control, a heating element, a stirrer, a thermometer, a 1-cm cell mount, and quartz windows for absorption or fluorescence measurements. These windows could be capped on the exterior of the compartment so that chemiluminescence measurements could be made. The compartment was used in this mode for the light emission measurements and the monochromator was set at the "zero-order" position so that all wavelengths of light were detected. A basic 60% aqueous methanol solution, containing fluorescein, was placed in a 1-cm quartz cell, which was contained in the thermostated bath at 29°. The peroxide was then introduced into the solution with a 250-μl Hamilton syringe and the solution was mixed. The final sodium hydroxide and fluorescein concentrations were 0.50 and 0.008 M, respectively. The initial chloro-*tert*-butyl hydroperoxide and **1b** concentrations were 2.0×10^{-2} and $4.0 \times 10^{-2} M$, respectively. Light emission increased to a maximum of 0.53 na and then began to decrease in the former solution. With **1b**, no light was detected within experimental error (±0.02 na).

Registry No.—**1a,** 16424-69-4; **1b,** 27492-18-8; **2a,** 35889-98-6; **2b,** 35889-99-7; **3a,** 35890-00-7; **3b,** 35890-01-8; **5,** 35890-02-9.

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Base-Induced Rearrangement of Epoxides. V. Phenyl-Substituted Epoxides[1]

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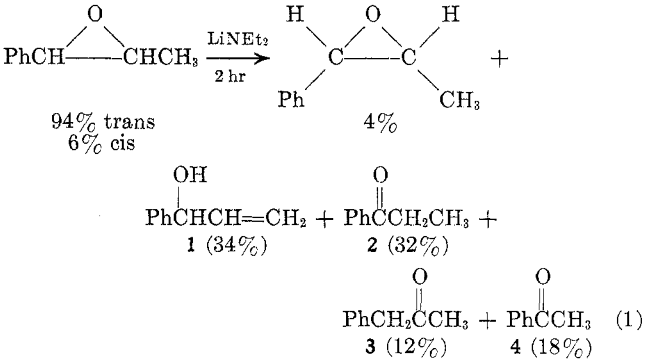
A number of α- and β-phenyl substituted epoxides have been subjected to lithium diethylamide treatment. The trans and cis isomers of β-methylstyrene oxide give different product distributions, but in both cases the β-elimination pathway is preferred over α-proton abstraction. The trans isomer leads to the formation of some acetophenone. Indene oxide gives a low yield of 1-indanone as the only isolable product. β-Phenyl substitution strongly affects the course of the epoxide to allylic alcohol rearrangement. For the first time in these reactions, some cis olefinic product is observed, formed preferentially from the trans isomer of 1-phenyl-2-butene oxide. The reactions of *trans*- and *cis*-3-phenylcyclohexene oxide substantiate a syn elimination mechanism.

Earlier work has established the strongly regioselective abstraction from the least substituted carbon in various alkyl-substituted epoxides,[2,3] the highly stereospecific formation of trans olefin[2,4] in these systems, and also the preferred syn elimination mechanism[5,6] in the reaction with lithium diethylamide. We have subsequently examined the base-induced reactions of various epoxides bearing substituents other than simple alkyl groups. This paper describes the results obtained with a number of α- and β-phenyl-substituted epoxides.

Cope and his coworkers[7] examined the reaction of some diarylethylene oxides with lithium diethylamide, and discovered some interesting stereochemical features. For example, *cis*-stilbene oxide gave 70% of deoxybenzoin, while *trans*-stilbene oxide gave 66% of diphenylacetaldehyde, both reactions occurring with high specificity. These illustrate the α-proton abstraction reaction pathway, various aspects of which have subsequently been explored in detail by Crandall, *et al.*[8]

Results and Discussion

Epoxidation of commercial β-methylstyrene gave a distilled epoxide mixture which contained 94% trans and 6% cis isomer. This material was treated with a twofold molar excess of lithium diethylamide in refluxing ether–hexane for 2 hr to give the product mixture shown in eq 1.



$$\mathrm{PhCH(OH)CH{=}CH_2} + \mathrm{PhC(O)CH_2CH_3} + \mathrm{PhCH_2C(O)CH_3} + \mathrm{PhC(O)CH_3}$$

Several interesting conclusions can be drawn from these data. First, the recovered epoxide proved to be essentially pure cis material (by vpc and ir), suggesting a considerable difference in rates of reaction for the isomeric epoxides;[9] this was substantiated by examining the reaction of isolated cis material, as discussed below. Second, examination of points taken during the course of eq 1 established that the allylic alcohol **1** was being converted fairly rapidly to the ketone **2** under the reaction conditions. In fact, extrapolation of these data suggests that no **2** is formed directly by an α-proton abstraction mechanism, but rather is generated exclusively by rearrangement of **1**. Similar allylic alcohol to ketone base-induced rearrangements have been previously observed[2,3,10] with terminal methylene allylic alcohols, and in the present system a more rapid reaction is anticipated because of the benzylic proton in **1**.

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(1) (a) This work was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society (5744-AC4). (b) Part IV: C. K. Kissel and B. Rickborn, *J. Org. Chem.*, **37**, 2060 (1972).

(2) B. Rickborn and R. P. Thummel, *ibid.*, **34**, 3583 (1969).

(3) J. K. Crandall and L. C. Lin, *ibid.*, **33**, 2375 (1968).

(4) A. C. Cope and J. K. Heeren, *J. Amer. Chem. Soc.*, **87**, 3125 (1965).

(5) R. P. Thummel and B. Rickborn, *ibid.*, **92**, 2064 (1970).

(6) R. P. Thummel and B. Rickborn, *J. Org. Chem.*, **36**, 1365 (1971).

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

(8) J. K. Crandall, L. C. Crawley, D. B. Banks, and L. C. Lin, *J. Org. Chem.*, **36**, 510 (1971).

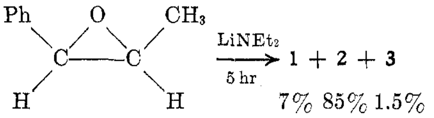
(9) This behavior stands in contrast to the reaction of *cis*- and *trans*-2-pentene oxide, where no significant difference in rates is observed.[2]

(10) C. K. Kissel and B. Rickborn, unpublished work.

Benzylmethyl ketone (**3**) is the only product clearly attributable to α abstraction; taking acidity into account suggests that the benzylic proton is attacked, followed by opening to a carbene and migration of the carbinol hydrogen to this center. This overall course of reaction must reflect the relative migratory aptitudes of hydrogen *vs.* methyl, since **3** arising by this mechanism from *trans*-β-methylstyrene oxide does not follow the stereochemical course observed by Cope[7] with the stilbene oxides. The relative amount of **1** plus **2** compared to **3** demonstrates the preference for β elimination as opposed to α abstraction.

The formation of acetophenone (**4**) was unexpected, and no obvious analogy for the production of this material exists in the literature. Analysis of the early points taken in the reaction support the view that **4** is formed as a primary product from *trans*-β-methylstyrene oxide. Further work is underway to determine the mechanism of this reaction.

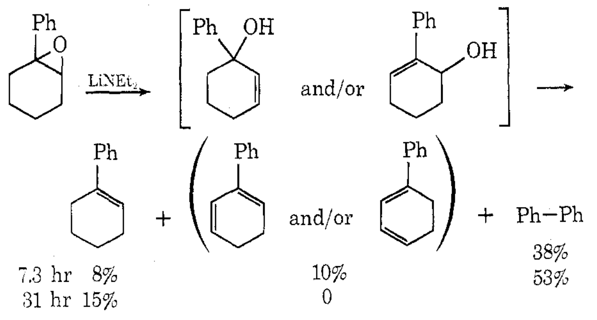
A sample of *cis*-β-methylstyrene oxide was obtained *via* epoxidation of predominantly cis olefin obtained by the Wittig reaction between ethylidenetriphenylphosphorane and benzaldehyde, and subsequent preparative vpc isolation. As anticipated from the results given in eq 1, the cis isomer was less reactive than the trans, 5 hr being required for >95% consumption of the epoxide. The results are given in eq 2.



(2)

The larger percentage of **2** relative to **1** is a reflection of the longer reaction time required in this reaction, and further substantiates the view that **2** is formed by a second-step rearrangement of **1** under the basic reaction conditions. An intriguing point is that the α-abstraction process leading to **3** appears to be even slower with the cis than the trans epoxide; one might have expected the opposite result assuming that the methyl group in the trans isomer could sterically impede attack of the α-benzylic hydrogen. No acetophenone was observed in the reaction of the cis epoxide.

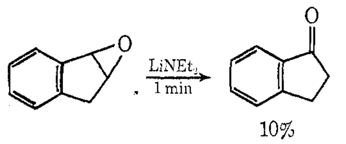
The reaction of 1-phenylcyclohexene oxide with lithium diethylamide was briefly explored. This system illustrates another secondary process that is facilitated by the phenyl substituent, namely further elimination and disproportionation. The presumed allylic alcohol intermediates, shown in eq 3, were not isolated but are inferred from subsequent products.[11]



(3)

A phenyl-substituted 1,3-cyclohexadiene is observed early in the reaction but disappears with time, presumably *via* disproportionation and by loss of LiH, forming 1-phenylcyclohexene and biphenyl by the first process, and biphenyl alone by the second. Literature precedents exist for both mechanisms under somewhat different reaction conditions,[12,13] as well a for the loss of Li_2O to form the diene intermediate.[3]

Indene oxide undergoes very rapid reaction with lithium diethylamide, but yields only 10% of 1-indanone product, the remainder being resinous intractable material (eq 4). This system is of interest because

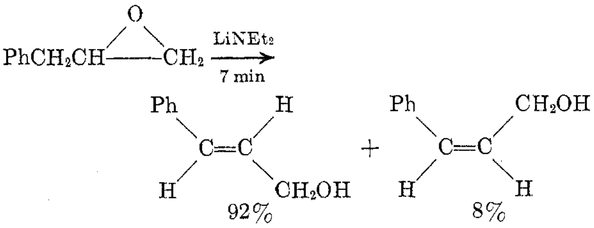


(4)

it has in effect both α- and β-phenyl substitution, but also the geometry of a cyclopentene oxide, which appears not to be ideal for the β-elimination process.[14] Although this has not been established, we suggest that the 1-indanone arises by β elimination followed by rearrangement of the allylic alcoholate. The intractable residue which accounts for most of the material could have arisen from the very reactive 2-indanone (a possible α-abstraction product), but no evidence for this material was obtained.

A number of interesting observations were made in the base-induced rearrangements of β-phenyl-substituted epoxides.

The major product obtained on treating a terminal methylene oxide with lithium diethylamide is usually[15] the amino alcohol adduct formed by nucleophilic attack at the primary center. It was of interest to determine whether the acidifying effect of a β-phenyl substituent could overcome this alternative reaction, and to this end 3-phenyl-1-propene oxide was treated with lithium diethylamide. Two products were formed in a very fast, high-yield reaction, as shown in eq 5. The



(5)

acidifying effect of the phenyl substituent is clearly evident; not only is nucleophilic attack completely suppressed, but the rate of the β-elimination reaction is much greater than with a simple alkyl-substituted epoxide (under the same reaction conditions, abstraction from a secondary carbon in an open-chain epoxide requires several hours). The minor product of eq 5, *cis*-cinnamyl alcohol, is of interest since it represents

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[11] Although not necessarily a good model for comparison with 1-phenylcyclohexene oxide, we have found that 1-*tert*-butylcyclohexene oxide undergoes a very slow reaction (47 hr) to give 95% of 1-*tert*-butyl-2-cyclohexenol and 5% of 2-*tert*-butyl-2-cyclohexenol.

[12] J. E. Hofmann, P. A. Argabright, and A. Schriesheim, *Tetrahedron Lett.*, 1005 (1964).

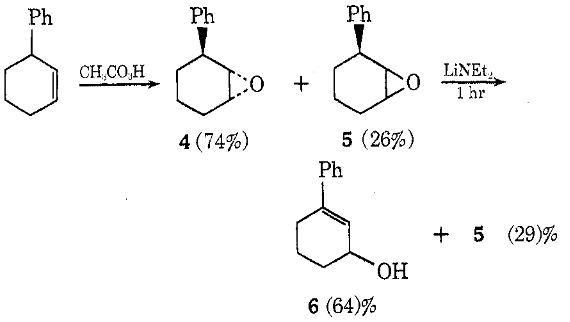
[13] R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *ibid.*, 199 (1967).

[14] J. K. Crandall and L. Chang, *J. Org. Chem.*, **32**, 435 (1967); these authors have reported that cyclopentene oxide on reaction with lithium diethylamide gives *mostly* amino alcohol adduct. A greater degree of elimination is obtained when a bulkier base (diisopropylamide) is employed.

[15] The course of these reactions is strongly dependent on other structural features of the substrate epoxide, the dialkylamide, and reaction conditions employed.[10]

the first example of any detectable cis olefin formed in a base-induced acyclic olefin oxide rearrangement. Both *cis*- and *trans*-cinnamyl alcohol are stable under the reaction conditions; so the distribution given in eq 5 represents a kinetically determined mixture rather than subsequent isomerization.

The formation of some cis olefin and the greatly enhanced rate of reaction associated with β-phenyl substitution raises the question of a possible difference in mechanism in these systems as compared to simple aliphatic epoxides. As noted earlier, the accumulated evidence dealing with alkyl-substituted epoxides all supports a syn elimination mechanism. In order to explore this question, 3-phenylcyclohexene was epoxidized and the resultant mixture of isomers was subjected to lithium diethylamide treatment (eq 6).

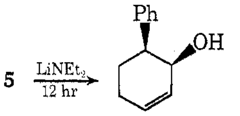


4 (74%) **5** (26%)

6 (64)% **5** (29)% (6)

The results of the short-time treatment with base show clearly that the *trans*-3-phenylcyclohexene oxide reacts considerably faster than the cis isomer [the product distribution given in eq 6 does not show the small amount of biphenyl and related materials (4%) formed (see eq 3) nor the minor (3%) allylic alcohol derived from the cis epoxide (see below)]. Note that the formation of allylic alcohol **6** involves the abstraction of a tertiary benzylic proton cis to the epoxygen; in the absence of the acidifying phenyl group, no tertiary proton abstraction is observed.[6]

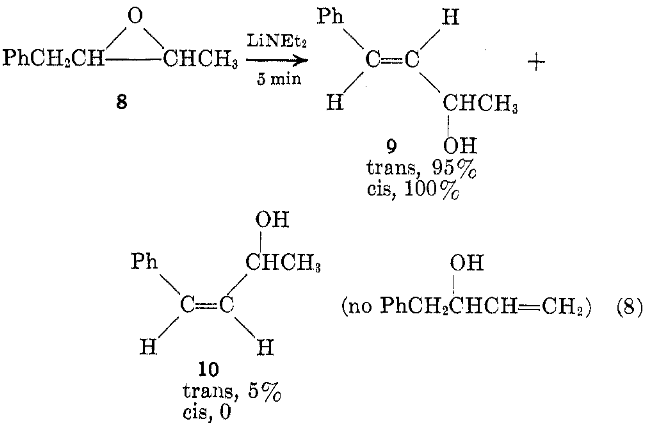
Distillation of the mixture obtained in eq 6 gave a sample of recovered epoxide which proved to be >98% pure cis material (**5**). This was in turn subjected to the basic reaction conditions, and in a much slower process gave **7**, derived from secondary proton abstraction, as the only allylic alcohol product (eq 7).



7 (7)

The results of eq 6 and 7 taken together strongly support the syn elimination mechanism, and demonstrate that, although the β-phenyl substituent exerts a significant acidifying effect, this is insufficient to overcome the geometrical requirements associated with the syn elimination process; *i.e.*, no anti elimination is observed with compound **5**.

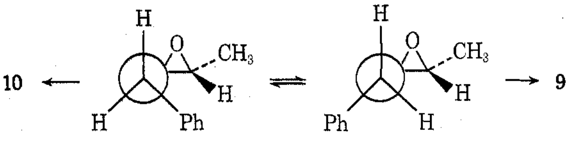
Competition for abstraction between primary aliphatic and secondary benzylic protons leads to exclusive reaction by the latter pathway. This is illustrated by the reaction of 1-phenyl-2-butene oxide (**8**), eq 8, where no 1-phenyl-3-buten-2-ol is formed. Interestingly, the two isomers of this epoxide give somewhat different product distributions; whereas the cis epoxide yields stereoisomerically pure trans olefin **9**, the trans epoxide, while giving 95% of the same product, also gives 5% of the cis allylic alcohol. The behavior of the trans epoxide in this respect resembles the reaction of 3-phenyl-1-propene oxide described earlier (eq 5). We can interpret these results in terms of a syn elimination mechanism as shown in eq 9 and 10. Considering first the trans epoxide, and viewing the Newman projections **11** and **12** as approximate models for the transition states for elimination, product **9** arises from conformer **12** in the favored process. Conformer **11** has an unfavorable 1,3-phenyl–hydrogen interaction (note that if phenyl is replaced by alkyl this process is excluded), leading to a smaller amount of cis olefin **10**.



8

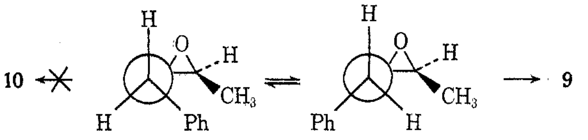
9 trans, 95% cis, 100%

10 trans, 5% cis, 0 (8)



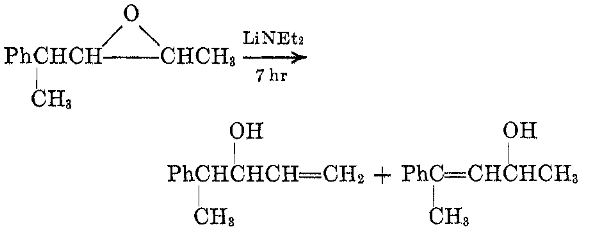
11 **12** (9)

Similar depictions for the cis epoxide, shown in eq 10, point out the sterically unfavorable 1,3-phenyl–methyl interaction in conformer **13**; as a consequence of this steric effect in the transition state, all of the cis epoxide reacts *via* conformer **14** to give product **9**.



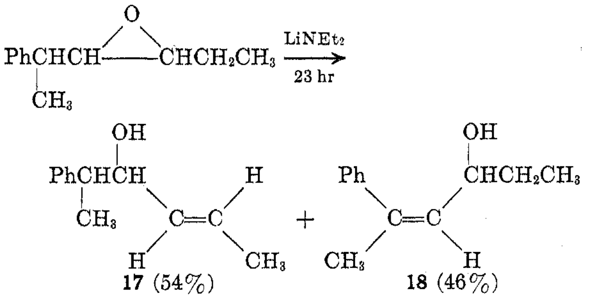
13 **14** (10)

Finally, the question of competition between benzylic and aliphatic proton abstraction was explored in two systems, as shown in eq 11 and 12. Unfortunately, we do not know the exact stereochemistry of the starting epoxides in either case; both systems contain three asymmetric centers and therefore may involve mixtures of four diastereomerically related isomers (of course two of these centers are fixed relative to each other by the geometry of the starting olefin, but these proved to be very difficult to separate, and, even had we worked with single olefin isomers, the epoxide would have been a mixture of two diastereomers; see Experimental Section). Nonetheless, the results are of interest in that they clearly show that even tertiary ben-



$$\underset{\displaystyle CH_3}{PhCH}\overset{O}{-\!\!-}CHCH_3 \xrightarrow[7\ hr]{LiNEt_2} \underset{\displaystyle CH_3}{PhCH}\overset{OH}{CH}CH{=}CH_2 + \underset{\displaystyle CH_3}{PhC}{=}CH\overset{OH}{CH}CH_3 \quad (11)$$

15 (93%) 16 (7%)

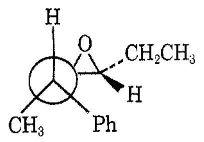


(12)

17 (54%) 18 (46%)

zylic proton abstraction can compete with primary aliphatic proton abstraction.

The geometry of the minor product in eq 11 was not determined directly, but the gross structure was demonstrated by catalytic reduction to the saturated alcohol which in turn was compared with a sample produced by an alternate route. By analogy with the results of eq 8 and 12, it is presumed that the phenyl group of **16** is cis to the hydroxyalkyl function. Two allylic alcohols were formed, along with a number of minor products, in the reaction shown in eq 12; both were isolated by preparative vpc and appear to be homogeneous by spectral analysis. Compound **17** is presumed to have the trans geometry by analogy with earlier work.[4] The structure of **18** was deduced from its nmr spectrum, and in particular the geometry shown is based on the chemical shift (δ 5.32 ppm) of the vinyl proton, indicating that it lies outside the deshielding region of the aromatic ring and hence is trans to the phenyl group. Typically, when this proton is cis to the phenyl substituent, as in *trans*-cinnamyl alcohol, the resonance is observed at δ 6.2 ppm. Product **18** can arise by syn elimination from two diastereomers, one (**19**) derived from trans olefin oxide, and the other (**20**) from cis olefin oxide. By analogy with eq 8, one would expect more facile reaction of **19** than of **20**; however, in view of the higher activation energy (longer reaction time) associated with the overall reaction in eq 12, formation of **18** from the cis olefin oxide **20** cannot be excluded on the basis of the present data. A substantial amount of epoxide (*ca.* 20%) is recovered even after the 23-hr time used in eq 12. It is likely that this material is diastereomerically enriched, but further efforts along these lines are hampered by the difficulty of separation of the epoxide diastereomers and the lack of a convenient method of assigning specific structures to these isomers.



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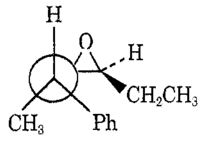

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Experimental Section

All epoxidations were carried out with peracetic acid following a literature procedure,[16] at room temperature for periods of 12–20 hr.

The base-induced rearrangement yields, as determined by vpc using an internal standard and in several cases by distillation of products, were high (70–90%), except where otherwise noted. The products were stable to the vpc analytical conditions, as shown by isolation and reinjection. In the slower reaction systems, aliquots were analyzed at early stages of reaction, and product distributions were invariant except where otherwise noted. Individual geometric isomers of allylic alcohols resubjected to the basic reaction conditions are not interconverted.

***trans*-1-Phenyl-1-propene Oxide.**[17]—Commerical β-methylstyrene was epoxidized in 78% yield, giving material which was 6% cis and 94% trans (longer retention time on a Carbowax 20M vpc calumn) isomer.

Treatment of this mixture with lithium diethylamide in refluxing ether–hexane 2 gave a product showing five peaks by vpc at 155° (Carbowax 20M columns were used exclusively in this analysis and those described below); in order of retention time the first peak (8%) was not characterized, the second was unreacted cis epoxide (4%, ir identical with that of authentic sample), the third was acetophenone (by ir, nmr, and vpc, 16%), the fourth (41%) was a mixture, analyzed by nmr of the collected sample, of propiophenone (30%) and 1-phenyl-2-propanone (11%), and the fifth peak (31%) was 1-phenylallyl alcohol (**1**), identified by its characteristic nmr spectrum: δ 7.17 (s, 5 H), 6.15–5.6 (m, 1 H), 5.3–4.9 (m, 3 H, $CH_2{=}CHCHOH$), and 3.1 ppm (s, OH); ir 3350, 1495, 1027, 991, 764, and 703 cm^{-1}. The ratio of products changed with time as described in the text, as determined by analysis of aliquots taken during the course of the reaction.

***cis*-1-Phenyl-1-propene Oxide.**—The procedure of Schlosser and Christmann[18] was followed to give a mixture of olefins which was spinning band distilled to give a sample enriched in the cis isomer (62%). Epoxidation gave 69% of material, bp 53–55° (3.5 Torr), which showed two peaks (63:37) by vpc. The major peak (cis epoxide)[17] was isolated by preparative gas chromatography.

Lithium diethylamide rearrangement of this isomer gave after 5 hr a mixture analyzed as above: unreacted cis epoxide (*ca.* 1%), propiophenone (85%), and 1-phenyl-2-propanone (1.5%), unidentified (4.5%), and 1-phenylallyl alcohol (7%).

1-Phenylcyclohexene Oxide.[19,20]—Commercial 1-phenylcyclohexanol was dehydrated by heating with phosphoric acid in acetic acid solution. The 1-phenylcyclohexene,[21] bp 122–124° (12 Torr), gave on peracetic acid treatment 68% of the epoxide, bp 147–149° (26 Torr).

Treatment of the epoxide with lithium diethylamide for 7.3 hr resulted in a mixture showing six peaks by vpc analysis at 180°. The first three were in a ratio of 8:10:37 and were identified as 1-phenylcyclohexene (by spectral comparison with an authentic sample), 1- or 2-phenylcyclohexadiene, nmr δ 7.1 (m, 5 H), 6.3–5.7 (m, 3 H), and 2.2 ppm (m, 4 H), ir 3060–3010, 2920, 1590, 1074, 944, 820, 760, 730, 695, and 670 cm^{-1}, and biphenyl (by spectral comparison with commercial material). The remaining longer retention time products were not isolated or characterized. After 31 hr of lithium diethylamide treatment the phenylcyclohexadiene peak had disappeared and the first and third peaks were present in a ratio of 15:53.

Indene Oxide.—Epoxidation of indene gave 66% of the desired oxirane,[22] bp 88° (1.2 Torr), mp 29°; when subjected to lithium diethylamide, the epoxide was consumed within 6 min. The sole volatile product by vpc was 1-indanone (10%), identified by comparison with a published infrared spectrum.[23] The large amount of residue obtained on evaporation of solvent was

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[16] M. Korach, D. R. Nielsen, and W. H. Rideout, *J. Amer. Chem. Soc.*, **82**, 4329 (1960).

[17] R. C. Fahey and C. Schubert, *ibid.*, **87**, 5172 (1965).

[18] M. Schlosser and K. F. Christmann, *Angew. Chem.*, **76**, 683 (1964).

[19] The authors are indebted to John Widosh for carrying out the preparation of this material.

[20] S. Nametkin and N. Ivanoff, *Chem. Ber.*, **56**, 1805 (1923).

[21] R. Huisgen, F. Jakob, and R. Grashely, *ibid.*, **92**, 2206 (1959).

[22] W. Whitmore and A. Gebhart, *J. Amer. Chem. Soc.*, **64**, 912 (1942).

[23] R. Mecke and F. Langenbucher, "Infrared Spectra of Selected Chemical Compounds," Heyden, 1965, p 1061.

a viscous, intractable material which was not further characterized.

3-Phenyl-1-propene Oxide.—Epoxidation of allylbenzene gave 47% of product, bp 63–64° (4 Torr).[24] The reaction with lithium diethylamide was complete within a few minutes, leading in good yield to a mixture of two volatile products. The minor product (8%) was identified as *cis*-cinnamyl alcohol by its nmr spectrum: δ 7.1 (s, 5 H), 6.4 (d, 1 H, J = 12 Hz, ArC**H**), 5.72 (d of t, 1 H, J_{23} = 12 Hz, J_{21} = 6 Hz, CH=C**H**CH$_2$OH), 4.25 (d of d, 2 H, J = 6, 1.5 Hz, C**H**$_2$OH), and 2.9 ppm (s, OH); ir 3350, 1600, 1030, 777, and 703 cm^{-1}. The major product (92%) was *trans*-cinnamyl alcohol, identified by spectral comparison with commercial material.

3-Phenylcyclohexene Oxide.—NBS treatment of cyclohexene was used to prepare 3-bromocyclohexene. This was in turn added to phenylmagnesium bromide in ether at 0° to give 3-phenylcyclohexene[25] in 93% distilled yield, bp 77° (3 Torr). Epoxidation gave 85% of material, bp 106° (3 Torr), which showed two peaks (area ratio 74:26) on vpc analysis at 180°.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.36; H, 3.34.

The stereochemical identification of the major epoxide as trans and the minor as cis is based on evidence presented below.

Treatment of the epoxide mixture with lithium diethylamide for 55 min gave a product which exhibited six peaks on vpc analysis at 188°. The first three peaks (4% total) were presumed to be phenylcyclohexadienes and biphenyl (the latter by coinjection); the fourth peak (29%) was unreacted cis epoxide; the fifth peak (3%) corresponded to 6-phenyl-2-cyclohexenol, presumably derived from the cis epoxide (see below). The last peak (64%) was identified as 3-phenyl-2-cyclohexenol:[26] nmr δ 7.02 (m, 5 H), 5.9 (s, OH), 4.13 (broad s, C**H**OH), and 2.5–1.2 ppm (m, 6 H); ir 3325, 3070–3010, 1490, 1440, 1160, 1055, 977, 760, and 698 cm^{-1}. This material on reinjection into the vpc underwent partial dehydration to give the phenylcyclohexadienes (peaks 1 and 2). Catalytic hydrogenation on Pd/C gave a mixture of 58% *cis*- and 42% *trans*-3-phenylcyclohexanol.

cis-**3-Phenylcyclohexene oxide** recovered from the above experiment was resubjected to lithium diethylamide treatment to give after 12 hr 6-phenyl-2-cyclohexenol[26] in high yield: nmr δ 7.0 (s, 5 H), 5.65 (m, 2 H), 3.7 (m, C**H**OH), 2.6 (m, ArC**H**), 1.9 (s, OH), 2.4–1.3 (m, 4 H); ir 3380, 3070–3010, 2910, 1605, 1072, 990, 940, 758, and 701 cm^{-1}.

Lithium aluminum hydride reduction of a sample of cis epoxide gave a mixture of 91% *cis*- and 9% *trans*-2-phenylcyclohexanol (the latter arising by the oxidative inversion mechanism[27]); these products were distinguishable by vpc from the 3-phenylcyclohexanols obtained above by catalytic hydrogenation.

trans-**1-Phenyl-2-butene Oxide.**—Commercial 1-phenyl-2-butene (Aldrich, 96% trans) was epoxidized in 83% yield, bp 107–108° (7.5 Torr), and a sample of pure trans epoxide was isolated by preparative vpc: nmr δ 6.9 (s, 5 H), 2.37 (s over m, 4 H), and 0.8 ppm (d, 3 H, J = 5 Hz); ir 3080–3020, 1610, 1500, 1460, 1390, 954, 858, 805, 743, and 704 cm^{-1}.

Reaction with lithium diethylamide was complete in 5 min, leading to two products in high yield. The major product (95%) was *trans*-4-phenyl-3-buten-2-ol:[28] nmr δ 7.08 (s, 5 H), 6.18 (m, 2 H), 5.0 (s, OH), 4.33 (d of q, C**H**OH), and 1.27 ppm (d, 3 H, J = 6 Hz), agrees well with *trans*-cinnamyl alcohol; ir 3340, 3080–3020, 2970, 1145, 1060, 968, 944, 750, and 696 cm^{-1}.

The minor product (5%) had the shorter vpc retention time, and was identified as *cis*-4-phenyl-3-buten-2-ol[28] by its spectra: nmr δ 7.06 (s, 5 H), 6.26 (d, J = 11 Hz, ArC**H**), 5.50 (d of d, J = 11, 8 Hz, CH=C**H**CHOH), 4.58 (d of q, J = 8, 6 Hz, C**H**OH), 2.48 (s, OH), and 1.22 ppm (d, 3 H, J = 6 Hz); ir 3340, 3070–3010, 2960, 1110, 1053, 930, 915, 870, 795, 768, and 700 cm^{-1}.

When the reaction with lithium diethylamide was carried out for 22 hr a new product (64%) appeared at the expense of the trans allylic alcohol so that the product ratio became 64:6:30. The new product was identified as 4-phenyl-2-butanone: nmr δ 7.0 (s, 5 H), 3.68 (two t, 4 H), and 1.97 ppm (s, 3 H); ir 1715 cm^{-1}.

cis-**1-Phenyl-2-butene Oxide.**—The procedure of Hauser, *et al.*,[29] was followed for the Wittig reaction of phenylacetaldehyde and ethylidenetriphenylphosphorane; 26% of olefin, bp 61–62° (11 Torr), was obtained, which by vpc analysis showed two poorly resolved peaks in a ratio of 25:75. The minor olefin was identical by coinjection with commercial trans material.

Epoxidation of this mixed olefin gave 66% of material which showed two peaks (ratio 79:21) on vpc analysis at 170°. The minor peak corresponded to *trans*-1-phenyl-2-butene oxide by coinjection. The major product (cis epoxide) was collected by preparative vpc.

The pure cis isomer again reacted very rapidly with lithium diethylamide to give a quantitative yield of *trans*-4-phenyl-3-buten-2-ol, analyzed as in the previous experiment. After 9-min reaction time, no other products could be detected.

4-Phenyl-2-pentene Oxide.—The procedure of Schlosser and Christmann[18] was followed, using 2-phenylpropionaldehyde and ethyltriphenylphosphonium bromide, to obtain 42% of 4-phenyl-2-pentene, bp 77.5–79° (20 Torr); attempts to separate the olefin isomers were unsuccessful. Epoxidation gave material, bp 82–84° (7 Torr), which showed only two peaks (9:91) on vpc analysis at 150°. Treatment of this epoxide mixture with lithium diethylamide for 6.6 hr gave two products in overall high yield. The major product (93%) was collected and identified as 4-phenyl-1-penten-3-ol by its characteristic nmr: δ 7.02 (s, 5 H), 5.9–4.8 (ABC pattern, 3 H, C**H**=C**H**$_2$), 4.0 (t, J = 5.5 Hz, C**H**OH), 2.73 (quintet, J = 7 Hz, ArC**H**), 2.13 (s, OH), and 1.25 ppm (d, 3 H, J = 7 Hz); ir 3400, 3070–3015, 2960, 1599, 1495, 1450, 1130, 995, 924, 764, and 703 cm^{-1}.

The minor product could not be isolated but was presumed to be 4-phenyl-3-penten-2-ol by catalytic hydrogenation of the product mixture and comparison with the products of lithium aluminum hydride reduction of the starting epoxide.

2-Phenyl-3-hexene Oxide.—The olefin was prepared as in the previous experiment by the modified Wittig reaction of 2-phenylpropionaldehyde and *n*-propyltriphenylphosphonium bromide. A 69% yield of material, bp 63–73° (6 Torr), was obtained; no separation of the cis and trans isomers could be effected. Peracetic acid treatment gave a product which showed four peaks (8:63:10:19) by vpc at 120°. Careful spinning-band distillation gave a sample containing only the second and third components in a ratio of 86:14, bp 88° (4.5 Torr). The latter mixture was subjected to lithium diethylamide treatment for 23 hr, after which it was analyzed by vpc at 175°, giving nine peaks. The first six peaks were collected in pairs and the last three separately. The first two peaks (9 and 1%) appeared to be dienes by virtue of their volatility and ir spectrum; of the second pair, peak three (18%) was unreacted epoxide, and the fourth (2%) was not identified. The fifth and sixth peaks (4 and 1%) were characterized only by ir: 3070–3020, 2960, 1495, 1450, 1380, 1200, 1170, 1068, 760, and 700 cm^{-1}. The seventh peak (27%) was *trans*-5-phenyl-4-hexen-3-ol: nmr δ 7.06 (s, 5 H), 5.32 (d, J = 9 Hz, C=CH), 3.85 (d of t, J = 9.6 Hz, C**H**OH), 3.2 (s, OH), 1.95 (s, 3 H, C=CCH$_3$), 1.38 (q, 2 H, J = 7 Hz), and 0.85 ppm (t, 3 H, J = 7 Hz); ir 3330, 3070–3015, 2960, 2930, 1495, 1445, 1075, 1030, 997, 961, 771, and 705 cm^{-1}. The eighth peak (33%) was identified as *trans*-2-phenyl-4-hexen-3-ol by its nmr: δ 7.0 (s, 5 H), 5.32 (m, 2 H), 3.96 (t, J = 5.5 Hz, C**H**OH), 2.7 (quintet, J = 6.5 Hz, ArC**H**), 2.1 (s, OH), 1.6 (d, 3 H, J = 4.5 Hz), and 1.25 ppm (d, 3 H, J = 6.5 Hz); ir 3375, 3080–3020, 2960, 1495, 1455, 1380, 1010, 968, 760, 705 cm^{-1}. The final vpc peak (5%) was an amino alcohol adduct, based on its mass spectrum: m/e 71, 91, 105, 249 (parent). The first six peaks, with the exception of the unreacted epoxide, all appear to be secondary reaction products or formed by minor decomposition of the allylic alcohols on vpc injection.

Registry No.—**1**, 4393-06-0; *trans*-**4**, 36004-00-9; *cis*-**5**, 36004-01-0; *trans*-**8**, 32215-84-2; *cis*-**8**, 36004-03-2; **9**, 36004-04-3; **10**, 31915-95-4; **15**, 36004-05-4; **17**, 36004-06-5; **18**, 36004-07-6; *trans*-1-phenyl-1-propene oxide, 23355-97-7; *cis*-1-phenyl-1-propene oxide, 4541-87-1; 1-phenylcyclohexene oxide, 4829-01-0; indene oxide, 768-22-9; 3-phenyl-1-propene oxide, 4436-24-2; *cis*-cinnamyl alcohol, 4510-34-3; 4-phenyl-2-pentene oxide, 36004-14-5; 2-phenyl-3-hexene oxide, 36004-15-6.

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