benzoate formed. The precipitate was filtered off and washed with 50 ml. of acetone. The combined filtrate and washings were treated with sodium thiosulfate solution to destroy the iodine. The acetone was taken off in the rotary evaporator, and the slurry remaining was extracted with 150 ml. of ether. The ether extracts were washed with 5% sodium carbonate and then dried over Drierite. Evaporation of the ether and two crystallizations from acetone yielded 9.8 g. of product and 2.2 g. of a straw-yellow gum.

1,1,1,3-Tetrachloro-3-triphenylsilylpropane.—A solution of 5 g. (0.017 mole) of triphenylvinylsilane in 60 ml. (95.7 g., 0.67 mole) of carbon tetrachloride was held at vigorous reflux for 20 hr. One gram (0.004 mole) of dibenzoyl peroxide was added in half-gram portions at 0 and 2 hours. The reaction was worked up as described above except that a 1:1 solution of ethanol and acetone was used to crystallize the product.

Reaction of 1,1,1-Trichloro-3-triethylsilylpropane with Triethylvinylsilane.—Fifteen grams (0.057 mole) of 1,1,1-trichloro-3-triethylsilylpropane was dissolved in a solution of 0.5 g. of benzoyl peroxide in 15 g. (0.105 mole) of triethylvinylsilane and held at 70° under a nitrogen atmosphere for 12 hours. Another 0.5 g. of peroxide (total of 1.0 g. or 0.0041 mole) was added and the solution held at 75° for an additional 12 hours. The reaction was worked up in the usual manner. Fractional distillation yielded 6.4 g. of triethylvinylsilane (b.p. 63-64° (44 mm.), $n^{20}\text{D}$ 1.4341), 13.1 g. of 1,1,1-trichloro-3-triethylsilylpropane (b.p. 56-57° (0.08 mm.), $n^{20}\text{D}$ 1.4760), and 2.5 g. of material boiling at 120–150° (0.015 mm.), $n^{20}\text{D}$ 1.4930. An infrared spectrum of the latter was superimposable on that of the material isolated from the reaction of triethylvinylsilane with chloroform.

Silver Nitrate Tests.—To establish whether halogen substituents were located alpha or beta to the silicon atom the stability of the compounds to silver nitrate was determined under conditions known to result in immediate and quantitative removal of halogen from trimethyl-β-bromoethylsilane.

Volhard titration of trimethyl-β-bromoethylsilane dissolved in methanol or acetone was conducted as follows: The sample (0.2591 g.) was added to 50 to 100 ml. of methanol containing 25.00 ml. of 0.0894 *N* silver nitrate solution, and 5 ml. of dilute nitric acid and allowed to stand for ten minutes. In all cases a precipitate formed immediately upon mixing; 1 ml. of 40% ferric alum indicator was added and the excess nitrate titrated with standard KCNS; theoretical Br content 44.11, found 43.11.

To test the compounds described in this paper, 5 ml. of 0.1022 *N* silver nitrate solution was mixed with 5 ml. of acetone and then 0.2 g. of the compound in question added as an acetone solution. Occasionally some turbidity occurred but this was caused by the insolubility of the compound since it disappeared when a little more acetone was added. As a check, after 15 minutes, a drop of *t*-butyl chloride was added to each solution and caused an immediate precipitate that was unchanged by further dilution with acetone.

Attempted Basic Hydrolysis of 1,1,1-Trichloro-3-triphenylsilylpropane.—Two grams (0.0049 mole) of the silane and 1.1 g. (0.0197 mole) of potassium hydroxide were dissolved in 50 ml. of 80% ethanol mixed with 25 ml. of tetrahydrofuran and refluxed for two hours. Application of the usual isolation procedure resulted only in the recovery of 1.7 g. of pure starting material.

Dehydrohalogenation of the *p*-Nitrophenyl Meerwein Adduct.—A solution of 500 mg. of the *p*-nitro adduct was refluxed in γ-picoline for 8 hours. The solution was then poured into water, extracted with ether, and the ether extract washed with aqueous acid. Evaporation of the ether deposited 0.37 g. (82%) of light yellow needles melting at 171.5–172.5° after crystallization from a 1:1 ethanol–acetone solution. A duplicate run utilizing 1.7 g. of nitro adduct resulted in an 81% yield. An infrared spectra showed a strong olefin band at 10.12 μ.

Anal. Calcd. for $C_{26}H_{21}O_2NSi$: C, 76.6; H, 5.19; N, 3.43. Found: C, 76.6; H, 5.19; N, 3.58.

Toluidide of Ethyl Bromoacetate Adduct.—A mixture of 10 g. (0.033 mole) of ethyl 4-bromo-4-triethylsilylbutanoate, 30 ml. of water, 30 ml. of ethanol and 10 ml. of 50% sodium hydroxide was refluxed on a steam-cone for 4 hours. The solution was concentrated and then acidified with dilute hydrochloric acid. This was extracted with ether and dried over calcium sulfate.

This ether solution of the lactone was refluxed for 20 minutes with a suspension of the magnesium salt of *p*-toluidine in ether. The latter was prepared by adding ethylmagnesium bromide (from 0.05 mole of ethyl bromide and 0.05 g. atom of magnesium in 50 ml. of dry ether) to 5.36 g. (0.05 mole) of *p*-toluidine in 30 ml. of dry ether.

After working up in the usual fashion a brown oil was obtained which eventually solidified. Crystallization of this material from 1:1 petroleum ether (60-70°) and ethyl ether yielded white needles melting at 67.5–69°. A qualitative test for nitrogen was positive and a halogen test negative.

Anal. Calcd. for $C_{17}H_{29}O_2NSi$: C, 66.39; H, 9.55; N, 4.55. Found: C, 66.46; H, 9.44; N, 4.70.

Acknowledgment.—This investigation was supported by the National Science Foundation whose financial assistance is gratefully acknowledged.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

An O-18 Tracer Study of the “Wet” and “Dry” Prevost Reactions

BY KENNETH B. WIBERG AND KLAUS A. SAEGEBARTH[1]

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The reaction of *erythro*-1-benzoxy-2-bromo-1,2-diphenylethane-carbonyl-O^{18} with silver benzoate under the conditions of the “dry” Prevost reaction followed by hydrolysis resulted in the formation of *meso*-hydrobenzoin having one-half the O-18 of the bromobenzoate. The bromobenzoate when treated with silver benzoate under the conditions of the “wet” Prevost reaction resulted in the formation of *threo*-2-benzoxy-1,2-diphenylethanol. The hydroxybenzoate on hydrolysis gave the D,L-hydrobenzoin which was found to have the same O-18 content as the bromobenzoate. These results are discussed in terms of the mechanisms of the reactions.

Introduction

Our interest in hydroxylation reactions has led us to investigate some aspects of the Prevost reaction.[2] This is particularly interesting since it has been shown recently that the reaction of an olefin with silver acetate and bromine in the presence of some water will give a product corresponding to *cis*-hydroxylation,[3] whereas the same reaction carried out in a dry solvent gives *trans*-hydroxylation. The wet reaction has been postulated to involve a cyclic acetoxonium ion intermediate which may add water and then be cleaved to the hydroxyacetate

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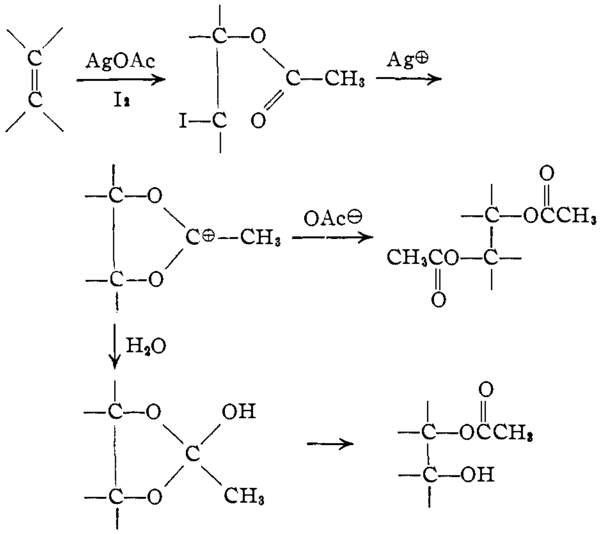
[1] Taken from part of a thesis submitted by K. A. Saegebarth to the University of Washington in partial fulfillment of the requirements for the Doctor of Philosophy degree, May, 1957.

[2] C. Prevost, *Compt. rend.*, **196**, 1129 (1933); **197**, 1661 (1933); C. Prevost and M. Losson, *ibid.*, **198**, 659 (1934); C. Prevost and R. Lutz, *ibid.*, **198**, 2264 (1934); C. Prevost and J. Weinman, *ibid.*, **204**, 700 (1937); C. Prevost, *Atti Xth cong. intern. chim.*, **3**, 318 (1939) (*C. A.*, **33**, 8187 (1939)).

[3] D. Ginsburg, THIS JOURNAL, **75**, 5746 (1953); L. B. Barkley, W. M. Farrar, W. S. Knowles, H. Raffelson and Q. E. Thompson, *ibid.*, **76**, 5014 (1954).

formed by *cis*- addition,[4] in analogy with the work of Winstein on the neighboring group displacement of a bromine by an acetoxy group.[5] The same acetoxonium ion intermediate probably is involved in the dry reaction; displacement by acetate will give the diacetate formed by *trans*-addition.



It is possible to test this scheme using O–18 as a tracer by labeling the carbonyl group of the acetoxybromide. In the cyclic acetoxonium ion intermediate, the two oxygens will become equivalent and each will have one-half of the original O^{18}. If the intermediate reacts with water giving the hydroxyacetate, the product will have the label distributed equally between the original oxygens, and no O^{18} will be lost in the hydrolysis to the diol.

If the intermediate reacts with acetate ion to give the diacetate, one of the carbon–oxygen bonds will be broken. The diacetate will have the same O^{18} content as the bromoacetate, but the diol formed by hydrolysis will have only one-half the original O^{18}, and the other half will be lost in the acetate ion. The olefin chosen for this study was stilbene since the two stereoisomeric 2-bromo-1,2-diphenylethanols are known and the respective configurations have been established. The benzoate group was used instead of the acetate group because it was felt that it would be more convenient in several ways.

trans-Stilbene was allowed to react with N-bromoacetamide in a buffered aqueous solution according to the method described by House[6] to give *erythro*-2-bromo-1,2-diphenylethanol (I). Treatment of the bromohydrin in the cold with benzoyl chloride in pyridine, a process known to have no effect on configuration, afforded the *erythro*-bromobenzoate (II). The same bromobenzoate may be obtained by the addition of a benzene solution of *trans*-stilbene to a cold (5°) slurry of the bromosilver complex obtained from silver benzoate and bromine.[7]

erythro-1-Benzoxy-2-bromo-1,2-diphenyl-ethane was converted readily to *meso*-hydrobenzoin dibenzoate (III) by its reaction with silver benzoate in refluxing xylene. The conversion of *trans*-stilbene to the same dibenzoate was effected by the action of the iodosilver benzoate complex in refluxing xylene. Saponification or lithium aluminum hydride reduction of the dibenzoate gave *meso*-hydrobenzoin (IV) in 80 and 86.5% yield, respectively. Therefore these results further confirm that the conversion of the *erythro*-benzoxybromide to the *meso*-dibenzoate is a stereospecific one proceeding with over-all retention of configuration. The reaction of *erythro*-1-benzoxy-2-bromo-1,2-diphenylethane with silver benzoate in N,N-dimethylformamide containing a stoichiometric amount of water resulted in the formation of *threo*-2-benzoxy-1,2-diphenylethanol (V). The same product also was obtained when the reaction was effected in moist acetic acid in the presence of silver acetate, indicating that the rate of the displacement is much more rapid than the possible ester interchange reaction. This result amounts to over-all inversion of configuration, which is analogous to the solvolysis of *trans*-1,2-acetoxyhalides in wet acetic acid.[5] The structure of the hydroxybenzoate was established by its conversion to D,L-hydrobenzoin dibenzoate and also by saponification or lithium aluminum hydride reduction to D,L-hydrobenzoin (VI).

erythro - 1 - Benzoxy - 2 - bromo - 1,2 - diphenylethane-carbonyl-O^{18}, containing 1.23% excess oxygen-18, was prepared by the benzoylation of parent bromohydrin with benzoyl chloride-O^{18}. Treatment of the labeled benzoxybromide with silver benzoate in wet N,N-dimethylformamide resulted in the formation of labeled *threo*-2-benzoxy-1,2-diphenylethanol. Saponification or lithium aluminum hydride reduction of the labeled hydroxyester gave D,L-hydrobenzoin-O^{18} containing 1.21 and 1.23% excess oxygen-18, respectively. When the displacement reaction was conducted with silver acetate in wet acetic acid, the labeled *threo*-hydroxybenzoate was again obtained. On saponification it gave the D,L-hydrobenzoin-O^{18} having 1.23% excess oxygen-18. When *erythro*-1-benzoxy - 2 - bromo - 1,2 - diphenylethane - carbonyl-O^{18} was allowed to react with silver benzoate in dry xylene there was obtained *meso*-hydrobenzoin dibenzoate-O^{18}. Saponification gave *meso*-hydrobenzoin having 0.604% excess oxygen-18, or one-half that of the reactant. It is clear from the data obtained that the extent of labeling which was predicted above has been obtained.

Further evidence for the formation of the intermediate orthoester could be obtained by allowing unlabeled *erythro*-1-benzoxy-2-bromo-1,2-diphenylethane to react with silver benzoate in dimethylformamide containing water-O^{18}. The O-18 content of the solvent was determined by an equilibration with carbon dioxide and was found to have an enrichment of 0.68% excess O-18. The *threo*-2-benzoxy-1,2-diphenylethanol contained 0.49% excess O-18, whereas the D,L-hydrobenzoin obtained from the hydrolysis of the hydroxyester contained no excess O-18.

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[4] G. W. Kenner, *Ann. Repts.*, **51**, 178 (1954).

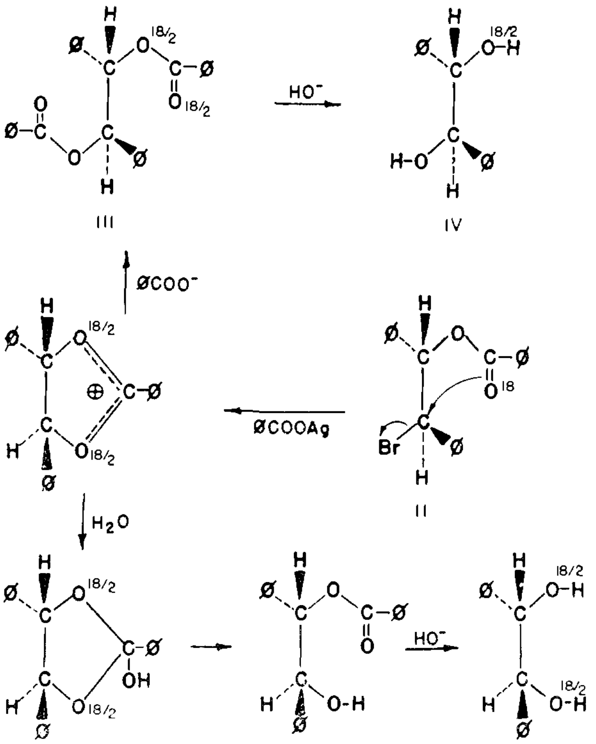
[5] S. Winstein and R. E. Buckles, This Journal, **64**, 2787 (1942); *cf.* A. Streitwieser, *Chem. Revs.*, **56**, 675 (1956).

[6] H. O. House, This Journal, **77**, 3074 (1955).

[7] The formation of the bromobenzoate was observed by Prevost (*Compt. rend.*, **197**, 1661 (1933)), but he gave no evidence concerning its stereochemistry.

It can be seen from the above data that only 72% of the excess oxygen-18 in the solvent has been transferred to the hydroxybenzoate for reasons that are not clear at this time. These results nevertheless confirm the formation of an intermediate orthoester since the excess O-18 appeared exclusively in the carbonyl oxygen of the hydroxyester.

The wet Prevost reaction appears to be particularly valuable for *cis*-hydroxylation. It has many advantages over osmium tetroxide in convenience and cost and it has certain advantages over potassium permanganate. An effort was therefore made to determine the order of the yields obtained in the wet Prevost reaction of certain olefins with silver acetate and bromine in moist acetic acid. The results are shown in Table I. It can be seen that from 50 to 65% yield of glycol may be obtained in these reactions and these yields are superior to those obtained by the other hydroxylation reactions. It thus appears that this is a particularly useful method for *cis*-hydroxylation.



ϕ indicates C_6H_5.

When the reaction was carried out using norbornylene, the product was found to be a mixture of 2-acetoxynortricyclene and *syn*-7-iodo-exo-2-norbornyl acetate. This is the expected product for an ionic addition of an iodine cation to the ring, for an electrophilic attack on this system always leads to rearrangement.[8] It also indicates the importance of the neighboring group participation in the subsequent step since here very little diacetate was formed, whereas the vicinal iodoacetates react readily with silver acetate.

TABLE I

cis-HYDROXYLATIONS IN PER CENT

	"Wet" prevost			
Compound	Glycol	Diacetate	KMnO$_4$	OsO$_4$ cat.
Acenaphthylene	..	55		
Cyclopentene	48	..	55[9]	2.5[11]
Cyclohexene	65	75	38[9]	58[12]
Cycloheptene	62		38[9]	
1,2-Dimethylcyclohexene-1	49		27[10]	
Stilbene	61			

Acknowledgment.—We wish to thank the National Science Foundation for a grant in support of this work.

Experimental[13]

Benzoyl Chloride-O^{18}.—A solution of 10 g. of benzoic acid in 125 ml. of water containing approximately 1.3% excess of O–18 was made 0.1 *N* in hydrochloric acid by the addition of 1 ml. of concentrated hydrochloric acid and the solution was heated under reflux for 20 hours. The solution was cooled in ice-water, the labeled benzoic acid was collected and dried in a vacuum desiccator, m.p. 121°. The labeled water filtrate was used in four subsequent runs to give a total yield of 47.2 g. (94.4%) of O–18 enriched benzoic acid. After the combined crystal crop had been dried it was thoroughly crushed to give a uniform sample. Oxygen-18 analysis by the pyrolytic method showed that the benzoic acid contained 2.47 ± 0.01% excess of O–18.

A mixture of 11.0 g. (0.09 mole) of the above labeled benzoic acid and 13.5 g. (0.113 mole) of freshly distilled thionyl chloride was allowed to stand at room temperature for two hours and then was refluxed for two hours. The solution was distilled giving 11.5 g. (90%) of enriched benzoyl chloride, b.p. 197–198°.

***erythro*-1-Benzoxy-2-bromo-1,2-diphenylethane. A. Benzoylation of *erythro*-2-Bromo-1,2-diphenylethanol.**—To 5.54 g. (0.02 mole) of *erythro*-2-bromo-1,2-diphenylethanol[6] in 20 ml. of dry pyridine was added 6.8 ml. (8.44 g., 0.06 mole) of benzoyl chloride with stirring and cooling. A large quantity of colorless precipitate was formed and the mixture was stirred for 15 minutes. Water (1.2 ml.) was added and the mixture was stirred for one hour. Chloroform (75 ml.), 60 ml. of water and 20 ml. of 6 *M* hydrochloric acid were then added and the mixture was stirred. The reaction mixture was transferred to a separatory funnel, the chloroform phase was separated and then washed with 100 ml. of 1 *M* hydrochloric acid, 100 ml. of 1 *M* sodium carbonate solution, 200 ml. of water and finally dried over anhydrous sodium sulfate. Evaporation of the solvent followed by recrystallization from benzene–hexane gave 6.30 g. (82%) of the *erythro*-benzoxybromide, m.p. 167.5–168.5°.[14]

Anal. Calcd. for $C_{21}H_{17}O_2Br$: Br, 21.0. Found: Br, 20.8.

erythro-1-Benzoxy-2-bromo-1,2-diphenylethane-carbonyl-O^{18} was prepared by the above procedure employing benzoyl chloride-O^{18}. This gave 83% of the theoretical amount, m.p. 167–168°, containing 1.23 ± 0.01% excess of oxygen-18.

B. Reaction of *trans*-Stilbene with Silver Benzoate and Bromine.—To a vigorously stirred suspension of 2.29 g. (0.01 mole) of silver benzoate in 50 ml. of dry benzene was added a solution of 1.60 g. (0.01 mole) of bromine in 10 ml.

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[8] J. D. Roberts, F. O. Johnson and R. A. Carboni, THIS JOURNAL, **76**, 5692 (1954); H. Kwart and L. Kaplan, *ibid.*, **76**, 4072 (1954); H. Kwart and W. G. Vosburgh, *ibid.*, **76**, 5400 (1954); H. M. Walborsky and D. F. Loncrini, *ibid.*, **76**, 5396 (1954).

[9] K. B. Wiberg and K. A. Saegebarth, *ibid.*, **79**, 2822 (1957).

[10] H. Meerwein, *Ann.*, **542**, 123 (1939).

[11] L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 4026 (1952).

[12] N. A. Milas and S. Sussman, THIS JOURNAL, **59**, 2345 (1937).

[13] Unless otherwise stated, the oxygen-18 analyses were performed using the method of W. E. Doering and E. Dorfman, *ibid.*, **75**, 5595 (1953). The analyses were performed in triplicate and the precision of the analyses was between ±0.002% and ±0.004%.

[14] C. Prevost, *Compt. rend.*, **197**, 1661 (1933), reported m.p. 170°.

of benzene and the mixture was stirred vigorously for a few minutes. The mixture was cooled to 5° and a solution of 1.80 g. (0.01 mole) of *trans*-stilbene in 50 ml. of dry benzene was then added with continuous stirring and cooling. The reaction mixture was allowed to warm to room temperature and the precipitated salts were removed and washed with benzene. The combined benzene solution was washed with 1 *M* sodium carbonate, water, and then dried over anhydrous magnesium sulfate. Evaporation of the solvent left a white crystalline residue which was recrystallized from benzene–hexene giving 1.2 g. (31.4%), of the bromobenzoate, m.p. 168–169°, undepressed on admixture with material from procedure A. The infrared spectra (Nujol mull) of these two samples were identical.

meso-**Hydrobenzoin Dibenzoate. A. Benzoylation of** *meso*-**Hydrobenzoin.**—To 2.14 g. (0.01 mole) of *meso*-hydrobenzoin in 20 ml. of dry pyridine was added 6.8 ml. (8.46 g., 0.06 mole) of benzoyl chloride with stirring and cooling. After the mixture had been stirred for 15 minutes, 1.5 ml. of water was added and the mixture was stirred for an additional hour. Water (45 ml.) and 15 ml. of 6 *M* hydrochloric acid were then added, the slurry was stirred and the white crystalline product was collected. The crude dibenzoate was triturated with 50 ml. of 1 *M* hydrochloric acid, 50 ml. of 1 *M* sodium carbonate, and finally with water until the washings were neutral. The material was air-dried and then recrystallized from boiling toluene to give 3.47 g. (82.5%) of pure *meso*-hydrobenzoin dibenzoate, m.p. 247–248°.[15]

B. The Reaction of *erythro*-**1-Benzoxy-2-bromo-1,2-diphenylethane with Silver Benzoate in Dry Xylene.**—A heterogeneous mixture of 1.14 g. (0.003 mole) of the *erythro*-benzoxybromide in 50 ml. of dry xylene and 0.87 g. (0.0038 mole, 25% excess) of silver benzoate was stirred and heated under reflux for 5 hours. The mixture was filtered while hot and precipitated silver salts were washed with hot xylene. The xylene solution was concentrated to about 30 ml. and the product allowed to crystallize giving 1.05 g. (83%) of the dibenzoate, m.p. 244–245°. Recrystallization from boiling toluene gave 1.0 g. (79%) of pure *meso*-hydrobenzoin dibenzoate, m.p. 247–248°, undepressed on admixture with a sample of authentic material. The infrared spectrum (Nujol mull) was identical in all respects with that of authentic material.

erythro-1-Benzoxy-2-bromo-1,2-diphenylethane-carbonyl-O^{18} was allowed to react with silver benzoate in dry xylene according to the above procedure to give 1.02 g. (80%) of hydrobenzoin dibenzoate, m.p. 247–248°.

C. The Reaction of *trans*-**Stilbene with Iodine and Silver Benzoate in Dry Xylene.**—To 4.58 g. (0.02 mole) of silver benzoate in 75 ml. of dry xylene was added 2.54 g. (0.01 mole) of finely pulverized iodine and the resulting yellow suspension was stirred and heated under reflux for 30 minutes. A solution of 1.80 g. (0.01 mole) of *trans*-stilbene in 25 ml. of dry xylene was added and the mixture was refluxed for 16 hours with stirring. The mixture was filtered while hot and the precipitate washed with hot xylene. The filtrate was allowed to cool to give 3.4 g. (80%) of the crude dibenzoate, m.p. 244–246°, which after recrystallization from toluene gave 3.1 g. (75%) of pure material, m.p. 247–248°.

meso-**Hydrobenzoin. A. Lithium Aluminum Hydride Reduction of** *meso*-**Hydrobenzoin Dibenzoate.**—The *meso*-dibenzoate (1.0 g., 0.0024 mole) was extracted for 51 hours in a Soxhlet apparatus with 250 ml. of anhydrous ether containing 1.0 g. (0.026 mole) of lithium aluminum hydride. Water (10 ml.) was added dropwise to destroy the excess lithium aluminum hydride and approximately 20 ml. of a 20% Rochelle salt solution was added with stirring to effect precipitation of the complex. The ether layer was decanted and the residue was washed with three 50-ml. portions of ether. The combined ether extracts were washed with three 50-ml. portions of water and then dried over anhydrous potassium carbonate. The solvent was evaporated and the white crystalline solid was recrystallized from benzene–hexane. This gave 0.37 g. (86.5% based on unrecovered starting material) of the diol, m.p. 136–137.5°.[16] The infrared spectrum (Nujol mull) was identical with that of an authentic sample.

B. Hydrolysis of *meso*-**Hydrobenzoin Dibenzoate.**—To 1.0 g. (0.0024 mole) of the dibenzoate was added 30 ml. of 95% ethanol and 10 ml. of 20% sodium hydroxide solution. The heterogeneous reaction mixture was heated under reflux for 2.5 hours, after which time all of the solid material had disappeared. The contents were cooled, most of the ethanol was evaporated, the residue was diluted with 50 ml. of water and extracted with three 100-ml. portions of ether. The combined ether solution was dried over anhydrous magnesium sulfate. Removal of the solvent left a white crystalline residue which was recrystallized from benzene–hexane. This gave 0.40 g. (78.5%) of *meso*-hydrobenzoin, m.p. 135.5–136.5°, identical in all respects with an authentic sample.

Saponification of 0.60 g. (0.00142 mole) of oxygen-18 enriched *meso*-hydrobenzoin dibenzoate by the above method gave 0.24 g. (80%) of *meso*-hydrobenzoin, m.p. 136.5–137°, containing 0.604 ± 0.002% excess O–18.

threo-**2-Benzoxy-1,2-diphenylethanol. A. The Reaction of** *erythro*-**1-Benzoxy-2-bromo-1,2-diphenylethane with Silver Benzoate in Wet N,N-Dimethylformamide.**—To a mixture of 1.74 g. (0.0076 mole, 25% excess) of silver benzoate, 50 ml. of redistilled dimethylformamide and 0.2 ml. (0.011 mole) of water was added to 2.28 g. (0.006 mole) of the *erythro*-benzoxybromide. The heterogeneous reaction mixture was stirred and heated in an oil-bath at 100° for 4.5 hours and then allowed to cool to room temperature. The precipitated silver salts were removed by filtration through a layer of filter-aid and washed with chloroform. The clear, colorless filtrate was diluted with 750 ml. of water and then extracted with three 100-ml. portions of chloroform. The combined chloroform extracts were washed with four 200-ml. portions of water and then dried over anhydrous sodium sulfate. Evaporation of the solvent and then recrystallization from benzene–hexane gave 1.60 g. (84%) of *threo*-2-benzoxy-1,2-diphenylethanol, m.p. 152.5–154°.

Anal. Calcd. for $C_{21}H_{18}O_3$: C, 79.2; H, 5.7. Found: C, 79.3; H, 5.5.

erythro-1-Benzoxy-2-bromo-1,2-diphenylethane-carbonyl-O^{18} was allowed to react with silver benzoate in wet dimethylformamide by the above method giving 1.58 g. (83%) of oxygen-18 labeled *threo*-2-benzoxy-1,2-diphenylethanol, m.p. 152–154°.

B. The Reaction of *erythro*-**1-Benzoxy-2-bromo-1,2-diphenylethane with Silver Acetate in Wet Acetic Acid.**—To a mixture of 0.64 g. (0.0038 mole, 25% excess) of silver acetate, 50 ml. of glacial acetic acid and 0.1 ml. (0.0056 mole) of water was added 1.14 g. (0.003 mole) of the *erythro*-benzoxybromide. The heterogeneous reaction mixture was stirred and heated in an oil-bath at 100° for 4.5 hours. The reaction mixture was allowed to cool, was filtered and the precipitated salts were washed with chloroform. The bulk of the solvent was removed from clear, colorless filtrate under reduced pressure. The residue was diluted with 100 ml. of water and the white crystalline precipitate was extracted with three 50-ml. portions of chloroform. The combined chloroform extracts were washed with two 20-ml. portions of 10% sodium bicarbonate, two 50-ml. portions of water and then dried over anhydrous sodium sulfate. Removal of the solvent and recrystallization from benzene–hexane gave 0.80 g. (85%) of *threo*-2-benzoxy-1,2-diphenylethanol, m.p. 152–154°, undepressed on admixture with a sample of the material obtained from the silver benzoate–wet dimethylformamide reaction. The infrared spectra (Nujol mull) of these two samples were identical in all respects.

The reaction of *erythro*-1-benzoxy-2-bromo-1,2-diphenylethane-carbonyl-O^{18} with silver acetate and wet acetic acid gave 0.83 g. (87.5%) of oxygen-18 enriched *threo*-monobenzoate, m.p. 152.5–154.5°.

D,L-**Hydrobenzoin Dibenzoate. A. Benzoylation of** D,L-**Hydrobenzoin.**—To 0.50 g. (0.0023 mole) of D,L-hydrobenzoin in 10 ml. of dry pyridine was added 1.6 ml. (1.97 g., 0.014 mole) of benzoyl chloride with stirring and cooling. The mixture was stirred for 15 minutes, 0.3 ml. of water was added and the mixture was stirred for an additional hour. Chloroform (50 ml.), 15 ml. of water and 5 ml. of 6 *M* hydrochloric acid were then added, the chloroform phase was separated and washed with three 25-ml. portions of 1 *M* hydrochloric acid, 25 ml. of 1 *M* sodium carbonate, 50 ml. of water and then dried over anhydrous sodium sulfate. The solvent was evaporated and the white crystalline residue

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[15] C. Forst and T. H. Zincke, *Ann.*, **182**, 278 (1876), reported m.p. 247°.

[16] J. Böeseken and G. Elsen, *Rec. trav. chim.*, **47**, 696 (1928), reported m.p. 138°.

was recrystallized from 95% ethanol to give 0.82 g. (85%) of the D,L-dibenzoate, m.p. 132–133°.[17]

B. Benzoylation of *threo*-2-Benzoxy-1,2-diphenylethanol.—To 0.50 g. (0.00157 mole) of the *threo*-monobenzoate in 5 ml. of dry pyridine was added 0.6 ml. (0.71 g., 0.005 mole) of benzoyl chloride. The D,L-hydrobenzoin dibenzoate was isolated as described above to give 0.60 g. (91%) of pure material after one recrystallization from 95% ethanol, m.p. 132–133°, undepressed on admixture with an authentic sample. The infrared spectrum (Nujol mull) was identical with that of authentic D,L-glycol dibenzoate.

D,L-Hydrobenzoin. A. Lithium Aluminum Hydride Reduction of *threo*-2-Benzoxy-1,2-diphenylethanol.—The *threo*-monobenzoate (0.50 g., 0.00157 mole) was extracted for five hours in a Soxhlet apparatus with 250 ml. of anhydrous ether containing 1.0 g. (0.026 mole) of lithium aluminum hydride. The excess lithium aluminum hydride was destroyed by the dropwise addition of 5 ml. of water, and approximately 20 ml. of a 20% Rochelle salt solution was added to precipitate the complex. The ether layer was decanted and the residue was washed with three 50-ml. portions of ether. The combined ether extracts were washed with three 50-ml. portions of water and then dried over anhydrous potassium carbonate. The solvent was evaporated and the residue was recrystallized from benzene–hexane to give 0.30 g. (88%) of D,L-glycol, m.p. 119–120°, identical with an authentic sample.

The reduction of 0.50 g. of oxygen-18 labeled *threo*-2-benzoxy-1,2-diphenylethanol, obtained from the silver benzoate–wet dimethylformamide reaction, afforded 0.30 g. (88%) of D,L-hydrobenzoin-O^{18}, m.p. 119–120°, containing 1.23 ± 0.01% excess oxygen-18.

B. Hydrolysis of *threo*-2-Benzoxy-1,2-diphenylethanol.—To 0.50 g. (0.00157 mole) of the *threo*-monobenzoate was added 25 ml. of 95% ethanol and 5 ml. of 20% sodium hydroxide solution. The homogeneous reaction mixture was heated under reflux for two hours. The solution was cooled and the bulk of the ethanol was removed under pressure. The residue was diluted with 50 ml. of water and the crystalline solid was extracted with three 50-ml. portions of ether. The ether solution was dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by recrystallization from benzene–hexane gave 0.29 g. (85.5%) of D,L-hydrobenzoin, m.p. 118.5–119.5°, undepressed on admixture with authentic material.

Saponification of 0.50-g. samples of oxygen-18 enriched *threo*-2-benzoxy-1,2-diphenylethanol, obtained from the silver benzoate–wet dimethylformamide and silver acetate–wet acetic acid reactions, gave 0.29 g. (85.5%) of D,L-hydrobenzoin-O^{18}, m.p. 119–120°, containing 1.21 ± 0.01% and 1.23 ± 0.01% excess of oxygen-18, respectively.

C. By the "Wet" Prevost Reaction on Stilbene.—To a solution of 1.80 g. (0.01 mole) of *trans*-stilbene in 100 ml. of glacial acetic acid and 0.3 ml. (0.015 mole) of water was added 4.18 g. (0.025 mole, 25% excess) of silver acetate and over a period of 0.5 hour, there was added 2.54 (0.01 mole) of finely pulverized iodine with vigorous stirring. The mixture was stirred for an additional hour at room temperature to consume all of the iodine and then stirred and heated at 100° in an oil-bath for 3 hours. The reaction mixture was allowed to cool, the precipitate removed by filtration and the filter cake washed with ether. The filtrate was concentrated under reduced pressure at 70° and the residue was dissolved in 50 ml. of 95% ethanol, filtered and then heated under reflux for two hours with 10 ml. of 20% sodium hydroxide solution. Most of the ethanol was removed under reduced pressure, the residue was diluted with 150 ml. of water and the crystalline solid precipitate was extracted with three 75-ml. portions of ether. The ether solution was dried over anhydrous magnesium sulfate. The solvent was evaporated to give a white crystalline residue which was purified by sublimation at 105–110° and 0.05 mm., followed by recrystallization from benzene–hexane giving 1.30 g. (61%) of pure D,L-hydrobenzoin, m.p. 118.5–119.5°.

The Reaction of Unlabeled *erythro*-1-Benzoxy-2-bromo-1,2-diphenylethane with Silver Benzoate in N,N-Dimethylformamide and Oxygen-18 Enriched Water.—A solution of redistilled dimethylformamide (25 ml.) and 0.2 ml. (0.011 mole) of water containing approximately 1.3% excess of oxygen-18 was equilibrated by shaking with ordinary carbon dioxide for 16 hours. Mass spectrometric analysis of the resultant carbon dioxide indicated that the solvent contained 0.79% excess of oxygen-18. To the dimethylformamide–water-O^{18} solution was added 0.87 g. of thoroughly dried silver benzoate and 1.14 g. of the unlabeled *erythro*-1-benzoxy-2-bromo-1,2-diphenylethane. The mixture was stirred and heated at 100° for 4.5 hours, precautions being taken to exclude moisture from the atmosphere. The reaction mixture was allowed to cool, filtered and the filtrate was equilibrated with ordinary carbon dioxide as described above. Analysis of the carbon dioxide indicated that the solvent contained 0.56% excess of oxygen-18. The filtrate was diluted with 500 ml. of water and then processed in the previously described manner to give 0.75 g. (79%) of *threo*-2-benzoxy-1,2-diphenylethanol-carbonyl-O^{18}, m.p. 153.5–154.5°, containing 0.484 ± 0.003% excess of oxygen-18.

Saponification of 0.50 g. of the carbonyl labeled *threo*-monobenzoate gave 0.30 g. (88%) of D,L-hydrobenzoin, m.p. 118.5–119.5°, containing 0.000 ± 0.002% excess of oxygen-18.

The Reaction of Olefins with Iodine and Silver Acetate in Wet Acetic Acid.—To a solution of 0.05 mole of the olefin in 150 ml. of glacial acetic acid containing 1.4 ml. (0.075 mole) of water was added 20.9 g. (0.125 mole) of silver acetate. Over a period of one hour, with vigorous stirring there was added 12.7 g. (0.05 mole) of finely pulverized iodine. The mixture was stirred for an additional hour at room temperature to consume all of the iodine. To ensure complete reaction the heterogeneous mixture was stirred for 3 to 4 hours in an oil-bath at 100°, allowed to cool, filtered and the precipitated silver salts were washed with ether. The filtrate was concentrated under reduced pressure at 50–60° to about 10–15 ml.

A. *cis*-1,2-Glycols.—The above residue was dissolved in 50 ml. of 95% ethanol, filtered to remove some insoluble material, and heated under reflux for two hours with 20 ml. of a 40% sodium hydroxide solution. The ethanol was evaporated and the residue was extracted with three 100-ml. portions of chloroform. The combined chloroform extracts were washed with 30 ml. of a 40% sodium bisulfite solution and then dried over anhydrous sodium sulfate. Evaporation of the solvent gave the crude diol which was recrystallized or distilled. The yield of pure material is given in Table I.

B. *cis*-1,2-Diacetates.—The residual oil, consisting of a mixture of mono- and diacetates, was treated with 50 g. of acetic anhydride and one drop of concentrated sulfuric acid. The solution was allowed to stand at room temperature for four hours. A small amount of calcium carbonate was added to neutralize the catalyst, and the mixture was shaken, filtered and concentrated under reduced pressure at 50–60°. The residue was taken up in 100 ml. of ether and the ether solution was washed with two 50-ml. portions of water, three 25-ml. portions of 10% sodium bicarbonate solution, 25 ml. of 40% sodium bisulfite solution and finally with water. The ether solution was dried over anhydrous magnesium sulfate. Evaporation of the solvent gave the crude *cis*-1,2-diacetate, which was recrystallized or distilled.

Treatment of Bicyclo[2.2.1]-2-heptene with Iodine and Silver Acetate in Wet Acetic Acid.—Bicyclo[2.2.1]-2-heptene (4.71 g., 0.05 mole) was allowed to react with iodine and silver acetate in moist acetic acid according to the previously described procedure for the isolation of *cis*-1,2-diacetates. Most of the solvent was evaporated and the residual oil was separated into two fractions by distillation: 1.67 g. (22%), b.p. 67–68° at 7 mm., and 5.56 g. (45%), b.p. 125–131° at 7 mm. The first fraction was redistilled for analysis, b.p. 71–71.5° (8 mm.), $n^{25}D$ 1.4674. This material was identified as 3-acetoxynortricyclene on the basis of the following elemental analysis, a negative Baeyer test for unsaturation and a prominent infrared absorption at 12.3–12.4 μ, which is characteristic for nortricyclene derivatives.[18]

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.0; H, 8.0. Found: C, 71.0; H, 7.9.

The elemental analysis and the infrared spectrum of the

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[17] S. H. Harper in E. H. Rodd, "Chemistry of Carbon Compounds," Vol. 3B, Elsevier Publishing Co., New York, N. Y., 1956, p. 1162, reported m.p. 133°.

[18] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3116 (1950).

higher boiling fraction, b.p. 125–131° at 7 mm., indicated that this material was *syn*-7-iodo-exo-2-norbornyl acetate which was contaminated with a small amount of a diacetoxy derivative. Further purification could not be effected by fractional distillation, but a fair separation was obtained by chromatography through a 2 × 20 cm. neutral alumina column using petroleum ether–benzene for elution.

Anal. Calcd. for $C_9H_{13}O_2I$: C, 38.6; H, 4.7; I, 45.3. Found: C, 39.3; H, 4.6; I, 44.5.

SEATTLE 5, WASH.

[CONTRIBUTION NO. 421 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Dehydrohalogenation Products of Hexahydroterephthaloyl Chloride. A Bifunctional Ketene and a Bicyclo[2.2.1]-heptan-7-one Derivative

BY W. R. HATCHARD AND A. K. SCHNEIDER

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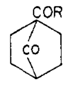
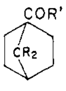
Two compounds of novel structure have been prepared by the dehydrohalogenation of hexahydroterephthaloyl chloride with triethylamine. With excess amine, the major product was 1,4-cyclohexanedimethenone, a crystalline reactive bisketene. Isolated in low yield by sublimation, the bisketene readily polymerized on slight warming. It reacted with moist air to form a mixture of *cis*- and *trans*-hexahydroterephthalic acids. Equimolar ratios of acid chloride and amine yielded 7-oxobicyclo[2.2.1]heptan-1-carbonyl chloride. Several derivatives retaining this structure were prepared by reaction of the keto-acid chloride with amines and alcohols.

Efforts of several investigators to apply the trialkylamine–acid halide synthesis of ketenes to adipoyl chloride and sebacoyl chloride,[1] to suberoyl chloride and longer chain diacid chlorides,[2] and to hexahydroterephthaloyl chloride[3] have resulted in the formation of polymeric resins and reactive intermediates which polymerized on attempted isolation. Recently, while the present paper was in preparation, Blomquist and Meinwald[4] described the reaction of 9,10-dihydroanthracene-9,10-dicarbonyl chloride with triethylamine to yield anthraquinoketene, the first reported bisketene, with the unique exception of carbon suboxide.

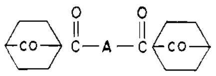
We have found that reaction of hexahydroterephthaloyl chloride with triethylamine can lead to two monomeric products: a bisketene, 1,4-cyclohexanedimethenone (I), and 7-oxobicyclo[2.2.1]-heptan-1-carbonyl chloride (II).

I





II, R = Cl V, R = R′ = OCH_3
IV, R = OH VI, R = OCH_3,
VII, R = $N(C_2H_5)_2$ R′ = OH

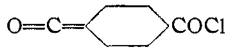


VIII, A = $-NHCH_2CH_2NH-$
IX, A = $-NH(CH_2)_4NH-$
X, A = $-OCH_2CH_2O-$

The bisketone I was prepared by the addition of the acid chloride to a fivefold excess of triethylamine in ethyl ether at 15–20°. Isolated in 8% yield by sublimation from the reaction mixture, it was a yellow, crystalline solid which spontaneously polymerized on slight warming. It reacted with moist air to form a mixture of *cis*- and *trans*-hexahydroterephthalic acids. It was identified by elemental analysis, by its infrared spectrum which exhibited a strong absorption band at 4.75 μ, and by its reaction with water. With 2,5-dimethylpiperazine in methylene chloride, the bisketene reacted to form a polyamide.

The bisketene also has been obtained in very low yield by the pyrolysis of hexahydroterephthaloyl chloride and of 7-oxo-bicyclo[2.2.1]heptan-1-carbonyl chloride at 575–625°.

The monodehydrohalogenation product II was formed concomitantly with the bisketene but was prepared in highest yield by the reverse addition of an equimolar quantity of triethylamine to a refluxing ether solution of the acid chloride. It was apparently not an intermediate in the formation of the bisketene since it was not further dehydrohalogenated under the conditions of the ketene preparation. Assignment of the bicyclic ketone structure II[5] rather than the isomeric ketene–acid chloride structure III was based on infrared spectra and failure of the product to undergo dimerization, halogen addition or dehydrohalogenation reactions. This compound exhibited a strong absorption band at 5.6 μ, similar to the spectra of previously described, more highly substituted bicyclo-[2.2.1]heptan-7-one derivatives.[6,7] No bicyclo-[2.2.1]-heptan-7-one derivatives having substitution only in the 1-position have been described previously.



III

Hydrolysis of II in water, dilute base or concentrated hydrochloric acid yielded a mixture of *cis*- and *trans*-hexahydroterephthalic acids. Attempts to prepare the keto-acid IV by stepwise hydrolysis of II failed, but this compound was obtained indirectly by reaction of the keto-acid chloride with acetic acid. The keto-acid readily hydrolyzed to the mixed hexahydroterephthalic acids. An attempt

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[1] J. C. Sauer, THIS JOURNAL, **69**, 2444 (1947).

[2] A. T. Blomquist and R. R. Spencer, *ibid.*, **70**, 30 (1948).

[3] J. M. Witzel, Doctoral Thesis, Cornell University, Ithaca, N. Y.

[4] A. T. Blomquist and Y. C. Meinwald, THIS JOURNAL, **79**, 2021 (1957).

[5] The structure was first suggested by Professor W. S. Johnson of the University of Wisconsin.

[6] C. F. H. Allen and J. A. Van Allan, *J. Org. Chem.*, **20**, 323 (1955).

[7] P. Wilder, Jr., and A. Winston, THIS JOURNAL, **78**, 868 (1956).