0.1%. It therefore appears that the X-rays have little effect in promoting the decomposition of diazomethane in benzene solution. Furthermore, the maximum possible *G*-value for "carbene" formation appears to be not greater than 1.

TABLE I

RESULTS OF VISIBLE AND ULTRAVIOLET LIGHT IRRADIATIONS OF SOLUTIONS OF DIAZOMETHANE-C^{14} IN BENZENE

	Sunlamp	Ultraviolet lamp
Percentages of total activity		
$C^{14}H_2N_2$-C_6H_6 soln., before irrad.	100	100
$C^{14}H_2N_2$-C_6H_6 soln., after irrad.	82	83
Residue after removal of C_6H_6	66	67
Cycloheptatriene/toluene ratio	3.5	3.5
Sp. act. cycloheptatriene, dis./min./mmole $\times 10^{-5}$	9.4	9.4
Sp. act. toluene, dis./min./mmole $\times 10^{-5}$	9.3	9.3
Toluene decarboxylation		
Sp. act. toluene (after diln.), dis./min./mmole $\times 10^{-5}$	1.43	1.04
Sp. act. benzoic acid, dis./min./mmole $\times 10^{-5}$	1.42	1.04
Sp. act. CO_2, dis./min./mmole $\times 10^{-5}$	1.39	1.01
Sp. act. benzene, dis./min./mmole $\times 10^{-2}$	<2.0	<1.5
C^{14} in methyl group, %	>99.8	>99.8
C^{14} in ring, %	< 0.2	< 0.2

Table I presents the results obtained from typical experiments using either the sun lamps or the ultraviolet lamp. With both types of irradiation the yields, based on diazomethane, of cycloheptatriene and toluene were approximately 30 and 8%, respectively. The data were obtained from 600 ml. of a 0.25 *M* solution of diazomethane in benzene. This solution was divided into two equal parts for the two irradiations, which were performed concurrently. The data of Table I show no significant differences between the visible and ultraviolet light irradiations.

The loss of about 18% of the radioactivity during the irradiations probably reflects a combination of "carbene" radicals to form ethylene and other low molecular weight hydrocarbons. More of this volatile material was removed during the benzene distillation, the bulk of it coming over in the first 50–100 ml. Gas chromatography (on polyethylene oxide) of the distilled benzene showed the presence of at least two compounds (probably polymers of "carbene") with retention times less than that of benzene. The same compounds appear to be present in both types of irradiations. No compounds other than toluene and cycloheptatriene were detectable (gas chromatography) after the removal of the benzene, *i.e.*, of all compounds boiling below 80°.

In the ultraviolet irradiations reported here, the "carbene" from the photolyzed diazomethane may have an imparted energy as high as 6 e.v. (corresponding to the radiation of around 2000 Å. transmitted through the quartz). Such an energy appears to be not high enough to permit the "carbene" to accomplish what a recoiling C^{14} atom, or radical, can accomplish—namely, to introduce activity into the benzene ring of toluene. These experiments therefore indicate a lower limit of energy, *i.e.*, the recoiling C^{14}-species probably has a kinetic energy above 6 e.v. when it interacts "chemically" with benzene.

BERKELEY 4, CALIF.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

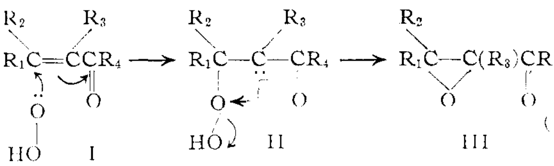
Overlap Control of Carbanionoid Reactions. I. Stereoselectivity in Alkaline Epoxidation

BY HOWARD E. ZIMMERMAN, LAWRENCE SINGER AND B. S. THYAGARAJAN

RECEIVED JULY 25, 1958

The alkaline epoxidation reaction of unsaturated carbonyl compounds has been found to be highly stereoselective. The energy of the carbanionic intermediate and that of the derived transition state is less responsive to ordinary steric interactions than to those diminishing electron delocalization. Overlap control favors the epoxide product with the unhindered carbonyl group. Thus epoxidation of α-phenylbenzalactone leads to the product with the large phenyl groups *cis* and the smaller acetyl group unhindered. The contrasting situation of epoxidation of α-phenylcinnamaldehyde, with an acyl group which can be planar even when *cis* to phenyl, and that of α-phenylcinnamonitrile, whose axially symmetric nitrile function has no conformational requirement, is discussed.

The epoxidation of polarized double bond compounds with alkaline hydrogen peroxide was first reported by Weitz and Scheffer[1] in 1921 and ever since this time has been the object of continued synthetic and mechanistic interest. In 1949, this mechanism was advanced by Bunton and Minkoff[2].



(1)

At first glance it might appear that the reaction, due to the intervention of the carbanionic intermediate II, would lead inevitably and prosaically to the more stable of the two possible stereoisomeric products. The literature affords little support for any other conclusion.

Thus the epoxidation reactions of known stereochemistry listed in Table I lead, with one exception,

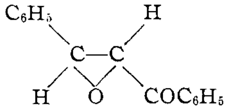
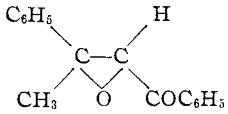
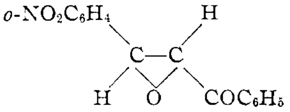
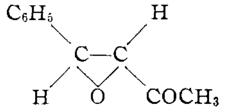
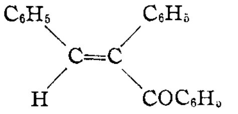
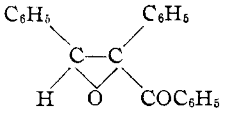
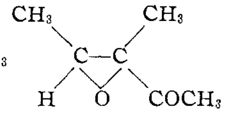
---

Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921).

(2) C. A. Bunton and G. J. Minkoff, *J. Chem. Soc.*, 665 (1949).

unambiguously to the stereoisomer with bulky groups *trans*. This accords with the observation of Cromwell and Setterquist[3] that the reaction seems to yield the *trans* product.

TABLE I

Reactant	Product	References
cis- or *trans*-$C_6H_5CH{=}CHCOC_6H_5$		4
trans-$C_6H_5C(CH_3){=}CHCOC_6H_5$		5
trans-*o*-$NO_2C_6H_4CH{=}CHCOC_6H_5$		3
trans-$C_6H_5CH{=}CHCOCH_3$		6
		7
cis- or *trans*-$CH_3CH{=}C(CH_3)COCH_3$		8

Furthermore, the finding of Lutz and co-workers[4] that both *cis*- and *trans*-benzalacetophenone afford the same stereoisomeric epoxide, the observation of Wasserman, Aubrey and Zimmerman[5] that *cis*-dypnone oxide accompanies the major *trans* epoxidation product, the recent description by House[8] of the formation of *trans*-epoxide from both stereoisomers of 3-methyl-3-penten-2-one—all[9] demonstrate, as has been pointed out by these three groups, the non-stereospecificity of the alkaline epoxidation reaction.

However, as has been intimated (*vide supra*) the literature affords one example which is not unambiguously in accord with the view that the reaction geometry is controlled by purely steric factors alone; this is the epoxidation of α-phenyl-*trans*-benzalacetophenone[7] to yield the stereoisomer with phenyl groups *cis*. Inspection of models and independent evidence[10] suggest that this is the isomer with larger groups *cis* and should exhibit slightly greater steric interaction than the stereoisomer with phenyl and benzoyl groups *cis*.

With the intent of resolving the intriguing problem of the stereochemistry of alkaline epoxidation, it was decided to investigate the alkaline epoxidation of some α-phenyl substituted polarized double bond compounds in which the delocalizing group was smaller than benzoyl and hence unambiguously smaller than phenyl. Thus our investigation began with a study of the stereochemistry of epoxidation of α-phenylbenzalacetone.

Necessary for this study were syntheses of the two possible epoxidation products and proof of their configurations. These syntheses began with the known[11] 56° isomer of α-phenylbenzalacetone and its stereoisomer, m.p. 66°, which was obtained by irradiation of the 56° compound.

That the 56° compound was α-phenyl-*trans*-benzalacetone (IVa)[12] while the 66° compound was α-phenyl-*cis*-benzalacetone (IVb) was demonstrated by relating the 56° isomer configurationally to α-phenyl-*trans*-cinnamic acid, m.p. 174°, whose configuration has been firmly established[13]; the details are depicted in Chart I and given in the Experimental section.[14]

Their configurations having been established, each of the stereoisomeric α-phenylbenzalacetones (IVa and IVb) was converted, as illustrated in Chart I, to the corresponding stereoisomer of 3,4-diphenyl-3,4-epoxybutan-2-one (IXa and IXb, resp.) using the stereospecific process first utilized by Wasserman and Aubrey[5]; the method depends on the facile and stereospecific epoxidation of the double bond by peracids once conjugation with the electron-withdrawing carbonyl group is destroyed by reduction.

The configurations of the possible products of alkaline epoxidation having been determined, it was possible to proceed with consideration of the alkaline epoxidation reaction itself. On treatment with alkaline hydrogen peroxide IVa led exclusively to 3,4-*cis*-diphenyl-3,4-epoxybutan-2-one (IXa). Neither the infrared spectrum of the crude product nor partition chromatography revealed any trace of

---

(3) N. H. Cromwell and R. A. Setterquist, THIS JOURNAL, **76**, 5752 (1954).

(4) The proof of configuration of the product is the work of H. H. Wasserman and N. E. Aubrey, *ibid.*, **77**, 590 (1955). That both stereoisomeric unsaturated ketones give the same product has been shown by Lutz and co-workers: R. E. Lutz and J. O. Weiss, *ibid.*, **77**, 1814 (1955); C. R. Bauer and R. E. Lutz, *ibid.*, **75**, 5995 (1953).

(5) H. H. Wasserman, N. E. Aubrey and H. E. Zimmerman, *ibid.*, **75**, 96 (1953); H. H. Wasserman and N. E. Aubrey, ref. 4.

(6) The 52° compound obtained from the alkaline epoxidation by Weitz and Scheffer (ref. 1) would appear to be the 56° epoxide shown in an unrelated study by H. Kwart and L. Kirk, *J. Org. Chem.*, **22**, 116 (1956), to be *trans*.

(7) The 116° compound of W. B. Black and R. E. Lutz, THIS JOURNAL, **75**, 5990 (1953), has been shown by H. O. House and D. J. Reif, *ibid.*, **77**, 6525 (1955), to have the indicated configuration.

(8) H. O. House and R. S. Ro, *ibid.*, **80**, 2428 (1958).

(9) The lack of stereospecificity has been shown by Lutz and co-workers[7] not to be due to a hydroxide-catalyzed isomerization of *cis* to *trans* reactant. House[8] has demonstrated a reversible addition of hydroperoxide anion with a slow subsequent ring closure of intermediate II.

(10) Unpublished results of H. E. Zimmerman with W. H. Chang. It must be recognized, however, that the effective bulk of groups is dependent on the molecular environment and hence that the relative size of closely similar groups as phenyl and benzoyl, deduced for one molecule may not completely validly be extrapolated to a second system.

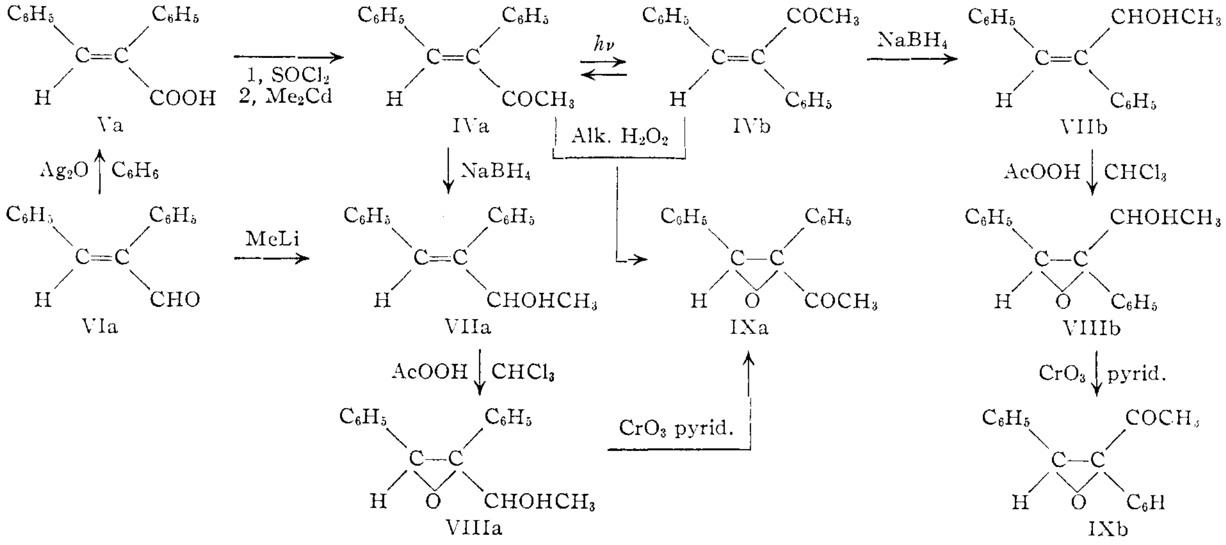
(11) A. Dornow and F. Boberg, *Ann.*, **578**, 112 (1952).

(12) The formation of the isomers with *cis*-phenyl groups in the condensations of benzaldehyde with phenylacetone and with phenylacetaldehyde has analogy in the formation of α-phenyl-*trans*-cinnamic acid in the Perkin reaction. The stereochemistry of this reaction is known to result from overlap control; these results of one of us with L. Ahramjian will be discussed in a forthcoming publication.

(13) R. Stoermer and co-workers, *Ann.*, **409**, 15 (1915), and immediately succeeding papers; *cf.* also L. Crombie, *Quart. Revs.*, **6**, 135 (1952).

(14) Also supporting this configurational assignment is the longer wave length carbonyl absorption in the infrared of isomer IVa, in which coplanarity and hence conjugation of the acetyl group with the double bond is readily achieved. Similarly, IVa absorbs at a longer wave length in the ultraviolet. See the Experimental section for details.

Chart I



the *trans* isomer IXb. Alkaline epoxidation of IVb also proceeded[15] completely stereoselectively[16] to IXa. Thus our suspicion that some factor other than ordinary steric repulsions governs the reaction was confirmed. Had avoidance of large groups in ring closure been controlling, the product with *trans*-phenyl groups would have been observed.

It is proposed that the formation of the stereoisomer with *cis*-phenyl groups but an unhindered carbonyl group is due to overlap control in the epoxidation transition state, an effect deriving from diminution of electron delocalization as a consequence of steric interaction between a large *cis* group and a delocalizing function having a conformational requirement for overlap, such as acetyl.

This may be understood as follows: Not only intermediate II but also the transition state derived therefrom and leading to product would be of extremely high energy were it not for delocalization of the electron pair and accompanying negative charge.[17] But this delocalization imposes a conformational restriction about the acyl to C-3 bond; maximum overlap of orbitals results only when the acyl group is coplanar with the other two carbon atoms (C-4 and phenyl carbon one) bonded to C-3. Should the acetyl group be forced 90° out of the preferred plane by a large *cis* group the transition state energy would be raised *ca.* 28 kcal./mole; less drastic interaction of the acetyl group with a *cis* group could still lead to an appreciable increase in transition state energy. It may be seen that these effects are more serious energetically than ordinary van der Waals repulsive forces.[18]

The two alternative transition states are pictured in Fig. 1, Xa (R = CH$_3$) leading to 2,3-*cis*-diphenyl-2,3-epoxybutan-2-one (IXa) and Xb (R = CH$_3$) leading to 2,3-*trans*-2,3-epoxybutan-2-one (IXb). Transition state Xa suffers only ordinary steric interaction between *cis*-phenyl groups and this may be minimized by assumption of the best conformations about the C–phenyl bonds. On the other hand, transition state Xb is confronted with mutually incompatible demands, one for electron delocalization, satisfied by coplanarity as pictured for Xb′, and the other for avoidance of serious van der Waals repulsions, satisfied by a non-coplanar conformation about the acyl–C-3 bond as pictured for Xb″. Thus it is not surprising that the transition state energy is more sensitive to interaction by *cis*-phenyl and acetyl groups than to that between two *cis*-phenyl groups with the result that the preferred transition state is the one (Xa) with phenyl groups *cis* but having an unhindered acetyl group.

The conclusion that alkaline epoxidation is overlap controlled not only rationalizes the presently described epoxidation of α-phenylbenzalacetone but also is compatible with the literature, for in every case the preferred product is the one with the less hindered acyl group.

Nevertheless, it seemed desirable to obtain further evidence bearing on the proposed mechanism. It was decided to study the reaction stereochemistry where the delocalizing group was the formyl or the nitrile function. In the first case coplanarity would be expected to be attained more readily than with acetyl due to the smaller size of formyl. Where

---

(15) It has been elegantly demonstrated by Lutz and co-workers (ref. 7a) that Michael addition may occur only where coplanarity of the unsaturated carbonyl system is possible. House (ref. 7b) has found this true of the alkaline epoxidation reaction where Michael addition of hydroperoxide is a requisite. He found that α-phenyl-*cis*-benzalacetophenone was completely unreactive. In the present work it is clear that hindrance to coplanarity is less severe.

(16) It seems desirable to distinguish between the terms "stereospecific" and "stereoselective." A stereospecific process is one in which the configuration of the product is related to that of the reactant; the relationship may be one of retention of the original configuration or one of reversal. A reaction in which a different distribution of products is obtained from the different reactants would be said to be only partially stereospecific. A stereoselective process is one in which there is no relationship between the configuration of the reactant and that of product but one in which there is a definite driving force for forming one of the possible stereoisomeric products. Thus alkaline epoxidation is not stereospecific but may, as in the case of epoxidation of IVa and IVb, be highly stereoselective.

(17) *Cf.* the *ca.* 28 kcal./mole difference in free energy of ionization of acetone (pK_a 20) *versus* methane (pK_a 40).

(18) An upper limit on the magnitude of the van der Waals *cis* effect of two phenyl groups is 5.7 kcal./mole, the total energy difference reported by R. B. Williams, This Journal, **64**, 1395 (1942), between *cis*- and *trans*-stilbene; this, however, includes a sizable difference in resonance energies.

the delocalizing group was the axially symmetric nitrile function there is no conformational requirement for overlap and delocalization should be possible even where this group is badly hindered by an adjacent phenyl substituent. Thus the concept of overlap control would admit as possible but not require the formation of the epoxyaldehyde stereoisomer having the hindered formyl group; and more definitively, it would predict the formation of the epoxynitrile stereoisomer having the hindered nitrile function but phenyl groups *trans*, since the unsaturated nitrile epoxidation would not be subject to overlap control.

For the study utilizing formyl as the electron-delocalizing group, α-phenylcinnamaldehyde was required. Only one isomer, m.p. 95°, seems to have been reported in the literature, this being most conveniently prepared from the base-catalyzed condensation of benzaldehyde and phenylacetaldehyde.[19] The 95° compound was found to be oxidized by either silver oxide in benzene or chromic anhydride in acetic acid to yield (Chart I) α-phenyl-*trans*-cinnamic acid and hence is α-phenyl-*trans*-cinnamaldehyde (VIa).[12] Also, this compound was converted stereospecifically (Chart II) to 2,3-*cis*-diphenyl-2,3-epoxypropan-1-ol (XIIa) of m.p. 119°, thus establishing the configuration of this latter compound.

Alkaline epoxidation of α-phenyl-*trans*-cinnamaldehyde under mild conditions afforded one stereoisomer of 2,3-diphenyl-2,3-epoxypropanal. To establish the configuration of this compound it was reduced with sodium borohydride; this afforded a stereoisomer which is different from XIIa and which must therefore be 2,3-*trans*-diphenyl-2,3-epoxypropan-1-ol (XIIb). This configurational assignment was checked by a stereospecific synthesis (Chart II) from the known α-phenyl-*cis*-cinnamic acid. Thus, the alkaline epoxidation product,[20] being the precursor to XIIb, must be 2,3-*trans*-diphenyl-2,3-epoxypropanal (XIIIb). Hence, where the very small formyl group is employed, electron delocalization must not be appreciably diminished by phenyl–formyl interaction with the consequence that avoidance of phenyl–phenyl interaction becomes dominant and transition state Xb′ (R = H) is of lower energy than Xa. Inspection of models does indicate a marked difference in phenyl–acyl interaction in transition state Xb′ depending on whether R is methyl or hydrogen.[21]

As a further test of these concepts it was of interest to consider the alkaline epoxidation of α-phenylcinnamonitrile. The axially symmetric nitrile function possesses no conformational requirement for overlap; therefore, overlap control should not be operative and the isomer with phenyl groups *trans* should result.

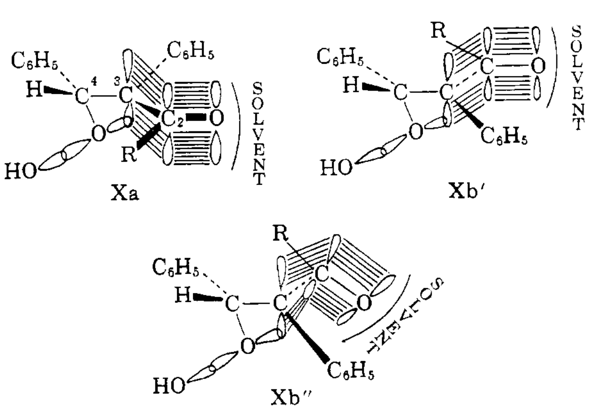


Fig. 1.

A survey of the literature revealed that the alkaline epoxidation of α-phenyl-*cis*-cinnamonitrile had been reported[22] to afford one isomer of 2,3-diphenyl-2,3-epoxypropionamide of melting point 204°; we have confirmed this finding. Our attempts to obtain an intermediate epoxynitrile or unsaturated amide by using milder reaction conditions led only to a mixture of starting material and epoxyamide.

This isomer of 2,3-diphenyl-2,3-epoxypropionamide and its stereoisomer melting at 124° had been reported by Kohler and Brown.[23] The 204° amide had been configurationally related to the 90° isomer of 2,3-diphenyl-2,3-epoxypropionic acid while the 124° amide was shown to be derived from the 121° isomer of 2,3-diphenyl-2,3-epoxypropionic acid, the latter being more readily available[24,25] from saponification of the product of the Darzens condensation of benzaldehyde with ethyl α-chlorophenylacetate or bromophenylacetate. Since in the present research the 121° acid has been configurationally related, as indicated in Chart II, to 2,3-*cis*-diphenyl-2,3-epoxypropan-1-ol (XIIa), this isomer of the acid must be 2,3-*cis*-diphenyl-2,3-epoxypropionic acid (XVIIa),[26] and the 204° amide must be the 2,3-*trans*-diphenyl-2,3-epoxypropionamide (XVb).

Thus the epoxidation of α-phenyl-*cis*-cinnamonitrile had led to the product with *trans*-phenyl groups as had been expected (*vide supra*). This expectation, however, was based on the assumption it was indeed the unsaturated nitrile which was being epoxidized and not an initially formed unsaturated amide. That epoxidation does precede hydrolysis may be seen as follows.

There are, *a priori*, two possible reaction routes, A and B as indicated in Chart III. Route A involves epoxidation followed by hydrolysis while in route B hydrolysis precedes epoxidation. The

---

[19] K. Alder, *et al.*, *Ann.*, **586**, 128 (1954), and earlier references cited therein. A compound melting at 84° and having this structure has been reported by Ruzicka, *C. A.*, **42**, 4200 (1948), U. S. Patent 2,435,018; due to insufficient information it is not clear whether this is the second isomer.

[20] Although XIIIb was the only isomer to be found, the formation and selective destruction by oxidation of small amounts of its stereoisomer during alkaline epoxidation cannot be excluded. Similarly, in the alkaline epoxidation of *cis*- and *trans*-α-phenyl-benzalacetone, the isolation of only 2,3-*cis*-diphenyl-2,3-epoxybutan-2-one (IXa) might conceivably be due to the selective destruction of its stereoisomer. However, the selective destruction of the *trans* product in one system and the destruction of the *cis* product in the other seems unlikely.

[21] Here and in Fig. 1 it is assumed that the oxygen atom, bearing a partial negative charge, is solvated and that of the two planar conformations of the acyl group, the one having the more accessible oxygen atom is favored.

[22] J. V. Murray and J. B. Cloke, THIS JOURNAL, **56**, 2749 (1934).

[23] E. P. Kohler and F. W. Brown, *ibid.*, **55**, 4299 (1933).

[24] F. Blicke, J. Faust and H. Raffelson, *ibid.*, **76**, 3161 (19 4).

[25] H. H. Morris, R. H. Young, Jr., C. Hess and T. Sottery, *ibid.*, **79**, 411 (1957).

[26] Thus the Darzens condensation leads to the product with the phenyl groups *cis*, an interesting result which will be discussed in another publication.

CHART II

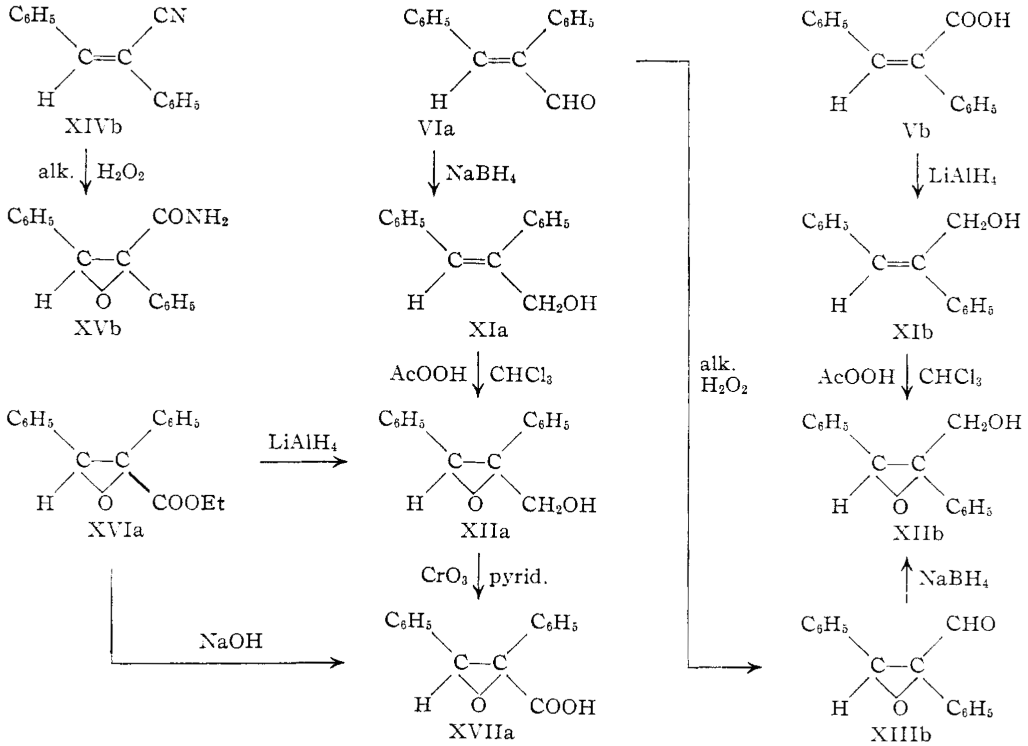
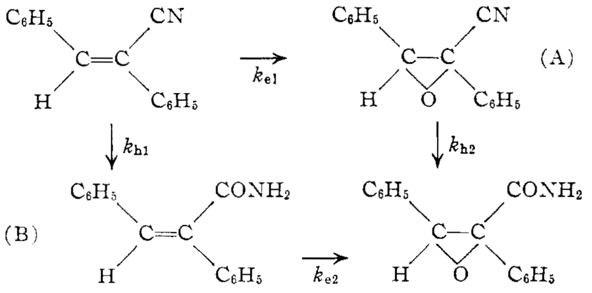


CHART III



information bearing on this problem falls into three categories: that defining the route preference, that bearing on certain relative rates and based on theoretical considerations and finally that derived from the experimental observation that under mild conditions only unsaturated amide starting material and epoxyamide product are present. This information is summarized in Table II. Only the second entry requires comment; this conclusion derives from the expectation that the rate of alkaline epoxidation of an unsaturated amide will be slower than that of the corresponding unsaturated nitrile, since in proceeding from the ground to the transition state, the electron density on the carbon alpha to the stabilizing group increases, and cyano is better able to stabilize this charge than carboxamide.

TABLE II

	Conclusion from route preference	Theoretical conclusions	Conclusion from experiment; non-isolability of intermediate
Route A	$k_{e1} > k_{h1}$	$k_{e1} > k_{e2}$	$k_{h2} > k_{e1}$
Route B	$k_{h1} > k_{e1}$	$k_{e1} > k_{e2}$	$k_{e2} > k_{h1}$

Inspection of Table II reveals that the conclusions which must be drawn if route B is correct are mutually incompatible while those for route A are not. Thus epoxidation of α-phenyl-*cis*-cinnamonitrile to yield the epoxynitrile with *trans*-phenyl groups occurred prior to hydrolysis of nitrile to amide.

Before proceeding to a final discussion of the stereoselectivity of epoxidation it should be noted that the present research provides further support for the lack of stereospecificity. While the epoxidation of α-phenyl-*cis*-cinnamonitrile led to product of the same configuration, the epoxidation of α-phenyl-*trans*-cinnamaldehyde afforded product with the reverse configuration and both isomers of α-phenylbenzalacetone afforded one stereoisomer, thus indicating that the reaction stereochemistry is controlled by factors other than retention of the original configuration.

Thus in the alkaline epoxidation of the polarized double bond compounds comprising the series $C_6H_5CH{=}CC_6H_5COC_6H_5$, $C_6H_5CH{=}CC_6H_5COCH_3$, $C_6H_5CH{=}CC_6H_5CHO$, $C_6H_5CH{=}CC_6H_5CN$, overlap control is dominant for the first two members of the series, the necessity for a planar carbonyl group outweighing the tendency for avoidance of van der Waals interactions. For the last two members of the series, overlap is not a problem; in the cases of the formyl group, with only a small hydrogen atom projecting toward the vicinal group, and the axially symmetric nitrile function, with no conformational requirement for overlap, overlap suffers negligible interference by a *cis* vicinal group with the result that a *trans* orientation of phenyl groups ensues.

Experimental[27]

α-Phenyl-*trans*-benzalacetone.—A mixture of 22.4 g. of α-phenyl-*trans*-cinnamic acid, m.p. 174.0–175.0°, and 20.0

---

[27] All melting points were taken on a Fisher–Johns block checked with compounds of known melting point.

g. of thionyl chloride in 200 ml. of anhydrous benzene was refluxed for 4 hr. The benzene and excess thionyl chloride were distilled off and the residue treated once more with 200 ml. of anhydrous benzene which was then distilled off to remove traces of thionyl chloride.

To a solution of methylmagnesium iodide in benzene, prepared in ether from 4.90 g. of magnesium and 30.0 g. of methyl iodide followed by addition of 100 ml. of anhydrous benzene and distillation of the ether, was added 19.6 g. of anhydrous cadmium chloride. The mixture was then stirred and refluxed for 0.5 hour. To this was then added a solution of the α-phenyl-*trans*-cinnamoyl chloride, prepared as described above, in 100 ml. of anhydrous benzene; the reaction was somewhat exothermic and addition was made at such a rate to maintain steady reflux. The mixture was then refluxed for an additional 30 min. During this time an insoluble complex formed which made stirring difficult. Then the mixture was decomposed with a mixture of ice and 50% sulfuric acid followed by ether extraction. The extracts were washed with water, dried over sodium sulfate and concentrated *in vacuo*. The residue solidified partially; treatment with 95% ethanol and filtration afforded 7.0 g. of yellow solid. This on recrystallization from ethanol melted at 169°; the infrared spectrum showed no carbonyl absorption. The combined filtrates were concentrated and the residue distilled *in vacuo* to give a pale yellow oil, b.p. 136–141° at 0.2–0.3 mm., and weighing 3.8 g. The oil crystallized on standing. Recrystallization from ether–pentane with strong cooling afforded a pale yellow solid melting at 55.0–56.0°. The infrared spectrum run in CS_2 possessed a doublet at 5.92 and 5.98 μ. The ultraviolet spectrum exhibited maxima at 226.5 mμ (log ε 3.22) and at 295 mμ (4.44) in 95% ethanol.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.48; H, 6.31. Found: C, 86.71; H, 6.34.

α-Phenyl-*trans*-benzalacetone from Benzaldehyde and Phenylacetone.—The following is essentially the method of Dornow and Boberg,[11] the details of which are given to corroborate the isolation of one isomer in good yield. A mixture of 19.5 g. of phenylacetone, 15.4 g. of benzaldehyde and 0.3 g. of piperidine in 100 ml. of anhydrous benzene was refluxed using a Dean and Stark water separator. At the end of 12 hr., 2.2 ml. of water had been collected. The reaction mixture was then concentrated *in vacuo* and distilled to give 26.0 g. of product boiling at 135° at 0.9 mm. and solidifying to α-phenyl-*trans*-benzalacetone of m.p. 55.0–56.0° and identical with the product of the previous preparation (reported[11] 56°).

3,4-*cis*-Diphenylbut-3-ene-2-ol.—To 4.0 g. of α-phenyl-*trans*-benzalacetone, m.p. 55.0–56.0°, in 40 ml. of methanol was added 0.75 g. of sodium borohydride with cooling to room temperature with an ice-bath. The mixture was stirred magnetically for 15 min., diluted with water and heated on the steam-bath for 5 min. This was then cooled and ether extracted. The extracts were dried over sodium sulfate and concentrated under vacuum. The residue was distilled to give 3.8 g. of 3,4-*cis*-diphenylbut-3-ene-2-ol as a viscous oil, b.p. 139° at 0.5 mm. The infrared spectrum showed the absence of carbonyl absorption and a strong O–H stretching band.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 86.09; H, 6.95.

3,4-*cis*-Diphenylbut-3-ene-2-ol from the Reaction of Methyllithium with α-Phenyl-*trans*-cinnamaldehyde.—To 0.28 g. of lithium metal cut in small pieces and placed in a 100-ml. flask equipped with magnetic stirrer, dropping funnel, reflux condenser and sodium hydroxide drying tube was added first 30 ml. of anhydrous ether followed by a solution of 2.84 g. of methyl iodide in 12 ml. of dry ether, the latter addition being made with stirring over one hour. The mixture then was stirred and refluxed in a nitrogen atmosphere for an additional hour. To the stirred solution of methyllithium was then added a solution of 4.16 g. of α-phenyl-*trans*-cinnamaldehyde in 40 ml. of dry ether at a rate to maintain steady refluxing without external heating. The reaction mixture was then stirred and refluxed for an additional 90 min. The mixture was decomposed by pouring into a cold and saturated solution of ammonium chloride. The product was extracted with ether and the extracts were dried over sodium sulfate and concentrated *in vacuo*. The residue was distilled to give a colorless oil boiling at 139° at 0.5 mm. and whose infrared spectrum was identical with that of 3,4-*cis*-diphenyl-but-3-ene-2-ol by the sodium borohydride reduction of the corresponding ketone; yield 4.17 g.

3,4-*cis*-Diphenyl-3,4-epoxybutan-2-one.—To 4.2 g. of α-phenyl-*trans*-benzalacetone dissolved in 140 ml. of methanol was added 21.0 ml. of 30% hydrogen peroxide and 7.0 ml. of 10% sodium hydroxide solution. The mixture was allowed to stand at room temperature for 6 hr. It was then diluted with an equal volume of water, saturated with sodium chloride and thoroughly ether extracted. The extract was washed with sodium thiosulfate solution and dried over sodium sulfate. The extracts were then concentrated to leave 2.5 g. of oil, whose infrared spectrum was that of 3,4-*cis*-diphenyl-3,4-epoxybutan-2-one and showed no trace of the *trans* isomer.

Chromatography on silica gel was found to cause decomposition. However, chromatography was successful with a silica gel column (Davidson, 60–200 mesh) packed using 10% ether in hexane solution saturated with ethylene glycol. The 500 × 15 mm. column was slurry packed and 50-ml. fractions were obtained by elution with the same solvent. Fractions 1 and 2 contained no material; fractions 3 and 4 contained a total of 130 mg. of pale yellow oil. Fraction 5 weighed 0.52 g.; fraction 6, 0.66 g.; fraction 7, 0.41 g.; fraction 8, 0.22 g.; fraction 9, 75 mg.; fraction 10, 60 mg.; fraction 11, nil. Elution with ether afforded no more material. Fractions 5 through 10 were colorless oils which solidified and melted in the range 60–63°; these were combined, the total weight being 1.9 g. Recrystallization from aqueous methanol yielded 1.3 g. of colorless needles melting at 64.0–64.5°. Further crystallization did not change the melting point.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.67; H, 5.88. Found: C, 80.59, 80.82; H, 5.94, 6.01.

Epoxidation of 3,4-*cis*-Diphenylbut-3-ene-2-ol.—To 2.16 g. of the 3,4-*cis*-diphenylbut-3-ene-2-ol dissolved in 50 ml. of chloroform were added 0.05 g. of sodium acetate and 0.57 g. of (Becco) 40% peracetic acid in acetic acid. The mixture was kept at room temperature for 4 hr., then diluted with water and extracted with ether. The extract was washed with sodium thiosulfate and then washed with water and dried over sodium sulfate. Concentration *in vacuo* left a residue which crystallized. Recrystallization from aqueous methanol afforded 1.2 g. of colorless needles, m.p. 98.0–99.9°.

Chromium Trioxide–Pyridine Oxidation of 3,4-*cis*-Diphenyl-3,4-epoxybutan-2-ol.—The method of Wasserman and Aubrey[4] for conversion of epoxyalcohols to epoxyketones by means of Sarett's complex[28] was used. To 15.0 ml. of pyridine which had been dried over KOH and distilled and then cooled to 0–5° was added slowly 0.95 g. of chromium trioxide with stirring and cooling below 10°. During 30 min. the yellow complex separated out. To the mixture was added at 0–5° a solution of 1.0 g. of 3,4-*cis*-diphenyl-3,4-epoxybutan-2-ol, prepared as described above, in 15 ml. of dry pyridine. Then the mixture was allowed to stir at room temperature overnight. Following this the reaction mixture was diluted with 100 ml. of ether and filtered free of some dark brown solid. The filtrate was washed first with water, then with dilute hydrochloric acid, dilute sodium carbonate solution and finally with water. The extract was then dried over sodium sulfate and concentrated *in vacuo* to leave an oil which solidified. Recrystallization of this from methanol–water gave 0.6 g. of colorless needles, m.p. 64.0–64.5°. There was no melting point depression with the 3,4-*cis*-diphenyl-3,4-epoxybutan-2-one obtained by the alkaline epoxidation reaction. Similarly, the infrared spectra were indistinguishable.

α-Phenyl-*cis*-benzalacetone.—A solution of 10.0 g. of α-phenyl-*trans*-benzalacetone in 30 ml. of hexane was irradiated for 12 hr. with a Hanovia-type immersion mercury discharge lamp; the solution was heated throughout to *ca.* 50° to prevent crystallization of the solute. The solution was then concentrated *in vacuo* leaving an oil whose infrared spectrum showed the presence of about 50% of the starting material together with a material whose carbonyl absorption band was at a shorter wave length.

The mixed ketones were dissolved in benzene and chromatographed on a silica gel column (20 × 1000 mm., slurry packed with benzene) by elution with 10% chloroform in benzene. The first 900 ml. of eluent contained only α-phenyl-*cis*-benzalacetone; this weighed 4.0 g. and melted at

---

(28) G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, This Journal, **75**, 422 (1953).

65–66°. Crystallization from pentane–ether brought the m.p. to 65.5–66.0°. No further material was eluted with 10% chloroform in benzene. By elution with chloroform there was obtained 6 g. of starting material, α-phenyl-*trans*-benzalacetone. In another run there was obtained from 4.0 g. of starting material, 1.7 g. of product and 2.2 g. of recovered reactant; the carbonyl band was at 5.86 μ. In the ultraviolet the compound had maxima at 226.5 mμ (log ε 3.08) and 285 mμ (4.44).

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.48; H, 6.31. Found: C, 86.30; H, 6.35.

3,4-*trans*-Diphenylbut-3-ene-2-ol.—The reduction of 4.0 g. of α-phenyl-*cis*-benzalacetone using 0.75 g. of sodium borohydride in 40 ml. of methanol was carried out exactly as described above for reduction of the stereoisomer. The product, weighing 3.1 g., was a colorless oil which was distilled. This boiled at 135° at 0.05 mm.; wt. 3.1 g. The infrared spectrum of this product exhibited marked differences from that of its stereoisomer; for example, this compound absorbed at 10.41 and 11.28 μ while the *cis*-diphenyl compound exhibited maxima at 10.30, 11.21, 13.20 and 13.60 μ (CS_2).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 85.62; H, 7.09.

Epoxidation of 3,4-*trans*-Diphenylbut-3-ene-2-ol.—A mixture of 3.01 g. of 3,4-*trans*-diphenylbut-3-ene-2-ol, 50 mg. of sodium acetate, 2.20 ml. of 40% peracetic acid (solution in acetic acid) and 50 ml. of chloroform was allowed to stand at room temperature for 4 hr. The mixture was then diluted with ether and washed with water, saturated sodium thiosulfate solution and dried over sodium sulfate. The extracts were then concentrated leaving a residual oil weighing 2.45 g. This material possessed an infrared spectrum which was decidedly different from that of the stereoisomer. It possessed absorption bands at 10.70, 10.93, 11.55 and 13.08 μ, while the *cis*-diphenyl isomer absorbed at 11.40 and 13.19 μ. The reaction product was apparently a mixture of diastereomers and would not crystallize. It was used directly for the next preparation.

2,3-*trans*-Diphenyl-2,3-epoxybutan-2-one.—The product of the previous experiment was dissolved in 30 ml. of anhydrous pyridine and was added to the chromium trioxide–pyridine complex in pyridine prepared from 2.00 g. of chromium trioxide and 30 ml. of pyridine. The mixture was stirred at room temperature for 12 hr. It was then diluted with ether and filtered. The filtrate was washed with water, dilute hydrochloric acid, water, sodium carbonate and finally with water. Concentration of the ether solution left 1.75 g. of an oily residue. This was subjected to chromatography on a 500 × 15 mm. silica gel column packed with 10% ether in hexane, the solution being saturated with ethylene glycol. The column was eluted first with 10% ether in hexane saturated with ethylene glycol and 50-ml. fractions were collected. Fractions 1 and 2 were void. Fractions 3, 4 and 5 contained a total of 0.75 g. of pale yellow oil which solidified. Fractions 6, 7 and 8 contained no material. Elution with 20% ether in hexane, this being saturated with ethylene glycol, was begun starting with fraction 9. This fraction as well as 10 was empty. Fractions 11, 12, 13 and 14 contained a total of 0.50 g. of an oil which solidified. Elution with ether afforded no further material.

The 0.75 g. of solid eluted with the 10% solvent was recrystallized from cold pentane bringing the m.p. to 65.0°. The infrared spectrum showed this to be the stereoisomer of the previously obtained epoxyketone; mixed m.p. with the latter 45°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.67; H, 5.88. Found: C, 80.97; H, 5.82.

The 0.50 g. of solid eluted with the 20% solvent was crystallized from cold pentane bringing the melting point to 74.0–74.5°. The infrared spectrum was essentially that of the starting material. Crystallization resulted, apparently due either to enrichment in one diasteromer or to purification by chromatography.

Alkaline Epoxidation of α-Phenyl-*cis*-benzalacetone.—A solution of 2.00 g. of α-phenyl-*cis*-benzalacetone in 70 ml. of methanol was treated with 10.0 ml. of 30% hydrogen peroxide and a solution of 0.030 g. of sodium hydroxide in 3.0 ml. of water. The mixture was kept at room temperature by cooling in ice-water and then was allowed to stand at room temperature for 6 hr. The mixture now was diluted with water, extracted with ether and the extracts washed with saturated sodium thiosulfate solution. The extracts next were dried over sodium sulfate and concentrated to leave 1.35 g. of an oil whose infrared spectrum was identical to that obtained by alkaline epoxidation of α-phenyl-*trans*-benzalacetone. Minor contamination, however not by the stereoisomer, as indicated by the infrared spectrum, prevented this essentially pure 2,3-*cis*-diphenyl-2,3-epoxybutan-2-one from crystallizing.

α-Phenyl-*trans*-cinnamaldehyde was prepared by the method of Alder[19]; in agreement with this author, no other isomer accompanied the product of m.p. 93.5–95.0° (reported 94°).

Proof of Configuration of α-Phenyl-*trans*-cinnamaldehyde; Chromic Acid Oxidation to α-Phenyl-*trans*-cinnamic Acid.—To an ice-cooled solution of 4.16 g. (0.02 mole) of α-phenyl-*trans*-cinnamaldehyde, m.p. 93.5–95.0°, in 30 ml. of acetic acid was added with stirring a solution of 1.33 g. (0.0133 mole) of chromium trioxide in a mixture of 40 ml. of acetic acid and 10 ml. of water. The temperature was kept at 20° during the addition which required 80 min. The reaction mixture now was allowed to remain at room temperature for 17 hr., at the end of which time the solution was green. The mixture was then diluted with water until there was no further separation of solid. This was taken up in ether and 20% sodium hydroxide solution. The ether phase was dried over sodium sulfate and concentrated *in vacuo*. The neutral fraction weighed 2.5 g., m.p. 80–84°. Crystallization from methanol brought the melting point to 94.5–95.5°, this being recovered starting material. The alkaline aqueous extract was acidified to a congo red end-point with hydrochloric acid and ether extracted. After drying over sodium sulfate the solution was concentrated under vacuum to leave 0.7 g. of solid, m.p. 174.0–174.5°, which showed no mixed melting depression with authentic α-phenyl-*trans*-cinnamic acid.

Oxidation of α-Phenyl-*trans*-cinnamaldehyde with Silver Oxide.—The following is the procedure of Meerwein[29] who reported this conversion without experimental details. Silver oxide was prepared by treating a solution of 1.0 g. (0.02 mole) of silver nitrate in 10.0 ml. of water with 3.0 ml. of 20% aqueous sodium hydroxide solution, filtering the precipitate, followed by washing and drying on the büchner funnel. The still damp silver oxide was added to a solution of 500 mg. of α-phenyl-*trans*-cinnamaldehyde in 20.0 ml. of thiophene-free benzene. The mixture was refluxed with magnetic stirring for 18 hr. at the end of which time a silver mirror had plated out on the reaction flask. The reaction mixture was filtered and the mixture of silver and silver salt reserved. The filtrate was diluted with ether and extracted with 10% sodium hydroxide solution. The alkaline extract was acidified to a congo red end-point and ether extracted; these extracts on drying over sodium sulfate and concentration *in vacuo* yielded only 8.2 mg. of non-crystalline residue which was discarded. The original ether–benzene solution on drying over sodium sulfate and concentration afforded 228 mg. of essentially pure starting material, m.p. 91.0–92.0°, exhibiting a mixed melting point of 91.5–92.5° with authentic starting material.

The originally filtered solid was digested with 20.0 ml. of concd. ammonium hydroxide solution and the mixture filtered. The filtrate, on acidification with dilute nitric acid, yielded a white precipitate which was filtered and washed with water. After drying this melted at 173.0–174.0° and weighed 162.3 mg. This did not depress the melting point of authentic α-phenyl-*trans*-cinnamic acid.

2,3-*trans*-Diphenyl-2,3-epoxypropanal.—To a solution of 5.0 g. of α-phenyl-*trans*-cinnamaldehyde in 175 ml. of methanol was added first 12.0 ml. of 30% hydrogen peroxide followed by 9.0 ml. of 10% sodium hydroxide solution. The reaction mixture tended to warm slightly at first but was kept below 40° by external cooling. At the end of 75 min. at room temperature the mixture was diluted with twice its volume of water and made distinctly alkaline with 10% sodium hydroxide solution. The product was then extracted with 1:1 ether–benzene. The extracts were dried over sodium sulfate and concentrated *in vacuo*. The residue which weighed 3.2 g. and melted at 46.0–49.0° was almost pure product. However, it was found that this material was quite sensitive to air oxidation unless immediately purified. Recrystallization of 1.2 g. of this material from hexane containing a small amount of ether afforded 1.1 g. of crystals, m.p. 51.0–52.0°. Another crystallization gave

---

(29) A. Meerwein and H. Doff, *J. prakt. Chem.*, [2] **97**, 281 (1918).

0.80 g. of melting point 51.0–52.0°. Further material could be obtained from the filtrates.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39. Found: C, 80.60; H, 5.46.

2,3-*trans*-Diphenyl-2,3-epoxypropan-1-ol.—To a magnetically stirred and ice-cooled solution of 2.0 g. of 2,3-*trans*-diphenyl-2,3-epoxypropanal in 40.0 ml. of methanol was added over 10 min. 0.80 g. of sodium borohydride; during the addition the temperature was kept at 15–20°. At the end of the addition 20 ml. of water was added and the reaction mixture was heated on the steam-bath for 5 min. and then cooled. The mixture now was diluted with water and benzene extracted. The extracts were dried over sodium sulfate and then concentrated *in vacuo*. The residual oil weighed 1.7 g. and soon solidified to yield solid of m.p. 47–50°, which represented nearly pure product. This was crystallized from hexane–ether to yield solid of m.p. 50.0–53.0°. Another crystallization afforded 0.7 g., m.p. 54.0–56.0°. The filtrates on further recrystallization gave another 0.5 g. of pure, 2,3-*trans*-diphenyl-2,3-epoxypropan-1-ol, m.p. 54.5–56.0°. The infrared spectrum of this compound differed markedly from that of its stereoisomer.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.95; H, 5.98.

Preparation of the Stereoisomeric 2,3-Diphenyl-2,3-epoxypropionitriles.—The following is a modification of the procedure of Kohler.[23] A shorter reaction time is used, since the extended reaction time of Kohler leads to a more complicated product mixture. To a solution of 80.0 g. (0.35 mole) of desyl chloride in 300 ml. of methanol was added a solution of 34.0 g. (0.53 mole) of potassium cyanide in 100 ml. of water. An immediate exothermic reaction was observed causing the mixture to warm slightly. The mixture was allowed to stand at room temperature for one hour with occasional swirling. At the end of this time 500 ml. of water was added and the mixture was ether extracted. The extracts were dried over sodium sulfate and concentrated *in vacuo;* the residual orange oil weighed 43.4 g.

The oil was taken up in a minimum of 1:1 ether–hexane and chromatographed on a silica gel column (Davidson 60–200 mesh, 1000 × 100 mm., slurry packed with 5% ether in hexane). Elution was with 5% ether in hexane and 200-ml. fractions were collected. Fractions 25 through 36 contained 8.46 g. of 2,3-*trans*-diphenyl-2,3-epoxypropionitrile while fractions 41 through 49 gave 13.52 g. of the *cis* isomer. The intermediate fractions, 37 through 40, yielded 10.42 g. of the mixed nitriles (total yield of nitrile thus obtained 42.5%). Crystallization of the *trans*-nitrile from ether–hexane brought the melting point to 65.0–66.0°. Similar crystallization of the *cis* isomer afforded 2,3-*cis*-diphenyl-2,3-epoxypropionitrile of m.p. 72.0–73.0° (reported[23] for the *trans* isomer, 52°; for the *cis* isomer, 72°). Useful infrared absorption bands found for the *cis*-isomer were 4.38, 7.54, 9.88, 11.08, 14.38 μ; for the *trans*-isomer: 4.38, 7.84, 10.20, 11.32, 14.38 and 15.50 μ.

Methyl 2,3-*trans*-Diphenyl-2,3-epoxypropionimidate.—The preparation of this compound and its stereoisomer was described by Kohler without experimental detail.[23] A solution of 1.0 g. (0.0045 mole) of 2,3-*trans*-diphenyl-2,3-epoxypropionitrile, 65.0–66.0°, in 75.0 ml. of reagent methanol saturated with sodium bicarbonate was refluxed for 2.75 hr. At the end of this time the methanol was removed *in vacuo* leaving an oily residue which was taken up in ether and washed with 5% sodium hydroxide solution. The ether solution was then dried over sodium sulfate and concentrated *in vacuo*. The crude product was crystallized from ether–hexane. After two crystallizations 0.25 g. of methyl 2,3-*trans*-diphenyl-2,3-epoxypropionimidate, m.p. 80.0–82.0°, was obtained. It was found by infrared analysis that the material in the filtrate was a mixture of product and unchanged starting material. While recycling proved practical, a longer reaction time did not improve the yield.

Anal. Calcd. for $C_{16}H_{15}O_2N$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.20; H, 5.86; N, 5.63.

Methyl 2,3-*cis*-Diphenyl-2,3-epoxypropionimidate.—In a similar manner from 2.5 g. of 2,3-*cis*-diphenyl-2,3-epoxypropionitrile in 100 ml. of reagent methanol saturated with sodium bicarbonate there was obtained 0.96 g. of methyl 2,3-*cis*-diphenyl-2,3-epoxypropionimidate, m.p. 104.0–105.0°.

Anal. Calcd. for $C_{16}H_{15}O_2N$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.73; H, 5.66; N, 5.70.

Methyl 2,3-*trans*-Diphenyl-2,3-epoxypropionate.—A solution of 1.13 g. (0.0045 mole) of 2,3-*trans*-diphenyl-2,3-epoxypropionimidate, m.p. 81.0–82.0°, in 75.0 ml. of methanol containing 0.186 ml. (0.0067 equiv.) of sulfuric acid and 1.3 ml. of water was refluxed for 1.75 hr. At the end of this time *ca.* 60 mg. of sodium acetate was added and the methanol removed *in vacuo*. The oily residue was taken up in ether. The ether solution was washed once with water and dried over sodium sulfate and concentrated under vacuum. The residue was chromatographed on silica gel (30 × 400 mm., slurry packed with 5% ether in hexane) collecting 200-ml. fractions. Fractions 2 and 3 afforded a total of 0.33 g. of methyl 2,3-*trans*-diphenyl-2,3-epoxypropionate as an oil. Characteristic infrared peaks were found at 5.86, 9.06, 9.90 μ. The infrared spectrum of the crude product before chromatography indicated the major by-product to be the corresponding amide.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.46; H, 5.62.

Methyl 2,3-*cis*-Diphenyl-2,3-epoxypropionate.—A solution of 0.75 g. (0.0030 mole) of methyl 2,3-*cis*-diphenyl-2,3-epoxypropionimidate, m.p. 104.0–105.0°, in 50.0 ml. of reagent methanol containing 0.121 ml. of sulfuric acid (0.0044 equiv.) and 1.0 ml. of water was refluxed for 3 hr. To the mixture was added 60 mg. of sodium acetate and the methanol was removed *in vacuo*. The residue was taken up in ether and washed with 10% sodium carbonate solution. The ether solution was then dried over sodium sulfate and concentrated *in vacuo*. The residue was chromatographed on silica gel (25 × 220 mm., slurry packed with 5% ether in hexane) by elution with 5% ether in hexane. From the first 400 ml. of eluent there was obtained 0.33 g. of solid. This on crystallization from ether–hexane melted at 78.0–79.0°. Characteristic infrared absorption bands were found at 5.87, 7.06, 7.87, 9.84, 11.94 μ.

Anal. Calcd. for $C_{16}H_{14}O_3N$: C, 75.57; H, 5.55. Found: C, 75.22; H, 5.56.

2,3-*trans*-Diphenyl-2,3-epoxypropionamide.—In a 500-ml. flask 3.0 g. of α-phenyl-*cis*-cinnamonitrile (m.p. 85–86°), 50.0 ml. of methanol, 4.0 ml. of 30% hydrogen peroxide and 3.0 ml. of 20% sodium hydroxide solution were mixed and the suspension was stirred magnetically for one hour. After the first 10 minutes of stirring the solid had gone into solution and was soon thereafter replaced by crystals of product. At the end of the hour the product was filtered and dried; the product thus obtained weighed 2.03 g. and melted at 202–204° (reported[22,23] 205°, 203–204°).

2,3-*cis*-Diphenylprop-2-ene-1-ol.—To 30 ml. of methanol cooled in ice and stirred magnetically was added first 2.0 g. of α-phenyl-*trans*-cinnamaldehyde, m.p. 93.5–95.0°, followed by 0.80 g. of sodium borohydride. The mixture was then allowed to warm to room temperature and stand for 15 min. To the mixture was then added 10 ml. of water and the solution heated on the steam-bath for several minutes. The methanol was removed *in vacuo* and the residue ether extracted. The extract was dried over sodium sulfate and concentrated under vacuum. Recrystallization of the residue afforded 1.15 g. of 2,3-*cis*-diphenylprop-2-ene-1-ol, m.p. 68.0–69.0°.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.91; H, 6.66.

Stereospecific Synthesis of 2,3-*cis*-Diphenyl-2,3-epoxypropanol.—To 75 ml. of chloroform was added 4.7 g. of (Becco) 40% peracetic acid (0.025 mole), 60 mg. of sodium acetate and 4.4 g. (0.021 mole) of 2,3-*cis*-diphenylprop-2-ene-1-ol, m.p. 68.0–69.0°. After standing for 4 hr. the mixture was washed with dilute sodium bicarbonate, then with water and finally was dried over sodium sulfate. Concentration *in vacuo* and crystallization of the residue from chloroform–hexane afforded 3.7 g. of 2,3-*cis*-diphenyl-2,3-epoxypropan-1-ol, m.p. 115.0–117.0°. Further crystallization brought the melting point to 118.0–119.0°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.57; H, 6.16.

Oxidation of 2,3-*cis*-Diphenyl-2,3-epoxypropan-1-ol with the Pyridine–Chromium Trioxide Complex.—To 5.0 ml. of pyridine was added 1.0 g. (0.0044 mole) of the epoxyalcohol. The oxidant was prepared by slowly adding 1.2 g. (0.012 mole) of chromium trioxide to 10.0 ml. of ice-cold pyridine.

To this mixture was then added the pyridine solution of the epoxyalcohol and the mixture was allowed to stand at room temperature for 16 hr. The mixture was then diluted with water and ether extracted after acidification with hydrochloric acid. The ether layer was washed with water and then dilute sodium bicarbonate. The latter extract was acidified with dilute hydrochloric acid and ether extracted. This extract was dried over sodium sulfate and concentrated. The residue weighed 70 mg. and melted at 111–114°. Its infrared spectrum was identical to that of the glycidic acid obtained from the Darzens reaction of benzaldehyde and ethyl α-chlorophenylacetate followed by saponification.

Lithium Aluminum Hydride Reduction of Ethyl 2,3-*cis*-Diphenylglycidate.—To a solution of 1.0 g. (0.0037 mole) of ethyl 2,3-*cis*-diphenylglycidate, m.p. 58.0–59.0°, in a flask equipped with magnetic stirring bar, dropping funnel, reflux condenser and drying tube was added 4.50 ml. of 0.44 molar lithium aluminum hydride solution. After five minutes, excess lithium aluminum hydride was decomposed by addition of water dropwise until a precipitate of aluminum hydroxide separated. The solution was filtered and concentrated *in vacuo*. After one crystallization from chloroform–hexane there was obtained 0.30 g. of product, m.p. 116.0–117.0°. The infrared spectrum of this material was identical with that of previously prepared 2,3-*cis*-diphenyl-2,3-epoxypropan-1-ol. The material in the filtrates was found by infrared analysis to contain unreacted starting ester.

2,3-*trans*-Diphenylprop-2-ene-1-ol.—The following is a slight modification of the procedure of Lutz.[30] To a solution of 1.00 g. (0.0045 mole) of α-phenyl-*cis*-cinnamic acid, m.p. 137°, in 40 ml. of anhydrous ether in a 100-ml. flask fitted with reflux condenser, sodium hydroxide drying tube, magnetic stirrer, dropping funnel and Glas-col heater was added over 5 minutes 20.0 ml. of a 0.44 molar lithium aluminum hydride solution in ether. During the addition and for an additional 50 min. the mixture was stirred and refluxed gently by means of external heating. Then water was added dropwise until a precipitate of alumina separated. The solution was diluted with ether and filtered. The filtrate was concentrated *in vacuo* leaving 0.70 g. of oil which later solidified to a solid of m.p. 67–70°. This was crystallized from hexane several times with negligible loss to the filtrate, affording 2,3-*trans*-diphenylprop-2-ene-1-ol, m.p. 73.0–74.0° (reported[30] 73–74°). The infrared spectrum of this compound differed considerably from that of its stereoisomer.

2,3-*trans*-Diphenyl-2,3-epoxypropan-1-ol.—A solution of 0.691 g. of 2,3-*trans*-diphenylprop-2-ene-1-ol, prepared as described above, in 30 ml. of chloroform was added 0.50 g. of sodium acetate and 1.50 ml. of 40% (Becco) peracetic acid solution in acetic acid. This mixture was allowed to remain at room temperature for 22 hr. The chloroform solution was then washed with water, dried over anhydrous potassium carbonate and concentrated *in vacuo* to leave 0.371 g. of oil which solidified. The infrared spectrum of this material showed it to be only slightly impure product. The material was then chromatographed on a 19 × 490 mm. silica gel column packed with 5% ether in hexane. Six fractions of 100 ml. each were obtained by elution with 10% ether in hexane. Fractions 7 through 18 were obtained with 15% ether in hexane. Only fractions 11 through 15 contained appreciable quantities of material; the weights and melting points were: fraction 11, 49.7 mg., m.p. 45–47°; fraction 12, 59.7 mg., m.p. 48.0–49.0°; fraction 13, 62.1 mg., m.p. 47.5–49.0°; fraction 14, 46.9 mg., m.p. 47.0–48.0°; fraction 15, 21.6 mg., m.p. 43.0–47.0°. These fractions were combined and crystallized once from aqueous methanol to yield 112.9 mg. of 2,3-*trans*-diphenyl-2,3-epoxypropan-1-ol, m.p. 50–52°, whose infrared spectrum was that of the pure material obtained previously by sodium borohydride reduction of the corresponding epoxyaldehyde.

Acknowledgment.—We wish to thank the Alfred P. Sloan Foundation for support of a postdoctoral fellowship for B. S. Thyagarajan. Also we would like to express our appreciation to the Office of Ordnance Research, U. S. Army, for a summer research assistantship for L. Singer.

EVANSTON, ILL.

---

[30] R. E. Lutz and E. H. Rinker, Jr., THIS JOURNAL, **77**, 368 (1955).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

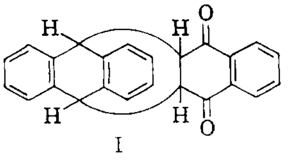
The *cis* and *trans* 12-Benzoyl-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic Acids

BY CHARLES D. HURD AND ALBERT TOCKMAN

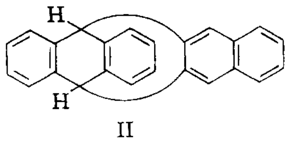
RECEIVED MAY 28, 1958

The *trans* acid III, prepared by reaction of benzene and aluminum chloride with the adduct of anthracene and maleic anhydride, does not cyclize to a diketone even when forced. The same *trans* isomer was made from the adducts of anthracene and benzoylacrylic acid (*cis* or *trans*) or fumaric ester. The *cis* isomer VI was prepared starting with the adduct of anthracene and methyl acetylenedicarboxylate; VI changed to III on alkaline treatment. Other adducts of anthracene that were studied included those of *trans*-dibenzoylethylene and *trans*-styrylacetic acid. Sodium borohydride was an efficient reducing agent toward the ketone function of III, whereas other methods of reduction failed.

The adduct of anthracene and 1,4-naphthoquinone (I) was examined unfruitfully in earlier work[1] as a source of 5,12-dihydro-5,12-*o*-benzenonaphthacene (II); but the conversion of I into II was not pursued exhaustively, in view of the successful synthesis of II by other methods.



I



II

In planning to test another synthesis of I, namely, by cyclization of 12-benzoyl-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid (III), we found that III had already been described by Barnett[2] and co-workers and that these investigators were unable to bring about such a cyclization. They prepared III by Friedel–Crafts reaction of benzene with the adduct of anthracene and maleic anhydride. They did not elaborate on their statement that compound I could not be made from III. The benzoyl carbonyl would, of course, deactivate the phenyl part of this radical toward electrophilic attack, but this should be no more true than in the benzoyl group of *o*-benzoylbenzoic acid which readily yields anthraquinone.

A more fundamental reason for non-formation of I from III is that III may be of *trans* structure,

---

[1] C. D. Hurd and L. H. Juel, THIS JOURNAL, **77**, 601 (1955).

[2] E. B. Barnett, N. F. Goodway, A. G. Higgins and C. A. Lawrence, *J. Chem. Soc.*, 1224 (1934). The m.p. was listed as 234°. Its empirical formula was given as $C_{20}H_{18}O_3$, but it should have been $C_{24}H_{18}O_3$.