared spectroscopy; C, chromatographic separation and isolation; Is, direct isolation. [c] Also isolated 1-chloro-2-propanol. [d] The range given indicates the uncertainty of the analysis. [e] Accidental loss; the actual yield was about three times as high. [f] Allyl bromide. [g] Presence probable but not absolutely certain.

oxide (XVIII), the hypothetical intermediate in the reduction of bromohydrin IX, should give rise to 1,1,2-triphenylethanol (XIX) (Fig. 2, path A) and not to 1,2,2-triphenylethanol (XIII) (Fig. 2, path B) which was the product actually obtained from IX. In fact, a careful reinvestigation of the reduction of a variety of epoxides with lithium

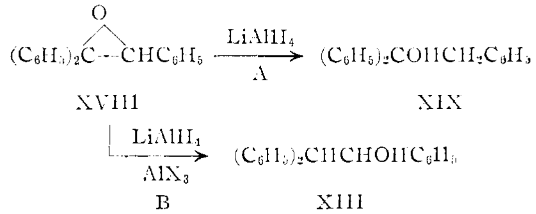


Fig. 2.

aluminum hydride, using mass spectrometry, infrared spectroscopy and chromatographic separation of products as analytical tools, confirmed that in all cases the overwhelmingly predominant if not exclusive product was the more highly substituted carbinol XX (Table II).

The only difference between the above reductions of epoxides and those of bromohydrins, such as IX, postulated to proceed *via* epoxides, such as XVIII (Fig. 2), is that in the ring-closure of the bromohydrins, bromide is released into solution. Thus it appeared that the presence of bromide would so modify the reduction as to reverse the direction of opening of the epoxide ring. That this is indeed so was shown by reducing triphenylethylene oxide XVIII with a lithium aluminum hydride solution in which a mole of allyl bromide had been reduced previously, so as to simulate the release of bromide from the bromohydrin. Under these conditions, the exclusive product was 1,2,2-triphenylethanol (Fig. 2, path B).

Subsequent experiments, summarized in Table III, indicated that the direction of reduction of most epoxides can be reversed by the addition of halide. It was found to be convenient to add the halide in the form of aluminum bromide or, better, aluminum chloride rather than allyl bromide; in fact maximum reversal of reduction is achieved with a mole ratio of epoxide to hydride to aluminum chloride of 1:0.25:1. Under these conditions, the direction of reduction of all the epoxides studied—with the exception of the primary-secondary aliphatic epoxide propylene oxide—was substantially reversed.

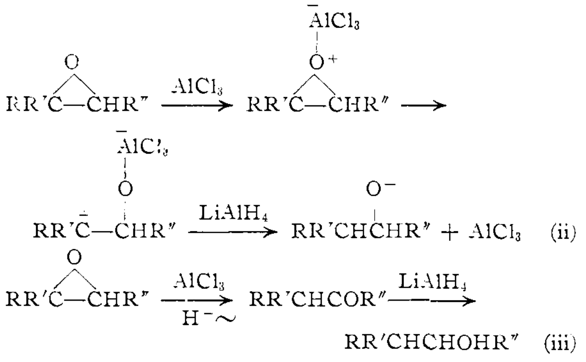
The question then arose as to the mechanism of the reversal. Two obvious possibilities come to mind. According to one (equation ii) aluminum halide coördinates with the epoxide and favors an

---

(12) Other instances of hindered epoxides which resist reduction are listed in ref. 11b, p. 74.

(13) R. F. Nystrom and W. G. Brown, THIS JOURNAL, **70**, 3738 (1948); L. W. Trevoy and W. G. Brown, *ibid.*, **71**, 1675 (1949).

SN1-like opening of the epoxide ring with subsequent attack of hydride at the more substituted carbon which bears the positive charge of the incipient carbonium ion.[14] According to the other (equation iii) the aluminum halide rearranges the epoxide to an aldehyde or ketone which is subsequently reduced to the product alcohol.



The former sequence (ii) resembles the reversal in direction of ring opening of epoxides observed with other nucleophiles (such as alcohols) upon addition of acid,[14] whereas the latter (iii) is reminiscent of the course of the reaction of epoxides with Grignard reagents.[15]

Reaction paths ii and iii may be differentiated by a tracer study employing lithium aluminum deuteride; if path ii is operative, the product should be RR'CDCHOHR'' whereas path iii should yield RR'CHCDOHR'', species which may be distinguished readily by mass spectrometry. The experiment was carried out with styrene oxide as a representative primary-secondary epoxide and with isobutylene oxide as a representative primary-tertiary epoxide, since mass spectra of the four possible products to be expected in reduction of these oxides (2-phenylethanol-2-*d*, 2-phenylethanol-1-*d*, isobutyl-2-*d* alcohol and isobutyl-1-*d* alcohol) were available from a previous investigation.[4] Reduction of styrene oxide with lithium aluminum deuteride–aluminum chloride gave a 2-phenylethanol fraction which was 94% of the 1-*d* species with only 5% of the 2-*d* isomer (the remaining 1% was unlabeled). Similarly, the isobutyl alcohol fraction from an analogous reduction of isobutylene oxide was 90% 1-*d* isomer $(CH_3)_2CHCHDOH$ and only 9% 2-*d* isomer, the remaining 1% being unlabelled. It follows therefore that path iii is by far the predominant course of the abnormal reduction of epoxides in the presence of aluminum halide and that therefore the reduction of epoxides with lithium aluminum hydride–aluminum halide resembles their reaction with Grignard reagents (whereas their reaction with lithium aluminum hydride alone resembles the reaction of epoxides with alkylmagnesiums).[16]

It is known from the extensive work of E. Wiberg and co-workers[17] that the addition of aluminum halides to lithium aluminum hydride leads to the formation of lithium halide (precipitated in the case of the chloride) and aluminum halohydrides of the type AlH_2X and $AlHX_2$. These halohydrides are, in general, weaker reducing agents than is lithium aluminum hydride[18]; thus, for example, they do not reduce *n*-octyl bromide[19] which is readily reduced by lithium aluminum hydride alone.[9] It is clear that in the above-described reductions, aluminum halohydrides are formed, and we believe that these are quite sluggish in attacking the epoxide as such, thus giving the excess aluminum halide, acting as a Lewis acid, an opportunity to rearrange the epoxide to a carbonyl compound first. This tendency for rearrangement prior to reduction is greatest in the case of triphenylethylene oxide (which suffers hardly any direct reduction even with lithium aluminum hydride alone, *cf.* Table II) and least in the case of propylene oxide, probably because in the latter the migration terminus for the hydride shift is secondary and aliphatic and therefore the rearrangement to aldehyde is sluggish[15] and not well able to compete even with the slowed-down direct reduction. However, the difference between propylene oxide on one hand and isobutylene and isoamylene oxide on the other may not be quite as large as implied in Table III. According to this table, the tertiary epoxides yield no tertiary alcohol XX, but the secondary epoxide yields very predominantly secondary alcohol XX. Unfortunately, in a control experiment in which a mixture of the two products XX $[(CH_3)_2COHCH_2CH_3]$ and XXI $[(CH_3)_2CHCHOHCH_3]$ to be expected from isoamylene oxide was treated with the lithium aluminum hydride–aluminum chloride, the tertiary alcohol XX was extensively destroyed by conversion to *t*-amyl chloride[20] (found) and possibly olefin (not found). Therefore it is possible that reduction of isobutylene and isoamylene oxide by the mixed reagent yielded substantially more of the tertiary alcohol than was isolated; nevertheless the total product yields are such that the conclusion that more XX is formed from propylene oxide than from isobutylene oxide remains valid, even though the contrast may not be as extreme as is implied in Table III.

In previous publications,[2,4] two paths have been indicated for the reduction of halohydrins to alcohols by lithium aluminum hydride, *viz.*, an assisted bimolecular displacement (Fig. 3, C) for primary and secondary halohydrins and a hydride shift

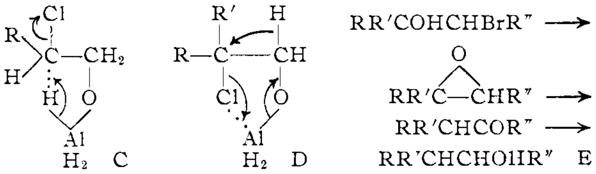


Fig. 3.

---

[14] *Cf.* E. L. Eliel in M. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, chapter 2, p. 112.

[15] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1956, pp. 965-967.

[16] Reference 15, p. 995.

[17] Summarized in ref. 11a, pp. 51-53; *cf.* also ref. 11b, p. 44.

[18] *Cf.* R. F. Nystrom, THIS JOURNAL, **77**, 2544 (1955).

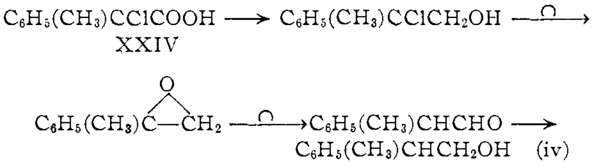
[19] E. Wiberg and A. Jahn, *Z. Naturforsch.*, **7b**, 580 (1952).

[20] The reduction of conjugated unsaturated ketones to hydrocarbons reported by J. Broome and B. R. Brown, *Chemistry & Industry*, 1307 (1956), also appears to proceed *via* the chlorides: C=CC=O → C=CCOH → C=CCCl → C=CCH, which, being allylic, may be further reduced to hydrocarbons by the mixed reagent[19]; *cf.* J. Broome, B. R. Brown and G. H. R. Summers, *J. Chem. Soc.*, 2071 (1957).

(Fig. 3, D) for halohydrins in which the halogen is tertiary. To these should now be added the path *via* the epoxide (Fig. 3, E) as a third possibility.[21] One must enquire, however, whether these three paths are really all separate. The possibility exists, *a priori*, that the epoxide intermediate is converted, by means of aluminum halide, to a halohydrin isomeric with that from which the epoxide was formed and that this halohydrin is then further reduced by path C or D. Conversely, the halohydrins previously studied[2,4] may have been first converted to epoxides which are then reduced by path E.[22]

Experimental evidence shows that the reduction of secondary halohydrins does *not* proceed *via* epoxides, or *vice versa*. Thus 2-chloro-1-propanol upon reduction yields 1-propanol as the only chlorine-free product[2,23] but propylene oxide yields largely 2-propanol, even in the presence of aluminum chloride. Again, 2-chloro-2-phenylethanol upon reduction with lithium aluminum deuteride yields largely 2-phenylethanol-2-*d*,[4] whereas styrene oxide with the same reagent in the presence of aluminum chloride yields largely 2-phenylethanol-1-*d*. Therefore path C represents a discrete course of reduction.

The evidence with respect to the tertiary halohydrins, RR′CClCH$_2$OH, is not so clear-cut. The products obtained from these by reduction[2,4,23] appear to be compatible with reaction *via* the epoxide. Nevertheless, we believe that reduction of these halohydrins does not involve the epoxide intermediate in a major way, but that, in the main, it involves the discrete path D (Fig. 3). There are several reasons for this assumption. Curtin and Meislich have found that the two diastereoisomeric 1-(*p*-chlorophenyl)-1,2-diphenyl-2-bromoethanols upon treatment with ethylmagnesium bromide give *distinct* rearrangement products, but the corresponding diastereoisomeric α-(*p*-chlorophenyl)-stilbene oxides with ethylmagnesium bromide give *the same* rearrangement product and have concluded that the epoxides are not intermediates in the rearrangement of the bromohydrins.[24] This observation shows that the rearrangement of halohydrins *need not* proceed *via* epoxides. There is experimental evidence that the reduction of $(CH_3)_2CClCH_2OH$ (XXII) and $(C_6H_5)_2CClCOOH$[2,4,22] (XXIII) *does not* involve the corresponding epoxides for in the formation of these epoxides only one gram-atom of halide per mole of compound would be liberated and the data in Table III show that this is not sufficient to suppress completely the formation of the tertiary alcohols, from the epoxides. Yet no tertiary alcohols whatsoever were obtained in the reduction of XXII and XXIII. Finally, if the reduction of 2-phenyl-2-chloropropionic acid (XXIV) were to proceed *via* the epoxide, equation iv shows that the over-all reduction should entail retention of optical configuration, since the reaction path involves *two* inversions.

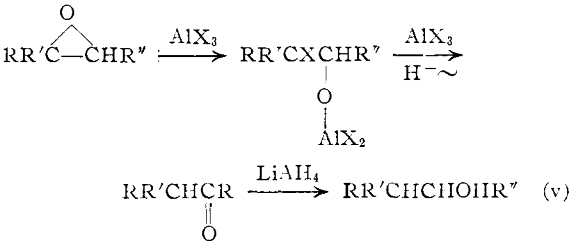


$$C_6H_5(CH_3)CClCOOH \longrightarrow C_6H_5(CH_3)CClCH_2OH \xrightarrow{\;\Omega\;}$$
XXIV

$$C_6H_5(CH_3)\overset{O}{C—CH_2} \xrightarrow{\;\Omega\;} C_6H_5(CH_3)CHCHO \longrightarrow C_6H_5(CH_3)CHCH_2OH \quad \text{(iv)}$$

Actually, however, predominant inversion was observed,[22] in agreement with the reaction course postulated previously. Nevertheless, since inversion of configuration was not complete,[22] a reaction path entailing retention, such as iv, may have made a minor contribution.

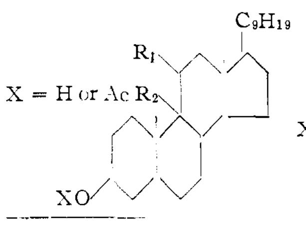
While thus it appears that not all halohydrin reductions proceed *via* epoxides, it is still a possibility that epoxide reductions proceed *via* halohydrins (equation v), at least in the case of tertiary epoxides. Such a possibility is suggested by



$$RR'\overset{O}{C—CHR''} \xrightarrow{AlX_3} RR'CX\underset{\substack{|\\O\\|\\AlX_2}}{C}HR'' \xrightarrow[H^-\sim]{AlX_3} RR'CH\underset{\substack{\|\\O}}{C}R'' \xrightarrow{LiAlH_4} RR'CHCHOHR'' \quad \text{(v)}$$

the work of House[25] on the reaction epoxides with magnesium bromide. Further experiments are required to clear up this point.

Some time ago it was found that 3-acetoxy-9-bromoergostanone-11 (XXV) is reduced, by means of lithium aluminum hydride, to 3-hydroxyergostanol-11 (XXVI) despite the fact that the bromine in this compound is tertiary.[26] It was suggested that reduction proceeds *via* the enolate of the ketone XXVII; but in view of the fact that enolates are usually resistant to further reduction,[23]



XXV, R_1 = =O, R_2 = Br
XXVI, R_1 = OH, R_2 = H
XXVII, R_1 = =O, R_2 = H
XXVIII, R_1,R_2 = >O
XXIX, R_1 = OH, R_2 = Br

---

[21] Paths D and E are analogous to those proposed by T. A. Geissman and R. I. Akawie, THIS JOURNAL, **73**, 1993 (1951), for the reaction of halohydrins with Grignard reagents.

[22] It has been stated previously—E. L. Eliel and J. P. Freeman, *ibid.*, **74**, 923 (1952)—that epoxides are not intermediates in the reduction of α-chloroacids and chlorohydrins to alcohols, since the alcohol, $C_6H_5(CH_3)COHCH_3$, obtained from α-methylstyrene oxide, $C_6H_5(CH_3)\underset{O}{C—CH_2}$, was isomeric with that, $C_6H_5(CH_3)CHCH_2OH$, obtained from α-chloro-α-phenylpropionic acid, $C_6H_5(CH_3)CClCOOH$. This argument now turns out to be invalid, since it neglected the effect of the aluminum chloride—formed in the reduction of the chloroacid—on the course of reduction of the potential epoxide intermediate.

[23] E. L. Eliel, C. Herrmann and J. T. Traxler, *ibid.*, **78**, 1193 (1956).

[24] D. Y. Curtin and E. K. Meislich, *ibid.*, **74**, 5905 (1952). See also ref. 25b for similar results with the positional isomers 2-bromo-3-pentanol and 3-bromo-2-pentanol.

[25] (a) H. O. House, *ibid.*, **77**, 3070 (1955); (b) **77**, 5083 (1955); (c) see also M. Tiffeneau and B. Tchoubar, *Compt. rend.*, **207**, 918 (1938).

[26] H. B. Henbest, E. R. H. Jones, A. A. Wagland and T. I. Wrigley, *J. Chem. Soc.*, 2477 (1955). More recently, Dr. Henbest (private communication) has obtained independent evidence (from the reduction of 1,2-cyclohexanediol monobrosylates) that epoxides may be intermediates in such reductions. See also H. B. Henbest and T. I. Wrigley, *ibid.*, 4596 (1957).

the epoxide XXVIII (formed from the bromoketone XXV *via* the bromohydrin XXIX) appears a more likely intermediate, especially in view of the fact that XXVIII itself was a by-product of the reduction. The epoxide XXVIII is formed along with aluminum bromide which is assumed to rearrange it to ketone XXVII which is finally reduced to the product XXVI.

Experimental

All melting and boiling points uncorrected. Infrared spectra by Mr. Rolland Ro; mass spectra by Mr. George Young; elementary analyses by Micro-Tech Laboratories, Skokie, Ill.

2,2-Diphenylethylene and its Epoxide.—Molten 2,2-diphenylethanol[23] (17.5 g., 0.088 mole) was added slowly from a pressure-equalized dropping funnel to an excess of solid potassium hydroxide contained in a vacuum distillation apparatus maintained at *ca.* 150° and 10 mm. The crude olefin distilled as it was formed. Redistillation gave 7.63 g. (48%) of material boiling at 135–139° (10 mm.), $n^{20}\text{D}$ 1.6015 (lit.[27] b.p. 134° (10 mm.), $n^{20}\text{D}$ 1.6100). Since the yield in this preparation was low, subsequent batches of 1,1-diphenylethylene were prepared by the method of reference 28. The olefin was converted to the bromohydrin VIII, m.p. 71–72.5° (lit.[29] 73–73.5°) by means of N-bromoacetamide.[29] 1,1-Diphenylethylene oxide, m.p. 56–58° (lit.[29] 55.5–56°), was obtained by treatment of either the bromohydrin VIII[29] or the monotosylate of 1,1-diphenylethylene glycol[30] with base.

Derivatives of 1,1,2-Triphenylethane.—1,1,2-Triphenylethanol, m.p. 87–88° (lit.[29] 86.5–87.5°) was prepared from benzophenone and benzylmagnesium chloride[31] and converted to 1,1,2-triphenyl-2-bromethanol (IX), m.p. 121–122° (lit.[32] 124–126°), by means of N-bromosuccinimide.[32] Treatment of the bromohydrin with base[32] gave triphenylethylene oxide, m.p. 74–76° (lit.[32] 75–77°). 1,2,2-Triphenylethanol (XIII) was prepared by lithium aluminum hydride reduction of phenyl benzhydryl ketone.[33] Since the ketone is not ether-soluble, it was added to the standardized hydride solution as ether slurry. The carbinol XIII melted at 86–88° (lit.[34] 87°).

2-(*p*-Chlorophenyl)-1,1-diphenyl-2-bromoethanol (XIV).—2-(*p*-Chlorophenyl)-1,1-diphenylethanol, m.p. 115–119° (lit.[35] 116°), was prepared from benzophenone and *p*-chlorobenzylmagnesium chloride.[35] It was brominated with N-bromosuccinimide in exactly the same way as the parent compound IX.[32] The bromohydrin XIV, obtained in 91% yield, melted at 128–130° after recrystallization from petroleum ether (b.p. 60–90°). The analytical sample melted at 129.5–130°.

Anal. Calcd. for $C_{20}H_{16}BrClO$: C, 61.95; H, 4.16. Found: C, 61.69; H, 4.27.

1-(*p*-Chlorophenyl)-2,2-diphenylethanol (XV).—A solution of 9.81 g. (0.05 mole) of diphenylacetaldehyde in[22] 100 ml. of sodium-dried ether was added to *p*-chlorophenylmagnesium bromide prepared from 1.22 (0.05 g.-atom) of magnesium and 9.57 g. (0.05 mole) of *p*-chlorobromobenzene in 100 ml. of ether and allowed to stand for 2.25 hr. at room temperature. The reaction mixture was cooled and hydrolyzed with a solution of 5.35 g. of ammonium chloride in 22 ml. of water followed by 150 ml. of dilute hydrochloric acid. Separation of the ether layer, drying over anhydrous potassium carbonate and concentration gave the product XV as a crystalline solid melting at 153–155.5° after crystallization from petroleum ether (b.p. 90–120°), yield 3.88 g. (25%). The analytical sample melted at 154–155.5°.

Anal. Calcd. for $C_{20}H_{17}ClO$: C, 77.79; H, 5.55. Found: C, 77.87; H, 5.73.

Lithium Aluminum Hydride Reductions. Reduction of 1,1-Diphenyl-2-bromoethanol (VIII).—A solution of 20.8 g. (0.075 mole) of VIII in 100 ml. of dry ether was added to a slurry of 6.85 g. (0.181 mole) of lithium aluminum hydride in 150 ml. of ether (prepared in the usual way) over a period of 30 minutes, followed by a 2-hour reflux. Hydrolysis was effected by means of sodium potassium tartrate.

The dried ether solution was concentrated to give 15.5 g. of an oil which, according to Beilstein and silver nitrate tests, contained little if any halogen. Comparison of the infrared spectrum of the oil with reference spectra suggested the presence of 1,1-diphenylethylene oxide, of some alcohol component(s) and of a small amount of benzophenone.[36] Diphenylacetaldehyde was absent. An entirely similar product mixture was obtained when the reaction mixture was worked up with 40% aqueous potassium hydroxide.

An aliquot of the product was chromatographed on basic alumina. Four fractions were identified in the eluate. The first one (15.5% recovery) was 1,1-diphenylethylene oxide, m.p. 50–56°, undepressed by admixture of an authentic sample (m.p. 55.5–56°[29]). The second one (2.2% recovery) was benzophenone, identified by its 2,4-dinitrophenylhydrazone, m.p. 228°, mixture melting point with authentic sample 228–230° (lit. 239°). The third fraction (16.5% recovery) was 1,1-diphenylethanol, m.p. after recrystallization from petroleum ether (60–90°) and mixture melting point with authentic sample 80–81° (lit.[37] 80–81°). The last fraction (20.1% recovery) was a mixture. Fractional crystallization from petroleum ether (b.p. 60–90°) gave 1,1-diphenylethanol, m.p. and mixture m.p. 80–81° (about 3 parts), and 2,2-diphenylethanol, identified by its phenylurethan, m.p. 127°, mixture m.p. with authentic sample 128–131° (lit.[38] 138–139°) (about 1 part).

By multiplying the crude yield with the recovery figures from the chromatogram, one obtains the yield, in grams, of each of the four products. Expressed as the usual mole percentage, this is: 1,1-diphenylethylene oxide, 16.3%; 1,1-diphenylethanol, *ca.* 33%; 2,2-diphenylethanol, *ca.* 5%; and benzophenone, 2.5%.

When the reduction mixture was worked up with sulfuric acid, the ratio of the yields of 1,1-diphenylethanol and 2,2-diphenylethanol was similar, but there was also obtained a substantial amount of diphenylacetaldehyde. It is believed that this compound is an artifact of the work-up process. A longer reaction time with acidic work-up led to more 2,2-diphenylethanol and less diphenylacetaldehyde. The data are summarized in Table I. It should be noted that with acidic work-up, 1,1-diphenyl-2-bromoethanol (VIII) was recovered, but with basic or tartrate work-up 1,1-diphenylethylene oxide was obtained instead, suggesting that the epoxide results from unchanged bromohydrin during the work-up. It is also significant that the 2,2-diphenylethanol:1,1-diphenylethanol ratio increases with increasing conversion. This may be due to the accumulation of halide ion in the reaction mixture as the reaction progresses, since this is known[18] to impede the reduction of halogen in halohydrins (a process by which 1,1-diphenylethanol may be formed from VIII) and to promote (*vide infra*) the formation of 2,2-diphenylethanol from 1,1-diphenylethylene oxide which may be a fleeting intermediate in the reduction.

Reduction of 1,1,2-Triphenyl-2-bromoethanol (IX).—A slurry of 14.12 g. (0.04 mole) of IX in 150 ml. of ether was added slowly to 87 ml. (0.096 mole) of 1.1 *M* ethereal lithium aluminum hydride. The mixture was heated at reflux for four hours and then worked up in the usual way to give 10.53 g. (96% recovery) of white solid, m.p. 76–82°. Recrystallization of this solid from petroleum ether (b.p. 60–90°) gave 1,2,2-triphenylethanol (XIII), m.p. 87–88° (lit.[34] 87°), in 96% recovery. The mixture melting point with authentic XIII was 86–88° and the infrared spectra of the two samples were identical. No additional bands appeared in the infrared spectrum of the crude product. The mixture melting point of the recrystallized product with 1,1,2-triphenylethanol was depressed to 83–88° and the infrared spectra of the two samples were distinct.

---

[27] R. N. Jones, This Journal, **65**, 1823 (1943).

[28] C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 226.

[29] S. J. Cristol, J. R. Douglass and J. S. Meek, This Journal, **73**, 816 (1951).

[30] E. L. Eliel and D. Delmonte, *J. Org. Chem.*, **21**, 596 (1956).

[31] C. Hell and F. Wiegandt, *Ber.*, **37**, 1429 (1904).

[32] J. F. Lane and D. R. Walters, This Journal, **73**, 4234 (1951).

[33] R. Anschütz and P. Förster, *Ann.*, **368**, 93 (1909).

[34] M. St. Pierre, *Bull. soc. chim. France*, [3] **5**, 292 (1891).

[35] W. Tadros, K. Farahat and J. M. Robson, *J. Chem. Soc.*, 439 (1949).

[36] For the possible origin of this product see ref. 23, footnote 41.

[37] M. Tiffeneau, *Ann. chim.*, [8] **10**, 359 (1907).

[38] P. Ramart and P. Amagat, *ibid.*, [10] **8**, 290 (1927).

Reduction of 2-(*p*-Chlorophenyl)-1,1-diphenyl-2-bromethanol (XIV).—A solution of 9.69 g. (0.025 mole) of XIV in 125 ml. of ether was added slowly to 55 ml. (0.06 mole) of 1.1 *M* ethereal lithium aluminum hydride and the mixture was heated at reflux for four hours. Hydrolysis followed by isolation of the product gave 5.64 g. (73%) of crude material melting at 141–147°. The mixture melting point with authentic 1-(*p*-chlorophenyl)-2,2-diphenylethanol (XV) (m.p. 153–155.5°) was 145–152° and the two samples had identical infrared spectra. The spectrum of the product differed from that of authentic 2-(*p*-chlorophenyl)-1,1-diphenylethanol.

Since recrystallization of the crude reaction product returned only 78% and raised the melting point to only 147–149°, it was suspected that perhaps the material might contain some of the isomeric 1,2-diphenyl-2-(*p*-chlorophenyl)-ethanol (XVI), the product of a phenyl shift. Therefore the crude material (1.00 g.) was oxidized with potsssium permanganate in pyridine and the acidic and neutral fractions of the oxidation product were isolated. The acid melted at 231–234° and had neut. equiv. 151.4 (*p*-chlorobenzoic acid melts at 242° and has neut. equiv. 156.5). After sublimation the acid weighed 0.32 g. (63%) and melted at 233–236°, mixture melting point 238–239.5°. The neutral fraction weighed 0.64 g. and gave a negative Beilstein test for chlorine, indicating absence of *p*-chlorobenzophenone, which would have resulted by oxidation of XVI. Treatment of the neutral oil with dinitrophenylhydrazine reagent gave benzophenone 2,4-dinitrophenylhydrazone, m.p. 231–235° (lit. 239°), mixture melting point 238–239.5°, corresponding in weight to 0.33 g. (56.5%) of benzophenone.

Reductions of Epoxides with Lithium Aluminum Hydride Alone.—These reductions were carried out by the standard procedure using 0.33–0.43 mole of 1.1 *M* standard lithium aluminum hydride solution per mole of oxide. All reaction mixtures were decomposed with water and sulfuric acid and the reaction products, except those from 1,1-diphenyl- and triphenylethylene oxide were isolated by continuous ether extraction.

Triphenylethylene Oxide.—Under the above conditions, 97% of the starting material, m.p. 70–73°, mixture m.p. 71–74°, was recovered. Using two moles of hydride per mole of oxide gave a mixture (92% material recovery). Two grams of the mixture on crystallization from petroleum ether (b.p. 60–90°) returned 0.90 g. of starting material, m.p. 73–74°. Chromatography of the mother liquor on basic alumina gave another 0.84 g. of starting material, m.p. 73–74°, and 0.26 g. of 1,1,2-triphenylethanol, m.p. 86–88°, undepressed by admixture of an authentic sample but depressed to 82–89° by admixture with 1,2,2-triphenylethanol. The infrared spectrum of the product was identical with that of 1,1,2-triphenylethanol and distinct from that of the 1,2,2-isomer.

1,1-Diphenylethylene Oxide.—The reduction product (94%) melted at 74.5–80°, mixture melting point with authentic 1,1-diphenylethanol 78–81°. The two samples had identical infrared spectra, different from the spectrum of 2,2-diphenylethanol. Recrystallization of the reaction product (97.5% recovery) raised the melting point to 80–81° (lit.[37] 80–81°). The crude product was chromatographically homogeneous.

Styrene Oxide.—The extracted reaction product was distilled to give 14.0 g. (82%) of material boiling at 62–69° (1.8 mm.), n^{20}_{D} 1.5280. Mass spectral analysis using the 107 peak for $C_6H_5CHOHCH_3$ and the 91 peak for $C_6H_5CH_2CH_2OH$ indicated a composition of 93% of 1-phenylethanol and 7% 2-phenylethanol. However, this analysis was somewhat untrustworthy, as synthetic mixtures of the two components, for reasons unknown, did not give accurate mass spectrometric analyses. The analysis was therefore checked by comparing the infrared spectrum of the mixture with synthetic mixtures containing 85, 90 and 95% of the 1-isomer and 15, 10 and 5% of the 2-isomer, respectively. This again suggested that the mixture contained 90–95% of 1-phenylethanol, the remainder being the 2-isomer. However, the presence of the latter could not be established with certainty, as the only characteristic band of the 2-isomer (at 9.6 μ) is masked in all mixtures rich in 1-isomer.

Trimethylethylene Oxide.—The reaction mixture was decomposed with base, as acid decomposition converted unchanged epoxide into glycol. Continuous extraction (36 hr.) followed by drying, concentration and distillation yielded 3.47 g. of *t*-amyl alcohol. The infrared spectrum indicated absence of methylisopropylcarbinol (diagnostic bands at 9.1, 9.8 and 10.23 μ), but there was some unchanged epoxide as indicated by a band at 11.6 μ. The amount of recovered starting material was estimated at 10–20% from the infrared spectrum and the yield of alcohol is accordingly 25–30%. The *p*-nitrobenzoate of the reduction product melted at 83–84° undepressed by admixture of *t*-amyl *p*-nitrobenzoate (lit. 85°).

Isobutylene Oxide.—The ether extract of the reaction mixture after drying over potassium carbonate was concentrated and distilled to give 26% of material boiling at 80–84° (737 mm.), n^{20}_{D} 1.3872. Mass spectrometric analysis of the product using the 59 peak for *t*-butyl alcohol and the 43 peak for isobutyl alcohol indicated a composition of 97.6% of *t*-butyl and 2.4% isobutyl alcohol. The infrared spectrum of a synthetic mixture containing 97% *t*-butyl and 3% isobutyl alcohol was in good agreement with that of the reaction product. There was no doubt whatever about the presence of the minor component (band at 9.58 μ).

Propylene Oxide.—The crude material, isolated as above, distilled at 79–82° (734 mm.), n^{20}_{D} 1.3778 (60% yield) (lit. b.p. 82.3°, n^{20}_{D} 1.3771 for isopropyl alcohol). The infrared spectrum of the product was identical with that of isopropyl alcohol and showed no bands due to *n*-propyl alcohol. Mass spectral analysis confirmed a composition of 99% isopropyl alcohol.

Reduction of Epoxides with Lithium Aluminum Hydride–Aluminum Halide.—The reduction of styrene oxide is described in detail as being typical. Other reductions were carried out similarly except as noted.

Styrene Oxide.—Standardized 1.1 *M* ethereal lithium aluminum hydride (36 ml., 0.04 mole) was added to a solution of 21.32 g. (0.16 mole) of anhydrous aluminum chloride in 50 ml. of cold sodium-dried ether. (The proportion of the reagents is important. The use of lithium aluminum hydride slurries did not give good results in this procedure.) A solution of 19.22 g. (0.16 mole) of styrene oxide in 75 ml. of sodium-dried ether was added to the mixed reagent over 48 minutes and the mixture boiled at reflux for two hours subsequently. Hydrolysis was effected by the addition of 10 ml. of water followed by 125 ml. 10% sulfuric acid. The ether layer was separated and the aqueous layer continuously extracted with ether for 18 hours. The combined ether layers were dried over potassium carbonate, concentrated and the residue distilled at 0.9 mm. to give 13.96 g. (71%) of product, n^{20}_{D} 1.5377. Mass spectral analysis indicated 98% of 2-phenylethanol and 2% 1-phenylethanol in the product. The infrared spectrum was in good agreement with that of a mixture containing 95% of the 2-isomer and 5% of the 1-isomer; however, it is difficult to demonstrate the definite presence of the 1-isomer by infrared, as the prominent band at 11.17 μ in the spectrum of this compound is absent in all mixtures rich in the 2-isomer. The reaction product was converted to the phenylurethan of 2-phenylethanol, m.p. 76–78°, mixture melting point with an authentic sample 77–79.5° (lit. 79°).

Other ratios of the reactant gave less complete reversal of the reduction, as indicated in Table III.

Trimethylethylene Oxide.—The reaction mixture was decomposed with base and extracted continuously with ether for 42 hours, dried, and concentrated to give 8.96 g. of crude product from 10.0 g. of epoxide. Distillation of the product yielded 3.29 g. (32%) of material boiling at 110–116°, n^{20}_{D} 1.4097 and 3.24 g. of high-boiling product. The infrared spectrum of the first fraction was identical with that of authentic methylisopropylcarbinol and the diagnostic bands of *t*-amyl alcohol at 7.8, 8.5 (broad), 10.65 and 13.73 μ were absent. The α-naphthylurethan of this fraction melted at 111–112° and did not depress the melting point of an authentic sample (alcohol purchased from Columbia Organic Chemicals Co.) (lit. m.p. 109°).

In a control experiment, a mixture of equal parts of *t*-amyl alcohol and methylisopropylcarbinol was added to the lithium aluminum hydride–aluminum chloride reagent. The infrared spectrum of the recovered product indicated that the *t*-amyl alcohol had been destroyed. In another experiment in which *t*-amyl alcohol alone was subjected to the mixed reagent, some *t*-amyl chloride was obtained.

Isobutylene Oxide.—The reduction was carried out as described for styrene oxide. The product (55%) was collected at 80–135° (746 mm.), n^{20}_{D} 1.4032. Mass spectral analysis indicated a composition of 93.4% isobutyl alcohol and 6.6% *t*-butyl alcohol. The infrared spectrum was in agreement with a composition of 95% isobutyl and 5% *t*-butyl alcohol. The presence of *t*-butyl alcohol appears to be real, as suggested by a shoulder at 10.97 μ which is absent in the spectrum of pure isobutyl alcohol (*t*-butyl alcohol has a prominent band at 10.99 μ).

A reduction with 0.5 mole lithium aluminum hydride in the presence of 0.25 mole of aluminum chloride gave a product containing 70% *t*-butyl alcohol and only 30% isobutyl alcohol.

Propylene Oxide.—The reaction was carried out as described for styrene oxide and the extracted product was distilled and collected in two fractions: (1) b.p. 80–96° (741 mm.), $n^{20}\text{D}$ 1.3808 and (2) b.p. 128–129° (739 mm.), $n^{20}\text{D}$ 1.4335. Fraction 1 by infrared spectrum appeared to be a mixture of *n*-propyl and isopropyl alcohol. Mass spectral analysis, using the 31 peak for *n*-propyl alcohol and the 45 peak for isopropyl alcohol, indicated 84% isopropyl and 16% *n*-propyl alcohol. The infrared spectrum of the product was very similar to that of a mixture of 81% isopropyl and 19% *n*-propyl alcohol. Fraction 2 was identical in infrared spectrum with an authentic specimen of 1-chloro-2-propanol (spectrum kindly provided by Professor C. A. VanderWerf), lit.[39] b.p. 64.5° (75 mm.), $n^{20}\text{D}$ 1.4387. The spectrum differed from that of 2-chloro-1-propanol.[23] Very little reversal was obtained using 0.3 mole of lithium aluminum hydride and 0.25 mole of aluminum chloride per mole of propylene oxide (*cf.* Table III).

1,1-Diphenylethylene Oxide. (a).—The reduction was carried out as described for styrene oxide, except that a 20% excess of the LiAlH_4–AlCl_3 reagent was employed, the reaction mixture was worked up with 20% sodium hydroxide solution, and the product was not extracted continuously. The crude product (89% yield) was an oil whose infrared spectrum was nearly identical with that of 2,2-diphenylethanol. Chromatography of this material on basic alumina gave, in over 85% recovery, a fraction whose infrared spectrum was identical with that of 2,2-diphenylethanol and which, after crystallization from mixed petroleum ether (b.p. 30–90°), melted at 60–62°, undepressed by admixture of authentic 2,2-diphenylethanol (lit.[38] m.p. 62°). No 1,1-diphenylethanol was evident in any of the fractions of the chromatogram.

(b) **Using Lithium Aluminum Hydride and Allyl Bromide.**—A solution of 3.02 g. (0.025 mole) of allyl bromide in 30 ml. of sodium-dried ether was added rapidly to 60.0 ml. (0.066 mole) of 1.1 *M* ethereal lithium aluminum hydride and the solution boiled at reflux for 40 minutes. A solution of 4.91 g. (0.025 mole) of 1,1-diphenylethylene oxide in 75 ml. of ether was then added over ten minutes and the mixture boiled for ten hours more. The mixture was worked up with dilute sulfuric acid in the usual way and the crude product analyzed as under (a) with the results entered in Table III. The diphenylacetaldehyde probably originated in the work-up by action of sulfuric acid on unchanged epoxide.

Triphenylethylene Oxide.—The reduction was carried out as described for 1,1-diphenylethylene oxide under (b). The crude product was obtained in 98% yield and melted at 83–85°, mixture melting point with authentic 1,2,2-triphenylethanol 83–86°. Recrystallization (93% recovery) raised the melting point to 84–87°. The infrared spectrum of the crude and the recrystallized product and authentic 1,2,2-triphenylethanol were identical and different from the spectrum of 1,1,2-triphenylethanol. However, the complete absence of the latter isomer was not established with certainty.

Reductions with Lithium Aluminum Deuteride–Aluminum Chloride. (a) **Isobutylene Oxide.**—The reduction was carried out with the same proportions of reagents as the corresponding reduction with the hydride; but since it is uneconomical to prepare clear solutions of lithium aluminum deuteride, the powdered deuteride (2.01 g., 0.048 mole, 20% excess) was added to a solution of 21.33 g. (0.16 mole) of anhydrous aluminum chloride in 100 ml. of dry ether. Another 50 ml. of ether was added and the mixture heated at reflux with stirring for 90 minutes. A solution of 11.54 g. (0.16 mole) of isobutylene oxide in 75 ml. of ether was added over 45 minutes to the deuteride mixture cooled previously to room temperature and the mixture was then heated at reflux for two more hours. Decomposition with 10 ml. of water and 150 ml. of 10% sulfuric acid was followed by continuous extraction for 72 hours of the aqueous layer. The combined ether layers were dried over potassium carbonate and fractionated and the fraction boiling at 106–108° (747 mm.), $n^{20}\text{D}$ 1.3980, weighing 3.86 g. was retained as deuterated isobutyl alcohol (isobutyl alcohol has b.p. 107.5° (752 mm.), $n^{20}\text{D}$ 1.3955). The fraction was analyzed mass spectrometrically using the reference spectra previously recorded.[4,40] The 32 peak (for isobutyl-1-*d* alcohol), 44 peak (for isobutyl 2-*d* alcohol) and 31 peak (for light isobutyl alcohol) were used in the analysis which indicated a composition of 90.0% $(\text{CH}_3)_2\text{CHCHDOH}$, 8.0% $(\text{CH}_3)_2\text{CDCH}_2\text{OH}$ and 2.0% $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$. As the infrared spectrum of the material showed slight contamination with a carbonyl compound, the fraction was converted to the hydrogen phthalate, m.p. 62.5–65° (lit.[41] 65°). The phthalate was saponified in the usual way and again analyzed mass spectrometrically: isobutyl-1-*d* alcohol, 90.1%; isobutyl-2-*d* alcohol 9.3%, light isobutyl alcohol 0.6%. (The slight change in the analysis suggests that failure to take into account the carbonyl contaminant in the previous analysis had caused a slight distortion.) The infrared spectrum of the purified reaction product was very nearly identical with that of a synthetic mixture of 90.2% isobutyl-1-*d* and 9.8% isobutyl-2-*d* alcohol.

(b) **Styrene Oxide.**—Optically active[30,42] styrene oxide (12.01 g., 0.1 mole, $[\alpha]\text{D}^{24.5}$ 18.76°) was reduced as described for isobutylene oxide and lithium aluminum deuteride. The product was collected in two fractions, b.p. 90.5–92° (5 mm.), $n^{20}\text{D}$ 1.5308 and b.p. 91–93° (5 mm.), $n^{20}\text{D}$ 1.5340, combined weight 6.83 g. (56%). The first fraction showed some carbonyl material in the infrared and was optically inactive. The second fraction had $[\alpha]^{24.5}\text{D}$ −0.15° (neat), but this rotation probably was due to slight contamination with $\text{C}_6\text{H}_5\text{CHOHCH}_2\text{D}$ (*ca.* 0.6% would suffice to give the observed activity). The 3,5-dinitrobenzoate of fraction 2, m.p. 106–108° (lit. 108°) was optically inactive. The infrared spectrum of fraction 2 resembled closely that of 2-phenylethanol-1-*d*[4] and differed considerably from that of a mixture containing over 90% of the isomeric 2-phenylethanol-2-*d*.[4] Mass spectrometric analysis,[4] using the 91 peak for 2-phenylethanol-1-*d*, the 92 peak for 2-phenylethanol-2-*d* and the 122 peak for light 2-phenylethanol, indicated 94.6% $\text{C}_6\text{H}_5\text{CH}_2\text{CHDOH}$, 4.5% $\text{C}_6\text{H}_5\text{CHDCH}_2\text{OH}$ and 0.9% $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$. The spectrum for authentic 2-phenylethanol-1-*d* was available from previous work[4,40] and that for authentic 2-phenylethanol-2-*d* was calculated from the spectrum of a mixture of known composition containing 92.6% 2-phenylethanol-2-*d*, 4.2% 2-phenylethanol-1-*d* and 3.2% 2-phenylethanol which was encountered in previous work.[4] (Details of the calculation may be found in the thesis of D. W. Delmonte.) The use of a calculated spectrum for what turns out to be a very minor component of the mixture of 2-phenylethanols encountered in the present work is not expected to introduce an appreciable error in the analysis.

Reaction of 2-(*p*-Chlorophenyl)-1,1-diphenyl-2-bromoethanol (XIV) with Mercuric Nitrate.—A solution of 4.65 g. (0.012 mole) of XIV and 1.95 g. (0.006 mole) of mercuric nitrate in 70 ml. of dioxane (purified over sodium and distilled) and 30 ml. of water was allowed to stand for 72 hours, neutralized with 1.01 g. (0.012 mole) of sodium bicarbonate, concentrated and extracted with ether. Distillation of the solvent followed by crystallization of the residue from ethanol gave 2.76 g. (75%) of material melting at 97–102°. Recrystallization of an aliquot from ethanol (94% recovery) gave *p*-chlorobenzhydryl phenyl ketone (XVII), m.p. 103–104° (lit.[43] 102–103°).

---

[39] W. Fickett, H. K. Garner and H. J. Lucas, THIS JOURNAL, **73**, 5064 (1951).

[40] The spectra have been deposited as Document number 4817 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints or $1.25 for 35 mm. microfilm payable to: Chief, Photoduplication Service, Library of Congress.

[41] W. Hückel and P. Ackermann, *J. prakt. Chem.*, [2] **136**, 23 (1933).

[42] Since active oxide was on hand, it was used in preference to the *dl*-material to observe the activity of $\text{C}_6\text{H}_5\text{CHDCH}_2\text{OH}$ if that product should result in major proportion.

[43] D. Y. Curtin and P. I. Pollak, THIS JOURNAL, **73**, 992 (1951).

Oxidation of an aliquot of the crude product with potassium permanganate gave an acidic fraction and a neutral fraction. The acid, m.p. 100–127°, was free of halogen as indicated by the Beilstein test, and upon recrystallization from water melted at 117–118° (benzoic acid melts at 121°). The yield in the oxidation was 71%. The neutral material melted at 59–61° (lit.[44] for *p*-chlorobenzophenone 75.5–76°), but recrystallization raised the melting point to 66–69°, mixture melting point with authentic *p*-chlorobenzophenone 69–75°, yield 51%.

The oxidation product had the same infrared spectrum as authentic *p*-chlorobenzophenone and gave a 2,4-dinitrophenylhydrazone melting at 184–186° (lit.[45] 184–185°).

Acknowledgment.—This work is a contribution from the Radiation Project of the University of Notre Dame supported, in part, under Atomic Energy Commission contract AT(11-1)-38 and Navy loan equipment contract Nonr-06900. We are grateful to Dr. H. O. House for a critical reading of the manuscript. Mr. Marck Rerick performed the reductions of trimethylethylene oxide and Mr. Mark Mersereau coöperated in the reductions of 1,1-diphenylethylene oxide and 1,1-diphenyl-2-bromoethanol.

Notre Dame, Indiana

---

(44) M. Kollarits and V. Merz, *Ber.*, **6**, 547 (1873).

(45) W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1806 (1934).

[Contribution from the Chemistry Department, University of Notre Dame]

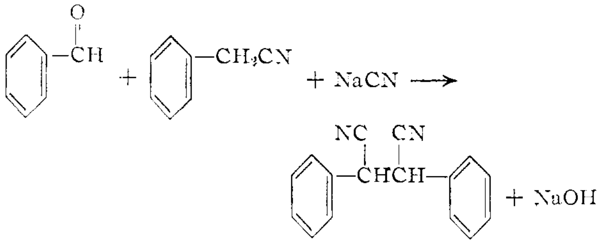
A New Method for Preparing Arylsuccinonitriles

By R. B Davis[1]

Received October 11, 1957

An aldehyde, an arylmethylene cyanide and an alkali metal cyanide react to form an arylsuccinonitrile. Some new arylsuccinonitriles have been prepared by this method.

Previously, the preferred method for preparing 2,3-diphenylsuccinonitrile was the method described by Lapworth and McRae[2] in which benzaldehyde benzyl cyanide were condensed to α-phenylcinnamonitrile using a base as a catalyst. Then hydrogen cyanide was added to the α-phenylcinnamonitrile to produce 2,3-diphenylsuccinonitrile. It has now been found that benzaldehyde, benzyl cyanide and sodium cyanide react to give this product in excellent yield.



Furthermore, it has been found that the reaction is general to the extent that other aldehydes and other arylmethylene cyanides may be used, and certain arylmethylene halides may be used in place of benzyl cyanide. Table I will serve to illustrate the versatility of the reaction.

The aldehyde, a slight excess of arylmethylene compound and the alkali metal cyanide are allowed to react in the presence of methanol or mixtures of methanol and water. Best results are obtained when about 2.5 to 3 moles of alkali metal cyanide per mole of the aldehyde are used. When the arylmethylene cyanide is produced *in situ* from an arylmethylene halide, a larger excess of the arylmethylene halide is employed as well as a corresponding larger excess of the alkali metal cyanide.

As the reaction proceeds alkali metal hydroxide is produced. During the early stages of the reaction, the base produced may actually be beneficial, but as its concentration increases, it may become detrimental. In one preparation of 2,3-diphenylsuccinonitrile, when a few grams of potassium hydroxide was added to the reaction mixture at the start and equivalent amounts of benzaldehyde and acetic acid gradually added, the product was obtained in improved yield.

Experimental[3]

Preparation of 2,3-Diphenylsuccinonitrile. A.—A mixture of 100 ml. of distilled water and 61.2 g. (1.25 moles) of sodium cyanide was warmed until nearly all the cyanide dissolved. Absolute, acetone-free methanol (400 ml.) was added, the mixture was heated to reflux, and 50 g. (0.425 mole) of benzyl cyanide was added all at once. A solution of 53 g. (0.5 mole) of benzaldehyde and 30 g. (0.256 mole) of benzyl cyanide was then added dropwise over 30 minutes with stirring at reflux. After the addition was completed, the reaction mixture was stirred at reflux for an additional 30 minutes. During the course of the reaction, a colorless solid precipitated and the liquid gradually took on a dark blue-green color. The reaction mixture was allowed to cool (2.5 hr.), was filtered with suction, and the solid was washed well with 75% methanol–water, with water, again with 75% methanol–water and then with ether. The colorless solid material weighed 89.5 g. (77% yield), m.p. 204–205°. A sample recrystallized from glacial acetic acid with practically quantitative recovery, as described by McRae and Bannard,[4] melted at 238–239° (lit.[4] 240–241° cor.).

B.—Following the same method as described in A, with the exception that 81 g. (1.25 moles) of potassium cyanide was used in place of the sodium cyanide, there was obtained 85.5 g. (74% yield) of product, m.p. 204–205°.

C.—A mixture of 100 ml. of distilled water, 61.2 g. (1.25 moles) of NaCN and 5 g. (0.089 mole) of potassium hydroxide was warmed until all solid had dissolved. Absolute, acetone-free methanol was added (400 ml.), the mixture heated to boiling and 50 g. (0.425 mole) of benzyl cyanide introduced all at once. This was followed by a mixture of 53 g. (0.5 mole) of benzaldehyde, 30 g. (0.256 mole) of benzyl cyanide and 30 g. (0.5 mole) of glacial acetic acid; the first 10 ml. was added over 20 minutes, precipitation then began and addition of the remaining aldehyde mixture was completed in 90 minutes. The mixture was refluxed for 15 minutes after addition and then cooled in an ice-bath with stirring. Filtration, washing of the solid with 250 ml. of 80% methanol, 300 ml. of H_2O at 60°, and another 250 ml.

---

(1) Reverend Ralph B. Davis, C.S.C.

(2) A. Lapworth and J. A. McRae, *J. Chem. Soc.*, **121**, 1709 (1922).

(3) Melting points are uncorrected.

(4) J. A. McRae and R. A. B. Bannard, *Org. Syntheses*, **32**, 63 (1952).