corresponding acid, and the 1,1,3,3-tetracyanopropenide ion as the barium salt. Spectra were obtained on a Perkin–Elmer model 21 double beam infrared spectrometer equipped with NaCl optics (2–15 μ) and with a CaF$_2$ prism (2–8 μ). The Raman spectrometer used to determine the position of the C=C stretching frequency in tetracyanoethylene is similar to that described by Rank, et al.[6] Ultraviolet spectra were obtained in water or methanol solution using a Cary model 11 ultraviolet spectrometer.

Vapor pressure vs. temperature data for tetracyanoethylene (Fig. 4) were determined by a vapor saturation method. A metered stream of nitrogen were saturated by passing it slowly over crystals of tetracyanoethylene held at the several temperatures. Tetracyanoethylene vapor in the metered volume of nitrogen was trapped in N,N-dimethylaniline and the amount determined quantitatively by measuring absorbance of the red dye formed by the reaction of N,N-dimethylaniline with tetracyanoethylene.[7]

(6) M. R. Fenske, W. G. Braun, R. V. Wiegand, Dorothy Quiggle, R. H. McCormick and D. H. Rank, Anal. Chem., 19, 900 (1947).

(7) Paper VI, B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, This Journal, 80, 2806 (1958).

The differential thermal analysis apparatus and procedures were conventional, using Pt vs. Pt–10% Rh thermocouples. Powdered samples and the alumina reference were packed against the thermocouples in $^1/_8$ in. platinum tubes fitted over the ceramics holding the thermocouple wires. The data were recorded on a standard 5 millivolt double-X strip-chart recorder. By using a preamplifier in the differential temperature channel, the over-all sensitivity was set at 200 microvolts full scale deflection. The heating rate was 15° per minute. The modified apparatus consisted of a horizontal electric tube furnace lined with a Pyrex tube and activated by a Powerstat to control the heating rate to about 25° per minute. An iron–constantan thermocouple was surrounded by 0.1 g. of powdered sample in a small test-tube placed in the center of the furnace. As the sample was heated, the temperature was recorded on a conventional strip-chart recording potentiometer with a range of 0 to 800°. The low temperature edge of the sharp temperature rise, which marked the onset of the rearrangement reaction, could be read with an accuracy of ±5° in most cases.

Base-catalyzed Rearrangement of Epoxides

By Arthur C. Cope, Patricia A. Trumbull and Elmer R. Trumbull

The reaction of a series of phenyl-substituted ethylene oxides with the base lithium diethylamide has been investigated. cis-Stilbene oxide was isomerized to desoxybenzoin (70%), trans-stilbene oxide gave diphenylacetaldehyde (66%), triphenylethylene oxide formed benzhydryl phenyl ketone (80%) and 1,1-diphenyl-2-p-tolylethylene oxide yielded benzhydryl p-tolyl ketone (41%). Tetraphenylethylene oxide and 1,1-diphenylethylene oxide did not rearrange when treated with lithium diethylamide. A mechanism based on abstraction of a proton from the oxirane ring by the base followed by ring opening or rearrangement is proposed.

The fact that cyclooctatetraene oxide is isomerized to cyclooctatrienone by treatment with lithium diethylamide[1] has prompted further study of the reaction of epoxides with bases. The acid-catalyzed and thermal rearrangements of epoxides to carbonyl compounds are well known,[2,3] but there are few examples of the rearrangement of epoxides by bases, except for the isomerization of the oxides of α,β-unsaturated ketones to α-diketones.[4] The reaction of Grignard reagents with epoxides in many instances gives rise to products whose formation may be explained by rearrangement of the epoxide to a carbonyl compound, followed by addition of the organometallic agent. However, in several cases it has been shown that the rearrangements are caused by the magnesium halide present in the Grignard reagents and that these reactions therefore may be considered to be acid catalyzed.[2,3,5]

The epoxides derived from phenyl-substituted derivatives of ethylene were chosen for the study, namely, 1,1-diphenylethylene, cis- and trans-stilbene, triphenylethylene, 1,1-diphenyl-2-p-tolylethylene and tetraphenylethylene. They were prepared conveniently by oxidation of the olefins with commercial peracetic acid. This method

failed only with 1,1-diphenylethylene, in which case the oxide was prepared from the corresponding bromohydrin.[6]

To bring about the isomerizations, the epoxides were treated with two equivalents of lithium diethylamide in ether at −20°. The stilbene oxides were found to have rearranged when the ether solutions were warmed to room temperature and refluxed for one hour. cis-Stilbene oxide gave desoxybenzoin, isolated in 70% yield, as the product of rearrangement. trans-Stilbene oxide yielded diphenylacetaldehyde which was isolated as its methone derivative in 66% yield.

Triphenylethylene oxide did not react completely under these conditions and required heating at 65° for several hours after replacement of the ether by benzene to bring about conversion to benzhydryl phenyl ketone in 80% yield.

1,1-Diphenyl-2-p-tolylethylene oxide was not converted cleanly to a ketone when subjected to conditions similar to those used with triphenylethylene oxide. By chromatographic separation of the mixture of products three pure compounds were isolated. These were the recovered oxide (23%), benzhydryl p-tolyl ketone (31%) and 2,2-diphenyl-1-p-tolylethanol (18%). The structures of the ketone and alcohol were established by comparison of melting points and infrared spectra with authentic samples. The isomeric ketone 2-phenyl-

(1) A. C. Cope and B. D. Tiffany, This Journal, 73, 4158 (1951).

(2) S. Winstein in Elderfield, "Heterocyclic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, Vol. 1, pp. 47–51.

(3) H. O. House, This Journal, 77, 3070 (1955).

(4) See ref. 2, p. 52.

(5) N. G. Gaylord and E. I. Becker, Chem. Revs., 49, 413 (1951).

(6) S. J. Cristol, J. R. Douglass and J. S. Meek, This Journal, 73, 816 (1951).

2-*p*-tolylacetophenone[7] and the alcohol 1,1-diphenyl-2-*p*-tolylethanol also were compared with the products isolated above and the isomers were shown to be readily distinguishable by infrared spectra and mixed melting points.

The rearrangements of 1,1-diphenylethylene oxide, triphenylethylene oxide and 1,1-diphenyl-2-*p*-tolylethylene oxide with boron trifluoride etherate also were studied, since their rearrangement in the presence of this Lewis acid apparently has not been reported. The products were diphenylacetaldehyde (isolated as the methone derivative in 76% yield), triphenylacetaldehyde (46%) and diphenyl-*p*-tolylacetaldehyde (49%). The structure of the latter compound was assigned on the basis of analysis, the fact that it was not identical with the isomeric ketones, and the close resemblance of its infrared spectrum to the spectrum of triphenylacetaldehyde (both show carbonyl absorption at 5.73 μ and have formyl hydrogen-stretching bands).

A melting point of 81.0–81.5° was observed for this aldehyde. Diphenyl-*p*-tolylacetaldehyde-1-C^{14} has been described as a solid, m.p. 60–61°.[8] A sample of this material, kindly supplied by the authors, was recrystallized and seeded with the higher melting form of the aldehyde. The sample then melted at 80–81°. It seems likely that the much higher melting point (171.0–172.5°) previously reported for the aldehyde[9] corresponds to the melting point of a polymeric form, possibly a cyclic trimer.

Tetraphenylethylene oxide was recovered unchanged (90% recovery) when treated with lithium diethylamide under conditions that caused triphenylethylene oxide and diphenyl-*p*-tolylethylene oxide to isomerize.

1,1-Diphenylethylene oxide also gave no evidence of rearrangement to either of the possible products, diphenylacetaldehyde or desoxybenzoin. However, some reaction did occur with opening of the oxide ring to give the aminoalcohol, 1,1-diphenyl-2-diethylaminoethanol. This compound was separated from the reaction mixture in 26% yield as the methiodide. The infrared spectrum of the crude reaction mixture showed a weak absorption in the carbonyl region but at a longer wave length than the carbonyl absorption of either desoxybenzoin or diphenylacetaldehyde. This absorption was found to be caused by the presence of a small amount (estimated as 5% from the intensity of absorption) of benzophenone, which was isolated as the oxime. The presence of as small an amount as 2–3% of diphenylacetaldehyde or desoxybenzoin would have been evident in the infrared spectrum of the crude product so it is certain that they were not formed to that extent. The source of the benzophenone is not known. It is not formed by further reaction of the aminoalcohol with base, because treatment of the aminoalcohol with lithium diethylamide under the conditions used for rearrangement of the oxide caused no cleavage to benzophenone.

(7) We are indebted to Dr. C. F. Koelsch for a sample of this ketone.

(8) B. M. Benjamin and C. J. Collins, THIS JOURNAL, **78**, 4336 (1956).

(9) A. McKenzie, R. Roger and W. B. McKay, *J. Chem. Soc.*, 2597 (1932).

Since these ethylene oxides are known to be sensitive to acid-catalyzed rearrangements, it was necessary to show that the isomerizations were not caused by the use of acids in the isolation procedure; samples of the oxides were subjected to the same procedure used in isolating products from the reactions and were recovered in high yields in all cases.

The results obtained in this study differ in two respects from those observed in the acid-catalyzed rearrangement of these same compounds. Tetraphenylethylene oxide, which is not isomerized with lithium diethylamide, reacts with various acids to form benzopinacolone.[10]

The other oxides studied may undergo rearrangement to produce an aldehyde or a ketone and the product actually observed depends on the exact reaction conditions.[3] For the purpose of comparison, the products obtained by treating these oxides with boron trifluoride etherate at room temperature are listed in Table I. In each case rearrangement leads to an aldehyde; the *cis* and *trans* forms of stilbene oxide give the same product.[8] 1,1-Diphenylethylene oxide which does not rearrange with lithium diethylamide reacts readily with boron trifluoride forming diphenylacetaldehyde. It has been shown that di- and trisubstituted aldehydes are rearranged to ketones by acids such as concentrated sulfuric acid or boiling formic acid.[8] Consequently the aldehydes listed in Table I would not be the expected products of the acid-catalyzed rearrangements if strong acids or high temperatures were used.

The reaction path suggested originally for the rearrangement of cycloöctatetraene oxide[1] seems best suited to explain the base-catalyzed reactions. The first step would be removal of a proton from the oxirane ring by the diethylamide ion. Accordingly the fully substituted tetraphenylethylene oxide does not react. In the case of the 1,1-diphenylethylene oxide the protons are not benzylic or allylic and therefore presumably are less acidic than in the other compounds. The methylenic carbon atom will be more susceptible to bimolecular attack by amide ion in this compound than will the more highly substituted carbon atoms in the other oxides and the combination of these factors probably accounts for the formation of an aminoalcohol instead of a carbonyl compound in this case.

Once the proton has been removed, ring opening can occur directly to give the anion of a carbonyl compound (path a) or rearrangement might occur
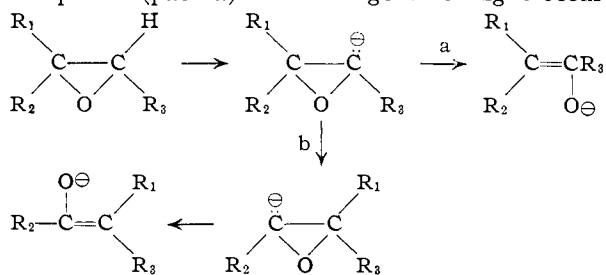
(path b) giving rise to an isomeric product. Unless the substituent groups are properly chosen it is

(10) H. E. Gebhart, Jr., and K. H. Adams, THIS JOURNAL, **76**, 3925 (1954).

Table I

Carbonyl Products from Rearrangement of Epoxides

Oxide	With LiN(C₂H₅)₂	With BF₃
1,1-Diphenylethylene	None	Diphenylacetaldehyde[a]
cis-Stilbene	Desoxybenzoin	Diphenylacetaldehyde[b]
trans-Stilbene	Diphenylacetaldehyde	Diphenylacetaldehyde[b]
Triphenylethylene	Benzhydryl phenyl ketone	Triphenylacetaldehyde[a]
1,1-Diphenyl-2-p-tolylethylene	Benzhydryl p-tolyl ketone	Diphenyl-p-tolylacetaldehyde[a]

[a] This work. [b] Ref. 3.

not possible to distinguish between these possibilities and only two of the compounds studied in this series allow such a choice.

With trans-stilbene oxide the product of reaction clearly shows that a phenyl group has migrated (reaction path b). It is of interest to note that the phenyl group which migrates is on the same side of the epoxide ring as the neighboring hydrogen atom which is assumed to be removed by the base. This cis migration is, of course, the opposite of the trans rearrangement observed in concerted migration to an electron-deficient center.[11] It is, however, the result to be expected of an electrophilic rearrangement similar to the Stevens and Wittig reactions.[12,13]
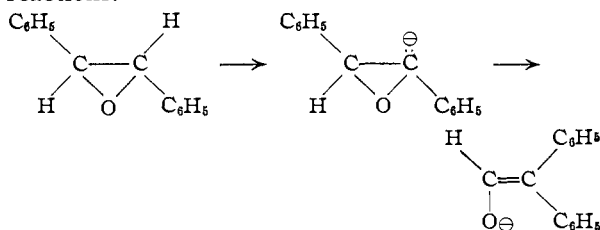
It has been shown that the group which migrates in the Stevens rearrangement does so with retention of configuration.[13] This was the result anticipated on the basis of the mechanism of the reaction proposed by Hauser and Kantor.[12] Frontal attack at the center to which migration occurs is one consequence of this mechanism. The rearrangement of trans-stilbene oxide to diphenylacetaldehyde appears to provide an example of such a frontal attack on an intermediate anion.

Grovenstein has pointed out that carbanion rearrangements in which a migrating group shifts from one carbon to another are rare.[14] The rearrangement of trans-stilbene oxide provides an example of this process if a carbanion is actually present during the reaction.

The other compound studied in which reaction
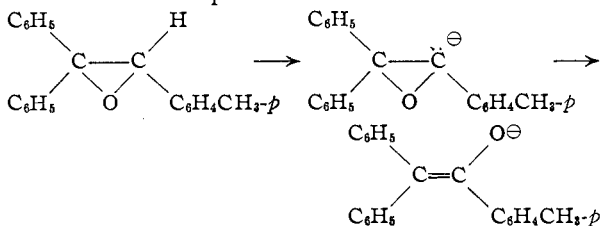
paths a and b are distinguishable is 1,1-diphenyl-2-p-tolylethylene oxide. The structure of the product formed by rearrangement of this oxide shows that no migration of an aryl group occurred in this case (reaction path a). The factors that are important in determining whether or not a group migrates in the base-catalyzed rearrangement are unknown at present. It is of interest that the 2,2-diphenyl-1-p-tolylethanol isolated as one of the products is the isomer that would be formed by reduction of the ketone, benzhydryl p-tolyl ketone, that was isolated.

A mechanism for these reactions based on attack of the diethylamide ion on a carbon atom of the epoxide ring also was considered. This seemed unlikely because such a reaction would give rise to a 1,2-aminoalkoxide, and 1,2-aminoalcohols are not reported to be isomerized by bases. Further, in the case of 1,1-diphenylethylene oxide the aminoalcohol was isolated but no carbonyl compound formed. Finally, an aminoalcohol was prepared from trans-stilbene oxide and diethylamine (presumably the erythro form) and treated with lithium diethylamide. The aminoalcohol was recovered unchanged (95%) under conditions that caused the oxide to rearrange, thereby eliminating it as a possible intermediate.

Experimental[15]

trans-Stilbene Oxide.—To a stirred solution of 40 g. (0.22 mole) of trans-stilbene in 200 ml. of chloroform was added, during a period of 0.5 hour, 45 ml. of a 40% peracetic acid solution (containing 0.26 mole of peracetic acid) in which 4 g. of sodium acetate trihydrate had been dissolved. The reaction mixture was stirred at room temperature for 2 days. Occasional cooling during the first few hours was necessary to keep the temperature from rising above 30°. The reaction mixture was poured into 200 ml. of an ice–water mixture, the layers were separated, and the aqueous layer was extracted with two 50-ml. portions of chloroform. The combined extracts were washed with 50-ml. portions of 10% sodium carbonate solution until the washings were basic, with 50-ml. portions of water until neutral, and were then dried over anhydrous magnesium sulfate. Removal of the drying agent by filtration and the solvent by distillation under reduced pressure left an oil which crystallized when cooled. Recrystallization from methanol gave 37.9 g. (87%) of trans-stilbene oxide, m.p. 67.0–69.0°. A second recrystallization from methanol gave the pure oxide, m.p. 68.6–69.8°.

Rearrangement of trans-Stilbene Oxide.—An ethereal solution of n-butyllithium containing 0.0544 g. of n-butyllithium per ml. was prepared.[16] To 60 ml. (0.051 mole) of

(11) G. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 2nd. ed., 1949, Chapter 12.

(12) C. R. Hauser and S. W. Kantor, This Journal, 73, 1437 (1951).

(13) J. H. Brewster and M. W. Kline, ibid., 74, 5179 (1952).

(14) E. Grovenstein, Jr., ibid., 79, 4985 (1957).

(15) Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses and for the spectra, which were determined with a Cary ultraviolet recording spectrophotometer, model 11 MS, and a Baird double beam infrared recording spectrometer, model B, fitted with a sodium chloride prism.

(16) H. Gilman and R. G. Jones, Org. Reactions, 6, 339 (1951).

this solution, cooled to $-15°$ and maintained under a slight positive pressure of dry nitrogen throughout the reaction, was added a solution of 5.2 ml. (0.051 mole) of dry diethylamine in 25 ml. of anhydrous ether. The solution was stirred for 15 minutes at $-15°$, and then a solution of 5.00 g. (0.0254 mole) of *trans*-stilbene oxide in 25 ml. of anhydrous ether was added dropwise. The reaction mixture was allowed to warm to room temperature and was refluxed for 1 hour. The solution was poured into 100 ml. of ice-water mixture and the layers were separated. The aqueous layer was extracted with two 50-ml. portions of ether and the combined ether solutions were washed with 50-ml. portions of saturated ammonium chloride until neutral, then with water, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left an oil that was allowed to stand in a desiccator at 0.1 mm. over potassium acid sulfate for 12 hours. The residue weighed 5.05 g. and the infrared spectrum indicated that it was composed largely of diphenylacetaldehyde. It proved impractical to isolate the aldehyde as such and instead its methone derivative was prepared. From 0.542 g. of the oil there was obtained 0.938 g. (74%) of product, m.p. 204–207°. Recrystallization from methanol gave 0.838 g. (66%) of the methone derivative, m.p. and mixed m.p. with the derivative prepared from an authentic sample of diphenylacetaldehyde, 208.8–210.0°.

Anal. Calcd. for $C_{30}H_{34}O_4$: C, 78.57; H, 7.47. Found: C, 78.63; H, 7.47.

The diphenylacetaldehyde was shown to be formed by the reaction with lithium diethylamide and not by rearrangement of the oxide during the process of isolation by a control experiment with *trans*-stilbene oxide. A mixture of 2 g. of the oxide and 2 g. of diethylamine in ether was shaken with lithium hydroxide solution, then washed with ammonium chloride solution and finally with water. The oxide was recovered quantitatively, unchanged in melting point and infrared spectrum. The stability of the other oxides described below was established in the same way.

Reaction of 1,2-Diphenyl-2-diethylaminoethanol with Lithium Diethylamide.—The aminoalcohol[17] was prepared by heating *trans*-stilbene oxide (2.90 g.), diethylamine (10 ml.) and two drops of concentrated hydrochloric acid at 150–160° in a bomb for 20 hours. After two recrystallizations from methanol-water the product weighed 2.14 g. (55%), m.p. 68–69°. A solution of 2.00 g. of this aminoalcohol in dry ether was refluxed with 2 equivalents of lithium diethylamide for 3 hours. Isolation of products from the reaction mixture in the usual way yielded 1.91 g. (96%) of the original aminoalcohol, m.p. 69–70°.

cis-**Stilbene Oxide.**—*cis*-Stilbene oxide was prepared from *cis*-stilbene by the method described above for the *trans* isomer. From 10.0 g. of the olefin there was obtained 9.8 g. (91%) of *cis*-stilbene oxide, m.p. 37.8–38.6°, purified by recrystallization from methanol.

Rearrangement of *cis*-Stilbene Oxide.—A solution of 5.02 g. of the *cis*-oxide was allowed to react with lithium diethylamide under the conditions described above for the *trans* isomer. The infrared spectrum of the crude product which was isolated (5.04 g.) indicated that it was impure desoxybenzoin. A sample of this crude material was used to prepare a 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. with an authentic sample of desoxybenzoin 2,4-dinitrophenylhydrazone, 200–201°.

The remainder of the crude product (4.49 g.) was recrystallized from ethanol to give 3.52 g. (70% from *cis*-stilbene oxide) of pure desoxybenzoin, m.p. and mixed m.p. with an authentic sample 54.5–55.7°.

Triphenylethylene Oxide.—A solution of 20 g. of triphenylethylene in 200 ml. of chloroform was allowed to react with peracetic acid for 40 hours. The crude product was recrystallized from hexane after removal of some relatively insoluble solid and gave 16.7 g. (78%) of triphenylethylene oxide, m.p. 73–76°. Further recrystallization from hexane gave the pure oxide, m.p. 75.0–76.4°.

Rearrangement of Triphenylethylene Oxide.—The product isolated after attempts to cause rearrangement under the conditions used for the stilbene oxides was a mixture of unchanged oxide and benzhydryl phenyl ketone. To achieve complete rearrangement, the oxide (5.0 g.) was added in

solution in 75 ml. of anhydrous benzene. After addition was complete and the solution had been heated to reflux, the ether was removed by distillation until the temperature of the refluxing solution reached 63°. This temperature was maintained for 5 hours and then the product was isolated as previously described. The crude product (5.0 g.) was recrystallized from ethanol, giving 4.0 g. (80%) of benzhydryl phenyl ketone, m.p. 133–135°. A second recrystallization raised the melting point to 137–139°. The mixed m.p. with an authentic sample was 136.5–138.5°.

Tetraphenylethylene Oxide.—To a solution of 33.2 g. (0.1 mole) of tetraphenylethylene in 600 ml. of chloroform was added 132 ml. (0.5 mole) of commercial 40% peracetic acid containing 1% of sulfuric acid. The mixture was stirred at room temperature for 95 hours after which the product was isolated as described above. Recrystallization from ethyl acetate gave 31.4 g. (90%) of tetraphenylethylene oxide, m.p. 209.7–210.2° (lit.[18] m.p. 208°).

Anal. Calcd. for $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found: C, 89.54; H, 5.84.

If the sulfuric acid in the peracetic acid solution was neutralized with sodium acetate, reaction products containing the unchanged olefin were isolated.

Treatment of 5.14 g. of this oxide with lithium diethylamide in the manner described for triphenylethylene oxide resulted in the recovery of 4.64 g. (90%) of tetraphenylethylene oxide, m.p. 208–210°. The recovered material showed no trace of absorption in the carbonyl region of its infrared spectrum.

1,1-Diphenylethylene Oxide.—1,1-Diphenylethylene oxide was prepared from the olefin *via* the bromohydrin by the method of Cristol, Douglass and Meek.[6] A solution of 5.0 g. of this oxide was treated with lithium diethylamide in ether as described for the stilbene oxides. The crude product could not be induced to crystallize. It was taken up in 25 ml. of acetonitrile and 5 ml. of methyl iodide and heated under reflux for 12 hours. The solvents were removed under reduced pressure, leaving a mixture of solid and oil. The mixture was washed with benzene, which dissolved the oil, leaving 2.80 g. (26%) of solid material. This product was recrystallized from acetonitrile, and yielded 1.98 g. of 1,1-diphenyl-2-diethylaminoethanol methiodide, m.p. 197–198°.

In order to obtain an authentic sample of the methiodide, 1,1-diphenyl-2-diethylaminoethanol was synthesized in nearly quantitative yield by reduction of N,N-diethylbenzilamide with lithium aluminum hydride.[19] The methiodide was prepared in acetonitrile and recrystallized from the same solvent; m.p. 196–197°.

Anal. Calcd. for $C_{19}H_{26}INO$: C, 55.48; H, 6.37; N, 3.40; I, 30.85. Found: C, 55.27; H, 6.19; N, 3.70; I, 30.81.

In another similar experiment a sample of the crude reaction product which had been kept at 0.2 mm. for several hours to remove diethylamine was analyzed for nitrogen. The oil contained 1.74% N which corresponds to 33% of 1,1-diphenyl-2-diethylaminoethanol in the mixture.

The benzene washings after removal of the methiodide were concentrated under reduced pressure, leaving 3.68 g. of an oil. The infrared spectrum of this product showed only one band in the carbonyl region; a weak absorption at 6.01 μ. The product was distilled at 90–110° (0.05 mm.) yielding 1.75 g. of a clear liquid. The infrared spectrum of this material showed absorption in the carbonyl region at 6.01 μ corresponding to a content of 5% of benzophenone and a new, weaker band at 5.80 μ due to a trace of diphenylacetaldehyde formed from the epoxide by thermal rearrangement during distillation. The oil was taken up in 10 ml. of ethanol and 2 ml. of water and treated with hydroxylamine hydrochloride and potassium hydroxide. After 15 minutes the mixture was poured into water and extracted with ether. The ether extract was concentrated under reduced pressure, leaving an oil which was triturated with pentane. Most of the oil dissolved leaving a small amount of solid. The solid was recrystallized twice from methanol and then from hexane, yielding 0.044 g. (1% from the oxide) of benzophenone oxime, m.p. 143–144°.

Treatment of 1,1-Diphenyl-2-diethylaminoethanol with Lithium Diethylamide.—A solution of 2.69 g. of the amino-

(17) R. E. Lutz, J. A. Freek and R. S. Murphey, THIS JOURNAL, **70**, 2015 (1948).

(18) J. Schmidlin and R. von Escher, *Ber.*, **43**, 1153 (1910).

(19) A. Uffer and E. Schlittler, *Helv. Chim. Acta*, **31**, 1397 (1948).

alcohol in ether was refluxed with 2 equivalents of lithium diethylamide for 2 hours. The crude reaction product showed no absorption in the carbonyl region of the infrared spectrum. It was heated with 12 g. of methyl iodide in 50 ml. of acetonitrile overnight and yielded 3.74 g. (91%) of the aminoalcohol methiodide, m.p. 195–197°.

1,1-Diphenyl-2-p-tolylethylene.—p-Xylene (100 g., 0.94 mole) was brominated with N-bromosuccinimide (54 g., 0.30 mole) in the manner described for the preparation of 3-thenyl bromide,[20] except that 115 ml. of carbon tetrachloride was used as solvent in place of dry benzene. The succinimide was removed by filtration and the solvent and excess xylene were removed by distillation at 13 mm. with a bath heated at 70°.

The crude residue from this distillation was added to a boiling solution of 26.4 g. (0.4 mole) of potassium cyanide in 200 ml. of 95% ethanol and 60 ml. of water in the manner described for the preparation of m-tolylacetonitrile.[21]

The p-tolylacetonitrile boiled at 83–84° (1.5 mm.), n^{25}D 1.5153, and weighed 34.2 g. (87% based on the N-bromosuccinimide).

The nitrile was converted to the ethyl ester by boiling with 250 ml. of absolute ethanol and 30 ml. of concentrated sulfuric acid for 2 days (18 hours was found to be insufficient time for complete reaction). The ethyl p-tolylacetate was collected by distillation at 72–74° (0.9 mm.), 33.1 g. (72%), n^{25}D 1.4930.

The ester was converted to 1,1-diphenyl-2-p-tolylethylene by a method similar to the one described for preparation of triphenylethylene.[22] A solution of phenyllithium in ether was prepared from 0.6 mole of bromobenzene and 1.30 moles of lithium. An ethereal solution of ethyl p-tolylacetate (26.7 g., 0.15 mole) was added to the phenyllithium and the mixture was refluxed for 17 hours. The reaction mixture was treated with water and sulfuric acid and heated to dehydrate the carbinol as described in ref. 22. After this treatment the non-aqueous layer was separated and distilled at 220–235° (13 mm.). The olefin solidified in the receiver and was crystallized from methanol, yielding 29.6 g. (73%) of product melting at 71–72° (lit.[23] m.p. 74°).

In one preparation using 0.01 mole of the ester and 0.04 mole of phenyllithium, the intermediate carbinol was isolated by treating the reaction mixture with ammonium chloride solution and extracting with ether. The 1,1-diphenyl-2-p-tolylethanol obtained was recrystallized from benzene to a constant melting point of 112–113°.

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.45; H, 6.99. Found: C, 87.45; H, 7.10.

1,1-Diphenyl-2-p-tolylethylene Oxide.—A solution of 11.2 g. (0.041 mole) of the olefin in 50 ml. of chloroform was treated with 15.5 ml. (0.043 mole) of peracetic acid to which had been added 2.0 g. of sodium acetate trihydrate. The mixture was stirred rapidly in a creased flask and cooled to keep the temperature below 30°. After a short time cooling was no longer needed and the reaction was stirred at room temperature for 19 hours. The product was isolated in the usual way and amounted to 6.2 g. (52%) of the oxide, purified by recrystallization from hexane, m.p. 70.5–72°.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.33. Found: C, 88.40; H, 6.33.

On one occasion, in which the sulfuric acid in the peracetic acid solution may not have been completely neutralized, an oil was isolated with an infrared spectrum that showed hydroxyl and carbonyl absorption. This oil, which was presumed to be an acetate, was heated with methanolic potassium hydroxide and yielded a solid that showed strong hydroxyl and no carbonyl absorption. Recrystallization from methanol and from chloroform gave pure 1,1-diphenyl-2-p-tolylethane-1,2-diol, m.p. 194–196°. Reference 8 reports m.p. 195–196° for this compound (isotopically labeled), but does not report an analysis.

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.85; H, 6.62. Found: C, 82.82; H, 6.76.

(20) E. Campaigne and B. F. Tullar, *Org. Syntheses*, **33**, 96 (1953).

(21) D. A. Shirley, "Preparation of Organic Intermediates," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 286.

(22) H. Adkins and W. Zartman, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 606.

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Rearrangement of 1,1-Diphenyl-2-p-tolylethylene Oxide. —A solution of lithium diethylamide in ether–benzene under nitrogen was prepared by adding 2.20 g. (0.030 mole) of diethylamine in 25 ml. of benzene to 0.0282 mole of butyllithium in 30 ml. of ether. The solution was stirred at room temperature for 5 minutes to ensure complete reaction. A solution of 4.00 g. (0.0140 mole) of the oxide in 25 ml. of benzene was added and rinsed into the flask with an additional 25-ml. portion of benzene. The solution was heated at 35° for 2 hours, and then the temperature was raised to 75° by allowing ether to distil. The mixture was kept at 75° overnight (18 hours heating in all). Water was added, and the layers were separated. The ether layer was washed with ammonium chloride solution until the washings had pH 6. The organic layer was dried over calcium sulfate and concentrated under reduced pressure. A brown, viscous residue was obtained (4.20 g.) with an infrared spectrum showing the presence of carbonyl (5.89 μ, medium) and hydroxyl (2.73 μ, weak) functions.

The residue was taken up in 40 ml. of hexane (0.20 g. failed to dissolve) and chromatographed on 100 g. of neutral alumina. Material eluted with 20% benzene in hexane weighed 1.809 g. and still showed carbonyl absorption. A second fraction eluted with 50% benzene in hexane weighed 0.698 g. The crude material (fraction 2) melted at 83–95°. After recrystallization from hexane and from methanol the melting point was raised to 101–102°, and a mixed melting point with benzhydryl p-tolyl ketone was 100–102°; with 2-phenyl-2-p-tolylacetophenone, 70–79°. The infrared spectra of both the crude and the purified ketone fractions were identical with that of benzhydryl p-tolyl ketone and different from the spectrum of the isomeric ketone. A third fraction was eluted from the column with ether. This fraction (0.700 g., 18% yield, 23% conversion) was recrystallized twice from ethyl acetate–hexane and melted at 132.0–133.5°. Its infrared spectrum indicated the presence of a hydroxyl group (2.73 μ) but no carbonyl group.

This compound (2,2-diphenyl-1-p-tolylethanol) was identical in melting point, mixed melting point and infrared spectrum with the alcohol prepared by reduction of benzhydryl p-tolyl ketone with lithium aluminum hydride in ether solution, and different from 1,1-diphenyl-2-p-tolylethanol, described above.

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.46; H, 6.99; mol. wt., 258. Found: C, 87.50; H, 6.97; mol. wt., 289 (Rast method in camphor).

The first fraction was rechromatographed on 50 g. of neutral alumina and by elution with 10% benzene in hexane gave 0.918 g. (23%) of the recovered oxide, crude m.p. 60–64°, showing no carbonyl or hydroxyl absorption in the infrared spectrum. Elution with benzene gave 0.548 g. of benzylhydryl p-tolyl ketone, m.p. 93–98°. The total of the ketone fractions was 1.25 g., 31% yield, 41% conversion, (taken together with the recovered oxide and the hydroxylic fraction, 72% of the starting material was collected as solid fractions). The remainder can be accounted for in many small intermediate fractions that failed to solidify.

Acid-catalyzed Rearrangement of 1,1-Diphenyl-2-p-tolylethylene Oxide.—A solution of 1.00 g. of the oxide in 50 ml. of dry ether was treated with 4 ml. of boron trifluoride etherate and allowed to stand at room temperature for 15 minutes. The solution was washed with two 50-ml. portions of water, dried over magnesium sulfate, and concentrated under reduced pressure. The residual oil crystallized from absolute ethanol, giving 0.49 g. (49%) of a product melting at 80.5–81.5°. An analytical sample melted at 81.0–81.5°. This compound showed infrared absorption in the carbonyl region at 5.73 μ, and is diphenyl p-tolylacetaldehyde.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.07; H, 6.47.

Rearrangement of 1,1-Diphenylethylene Oxide and Triphenylethylene Oxide with Boron Trifluoride.—In a manner similar to the one described above, 1.00 g. of 1,1-diphenylethylene oxide was treated with boron trifluoride etherate in anhydrous ether. Diphenylacetaldehyde was isolated as the methone derivative, which was recrystallized from ethanol and gave 1.77 g. (76%) of product, m.p. 208–209°.

Similarly, 1.10 g. of triphenylethylene oxide yielded 0.76 g. (69%) of triphenylacetaldehyde, m.p. 98–102°. One recrystallization from absolute ethanol gave the pure aldehyde, 0.51 g. (46%), m.p. 104–105° (lit.[24] m.p. 105.5°).

(24) S. Danilov, *Zhur. Russ. Fiz. Khim. Obshchestva*, **51**, 97 (1919); *C. A.*, **18**, 1488 (1924).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Proximity Effects. XII. Reaction of *cis-* and *trans*-Cyclooctene Oxide with Bases

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The reaction of *cis*-cyclooctene oxide with the strong bases phenyllithium and lithium diethylamide has been shown to result in the formation of an intramolecular alkylation product, *endo-cis*-bicyclo[3.3.0]octan-2-ol (I) as the major product, and a smaller amount of 2-cycloocten-1-ol (II). The reaction of *trans*-cyclooctene oxide with lithium diethylamide formed cycloheptanecarboxaldehyde, *exo-cis*-bicyclo[3.3.0]octan-2-ol (IV) and 2-cycloocten-1-ol.

The acid-catalyzed solvolysis of cycloheptene oxide[2] and *cis-*[3] and *trans*-cyclooctene oxides[4] and the hydroxylation with performic acid of the nine-,[5] ten-[6] and eleven-membered[7] ring olefins are known to yield products other than the expected *trans*-1,2-glycols. Formation of the abnormal products has been explained as due to a transannular hydride shift for which the conformations of the medium-sized rings may be responsible. In the present paper, we report a different type of transannular reaction that takes place upon treatment of *cis*- and *trans*-cyclooctene oxides with strong bases.

When a mixture of *cis*-cyclooctene oxide and excess lithium diethylamide in ether was refluxed for forty-eight hours, and the products were separated by chromatography on alumina, they were found to be: 5.5% of recovered *cis*-cyclooctene oxide, 69.5% of a liquid alcohol, $C_8H_{13}OH$ (I), 16% of another liquid alcohol, $C_8H_{13}OH$ (II), and 2% of *trans*-1,2-cyclooctanediol, identified as the bis-*p*-nitrobenzoate. The major product I was identified as *endo-cis*-bicyclo[3.3.0]octan-2-ol by comparing its infrared spectrum with the spectrum of an authentic specimen,[8] and by preparation of identical *p*-nitrobenzoates from the two samples. The minor product II was identified by its infrared spectrum and *p*-nitrobenzoate as 2-cycloocten-1-ol.[9]

This conversion of *cis*-cyclooctene oxide into the bicyclic alcohol I and 2-cycloocten-1-ol through reaction with a base was first observed upon treating the oxide with an excess of phenyllithium. The bicyclic alcohol I was isolated in 50% yield, and 2-cycloocten-1-ol in 27% yield. From a reaction mixture in which *cis*-cyclooctene oxide was present in 37% excess over phenyllithium, lower yields of

(1) American Cyanamid Co. Fellow, 1955–1956.
(2) A. C. Cope, T. A. Liss and G. W. Wood, *Chemistry & Industry*, 823 (1956); THIS JOURNAL, **79**, 6287 (1957).
(3) A. C. Cope, S. W. Fenton and C. F. Spencer, *ibid.*, **74**, 5884 (1952).
(4) A. C. Cope, A. Fournier, Jr., and H. E. Simmons, Jr., *ibid.*, **79**, 3905 (1957).
(5) V. Prelog, K. Schenker and W. Küng, *Helv. Chim. Acta*, **36**, 471 (1953).
(6) V. Prelog and K. Schenker, *ibid.*, **35**, 2044 (1952).
(7) V. Prelog and V. Boarland, *ibid.*, **38**, 1776 (1955).
(8) A. C. Cope, M. Brown and H. E. Petree, THIS JOURNAL, **80**, 2852 (1958).
(9) A. C. Cope, M. R. Kinter and R. T. Keller, *ibid.*, **76**, 2757 (1954).

I and II were obtained, 30% of the oxide was recovered and 13% of *trans*-1,2-cyclooctanediol was isolated. In neither case was 2-phenylcyclooctanol found among the products.

A base stronger than sodium ethoxide in ethanol is required for the transannular alkylation reaction leading from *cis*-cyclooctene oxide to I under the conditions that were investigated. When a mixture of *cis*-cyclooctene oxide and sodium ethoxide in absolute ethanol was refluxed for forty-eight hours, the products isolated were 81% of the recovered oxide, 7% of *trans*-1,2-cyclooctanediol and 3% of *trans*-2-ethoxycyclooctanol. The identity of the *trans*-2-ethoxycyclooctanol was established by comparison of its *p*-nitrobenzoate with the corresponding derivative obtained from an authentic sample prepared from the monosodium salt of *trans*-1,2-cyclooctanediol and ethyl iodide.

From the reaction of *trans*-cyclooctene oxide with lithium diethylamide, there was isolated 32% of cycloheptanecarboxaldehyde (III), identified as the 2,4-dinitrophenylhydrazone and semicarbazone. In addition there was isolated 68% of a mixture of liquid alcohols, with an infrared spectrum indicating that it contained 2-cycloocten-1-ol and an alcohol of unknown structure. A *p*-nitrobenzoate prepared from the mixture was shown by mixed melting point to be the *p*-nitrobenzoate of *exo-cis*-bicyclo[3.3.0]octan-2-ol (IV).[8] Indirect separation of the mixture of II and IV was effected by treatment with phenyl isocyanate to form a mixture of phenylurethans, which was then ozonized. The ozonization product was treated with sodium borohydride and then with phenyl isocyanate. Chromatography on alumina of the mixture of phenylurethans that was formed separated as the major component the phenylurethan of *exo-cis*-bicyclo[3.3.0]octan-2-ol, identified by mixed melting point and comparison of the infrared spectrum with the spectrum of an authentic sample.[8] The minor component was similarly identified as 1,2,8-octanetriol tris-phenylurethan.[10] Based on this separation, the yields of II and IV from the reaction of *trans*-cyclooctene oxide with lithium diethylamide are calculated to be 10–15% and 55–60%, respectively.

(10) A. C. Cope and G. W. Wood, *ibid.*, **79**, 3885 (1957).