Acknowledgments.—We gratefully acknowledge the use of the laboratory facilities of the Cosmetics Division of the U. S. Food and Drug Administration for the early phases of this work. C. D. R. also wishes to express his appreciation to the Robert A. Welch Foundation for a Post-doctoral fellowship under which much of the present work was carried out, and to the Department of Chemistry, University of Buffalo, for clerical assistance in preparing the manuscript.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY[1] OF THE UNIVERSITY OF NOTRE DAME, NOTRE DAME, IND., AND THE DEPARTMENT OF CHEMISTRY OF PROVIDENCE COLLEGE, PROVIDENCE, R. I.]

Reduction with Metal Hydrides. IX. Reaction Paths in the Reduction of Epoxides with Lithium Aluminum Hydride and Aluminum Chloride[2]

BY MARK N. RERICK AND ERNEST L. ELIEL

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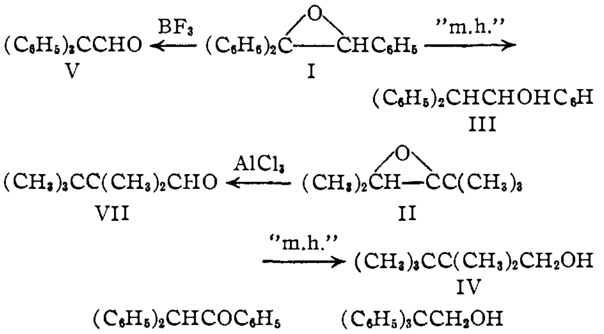
The nature of the reduction products of triphenylethylene oxide with "mixed hydride" (lithium aluminum hydride–aluminum chloride) has been found to depend on the proportions of $LiAlH_4$ and $AlCl_3$ in the reagent. With a 1:3 ($AlCl_3$: $LiAlH_4$) reagent, presumably containing AlH_3 as the active reducing agent, the product is the previously observed phenylbenzhydrylcarbinol, $Ph_2CHCHOHPh$, probably formed by direct, electrophilically assisted reductive ring opening of the epoxide. With a 4:1 reagent, presumably $AlHCl_2$ and excess $AlCl_3$, the main product is Ph_3CCH_2OH, accompanied by hydrogenolysis products of $Ph_2CHCHOHPh$. With this reagent, reduction seems to be preceded by rearrangement of the epoxide to the aldehyde Ph_3CCHO (phenyl shift) as the major product and the ketone $Ph_2CHCOPh$ (hydride shift) as the minor product. Treatment of the epoxide with $AlCl_3$ gave the aldehyde and ketone in a 3:1 ratio, as distinct from treatment with BF_3 which gives almost entirely the aldehyde. The reaction of the epoxide with $AlCl_3$ seems to involve a complex of the chlorohydrin $Ph_2CClCHOHPh$ as the first intermediate. This unstable chlorohydrin was prepared by treatment of the epoxide with hydrogen chloride. Upon treatment with a limited amount of $LiAlH_4$ (<0.25 mole) it also gave a mixture of Ph_3CCHO and $Ph_2CHCOPh$ with the aldehyde predominating, and upon reduction with mixed (4:1) hydride it gave Ph_3CCH_2OH, whereas with excess $LiAlH_4$ alone it gave mainly $Ph_2CHCHOHPh$. In this latter reduction, the ketone $Ph_2CHCOPh$ is not an intermediate, since deuteride reduction gave $Ph_2CDCHOHPh$, as shown by n.m.r. spectrum, rather than $Ph_2CHCDOHPh$. Similar results are obtained with β-diisobutylene oxide which gives mainly $Me_3CCMe_2CH_2OH$ with the 4:1 reagent but mainly $Me_3CCHOHCHMe_2$ with the 1:3 reagent.

In previous publications[3,4] from this Laboratory, the reduction of epoxides with lithium aluminum hydride–aluminum halide mixtures ("mixed hydrides"[5]) has been described. Of particular interest in connection with the present investigation is the reduction of triphenylethylene oxide (I) and of β-diisobutylene oxide (II). The former gave rise to phenylbenzhydrylcarbinol (III) and the latter to 2,2,3,3-tetramethylbutanol-1 (IV). It was postulated that the reduction of I to III involved a hydride shift in the acidic reaction medium producing phenyl benzhydryl ketone (VI) as an intermediate. This postulate was based on the demonstration[3] that reduction of styrene oxide with lithium aluminum deuteride–aluminum chloride gave 2-phenylethanol-1-*d*, evidently *via* phenylacetaldehyde, and that similar reduction of isobutylene oxide gave isobutyl-1-*d* alcohol *via* isobutyraldehyde. The mechanism of reduction of I to III was inferred by analogy, passing over the fact that in this reduction lithium aluminum hydride pre-treated with allyl bromide was used rather than lithium aluminum chloride–aluminum halide. At the time, this did not seem to matter, since allyl bromide (believed to be a generator of inorganic bromide *in situ*) had been employed interchangeably with aluminum halides in other reductions.[5] The reduction of II to IV was similarly postulated to involve shift of a *t*-butyl group to give tetramethylbutyraldehyde (VII) as an intermediate.[4] In this case the reality of the intermediate was demonstrated by isolating it from the reaction of II with aluminum chloride in the absence of hydride.[4]



$(C_6H_5)_2CHCOC_6H_5$
VI

$(C_6H_5)_3CCH_2OH$
VIII

$(CH_3)_3CCHOHCH(CH_3)_2$
IX

The postulated rearrangement of I to VI became a matter of concern in the light of a recent survey[6] which suggests that phenyl usually migrates in preference to hydrogen and especially in view of the demonstration[7] that treatment of triphenylethylene oxide (I) with boron trifluoride etherate gives triphenylacetaldehyde (V) by a phenyl shift rather

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(1) The Radiation Laboratory is operated under contract with the Atomic Energy Commission. Enquiries regarding this paper should be directed to E. L. E., University of Notre Dame. Presented before the Division of Organic Chemistry at the meeting of the American Chemical Society at New York, N. Y., September 12, 1960.

(2) Paper VIII, E. L. Eliel and M. N. Rerick, *J. Am. Chem. Soc.*, **82**, 1367 (1960).

(3) E. L. Eliel and D. W. Delmonte, *ibid.*, **80**, 1744 (1958).

(4) E. L. Eliel and M. N. Rerick, *ibid.*, **82**, 1362 (1960).

(5) For a review of mixed hydride reductions *cf.* M. N. Rerick, "Selective Reduction of Organic Compounds with Complex Metal Hydrides," Metal Hydrides, Inc., 33 Congress Street, Beverly, Mass., 1959, and E. L. Eliel, *Rec. Chem. Progr.*, **22**, 129 (1961).

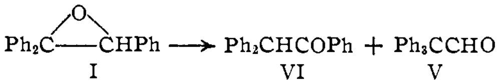
(6) R. E. Parker and N. S. Isaacs, *Chem. Revs.*, **59**, 737 (1959).

(7) A. C. Cope, P. A. Trumbull and E. R. Trumbull, *J. Am. Chem. Soc.*, **80**, 2844 (1958).

than phenyl benzhydryl ketone by a hydride shift. An investigation of the rearrangement of I with various Lewis acids was therefore carried out with the results shown in Table I. It may be seen that whenever rearrangement does take place, the predominant product is V and not VI, in agreement with the finding of Cope and co-workers,[7] although the predominance of phenyl shift over hydride shift is not as great with the aluminum halides as it is with boron trifluoride.

TABLE I

REARRANGEMENTS OF TRIPHENYLETHYLENE OXIDE (I)



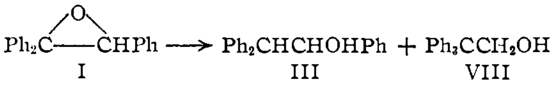
Reagent	Moles[a]	Reaction time, min.	Yield, %	VI,[b] %	V,[c] %
$BF_3 \cdot Et_2O$	7.8	15	74[d]	4–5	95–96
$AlCl_3$	3.0	15	87	24–28	72–76
$AlCl_3$	3.0	120	87	24–28	72–76
$AlCl_3$	0.66	120	90	24–28	72–76
$AlBr_3$	3.0	120	95	24–28	72–76
$ZnCl_2$	3.0	120	92[e]	...	...
Al_2O_3	3.0	120	91[e]	...	...

[a] Reagent per mole of epoxide; most runs were carried out on a 0.01-mole scale. [b] Benzhydryl phenyl ketone—by infrared spectroscopy. [c] Triphenylacetaldehyde—by infrared spectroscopy (*cf.* Experimental). [d] V (69% yield) is reported as the only product in ref. 7. [e] Recovered-epoxide.

The finding that VI is not the main product of the reaction of I with aluminum halides reopens the question as to how I is reduced to III by mixed hydride, or whether, in fact, it is reduced to III under all circumstances. In this connection, the reductions shown in Table II were carried out, the ratio of aluminum halide to lithium aluminum hydride (LAH) being varied. The first entry refers to the already mentioned work[3] in which allyl bromide was used in conjunction with LAH. In the experiments corresponding to the second and third entry, enough aluminum halide was added to produce lithium halide and aluminum hydride, according to the equation[8]: $3LiAlH_4 + AlX_3 \rightarrow 3LiX + 4AlH_3$. Regardless of whether X was bromine or chlorine, these experiments produced only phenylbenzhydrylcarbinol (III). But when (last entry in Table II) four moles (rather than one-third mole) of aluminum halide was used per mole of LAH, the only alcohol isolated (67% of product) was 2,2,2-triphenylethanol. In addition, however, 15% of 1,2,2-triphenyl-1-chloroethane (X) and 18% 1,1,2-triphenylethane (XI) were obtained by column chromatography.

TABLE II

REDUCTION OF TRIPHENYLETHYLENE OXIDE WITH MIXED HYDRIDES



Halide	Moles[a]	Yield, %	III, %	VIII,[b] %	Ref.
$CH_2{=}CHCH_2Br$	0.38	91	100	0	3
$AlBr_3$	.33	80	100	0	[c]
$AlCl_3$	.33	80	100	0	[c]
$AlCl_3$	4.00	94	0	67[d]	[c]

[a] Moles of halide per mole of LAH; an eightfold excess of hydride was used per mole of epoxide. [b] Analysis by isolation and/or elution chromatography. [c] This work. [d] There was also isolated 15% 1,2,2-triphenyl-1-chloroethane, $Ph_2CHCHClPh$ (X) and 18% 1,1,2-triphenylethane, Ph_2CHCH_2Ph (XI).

It is evident from Table II that the "mixed reagent" is not one single species but that the proportions of lithium aluminum hydride and aluminum chloride are of vital importance. With a 4:1 ($AlCl_3$:LAH) reagent, reduction is preceded by rearrangement of the epoxide I to triphenylacetaldehyde (V). As indicated in Table I, aluminum halides rearrange I to approximately 75% V and 25% phenyl benzhydryl ketone (VI). With the 4:1 mixed hydride, V is reduced to the corresponding carbinol VIII which is found as a product. Ketone VI should be reduced to the corresponding carbinol III, but this is not present among the reduction products. The reason for this became clear when, in a control experiment, phenylbenzhydrylcarbinol (III) was treated with 4:1 mixed hydride. Two-thirds of the carbinol did not survive this treatment but was converted to a mixture of approximately equimolar amounts of the corresponding chloride X (presumably by action of aluminum chloride on the carbinol III) and the hydrocarbon XI. The latter is formed by hydrogenolysis of III by the mixed hydride, analogous reactions having been observed in the case of other benzylic alcohols.[5,9,10]

The reduction with a 1:3 ($AlCl_3$:$LiAlH_4$) reagent takes an entirely different course, the sole product now being phenylbenzhydrylcarbinol (III) (Table II). This carbinol is *not* formed *via* the ketone VI, for reduction of the epoxide I with a 1:3 $AlCl_3$:$LiAlD_4$ reagent gave $Ph_2CDCHOHPh$ and not $Ph_2CHCDOHPh$, as shown by n.m.r. spectrum. Since the 1:3 reagent is known[8] to give rise to AlH_3, III may well be the product of reduction of the epoxide I by AlH_3. In fact, when AlH_3 was prepared by addition of one mole $AlCl_3$ to three moles LAH in ether, followed by filtration from the precipitated lithium chloride, the resulting clear solution did reduce I to nearly pure III. The significance of this experiment is somewhat marred, however, by the fact that the AlH_3 solution contained some chloride (*vide infra*).

It is, of course, entirely reasonable that the nucleophilic LAH should reduce I to diphenylbenzylcarbinol,[3] Ph_2COHCH_2Ph, by attack at the least substituted carbon of the epoxide, whereas the partially electrophilic AlH_3 would lead to incipient ring opening to the more stable carbonium ion followed by attack of hydride at the tertiary carbon to give III, since an analogy exists in the general behavior of epoxides upon ring opening in basic media on one side and acidic media on the other.[11]

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(8) A. E. Finholt, A. C. Bond and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

(9) B. R. Brown and A. M. S. White, *J. Chem. Soc.*, 3755 (1957); R. F. Nystrom and C. R. A. Berger, *J. Am. Chem. Soc.*, **80**, 2896 (1958).

(10) J. H. Brewster, private communication; S. F. Osman, Ph.D. Dissertation, Purdue University, 1960; *cf. Dissertation Abstr.*, **21**, 1733 (1961).

(11) E. L. Eliel in M. S. Newman, ed., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, 1956, pp. 106–114.

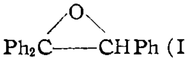
There is, however, an alternative possibility: namely that I is opened by lithium chloride to the tertiary chlorohydrin $Ph_2CClCHOHPh$ (XII)[12] which is then reduced by LAH to III. This possibility suggested itself when we succeeded in preparing a fairly pure sample of the very unstable chlorohydrin XII and found that it is reduced to III by lithium aluminum hydride and to $Ph_2CDCHOHPh$ by lithium aluminum deuteride.[13] However, the direct reduction of a tertiary chloride such as XII by lithium aluminum hydride is unlikely[3] (even though the chloride is benzylic) and a more plausible assumption is that under the influence of LAH, XII gives I and AlH_3 which in turn yield III. Both possibilities are outlined in Chart I, but we favor the route XII → I → III.

The chlorohydrin XII was prepared by action of ethereal hydrogen chloride on the epoxide I and, according to chlorine analysis, ranged in purity from 75 to 95% in different preparations. Its infrared spectrum was in accordance with the assigned structure, and suggested that the contaminant (5–25%) was phenyl benzhydryl ketone (VI). Compound XII is evidently different from the isomeric chlorohydrin $Ph_2COHCHClPh$ which has been reported in the literature[14] without any indications of lack of stability. Although we did not prepare a sample of this compound, the corresponding bromohydrin $Ph_2COHCHBrPh$ has been prepared in this Laboratory[3] and stored for several years without evidence of extensive decomposition. Upon treatment with ethanolic sodium hydroxide, chlorohydrin XII reverted to the epoxide I, but on solvolysis in boiling ethanol it rearranged to ketone VI. On standing in a desiccator over potassium hydroxide for 4 days, XII also lost hydrogen chloride to give mainly VI whose infrared spectrum showed however contaminants absorbing at 6.05 and 10.62 μ. We believe that these bands may have been caused by the enol $Ph_2C{=}C(OH)Ph$. In accordance with this hypothesis is the finding that reduction of XII with LAH gave, in addition to III, about 10% of ketone VI. Since this ketone does not survive hydride treatment as such, it must have been present in the reduction mixture as the enolate. The reactions of the chlorohydrin XII are summarized in Chart II.

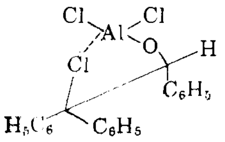
We must now return to the reaction of I with boron trifluoride and with aluminum chloride and bromide. The boron trifluoride-catalyzed rearrangement gives largely V by a phenyl shift, in analogy to the rearrangement of the stilbene oxides to diphenylacetaldehyde.[15] Aluminum halides give appreciably more hydride shift to ketone VI than BF_3, although the aldehyde product still predominates (Table I). In analogy with related work by House on the reaction of the stilbene oxides with magnesium bromide,[15] it is proposed that aluminum halide first opens the epoxide to a complex of the chlorohydrin XII which then undergoes a concurrent phenyl and hydride shift to a mixture of aldehyde V and ketone VI. In fact, when XII was treated with one equivalent of LAH to produce a similar salt or complex, it also rearranged to a mixture of V and VI in which V predominated.[16] Moreover, the reduction of XII with the 4:1 reagent entirely paralleled the corresponding reaction of I in that the products were VIII (52%), X (26%) and XI (22%). (The smaller proportion of VIII and the larger proportion of X and XI in the reduction of XII—as compared to I—again reflects the presence of some VI in the sample of XII used. As was shown before, reduction of III with the 4:1 reagent gives X and XI.) The data are summarized in Table III and our interpretation is shown in Chart III.

Table III

Reductions with the 4:1 $AlCl_3$:$LiAlH_4$ Reagent

Starting material	% Ph_3CCH_2OH (V)	% $Ph_2CHCHOHPh$ (III)	% $Ph_2CHCHClPh$ (X)	% Ph_2CHCH_2Ph (XI)
$Ph_2CHCHOHPh$ (III)	0	32	33	35
 (I)	67	0	15	18
$Ph_2CClCHOHPh$ (XII)	52	0	26	22

There are, then, three ways in which the systems studied here may rearrange. The first is brought about by the action of boron trifluoride on epoxide I in anhydrous medium and leads to very predominant migration of phenyl as compared to hydrogen, presumably because of the greater ability of the migrating phenyl to delocalize positive charge. This migration may be concerted with ring opening and follows precedent.[6,15] The second type of rearrangement involves the $ROAlCl_2$ complex of the chlorohydrin XII and is pictured to entail intramolecular electrophilic catalysis in the transition state XIII. A similar picture has been drawn by House[15] for the reaction of stilbene oxide with magnesium bromide or stilbene bromohydrin with Grignard reagents. Our case is intermediate between that of *cis*-stilbene oxide (which undergoes almost exclusive phenyl shift) and *trans*-stilbene oxide (which undergoes largely hydrogen shift in ether-containing media) so that the approximately 3:1 ratio of phenyl to hydrogen shift in our case is not unexpected. A third type of rearrangement occurs in the solvolysis of the chlorohydrin XII; this rearrangement probably proceeds *via* the solvated carbonium ion XIV which either undergoes



XIII

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[12] Sr. Lucetta Barnard, C.S.C., in our laboratory has observed the formation of $PhCHClCH_2OH$ from styrene oxide and lithium chloride in tetrahydrofuran although in low conversion.

[13] Actually a mixture of 80% $Ph_2CDCHOHPh$ and 20% $Ph_2CHCDOHPh$ as shown by n.m.r. spectroscopy. However, the latter product clearly originates from about 20% VI shown, by infrared spectroscopy, to be a contaminant of the sample of XII which was subject to the deuteride reduction.

[14] H. Felkin, *Compt. rend.*, **227,** 1383 (1948).

[15] H. O. House, *J. Am. Chem. Soc.*, **77,** 3070 (1955). It is not yet clear whether a direct rearrangement of the oxide is involved or whether fluorohydrin complexes intervene; *cf.* H. O. House and G. D. Ryerson, *ibid.*, **83,** 979 (1961).

[16] The proportion of VI was somewhat greater (35%) than in the treatment of I with aluminum chloride, but this may be ascribed to the initial presence of 5–10% of VI in the sample of XII used for the reaction with LAH.

CHART I
REDUCTIONS WITH ALUMINUM CHLORIDE–LITHIUM ALUMINUM HYDRIDE (1:3)

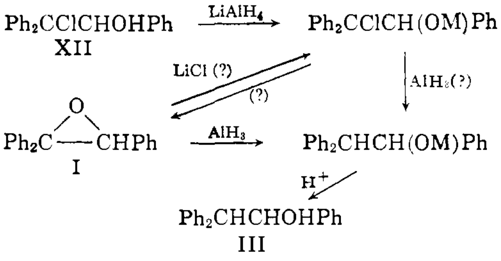


CHART II
REACTIONS OF 1,2,2-TRIPHENYL-2-CHLOROETHANOL

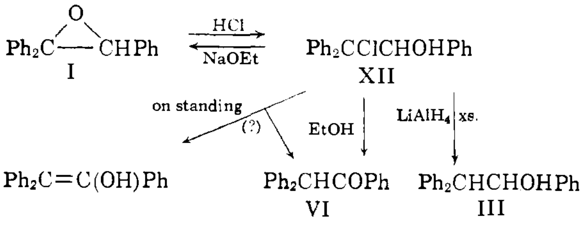
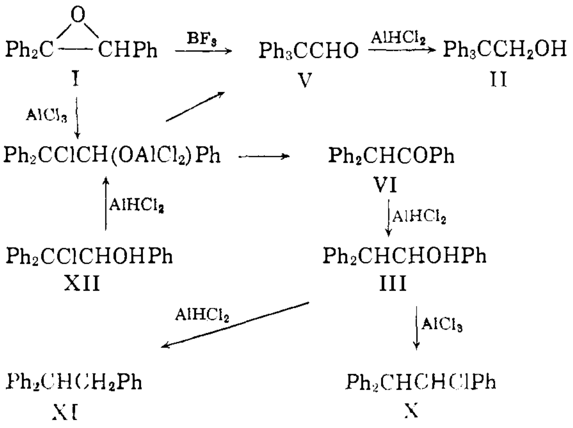
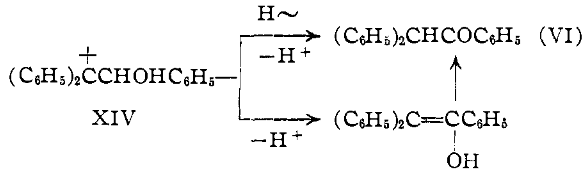


CHART III
REACTIONS OF TRIPHENYLETHYLENE OXIDE AND OF 1,2,2-TRIPHENYL-2-CHLOROETHANOL WITH LEWIS ACIDS AND/OR WITH 4:1 MIXED HYDRIDE

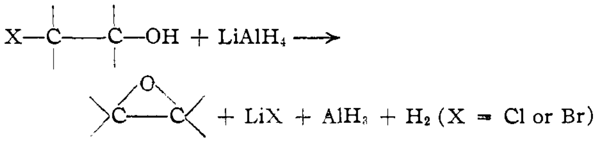


hydrogen shift to ketone VI or proton loss to the enol of VI.



It is now appropriate to consider our present results in the context of the general problem of the mechanism of reduction of halohydrins and epoxides with LAH and LAH–Lewis acid combinations.[3–5,17–20] We have previously[3] discerned three paths for the reduction of halohydrins. One involves a direct, assisted displacement, exemplified by $CH_3CH_2CHBrCH_2OH \rightarrow CH_3CH_2CHDCH_2OH$. The second involves a hydride shift, *e.g.*, $(Me)_2CClCH_2OH \rightarrow (Me)_2CHCHDOH$ *via* $(Me)_2CHCHO$.[21] The third involves an epoxide intermediate, for example $PhCHBrCOHPh_2 \rightarrow PhCHOHCHPh_2$. (The mode of further reduction of this epoxide will be examined below.) A fourth possibility has now been observed in the reduction of $Ph_2CClCHOHPh$ with the 4:1 $AlCl_3$:LAH reagent which gives not only hydride shift to $Ph_2CHCOPh$ (which is then further reduced) similar to path 2 above, but also a phenyl shift to Ph_3CCHO which is then further reduced to Ph_3CCH_2OH. This is the first time we have observed an alkyl shift in the reduction of a halohydrin, and it is noteworthy that such alkyl shift requires added Lewis acid and does not occur in the reduction of halohydrins with LAH alone.

Previously,[3,4] also, we have discerned two paths for the reduction of epoxides, direct reduction by LAH involving attack at the least substituted position and reduction in the presence of halides or Lewis acids involving apparent attack at the more highly substituted position, this latter being ascribed to prior rearrangement to an aldehyde or ketone. The present work shows, however, that our previous diagnosis of the second path was both incomplete and, in part, incorrect. Rearrangement only occurs in the presence of a large excess of Lewis acid (the 4:1 reagent) and then probably involves the chlorohydrin and not the epoxide directly; moreover it may lead to alkyl shift in preference to hydride shift.[22] In the presence of a small amount of $AlCl_3$ (1:3) reagent, rearrangement often does not occur at all, but rather a reverse, electrophilically assisted ring opening may occur, involving AlH_3 formed from the reagents.[23] This is also the mode of reduction of those halohydrins which react *via* epoxides, since by-products of the first step are lithium halide and aluminum hydride



It is of interest that the three modes of ring opening of epoxides may sometimes be produced at will, depending on the amount of aluminum halide used along with LAH. Two examples are shown in Chart IV. The case of I has already been discussed in detail. β-Diisobutylene oxide (II) is

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(17) E. L. Eliel and J. P. Freeman, *J. Am. Chem. Soc.*, **74**, 923 (1952).

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

(19) E. L. Eliel and T. J. Prosser, *ibid.*, **78**, 4045 (1956).

(20) E. L. Eliel and J. T. Traxler, *ibid.*, **78**, 4049 (1956).

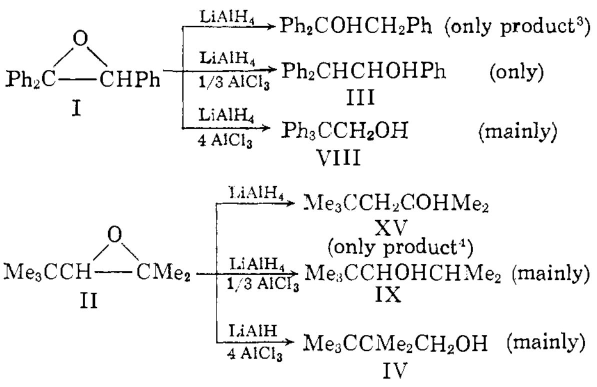
(21) A minor product of this reduction is $(CH_3)_2CDCH_2OH$. This is probably formed analogously to $Ph_2CDCHOHPh$ from $Ph_2CClCHOHPh$ in the present investigation—either by direct displacement, or, more likely, by closure to epoxide followed by opening by AlD_3. The contrast between Me_2CClCH_2OH and $Ph_2CClCHOHPh$ is interesting, reflecting either greater tendency to ring closure in the latter (because of trisubstitution; *cf.* ref. 11, pp. 117–120) or lesser tendency to direct displacement in the former; in either case the hydride shift has a better chance to compete in Me_2CClCH_2OH.

(22) It would be of interest to investigate the reaction of epoxides with LAH and BF_3. Barring complications due to the formation of diborane, BF_3 may promote alkyl shifts more extensively and more generally than $AlCl_3$.

(23) It is not clear whether one molecule of AlH_3 fulfills both the electrophilic and nucleophilic function (in S_N1 fashion) or whether two molecules are involved. Alternatives are intervention of an ether-solvated carbonium ion or of a halohydrin formed by attack of LiX on the epoxide.

CHART IV

REDUCTION PRODUCTS OF OXIDES WITH LAH



reduced to dimethylneopentylcarbinol (XV) by LAH alone[4] and to a mixture of IV (77%), IX (15%) and 2,4,4-trimethylpent-1-en-3-ol, (XVI) (8%) in which IV is the predominant product by 4:1 mixed hydride.[4] It is now believed that this reaction involves 2,4,4-trimethyl-2-chloro-3-pentanol, $Me_3CCHOHCClMe_2$ (XVII), as an intermediate, in analogy with the reduction of I *via* XII. Compound XVII undergoes predominant *t*-butyl shift to give tetramethylbutyraldehyde (VII) which is then reduced to IV; but this is accompanied by a lesser hydride shift to isopropyl *t*-butyl ketone (XVIII) which is reduced to the corresponding carbinol IX. Unlike III formed from I by 4:1 mixed hydride, however, IX survives the reduction because, not being a benzyl alcohol, it is not subject to hydrogenolysis by the mixed reagent. In fact, both VII and XVIII are formed when II is treated with aluminum chloride. The unsaturated alcohol XVI is not formed under these circumstances, possibly because it originates from the intermediate chlorohydrin XVII only in presence of the basic LAH reagent. Finally, it was shown in the present work that reduction of II with a 1:3 reagent gives largely IX (83%), probably[23] through reversed (*i.e.*, electrophilically assisted) ring opening by AlH_3. A small amount (5%) of *t*-butyl migration does, however, occur and some of the elimination product XVI is also formed. At an intermediate LAH:$AlCl_3$ ratio, the product composition is intermediate between that observed with AlH_3 and that observed with the 4:1 reagent.

TABLE IV

REDUCTION OF β-DIISOBUTYLENE OXIDE (II) WITH MIXED HYDRIDE

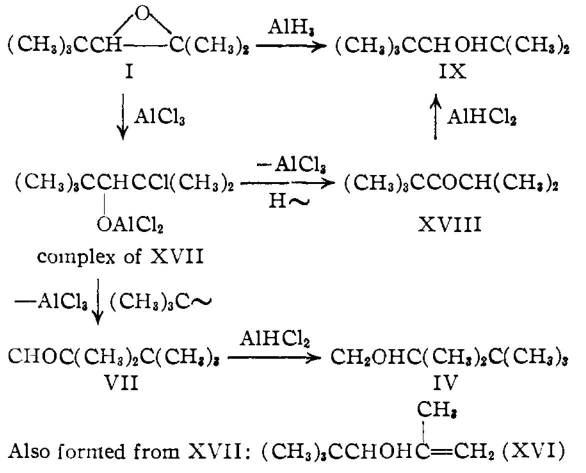
Moles $AlCl_3$[a]	Yield, %	IV, %	IX, %	XVI, %	Ref.
0.3	99	5	83	12	[b]
1.0	99	42	52	6	[b]
4.0	83	77	15	8	4

[a] Per mole LAH; a threefold excess of hydride over epoxide was used throughout. [b] This work.

The results are summarized in Table IV and our interpretation is shown in Chart V.

CHART V

REACTIONS OF β-DIISOBUTYLENE OXIDE WITH MIXED HYDRIDE



Experimental

All melting points were recorded on a calibrated Kofler block. Infrared spectra were recorded on Baird Associates model 4-55 and Beckman model 7 instruments. N.m.r. spectra were recorded on a Varian 4300B instrument.

Epoxides.—Triphenylethylene oxide was prepared according to a method previously described[4]; m.p. 74–76° (lit.[4] 74–76°). β-Diisobutylene oxide was commercial material kindly provided by Carbide and Carbon Chemicals Co. and used without further purification.

Rearrangements of Triphenylethylene Oxide (I).—Solutions (or slurries) of the Lewis acids in ether were prepared at ice-bath temperature with the exception of aluminum bromide solutions, which were prepared at acetone–Dry Ice-bath temperature. The solutions were allowed to come to room temperature and a solution of I in anhydrous ether was added, the reaction mixtures being stirred for various times as shown in Table I, and then hydrolyzed with water. Extraction, drying over anhydrous sodium sulfate and concentration gave crude product containing triphenylacetaldehyde (V) and phenyl benzhydryl ketone (VI). Quantitative infrared analysis using peaks characteristic of V at 3.65 and 5.83 μ and peaks characteristic of VI at 5.95 and 10.04 μ was effected by comparison of spectra with calibration curves obtained from authentic samples of aldehyde and ketone. The reference sample of triphenylacetaldehyde was obtained by recrystallization of the crude product, m.p. 80–105°, from the boron trifluoride rearrangement of I to constant m.p. 106–107° (from ethanol) (lit.[24] 105–106°). The authentic sample of benzhydryl phenyl ketone, m.p. 135–137° (lit.[3] 135–137°), was prepared as previously described.[3]

The products of rearrangement of I with BF_3 were not altered in composition by subsequent treatment with $AlCl_3$.

Reduction of Epoxides with Mixed Hydrides.—Reductions were carried out as previously described.[3,4] Alcohols obtained by reduction of β-diisobutylene oxide were analyzed by vapor phase chromatography on a Ucon-polar column at 129°. Carbinols from triphenylethylene oxide were analyzed by isolation and/or elution chromatography. Authentic carbinols resulting from the former reduction were available as described.[4] Authentic 2,2,2-triphenylethanol (VIII) was prepared by the lithium aluminum hydride reduction of triphenylacetaldehyde; m.p. 105–106° (lit.[25] 103–105°) after one recrystallization from *n*-hexane. 1,2,2-Triphenylethanol (III) was prepared by LAH reduction of benzhydryl phenyl ketone; m.p. 88–90° (lit.[3] 86–88°).

Reduction of Triphenylethylene Oxide (I) **with Lithium Aluminum Hydride–Aluminum Chloride.**—To 5.3 g. (0.04 mole) of anhydrous aluminum chloride was added 50 ml. of anhydrous ether at ice-bath temperature, followed by 11.1 ml. (0.01 mole) of 0.91 *M* ethereal lithium aluminum hydride. After stirring the clear ethereal solution for 0.5 hour, 1.35 g. (0.005 mole) of triphenylethylene oxide in 50 ml. of ether was added. The mixture was refluxed for 2 hours and hydrolyzed with water. The clear ether layer

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[24] S. Danilov, *Zhur. Russ. Fiz. Khim. Obshch.*, **49**, **282** (1917); *C. A.*, **18**, 1488 (1924).

[25] J. L. Greene, D. Abraham and H. D. Zook, *J. Org. Chem.*, **24**, 132 (1959).

was dried over anhydrous potassium carbonate and concentrated to give 1.21 g. of a semi-solid whose infrared spectrum was identical with that of authentic 2,2,2-triphenylethanol. Chromatography of a small sample on basic alumina gave no clear-cut separation, but the infrared spectra of the first, second, third and fourth quarters of material eluted from the column were identical and identical to the crude product. A 0.80-g. sample of the crude product was recrystallized from petroleum ether (b.p. 60–70°) and gave 0.413 g. of 2,2,2-triphenylethanol, m.p. 103–105°. On cooling to −60° a second crop of crystals (0.102 g.) which melted on warming to room temperature was obtained. The remaining mother liquor was concentrated to give 0.230 g. of an oil. The infrared spectrum of the second crop of material was that of 2,2,2-triphenylethanol, but contained peaks of the oil obtained by concentration of the mother liquor at 7.9, 9.35 and 9.73 μ. Eighty milligrams of each of these two fractions samples were combined and the mixture chromatographed on 5.0 g. of basic alumina. Three main fractions (85% recovery) were obtained. The first fraction (0.055 g.), m.p. 33–47°, raised to 45–50° after distillation, was shown to be 1,1,2-triphenylethane by comparison of the infrared spectrum with that of an authentic sample,[26] m.p. 53–55° (lit.[27] 52–54°). The second fraction (0.046 g.), m.p. 85–95°, was identical in infrared spectrum with an authentic sample of 1,2,2-triphenyl-1-chloroethane, m.p. 97–99° (lit.[28] 99–100°), prepared according to the method previously described.[28] The third fraction (0.034 g.), m.p. 102–105°, was identical with authentic 2,2,2-triphenylethanol. Thus, the reduction product contained 2,2,2-triphenylethanol (*ca.* 67%), 1,2,2-triphenyl-1-chloroethane (*ca.* 15%) and 1,1,2-triphenylethane (*ca.* 18%).

Reduction of Triphenylethylene Oxide (I) with Lithium Aluminum Deuteride and Aluminum Chloride.—To a solution of 0.44 g. (0.0033 mole) of anhydrous aluminum chloride in 50 ml. of anhydrous ether was added 0.42 g. (0.01 mole) of lithium aluminum deuteride at ice-bath temperature. After stirring 0.5 hour at room temperature, a solution of 1.35 g. (0.005 mole) of I in 50 ml. of anhydrous ether was added dropwise. The reaction mixture was hydrolyzed, after 2 hours stirring, with water and dilute sulfuric acid. Extraction, drying and concentration gave 1.23 g. of a white solid, m.p. 83–88°. Recrystallization of a 0.50-g. aliquot from petroleum ether, b.p. 60–70°, gave 0.46 g. of solid, m.p. 88–90°. The infrared spectrum was significantly different from that of a specimen of 1,2,2-triphenylethanol-1-*d* prepared by LAD reduction of phenyl benzhydryl ketone. The latter melted at 87–90° after two recrystallizations from petroleum ether, b.p. 60–70°. The n.m.r. spectrum of the 1,2,2-triphenylethanol-1-*d* showed three proton resonances due to Ph-*H*, Ph_2CH and O*H*, while the n.m.r. spectrum of 1,2,2-triphenylethanol showed four bands: Ph-*H*, Ph_2CH, C*H*OH and O*H*, the band at lowest field being attributed to Ph*H* and that at highest field to O*H*, the intermediate bands being due to the two benzylic hydrogens. Of these two, the one at lower field is absent in 1,2,2-triphenylethanol-1-*d*. Thus in the perhydro compound the CH band at low field is due to the hydrogen on the carbinol carbon and the CH band at higher field is due to Ph_2CH hydrogen.

The n.m.r. spectrum of the product obtained in the reduction of I with LAD-$AlCl_3$ shows only one CH band, its position corresponding to that of the C*H*OH in the perhydro compound. It is clear that the product obtained was 1,2,2-triphenylethanol-2-*d*.

Similar reduction of I (1.1 g., 0.004 mole) with lithium aluminum hydride (8.5 ml. of 0.94 *M* ethereal solution, 0.008 mole) and aluminum chloride (0.36 g., 0.0027 mole) gave 1.0 g. (90%) of III, m.p. 84–88°, raised to 89–90° upon recrystallization (93% recovery) from petroleum ether, b.p. 60–70°. The infrared spectra of both the crude and recrystallized material were identical with that of an authentic specimen of III. The results of other reductions of I with LAH-$AlCl_3$ or -$AlBr_3$ (3:1 mole ratio) are shown in Table II.

Reduction of Triphenylethylene Oxide (I) with Aluminum Hydride.—To a solution of 0.36 g. (0.002 mole) of aluminum chloride in 25 ml. of anhydrous ether was added 8.5 ml. of 0.94 *M* ethereal lithium aluminum hydride (0.008 mole). After stirring for 0.5 hr., the solution was separated from the precipitated lithium chloride by allowing it to flow through a stopcock plugged with glass wool at the bottom of the flask into another reaction vessel. An aliquot (1 ml.) of the filtered solution gave a very slight precipitate when treated with aqueous nitric acid followed by silver nitrate.

To the body of the filtered solution was added 1.1 g. (0.004 mole) of I in 50 ml. ether. After 2 hr. of stirring the solution was worked up in the usual way. The product (1.0 g., 90%) melted at 84–88°, raised to 87–89° by recrystallization (90% recovery). The infrared spectra of both the crude and recrystallized product were identical with that of an authentic sample of III.

Preparation of 1,2,2-Triphenyl-2-chloroethanol (XII).—Anhydrous hydrogen chloride was passed into 250 ml. of anhydrous ether for 30 minutes and 5.40 g. (0.02 mole) of triphenylethylene oxide (I) was added. The mixture was diluted with 250 ml. of ether. After stirring 10 minutes, a 50-ml. aliquot was removed and added to 50 ml. of saturated sodium bicarbonate solution at ice-bath temperature. The ether layer was washed with 50 ml. of saturated bicarbonate and two 50-ml. portions of brine. After drying for 2 hours over sodium sulfate, concentration under vacuum gave 0.65 g. of solid, m.p. 85–87° dec., recrystallizing to a new compound, m.p. 120–136° (lit.[3] for phenyl benzhydryl ketone, m.p. 135–137°). The sample fumed in air (HCl) and gave strong positive tests for halogen. The infrared spectrum of the product showed bands at 2.8, 2.95, 7.2, 9.45, 10.85, 11.4 and 15.5 μ. In addition, a small carbonyl band appeared at 5.95 μ (*ca.* 5%). Attempts to recrystallize the chlorohydrin from non-hydroxylic solvents were unsuccessful.

The bulk of the reaction mixture was worked up in an identical manner after 2 hours reaction time to give 4.05 g. of the chlorohydrin. The infrared spectrum of this sample was identical with that previously obtained. A 1.0493-g. sample was dissolved in ethanol and treated with excess standard sodium ethoxide. Back titration indicated the sample to contain 94.5% of chlorohydrin. The titration mixture was extracted with ether, dried and concentrated to give 0.81 g. of I, m.p. 72–77°. Its infrared spectrum was identical with that of authentic I, but contained a small carbonyl band at 5.95 μ. Treatment of 1.00 g. of the chlorohydrin with boiling ethanol for 30 minutes, followed by cooling, gave 0.65 g. (74% yield) of phenyl benzhydryl ketone (VI), m.p. 136–138°. Its infrared spectrum was identical with that of an authentic sample.

When the chlorohydrin was allowed to stand at room temperature for 3 days, the infrared spectrum of the sample was identical with that of benzhydryl phenyl ketone. However, after a 1.68-g. sample containing 20–25% ketone from a different preparation was stored in an open vial over (*vide infra*) solid potassium hydroxide in a desiccator for 94 hours, the sample weighed only 1.52 g. (corresponding to a loss of 84% of the theoretical amount of hydrogen chloride considering the sample to be 80% chlorohydrin) and its infrared spectrum was mainly that of benzhydryl phenyl ketone. In addition, bands at 6.05 and 10.62 μ of medium intensity were also present. These bands are attributed to the enol of phenyl benzhydryl ketone formed by loss of hydrogen chloride from the product. On the basis of this and other information given below and previously discussed (*vide supra*), the product is undoubtedly 1,2,2-triphenyl-2-chloroethanol (XII).

Other similar preparations of XII gave a product contaminated with 15–25% phenyl benzhydryl ketone and in only one instance was it prepared containing only *ca.* 5% ketone.

Reduction of 1,2,2-Triphenyl-2-chloroethanol (XII) with LAH.—A solution of 1.54 g. (0.005 mole) of XII (containing 5% ketone) in 50 ml. of anhydrous ether was added to 10.0 ml. (0.01 mole) of 1.0 *M* ethereal lithium aluminum hydride. The mixture was refluxed for 2 hours and hydrolyzed in the usual manner. Extraction, drying and concentration gave 1.10 g. of solid, m.p. 72–84°. Recrystallization of a portion raised the m.p. to 88–101°. The infrared spectrum of the crude product was similar to that of 1,2,2-triphenylethanol (III) but contained a band at 5.95 μ diagnostic of phenyl benzhydryl ketone (VI). Chromatography of a 0.200-g. sample on alumina gave as a first fraction, 0.021 g. of benzhydryl phenyl ketone, m.p. 132–136° (lit.[3] 135–

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(26) Obtained from Eastman Kodak Co., Rochester, N. Y.

(27) D. Y. Curtin and M. J. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952).

(28) T. Nagano, *ibid.*, **77**, 6680 (1955).

137°), whose infrared spectrum was identical to that of the authentic ketone VI. A second fraction, 0.168 g., melted at 80–87°. Its infrared spectrum was identical with that of 1,2,2-triphenylethanol. Recrystallization from petroleum ether, b.p. 60–70°, raised the m.p. to 88–90° (lit.[3] 86–88°).

Reduction of 1,2,2-Triphenyl-2-chloroethanol (XII) with Lithium Aluminum Deuteride.—To a slurry of 0.42 g. (0.01 mole) of lithium aluminum deuteride in 50 ml. of anhydrous ether was added a solution of 1.54 g. of XII (containing *ca.* 20% ketone) in 50 ml. of anhydrous ether. The reaction mixture was refluxed for 2 hours and hydrolyzed in the usual manner. Extraction, drying and concentration gave 1.13 g. of crude product, m.p. 74–85°. Chromatography on alumina of a 0.400-g. portion gave 0.037 g. of benzhydryl phenyl ketone (VI), m.p. 134–136° (lit.[3] 135–137°), as a first fraction. Its infrared spectrum was identical with that of an authentic sample. A second fraction, 0.335 g., m.p. 82–88°, was also obtained. Its infrared spectrum was indistinguishable from that of 1,2,2-triphenylethanol-2-*d* (*vide supra*). Recrystallization from petroleum ether, b.p. 60–70°, gave 0.30 g. of solid, m.p. 88–90°. The n.m.r. spectrum showed four bands, including two carbon–hydrogen bands at intermediate field (*vide supra*), in a ratio of *ca.* 3:1, the C*H*OH band predominating. That the $Ph_2C\mathit{H}$ band is present to some extent is in accord with the observation that the starting material contained *ca.* 20% ketone.

Reaction of 1,2,2-Triphenyl-2-chloroethanol (XII) with a Limited Amount of LAH.—To 1.54 g. (0.005 mole) of XII (containing *ca.* 5% ketone) in 25 ml. of anhydrous ether was delivered 0.94 ml. (0.00094 mole) of 1.0 *M* ethereal lithium aluminum hydride. After standing for 2 hours at room temperature the reaction mixture was poured into 50 ml. of saturated sodium bicarbonate solution at ice-bath temperature. The ether layer was washed with cold saturated bicarbonate and brine. After drying over sodium sulfate for 1 hour, concentration gave 1.1 g. of solid, m.p. 74–109°. Infrared spectral analysis (*vide supra*) showed the sample to contain 60–65% of triphenylacetaldehyde (V) and 35–40% phenyl benzhydryl ketone (VI). A band characteristic of chlorohydrin at 9.45 μ was absent.

In a similar experiment, using 1.54 g. of XII (containing *ca.* 15% ketone) and 1.12 ml. of 1.0 *M* ethereal lithium aluminum hydride, 1.20 g. of a solid, m.p. 75–112°, was obtained. Infrared analysis showed 65–70% V and 30–35% VI.

Reduction of XII with $LiAlH_4$-$AlCl_3$ (1:4).[29]—The chlorohydrin XII was prepared from 5.40 g. (0.02 mole) of I as described above. The crude product, after removal of ether, weighed 5.6 g. and, according to its infrared spectrum, consisted of chlorohydrin with some ketone present.

Part of the above material (1.93 g., 0.0062 mole calculated as XII) was immediately reduced by means of a reagent prepared from 10 g. (0.075 mole) of aluminum chloride and 15.3 ml. of 1.24 *M* ethereal lithium aluminum hydride (0.019 mole). After 2 hours of stirring and boiling at reflux, the reaction mixture was hydrolyzed by the addition of 100 ml. of a 10% solution of sodium potassium tartrate. The ether layer was separated and the aqueous layer twice extracted with 50-ml. portions of ether. Drying of the combined ether layers followed by concentration gave 1.2 g. of crude product.

Chromatography of 1.00 g. of this material on 25 g. of acid-washed alumina gave three fractions, two weighing 0.27 g. and 0.11 g., eluted with 1:1 petroleum ether–benzene, and one (totaling 0.41 g.) eluted in part with benzene–ether and in part with ether. The last fraction crystallized, m.p. 103–106°, and did not depress the melting point of VIII on admixture. Thus VIII constituted 0.41 out of 0.79 g. or 52% of the mixture. Fraction two was solid and melted at 76–96°. Its infrared spectrum suggested that it was almost entirely chloride X. Fraction I was semi-solid and, upon repeated chromatography, was partially resolved into XI, m.p. 46–52° (lit.[27] 52–54°), and X, m.p. 97–100° (lit.[28] 99–100°), as evidenced by infrared spectra. From the chromatograms, the proportions of X and XI in the crude material were estimated as 26% and 22%, respectively.

Reaction of 1,2,2-Triphenylethanol (III) with Lithium Aluminum Hydride–Aluminum Chloride.—The mixed hydride was prepared in the usual manner from 1.56 g. (11.68 mmoles) of anhydrous aluminum chloride in 25 ml. of ether and 3.2 ml. (2.92 mmoles) of 0.94 *M* ethereal lithium aluminum hydride. A solution of 0.4 g. (1.46 mmoles) of 1,2,2-triphenylethanol in 25 ml. of ether was added dropwise and the mixture refluxed. The reaction mixture was hydrolyzed with water and the ether layer dried and concentrated to give 0.375 g. of product. Chromatography on basic alumina of 0.265 g. of material gave four main fractions. The first (0.028 g.) was an oily solid, m.p. 49–53°. Its infrared spectrum was similar to that of the 1,1,2-triphenylethane except for a strong band at 7.9 μ, shown to be due to silicone stopcock grease. The third fraction (0.047 g.), m.p. 97–99°, was identified by comparison of the infrared spectrum with that of authentic 1,2,2-triphenyl-1-chloroethane, m.p. 97–99°. The second fraction (0.076 g.), m.p. 65–80°, was considered to be a mixture of the hydrocarbon and the chloride in a ratio of *ca.* 2:1 by inspection of the infrared spectrum. The fourth fraction (0.070 g.), m.p. 82–89°, was shown to be 1,2,2-triphenylethanol by comparison of its spectrum with that of an authentic sample, m.p. 87–89°. Thus the crude product contained 1,1,2-triphenylethane (35%), 1,2,2-triphenyl-1-chloroethane (33%) and 1,2,2-triphenylethanol (32%).

The absence of triphenylethylene in this product and the epoxide reduction product was ascertained by the absence of the bands at 10.5 or 11.4 μ, characteristic of triphenylethylene, m.p. 67–69° (lit.[30] 67–68°), prepared by dehydration of the available 1,1,2-triphenylethanol[3] as described elsewhere.[30]

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(29) This experiment was performed with the assistance of Sr. Lucetta Barnard, C.S.C.

(30) J. van de Kamp and M. Sletzinger, *J. Am. Chem. Soc.*, **63**, 1879 (1941).