give a water-white solution from which long white needles separated on cooling; m.p. 96.5–97.5°. The melting point of this material was not depressed by admixture with authentic "α"-1,2-diphenyl-1,2-propanediol, but was depressed by similar admixture with authentic "β"-diol. An oily sample of the authentic "α"-diol crystallized readily when seeded with a small sample of this product.

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LAFAYETTE, IND.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The *cis*-Oxidation of Olefins to Glycol Monobenzoates with Perbenzoic Acid.[1] Evidence of Epoxide Ring Opening with Retention of Configuration

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cis- and *trans*-*p*-methoxystilbene have been found to react with perbenzoic acid to give predominately in each case that glycol monobenzoate formed by over-all *cis*-addition of the elements of perbenzoic acid to the double bond. If, as has been commonly assumed, the epoxides are intermediates in these reactions the conclusion is suggested that the epoxides react with benzoic acid in chloroform to give predominately glycol monobenzoates formed with retention of configuration—contrary to the generally held belief about such reactions. *dl*-*trans*-*p*-Methoxystilbene oxide does, in fact, react with benzoic acid under the conditions employed above to give the *threo*-hydroxy benzoate with predominant retention. All efforts to prepare *cis*-*p*-methoxystilbene oxide in order to test its behavior have failed. Results similar to those above have also been obtained with the *p*-methoxy-*p*'-methylstilbenes. It is concluded that such epoxide ring openings are at present of dubious reliability for demonstrating configurational relationships.

Although the reaction of perbenzoic acid with olefins in general leads to epoxides, an alternative reaction resulting in the addition of a hydroxyl and a benzoate residue to the carbon atoms of the double bond frequently has been observed.[4] Such glycol monobenzoate formation commonly has been assumed to consist of two stages: first, the oxidation of the olefin to the epoxide and then ring-opening of the epoxide by benzoic acid known to be present.[4] The stereochemistry of the epoxidation step has, furthermore, been shown not to involve any change of configuration about the olefinic double bond[4] and the opening of epoxide rings with acids has, in general, occurred with predominant inversion of configuration.[5] The conclusion which follows from these assumptions is that the glycol monobenzoate formed by the reaction of a peracid with an olefin should be the racemate with the hydroxyl and benzoate groups added in a *trans* fashion.

In an attempt to prepare *trans*-*p*-methoxystilbene oxide, *trans*-*p*-methoxystilbene (*trans*-I) was treated with perbenzoic acid in chloroform. The product, was, however, a glycol monobenzoate ester II, m.p. 120–121°, as shown by its analysis, saponification equivalent and infrared spectrum.[6] On hydrolysis, the hydroxy benzoate II was converted to a racemic glycol which was not, however, the anticipated *erythro*-racemate but was instead the *threo*-isomer (*threo*-III) formed by a net *cis* addition of the elements of perbenzoic acid to the double bond. The estimated yield of *threo*-glycol (*threo*-III) from *trans*-olefin (*trans*-I), was 43% and no evidence for the formation of the *erythro*- isomer was obtained.

Oxidation of *cis*-*p*-methoxystilbene (*cis*-I) in an analogous fashion yielded, after saponification of the intermediate glycol monobenzoate(s), an over-all 42% yield of a mixture of glycols from which the only product which could be separated was the *erythro*-glycol (*erythro*-III) in 12% yield. The crude glycol mixture consisted, according to an infrared analysis, of approximately 76% of the *erythro*-racemate (*erythro*-III) and 20% of the *threo*-glycol. It seems clear, therefore, that although the oxidation of the *cis* isomer was somewhat less stereospecific than that of the *trans*, the predominant steric course was again that of over-all *cis* addition of the elements of perbenzoic acid (see Chart I).

The possibility that an inversion of configuration occurred in the alkaline hydrolysis of the glycol monobenzoates was excluded by the observation that each ester could be converted to the same glycol with lithium aluminum hydride as with alkaline hydrolysis.

Configurations of the olefins (*cis*- and *trans*-I) had been assigned by Stoermer and Prigge[7] and were confirmed by a comparison of the ultraviolet absorption spectra with those of *cis*- and *trans*-stilbene. The *p*-methoxy glycols (*erythro*- and *threo*- III) had been prepared previously by the reduction of *p*-methoxybenzoin.[8] While no ex-

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(1) From the Ph.D. Dissertation submitted to Columbia University in 1952 by Arthur Bradley and the Ph.D. Thesis submitted to the University of Illinois in 1955 by Yngve Gust Hendrickson.

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(4) (a) D. Swern, *Chem. Revs.*, **45**, 30 (1949); (b) "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, Chapter 7.

(5) See S. Winstein and R. B. Henderson, "Heterocyclic Compounds," Vol. I, R. C. Elderfield, Editor, John Wiley and Sons, Inc., New York, N. Y., p. 27.

(6) It had been reported by M. Tiffeneau and J. Levy [*Bull. soc. chim. France*, **39**, 763 (1926)] that *trans*-*p*-methoxystilbene gave one of the racemic epoxides (m.p. 118–119°). The only evidence for this structural assignment was the elementary analysis which was, however, 1% low in carbon, and the observation that the substance rearranged to α-*p*-anisylacetophenone on distillation. The question of which of the two glycolic hydroxyl groups of the ester II is esterified cannot be answered at present and the structures have been written, therefore, with this detail unspecified.

(7) R. Stoermer and L. Prigge, *Ann.*, **409**, 30 (1915).

(8) S. S. Jenkins, THIS JOURNAL, **54**, 1157 (1932).

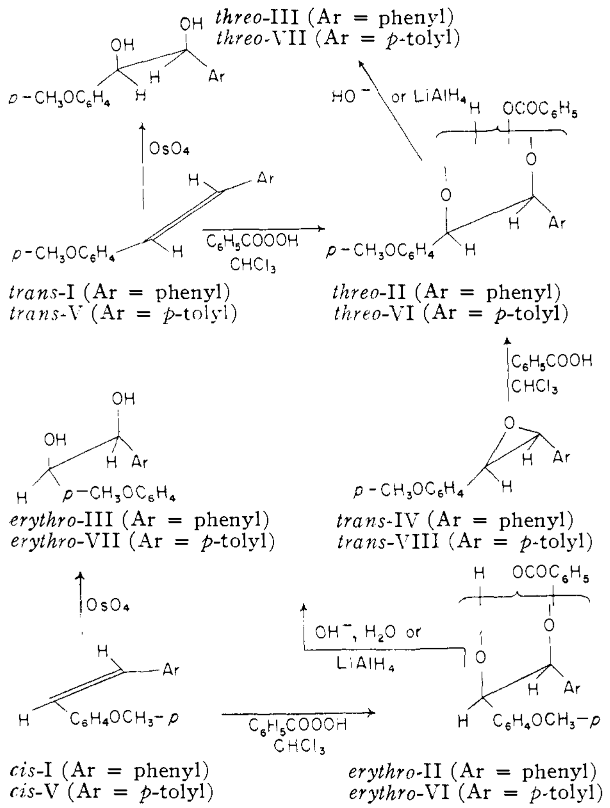
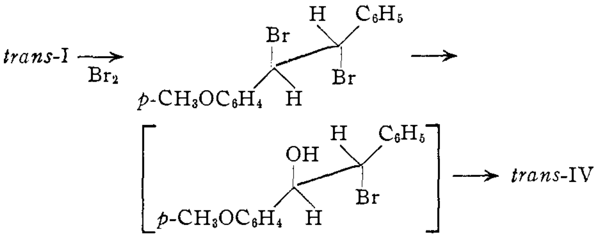


CHART I

plicit configurational assignment had been made, one was perhaps implied since the higher-melting isomer obtained in greater amount from the reduction with sodium amalgam of *p*-methoxybenzoin was called "hydrobenzanisoin," while the lower melting isomer formed in lesser amount was termed "isohydrobenzanisoin," presumably by analogy with "hydrobenzoin" and "isohydrobenzoin."[9] Hydrobenzoin (the major product from the sodium amalgam reduction of benzoin[9]) is known to be the *meso* isomer and isohydrobenzoin (which has been resolved) the *dl*. Since it is not likely that the introduction of a *p*-methoxyl group into a benzene ring of benzoin would appreciably change the relative amounts of the two diastereoisomers obtained on reduction with sodium amalgam, it follows that the "isohydrobenzanisoin" has the two hydroxyl groups *trans* to each other in the usual projection formula and is the *threo* isomer while the "hydrobenzanisoin" is *erythro*. These configurations were confirmed by relating the glycols directly to the stilbenes, *cis*- and *trans*-I. *cis*-I, when treated with osmium tetroxide, gave the *erythro*-glycol *erythro*-III, while the *trans*-olefin gave *threo*-III. Osmium tetroxide has been shown in a number of examples to be a reliable reagent for the *cis* addition of hydroxyl groups to double bonds.[10] These relationships are summarized in Chart I.

Apparently, then, either the epoxides (*cis*- and *trans*-IV) were not intermediates in the conversions of the olefins (*cis*- and *trans*-I) to hydroxybenzoates or else the epoxides were opened with retention of configuration. In order to examine this latter possibility it was desirable to prepare the *cis*- and *trans*-epoxides (*cis*- and *trans*-IV) and to examine their behavior with benzoic acid in chloroform solution.

trans-*p*-Methoxystilbene oxide (*trans*-IV) was prepared from the olefin (*trans*-I) by the addition of bromine to give a dibromide (presumably the *erythro*-dibromide) which was converted directly to the *trans*-epoxide by treatment with sodium carbonate dissolved in aqueous acetone.[11] A convincing argument was provided by a comparison of the ultraviolet spectra of the *p*-methoxy epoxide (*trans*-IV) with the spectra of *cis*- and *trans*-stilbene oxides. The *p*-methoxy epoxide spectrum had an absorption maximum at 238 mμ (ε 23,000) which compares favorably with that of *trans*-stilbene oxide ($\lambda_{\max}$ 228 mμ, ε 22,000) but not with that of *cis*-stilbene oxide which has only a shoulder at 218 mμ (ε 1300). The reactions leading to the *trans*-epoxide are



As anticipated, the *trans*-epoxide (*trans*-IV) reacted readily with benzoic acid in chloroform solution with retention of configuration. Under conditions approximating those which had been used for the perbenzoic acid oxidation of the *trans*-olefin (*trans*-I) a 70% yield of the same *threo*-hydroxy benzoate (*threo*-II) which had been formed from *trans*-I was obtained. It was strongly suggested, then, that the two olefins (*cis*- and *trans*-I) were undergoing normal oxidation to the *cis*- and *trans*-epoxides, respectively, and that each epoxide was being opened with benzoic acid with predominant retention of configuration.

It was most desirable to confirm this conclusion by examining the behavior of the *cis*-epoxide (*cis*-IV) with benzoic acid. For this reason, numerous attempts were made to obtain this epoxide but none was successful. The methods attempted are indicated in the Experimental section.[13]

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(9) A. Breuer and T. Zincke, *Ann.*, **198**, 151 (1879).

(10) R. Criegee, *ibid.*, **522**, 75 (1936); R. Criegee, B. Marchand and H. Wannowius, *ibid.*, **550**, 99 (1942); M. Mugdan and D. Young, *J. Chem. Soc.*, 2997 (1949).

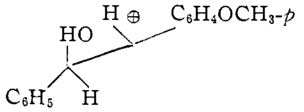
(11) The epoxide was initially assigned the *trans* configuration on the basis of the probable mechanism of its formation. It might be expected that the *erythro*-dibromide from *trans*-*p*-methoxystilbene would initially undergo solvolysis to the corresponding *erythro*-bromohydrin (with over-all retention of the configuration due to neighboring group participation of the adjacent bromine).[12] The bromohydrin should then give *trans*-epoxide with inversion of configuration.

(12) See (a) S. Winstein and D. Seymour, THIS JOURNAL, **68**, 119 (1946); (b) ref. 46, pp. 8-13.

(13) B. M. Lynch and K. H. Pausacker [*J. Chem. Soc.*, 1525 (1955)] have carried out a kinetic study of the reaction with perbenzoic acid of several olefins including *p*-methoxystilbene oxide. The product from the latter oxide was reported to be *p*-methoxystilbene oxide (95% yield), but its m.p. of 119° suggests that it was actually the glycol benzoate (*threo*-II). The log *k* for the methoxystilbene reaction falls where it would be expected on a plot of log *k* *vs.* σ for a number of *m*- and *p*-substituted stilbenes. This provides some support for the point of view that the epoxide is the product formed initially.

Results similar to those just described also were obtained with *cis-* and *trans-p*-methoxy-*p'*-methylstilbene (*cis-* and *trans*-V); *trans*-stilbene oxide, however, failed to react with benzoic acid and was recovered (64%) even after 3 hours of refluxing with benzoic acid in xylene.

The results reported above show that the over-all addition of the elements of perbenzoic acid to *cis-* and *trans-p*-methoxystilbene and to *cis-* and *trans-p*-methoxy-*p'*-methylstilbene is predominately *cis*. It seems probable that the epoxides are intermediates in each case and are opened with retention of configuration, but this latter conclusion is by no means certain since only the *trans*-epoxides could be studied. The demonstration that *trans*-epoxide leads to benzoate ester of *threo*-glycol is not evidence for a generalized opening of epoxides with retention of configuration since it is possible that a carbonium ion (A) is an intermediate and, since it still has a center of asymmetry, (A) might well give predominantly the *threo*-product. Under these circumstances the *cis*-isomer (assuming that it also reacted by way of the same carbonium ion (A)) would also give predominantly *threo*-hydroxy benzoate but with over-all inversion.[14]



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The suggested stereospecific *cis-* ring-opening is, however, not unreasonable, particularly in a relatively non-polar solvent such as chloroform. For example, the reaction of thionyl chloride with alcohols may proceed with retention of configuration[17] under certain conditions as do the reactions of some alcohols with hydrogen bromide in hydrocarbon solvents at low temperatures.[18] The cleavage of phenyl α-phenylethyl ether with hydrogen chloride[19] has also been shown to proceed with retention.

Boeseken and Elsen[20] oxidized *cis-* and *trans*-stilbenes with peracetic acid and, after saponification of the glycol acetates, obtained a mixture of *dl-* and *meso*-hydrobenzoins in each case. They presented evidence from melting point data on the crude mixture that predominant retention of configuration occurred in each case but the data do not permit this conclusion to be drawn with any finality.

In order to determine whether a predominantly *cis* opening occurred in aqueous solution as well as under the conditions used above, *trans-p*-methoxy-*p'*-methylstilbene oxide was treated with 2% aqueous sulfuric acid. A mixture of glycols was obtained in contrast to the results with benzoic acid in chloroform solution but this phase of the work has not been pursued further.

Experimental[21]

Reaction of *trans-p*-Methoxystilbene (*trans*-I) with Perbenzoic Acid.—*trans*-I (1.04 g., 4.94 × 10^{-3} mole, m.p. 136–137°; λ_{max} 303 mμ, ε 28,000), prepared by the method of Kinney[22] from 1-anisyl-2-phenylethanol, was treated in the dark with 12.1 ml. of 0.452 *M* perbenzoic acid in chloroform for 48 hours at 0°.[23] The chloroform solution was washed with 2% sodium carbonate and dried over sodium carbonate. Evaporation of the solvent gave solid glycol monobenzoate (*threo*-II) which in one experiment was isolated and recrystallized twice from benzene after which it amounted to 45% of the theoretical yield and had m.p. 118–119°.

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.8; H, 5.7. Found: C, 75.8; H, 5.5.

In a subseqent experiment, however, the ester was hydrolyzed directly by treatment with 120 ml. of 0.5 *M* potassium hydroxide and 50 ml. of water under reflux for 3.5 hours. An oil layer (1.11 g.) which separated at this point was shown to consist largely of unsaponified hydroxy ester and was separated by decantation and treated further with potassium hydroxide (10.5 hours of reflux with 86 ml. of 0.5 *M* base). Evaporation of the solutions remaining after saponification yielded a number of fractions of *threo*-glycol (*threo*-III) with m.p. ranging from 114.5–116.5° to 119–120°. Infrared examination of these fractions and comparison of the spectra with spectra of the authentic *threo-* and *erythro*-glycols (*threo-* and *erythro*-III) showed no evidence of the presence of the *erythro* isomer. Recrystallization of the combined crude *threo* isomer fractions yielded three fractions: 0.26 g., m.p. 120.5–121°; 0.11 g., m.p. 118–119.5°; and 0.07 g., m.p. 116–119°. The combined weight of 0.44-g. amounts to a yield of 43% based on the olefin (*trans*-I).

The monobenzoate (0.22 g.) described above was also converted to the same *threo*-glycol (*threo*-III) (0.12 g., 80% yield), m.p. 121°, by treatment with excess lithium aluminum hydride in ether.

Reaction of *cis-p*-Methoxystilbene (*cis*-I) with Perbenzoic Acid.—*cis*-I (1.04 g., 4.94 × 10^{-3} mole), $n^{25}D$ 1.6194, λ_{max} 285 mμ, ε 12,000, prepared by the method of Stoermer and Prigge[7] from *cis*-3-[*p*-methoxyphenyl]-2-phenylacrylic acid with copper chromite, was treated in the dark for 48 hours at 0° with 25.5 ml. of 0.452 *M* perbenzoic acid in chloroform. The chloroform solution was washed with 2% sodium carbonate and water and evaporated. The resulting oil partially crystallized and, in one experiment, collection of the crystals gave, after recrystallization from petroleum ether, a 30% yield of a monobenzoate, *erythro*-II, m.p. 153–154°, of *erythro-p*-methoxyhydrobenzoin.

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.8; H, 5.7. Found: C, 75.5; H, 5.6.

This ester (100 mg.) could be hydrolyzed by treatment with 8 ml. of 0.5 *N* potassium hydroxide until it had all dissolved to give a solution from which the *erythro*-glycol

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(14) It has been pointed out by Brewster[15] that configurations assigned to the α-methylstilbenes and to the α-methylhydrobenzoins lead to the conclusion that the dilute acid hydrolysis of α-methylstilbene oxide to α-methylhydrobenzoin by Tiffeneau and Levy[16] occurred with retention of configuration. Until the *cis*-epoxide is investigated, however, the detailed stereochemical courses of such reactions will not be clear. In other reactions where retention is observed (referred to later), the amount of retention as compared with inversion is very solvent-dependent. It is possible that stereospecific retention in epoxide ring-openings is a general phenomenon in non-polar solvents such as chloroform but not in aqueous solution.

(15) J. H. Brewster, THIS JOURNAL, **78**, 4061 (1956).

(16) M. Tiffeneau and J. Levy, *Bull. soc. chim.*, [4] **41**, 1351 (1927).

(17) W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1252 (1937); E. S. Lewis and C. E. Boozer, THIS JOURNAL, **74**, 308 (1952); **75**, 3182 (1953); D. J. Cram, *ibid.*, **75**, 332 (1953).

(18) P. Levene and A. Rothen, *J. Biol. Chem.*, **127**, 237 (1939); D. Y. Curtin and D. B. Kellom, THIS JOURNAL, **75**, 6011 (1953).

(19) H. Hart and H. S. Eleuterio, *ibid.*, **76**, 1379 (1954).

(20) J. Boeseken and G. Elsen, *Rec. trav. chim.*, **47**, 694 (1928).

(21) All melting points are corrected. Microanalyses were carried out by Mr. Josef Nemeth, Mrs. Katherine Pih, Mrs. Esther Fett, Mrs. Lucy Chang, Mr. Rollo Nesset, Mrs. Doreen Mosier and Mrs. Marie Benassi of the University of Illinois Microanalytical Laboratory and by the Clark Microanalytical Laboratory, Urbana, Ill., and the Schwarzkopf Microanalytical Laboratory, Middle Village, Long Island, N. Y. Infrared spectra were measured by Miss Helen Miklas, Mrs. Rosemary Hill and Mr. James Brader. Ultraviolet spectra were obtained by Mrs. Barbara Burnett, Mrs. Rosemary Hill and Miss Gerardine Meerman.

(22) C. Kinney, THIS JOURNAL, **51**, 1598 (1929).

(23) See ref. 4b, p. 392, for titration method.

(*erythro*-III) (45 mg., 60%), m.p. 132–134°, crystallized on cooling. After one recrystallization the product had m.p. 134–135° and the m.p. of a mixture with the authentic glycol showed no depression.

In another experiment the glycol ester was not isolated but was hydrolyzed directly by treatment for 3.5 hours under reflux with 120 ml. of 0.5 *M* potassium hydroxide. From the reaction mixture was isolated 0.51 g. (42%) of a mixture of *erythro*- and *threo*-III, m.p. 120.5–123.5°. Insoluble oil (0.38 g.) which still remained was extracted and hydrolyzed for an additional 10 hours with 28 ml. of 0.5 *M* potassium hydroxide under reflux. This gave an additional 7% of mixed glycols. Repeated recrystallization of the solid product from 50% aqueous ethanol led to the isolation of *erythro*-*p*-methoxyhydrobenzoin (0.046 g., m.p. 127–129.5°, and 0.081 g., m.p. 133–134°; total, 0.127 g. 12%).

A somewhat more refined estimate of the composition of this mixture, made by comparing infrared spectra of the various fractions (in Nujol mull) with spectra of authentic *erythro*- and *threo*-glycols, gave for the 42% of mixed glycols obtained from the first saponification an estimated composition of 76% of the *erythro* and 20% of the *threo* isomer. The *erythro* isomer has a strong band at 750 cm.$^{-1}$ which is absent in the *threo* spectrum while the latter has bands at 760 and 855 cm.$^{-1}$ absent in the *erythro*. Although it was undesirable to measure the spectra in Nujol, no satisfactory solvent could be found for use in this region. The total mull concentration could be estimated by comparing the height of the monosubstituted phenyl bands at 700 cm.$^{-1}$ and assuming that these had nearly equal extinction coefficients in the pure samples.[24] Although this analytical method leaves something to be desired, it leads to results which, together with the isolation experiments discussed above, leave no doubt that the *cis*-olefin gives as the major product the *erythro*-glycol.

***trans*-*p*-Methoxystilbene Oxide (*trans*-IV).**—*erythro*-*p*-Methoxystilbene dibromide (7.0 g., m.p. 177°), prepared by the addition of bromine to *trans*-I in chloroform solution,[25] was treated with 150 ml. of acetone and 150 ml. of 7% sodium carbonate solution under reflux for 3 minutes. Removal of the solvent by distillation gave a clear oil which, after extraction with benzene and evaporation to about 10 ml. volume and dilution with ligroin gave, after cooling, 2.6 g. (60%) of *p*-methoxystilbene oxide (*trans*-IV), m.p. 80–82°. The m.p. was brought to 82–83° by recrystallization from hexane.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 79.68; H, 6.2. Found: C, 79.7; H, 6.4.

Attempted Synthesis of *cis*-IV.—When *cis*-I was treated with bromine under the conditions used for *trans*-I above the same *erythro*-dibromide was obtained. This method of preparing the *cis*-epoxide (*cis*-IV) was not, therefore, pursued further.

Since it was believed that the epoxide was the first-formed product in the perbenzoic acid oxidation of *cis*-I, attempts were made to isolate it from experiments in which purified[26] (99.3% by titration) perbenzoic acid, m.p. 41–43.8°, in redistilled chloroform, was allowed to react with *cis*-I at 0°. The disappearance of perbenzoic acid was followed by titration. After 12 hours (titration showed 20% of the perbenzoic acid still unreacted) the product was passed through an alumina column and eluted with chloroform. An oil was obtained which failed to crystallize and which failed to give a correct elementary analysis for the oxide (*cis*-IV). It yielded little, if any, glycol benzoate on treatment with benzoic acid in chloroform.

Attempts to purify the product by oxidizing olefin or other impurities with potassium permanganate to more readily separable impurities were unsuccessful. The infrared spectrum showed a small amount of absorption at 3500 cm.$^{-1}$ and a small amount of carbonyl absorption at 1700 and 1720 cm.$^{-1}$.

Reaction of *trans*-Epoxide (*trans*-IV) with Benzoic Acid in Chloroform.—The epoxide (0.5 g.) was allowed to stand for 2 days with 0.5 g. of benzoic acid in 6 ml. of chloroform. The solution was washed with dilute sodium carbonate and water and dried and the solvent evaporated. Recrystallization of the residue gave 0.5 g. (70%) of the hydroxy benzoate, *threo*-II, m.p. and mixture m.p. with authentic *threo*-II, 119–120°.

Conversion of *trans*-I to *threo*-Glycol (*threo*-III) with Osmium Tetroxide.—*trans*-Olefin (*trans*-I) (0.5 g., 0.0024 mole) in 1 ml. of pyridine and 15 ml. of ether was added to 0.50 g. of osmium tetroxide (0.0020 mole) in 15 ml. of dry ether. The mixture changed color immediately and a precipitate formed. After 12 hours at room temperature the purple olefin–pyridine–osmium tetroxide complex was collected by filtration and washed with ether. The crystals were dissolved in 20 ml. of chloroform and shaken for 20 minutes with 0.5 g. of potassium hydroxide in 40 ml. of water containing 2.0 g. of mannitol.[13] Separation of the organic layer, decolorization with activated charcoal and evaporation of the solvent gave 0.33 g. (57%) of glycol (*threo*-III), m.p. 118–120°. Recrystallization gave m.p. 120–121°. A mixed m.p. with the glycol, m.p. 118–119°, obtained as described above from *trans*-I with perbenzoic acid showed no depression. The analysis reported below was carried out with a sample of the latter glycol.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.8; H, 6.6. Found: C, 73.7; H, 7.0.

Conversion of *cis*-I to *erythro*-Glycol (*erythro*-III) with Osmium Tetroxide.—The olefin (*cis*-I) (0.5 g.) was converted to *erythro*-glycol (0.36 g., 0.0015 mole, 62%, m.p. 130–132°) by the procedure described above. Recrystallization from chloroform–petroleum ether gave m.p. 134–135° as previously reported.[8]

***trans*-*p*-Methoxy-*p*′-methylstilbene (*trans*-V).**—Anisaldehyde was added to *p*-methylbenzylmagnesium bromide in ether and the crude alcohol formed by hydrolysis with dilute hydrochloric acid was dehydrated by distillation (200–215° at 12 mm.) to give a 20% yield of *trans*-V, m.p. 166–167°; ultraviolet spectrum, λ_{max} 310, ϵ 23,000.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.8; H, 7.1. Found: C, 86.1; H, 7.1.

***cis*-2-*p*-Tolyl-3-*p*-anisylacrylic Acid.**—*p*-Tolylacetic acid (9.5 g., 0.063 mole) was heated with anisaldehyde (12 ml.) and piperidine (1.5 ml.) for 6 hours at 160°. Acetic acid (15 ml.) was added to the product which crystallized on standing for 12 hours at 0°. The product was collected by filtration, washed with 30 ml. of acetic acid and 30 ml. of methanol and dried after which it amounted to 5.3 g. (0.020 mole) of 30% and had m.p. 217–219°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.1; H, 6.0. Found: C, 76.2; H, 6.0.

***cis*-*p*-Methoxy-*p*′-methylstilbene (*cis*-V).**—The *cis*-acrylic acid (8.7 g., 0.032 mole) prepared above underwent decarboxylation by the procedure previously described[18] to give 4.7 g. (0.021 mole, 65%) of *cis*-V as an oil (λ_{max} 280 mμ, ϵ 13,000).

Reaction of *trans*-*p*-Methoxy-*p*′-methylstilbene (*trans*-V) with Perbenzoic Acid.—The olefin (*trans*-V) (3.0 g., 0.013 mole) was allowed to react for 2 days at 0° with perbenzoic acid (0.02 mole) in 100 ml. of dry chloroform. The solution was washed with excess sodium carbonate solution, dried, evaporated to a volume of 10 ml. and diluted with 10 ml. of heptane. The solid hydroxy benzoate (*threo*-VI) separated and, when filtered, amounted to 2.9 g. (60%), m.p. 130–134°. Recrystallization from benzene–petroleum ether raised the m.p. to 138°.

Anal. Calcd. for $C_{23}H_{22}O_4$: C, 76.2; H, 6.1. Found: C, 76.1; H, 6.1.

Saponification of the benzoate ester, *threo*-VI (0.9 g.), by 1 hour of refluxing with 100 ml. of 1 *M* potassium hydroxide gave, after the solution cooled, 0.24 g. (38%) of *threo*-*p*-methoxy-*p*′-methylhydrobenzoin (*threo*-VII), m.p. 130°.

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.4; H, 7.0. Found: C, 74.6; H, 7.0.

A mixture m.p. with *threo*-VII, m.p. 128–129°, obtained from the reaction of *trans*-olefin (*trans*-V) with osmium tetroxide was undepressed.

Reaction of *trans*-V with Osmium Tetroxide.—The procedure employed with the other olefins (*cis*- and *trans*-I) had to be modified because of the insolubility of *trans*-V. To *trans*-V (0.45 g., 0.018 mole) in 40 ml. of a mixture of benzene (1 part), ether (3 parts) and pyridine (1 ml.) was

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[24] The infrared curves and detailed method of calculation are available in the Ph.D. Thesis of Dr. Y. G. Hendrickson and reproduced (Film #M16 55-822) by Univ. Microfilms, Ann Arbor, Mich.

[25] M. Tiffeneau and A. Orekhoff, *Bull. soc. chim.*, **37**, 1410 (1925).

[26] J. D'Ans, J. Mattner and W. Busse, *Angew. Chem.*, **65**, 57 (1953).

added 0.5 g. (0.020 mole) of osmium tetroxide in 25 ml. of ether. Since some of the olefin had a tendency to precipitate with the osmium tetroxide complex, best results were obtained by mixing the hot solutions. In the most successful experiment, 1.0 g. (80%) of the complex was obtained which was converted to the glycol as described for the oxidation of *trans*-I to give 0.24 g. (46% yield) of glycol (*threo*-VII), m.p. 128–129°.

Reaction of *cis*-*p*-Methoxy-*p*′-methylstilbene (*cis*-V) with Perbenzoic Acid.—*cis*-V (2.1 g., 0.010 mole) was treated with 1.6 g. (0.012 mole) of perbenzoic acid in 80 ml. of chloroform at 0° for 48 hours, after which the solution was washed with dilute sodium carbonate solution, and the solvent evaporated. The oily product crystallized from benzene–petroleum ether solution, and, after recrystallization, amounted to 1.4 g. (0.004 mole, 40%) of hydroxy benzoate, *erythro*-VII, m.p. 139–142°. Two additional recrystallizations raised the m.p. to 144°.

Anal. Calcd. for $C_{23}H_{22}O_4$: C, 76.2; H, 6.1. Found: C, 76.3; H. 5.9.

The hydroxy benzoate (0.65 g.) was hydrolyzed by treatment under reflux with 80 ml. of 1.7 *M* potassium hydroxide to which had been added 20 ml. of methanol. On cooling of the reaction mixture, the glycol (*erythro*-VII) crystallized and was recrystallized from benzene–ligroin. When purified it amounted to 0.27 g. (58%) and had m.p. 134–135° both alone and when admixed with the product, m.p. 134–135°, obtained from the osmium tetroxide oxidation described below.

Reaction of *cis*-V with Osmium Tetroxide.—The oxidation of *cis*-V (0.44 g., 0.0020 mole) was carried out by the method employed for *cis*-I to give 0.32 g. (0.0012 mole, 63% yield) of glycol (*erythro*-VII), m.p. 134–135°.

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.4; H, 7.0. Found: C, 74.3; H, 6.8.

***trans*-*p*-Methoxy-*p*′-methylstilbene Oxide (*trans*-VIII).**—The conversion of the *trans*-olefin (*trans*-V) to the epoxide was carried out by way of the dibromide in a method completely analogous to that employed with *trans*-I. The epoxide, m.p. 78–82°, was obtained from dibromide in 57% yield and when recrystallized had m.p. 84–85°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7. Found: C, 79.8; H, 7.0.

Reaction of the Epoxide (*trans*-VIII) with Benzoic Acid.—The epoxide (0.30 g.) was treated with benzoic acid (0.30 g.) in 10 ml. of chloroform for 1 hour at room temperature after which 30 ml. more of chloroform was added, the solution was washed with aqueous sodium carbonate, dried and evaporated to 5-ml. volume. On dilution with 20 ml. of petroleum ether the hydroxy benzoate (*threo*-VI) crystallized and was collected by filtration and washed with petroleum ether to give 0.29 g. (64%) of crystals, m.p. 139–140°. The m.p. of a mixture with a sample of *threo*-VI obtained above showed no depression.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE SANITARY CHEMISTRY BRANCH, CHEMICAL CORPS MEDICAL LABORATORIES]

The Chlorine-catalyzed Hydrolysis of Isopropyl Methylphosphonofluoridate (Sarin) in Aqueous Solution

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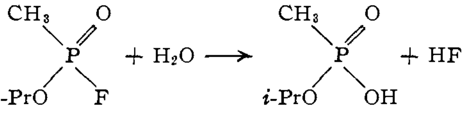
The decomposition of isopropyl methylphosphonofluoridate (Sarin) in aqueous solutions of chlorine has been studied in the *p*H region 5 to 9. Sarin decomposes, as in a simple hydrolysis, with the formation of two acids. The hydrolysis is catalyzed by hypochlorite ion, and the rate is proportional to the first powers of hypochlorite ion and Sarin. The bimolecular rate constant has a value of approximately 600 l. mole^{-1} min.$^{-1}$ at 25°. A mechanism for the reaction consistent with observations is proposed. An explanation for the high nucleophilicity of the hypochlorite ion toward Sarin is advanced.

Introduction

In connection with drinking water purification studies carried out in these laboratories it was of interest to study the behavior of the nerve gas Sarin (isopropyl methylphosphonofluoridate) in dilute aqueous solution containing an approximately equivalent concentration of active chlorine compounds.

In slightly acid and slightly alkaline solutions of chlorine, Sarin decomposes with the formation of two moles of acid as in a simple hydrolysis, but at



a much more rapid rate than is observed for a spontaneous hydrolysis.[1]

The decomposition of Sarin at constant *p*H, even in solutions containing approximately equivalent concentrations of Sarin and chlorine, followed by both the disappearance of Sarin and the appearance of acid, is kinetically of first order (Fig. 1). Moreover, the concentration of the active chlorine compound remains constant during the course of the hydrolysis.

Analysis of rate data at constant *p*H (Table I) by the differential method[2] indicates that the reaction is bimolecular, the rate of decomposition of Sarin being proportional to the first powers of the Sarin and chlorine concentrations.

TABLE I

RATE DATA OF SARIN DECOMPOSITION[a] IN AQUEOUS CHLORINE SOLUTION[b]

Sarin, $M \times 10^4$	Chlorine, $M \times 10^3$	$k_{obs.} \times 10^2$, min.$^{-1}$
2.14	2.12	4.6
4.28	2.12	4.0
8.56	2.12	4.6
2.14	0.71	1.6
2.14	2.82	6.1

[a] All experiments performed at constant *p*H 6.0 and temperature 24.0 ± 0.5°. [b] High test hypochlorite (HTH) manufactured by Mathieson Chemical Corp. used as the source of chlorine.

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(1) In fact, for many of the experiments described herein, the spontaneous hydrolysis rate was negligible (*i.e.*, <1%), as compared to the hydrolysis rate of Sarin in the presence of chlorine. The spontaneous hydrolysis rate constant of Sarin determined at 25° at *p*H 5 and 6 is approximately 6×10^{-5} min.$^{-1}$, at *p*H 7, 2×10^{-4} min.$^{-1}$, at *p*H 8, 2×10^{-3} min.$^{-1}$ and *p*H 9, 2×10^{-2} min.$^{-1}$.

(2) S. Glasstone, "Textbook of Physical Chemistry," 2nd Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 1067.