and treated dropwise with a solution of 32 g. (0.32 mole) of concentrated sulfuric acid in 150 ml. of ether. After an hour at 5–10°, the mixture was stirred overnight at room temperature. After removal of barium sulfate by filtration, the filtrate was dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure, leaving 39 g. (94%) of a brown solid. Treatment of this material in ether with diazomethane, or the use of other methods to form esters, produced complex mixtures of products.

Reactions of Desyl Chloride with Organic Bases. 1. Triphenylmethylsodium.—To a solution of 7.0 g. (0.03 mole) of desyl chloride in 250 ml. of anhydrous ether cooled in a salt–ice bath was added 7.5 g. (0.028 mole) of triphenylmethylsodium [prepared by treatment of 15 g. (0.054 mole) of triphenylchloromethane in 300 ml. of anhydrous ether with 1% sodium amalgam (0.125 mole sodium) according to Renfrow and Hauser[35]] via a nitrogen inlet tube from the reaction vessel used to prepare the base. A steady nitrogen sweep was continued during the entire reaction. The dark blood-red reaction mixture was stirred with a magnetic stirrer and after several hours the reaction mixture turned to a dull orange color. Stirring was continued for 24 hr. The reaction mixture was acidified with a 1% acetic acid solution. A solid remained insoluble in both the aqueous or the organic layer and was filtered off to give 3.0 g. (0.006 mole) of bistriphenylmethyl peroxide, m.p. 185–186° (lit.[36] m.p. 185–186°).

The organic layer was separated and dried over anhydrous sodium sulfate. After removal of solvent under reduced pressure, 4.0 g. (0.016 mole) of triphenylmethane remained, m.p. 91–92° (lit.[37] m.p. 92°). The aqueous layer was acidified with a 20% hydrochloric acid solution and extracted with two 100-ml. portions of ether, dried over anhydrous sodium sulfate, and the solvent removed under reduced pressure, leaving a solid residue. Fractional crystallization from alcohol followed by recrystallization from Skelly B afforded 2.9 g. (40% yield) of benzoic acid, m.p. 121–122°, and 1.8 g. (25% yield) of benzilic acid, m.p. 148–149°. The infrared spectra of these two acids were identical with those of authentic compounds.

(35) W. B. Renfrow and C. R. Hauser, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 607.

(36) M. Gomberg, *Ber.*, **33**, 3150 (1900).

(37) J. F. Norris, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 548.

2. Potassium *t*-Butoxide in Dimethyl Sulfoxide.—The dimethyl sulfoxide was distilled at 20 mm. collecting a center fraction. This was dried over Molecular Sieves and redistilled at 20 mm. to yield a center fraction. Three grams (0.013 mole) of desyl chloride in 120 ml. of purified dimethyl sulfoxide was added slowly under a nitrogen atmosphere at room temperature to 1.4 g. (0.013 mole) of potassium *t*-butoxide, prepared by adding 0.5 g. (0.013 mole) of potassium metal to 11 ml. of anhydrous *t*-butyl alcohol and evaporating *in vacuo* to dryness. The solution turned dark red and was allowed to react for 30 hr. This dark reaction mixture was added to 500 ml. of water and extracted with two 250-ml. portions of ether. These were combined and washed with two 250-ml. portions of water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure leaving a dark yellow oil which could be crystallized from Skelly B, giving 2.8 g. of a light yellow solid. The infrared spectrum of this solid showed a strong band at 6.1 μ, indicating a conjugated carbonyl compound; its n.m.r. spectrum (in CDCl₃) showed that it had no protons other than phenyl protons. Fractional crystallization from benzene afforded 0.1 g. of *trans*-dibenzoylstilbene, m.p. 232° (lit.[38] m.p. 232–234°). The remaining solid, 2.7 g., was dissolved in benzene and chromatographed on a 9 × 0.75 in. Woelm alumina column (neutral, activity grade 1). The *cis* isomer was eluted with a 1:1 mixture of ether and chloroform. After recrystallization from benzene an additional 0.5 g. of the *trans* isomer was obtained (24% total yield). Recrystallization from 1:1 benzene–ethanol gave 1.3 g. (52% yield) of the *cis* isomer, m.p. 211–213° (lit.[38] m.p. 212–213°).

(38) R. E. Lutz, C. R. Bauer, R. G. Lutz, and J. S. Gillespie, *J. Org. Chem.* **20**, 218 (1955).

[Contribution from the Department of Chemistry, State University of Iowa, Iowa City, Iowa]

Oxirene.   An Intermediate in the Peroxyacid Oxidation of Acetylenes[1]

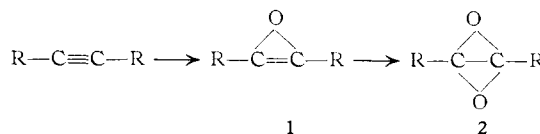By J. K. Stille and D. D. Whitehurst

Received April 1, 1964

Diphenylacetylene has been oxidized with organic peroxyacids to give a variety of products which indicate that diphenyloxirene is an intermediate in the reactions. The mechanistic fate of this intermediate was found to be quite sensitive to solvent polarity and acidity. In an acetic acid solvent, oxidation with *m*-chloroperoxybenzoic acid resulted mainly in the formation of benzoic acid and the production of smaller amounts of benzil and O-acetylbenzoin. In a benzene solvent, with sodium carbonate as an insoluble base, no benzoic acid was formed; the major products were benzophenone and O-benzoyl-O′-(*m*-chlorobenzoyl)dihydroxyphenylmethane. Benzoic acid and ethyl diphenylacetate were the main products when the oxidation was conducted in ethanol.

Introduction

Although the products of peroxyacid oxidation of olefins are well known,[2] the analogous peroxyacid oxidation of acetylenes has not been well studied. The first report of the oxidation of an acetylene with organic peroxyacids[3] indicated that oxidation of phenylacetylene with peroxybenzoic acid in ether solution led to the production of methyl phenylacetate. Later work[4] demonstrated that oxidation of acetylenes with peroxyacetic acid resulted only in cleavage products. The rates of the reactions of peroxyacids with acetylenic

compounds have been shown[5] to be about one-thousandth those of the corresponding olefins.

By analogy to the epoxidation of olefins, it might be expected that an oxirene (1) would be the first product of the oxidation of an acetylene and that a product (2) could also be formed by further oxidation of the oxirene. Products of the type 1 have been claimed[5] as a result of

$$R-C{\equiv}C-R \longrightarrow R-\overset{\displaystyle O}{\overset{\displaystyle /\backslash}{C}}{=}C-R \longrightarrow R-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\displaystyle /\backslash}{C}}-\overset{}{C}}-R$$

1   2

acetylene epoxidations. Later work[6] revealed, how-

(1) This paper is taken in part from the Ph.D. Thesis of D. D. W., State University of Iowa, June, 1964.

(2) D. Swern, *Org. Reactions*, **7**, 378 (1960).

(3) N. Prileshajew, *Chem. Zentr.*, **82**, 1281 (1911).

(4) J. Böesken and G. Slooff, *Rec. trav. chim.*, **49**, 95 (1930).

(5) H. Schlubach and V. Franzen, *Ann.*, **577**, 60 (1952).

(6) V. Franzen, *Chem. Ber.*, **87**, 1479 (1954).

ever, that the product in question was in fact an α,β-unsaturated ketone and that by-products from ketene intermediates were also formed.[7]

Even though the α,β-unsaturated ketone and the other products were explained according to the following reaction scheme,[6] it is not unreasonable to expect that an oxirene could be the initial oxidation product. It is clear, however, that if no hydrogens are adjacent
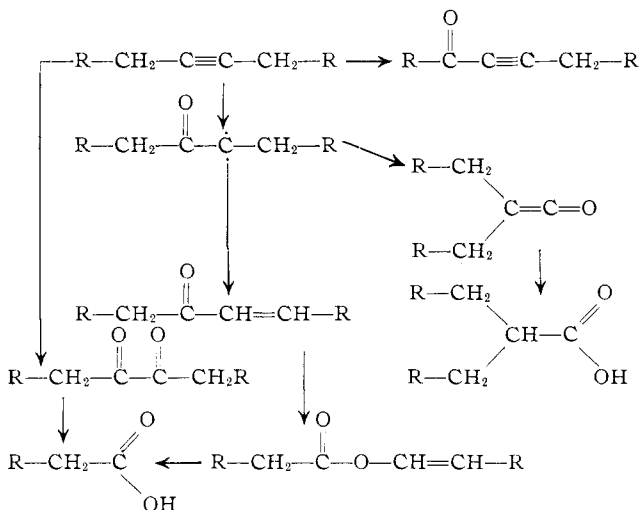
to the acetylenic carbons, any intermediate formed could not be destroyed by a 1,2-shift of hydrogen to afford an α,β-unsaturated ketone and the chances of isolation of the oxirene would be greater.

Our interest in the chemistry of oxirene stemmed from the consideration that this small-ring heterocycle is π-isoelectronic with butadiene.

Results

In hope that an oxirene could be isolated, diphenylacetylene was oxidized with peroxybenzoic, m-chloroperoxybenzoic, and p-nitroperoxybenzoic acids in a variety of solvents. Preliminary rate studies in chloroform solution revealed that diphenylacetylene could be successfully oxidized with peroxybenzoic acid at room temperature. The reaction had second-order kinetics with $k = 5 \times 10^{-5}$ sec.$^{-1}$ and oxidation required 2 to 3 days under the usual conditions for preparative oxidations.

The product·characterization from the oxidation in chloroform was difficult, however, as appreciable amounts of decomposition products were formed by the reaction of peroxybenzoic acid with chloroform. The oxidation was found to proceed with much less decomposition in benzene solutions.

When peroxybenzoic acid was used as the oxidizing agent, addition of a co-solvent was necessitated as the preparation of peroxybenzoic acid was carried out at $-5°$ or below. It was found that the co-solvent used had a marked effect on the product character and distribution. A study was then conducted to note these effects in a variety of solvents. The results of this study are presented in Table I.

Product separation was achieved by column chromatography either on alumina or silica followed by various crystallization techniques. After several oxidations, it was discovered that large-scale decomposition of the reaction products occurred on alumina. This

(7) V. Franzen, Chem. Ber., 87, 1218 (1954).

Table I[a]

PRODUCT YIELDS FROM VARIOUS OXIDATIONS

	$C_6H_6/$ $(C_2H_5)_2O$ 4/1	$C_6H_6/$ $CHCl_3$, 7/3	$C_6H_6 +$ Na_2CO_3	CCl_4	C_2H_5OH	CH_3- CO_2H
	Peroxybenzoic acid			m-Chloroperoxybenzoic acid		
Products	—Yield, %—			————Yield, %————		
7	9.6	Trace		5.8	3.2	17.3
12	7.8[b]				18.3[b]	5.2[c]
14	[d]	[d]	Trace	19.2		4.4
15	8.3[e]	3.0[e]		Trace[f]		21.4[g]
16				17.1[h]		
17	3.5	20.3	15.2	6.4		
18	[d]	[d]			66.2	44.3
19	9[i]	18.6[i]	24.2[j]	10.7[j]		
Ethyl benzoate					5.3	

[a] All yields were based on the diphenylacetylene consumed in the reaction. Completely quantitative separation of the products could not be achieved; thus the reported yields are slightly lower than actual. [b] $R = C_2H_5$. [c] $R = H$. [d] When peroxybenzoic acid was used as the oxidizing agent the yields of 14 and 18 could not be determined directly. The yield of 14 and 18 was approximated by difference. This yield in benzene–ether solvent was 60%. In benzene–chloroform solvent, the yield was 40%. [e] $X = H$. [f] $X = Cl$. [g] When acetic acid was used as solvent, the acetate ester was formed rather than the benzoate or m-chlorobenzoate ester. [h] $R = H$. [i] $X = H$. [j] $X = Cl$.

was not the case with silica, so most chromatographies were conducted on this column packing. No work-up procedure was found, however, which completely excluded some product decomposition.

The yields of cleavage products 7, 14, 18, and rearrangement products 12, 16 were largest when diphenylacetylene (3) was oxidized in polar solvents. In nonpolar solvents, O-benzoyl-O'-(m-chlorobenzoyl)dihydroxyphenylmethane (19) was produced in appreciable quantities. The highest yields of 19 were obtained when 3 was oxidized in benzene in the presence of sodium carbonate as an insoluble base. It should be noted that the yields of 19 are probably higher than the yields reported as this compound suffers appreciable decomposition during work-up.

The structures of all compounds listed in Table I were determined by comparison with authentic samples. Compounds 15e–g were prepared by treating benzoin in pyridine solution with the corresponding acid chloride. The preparation of authentic samples of 19i,j was accomplished by treating the addition compound of benzaldehyde and benzoyl bromide with silver m-chlorobenzoate.[8] Chemical evidence for the identification of 19j is outlined
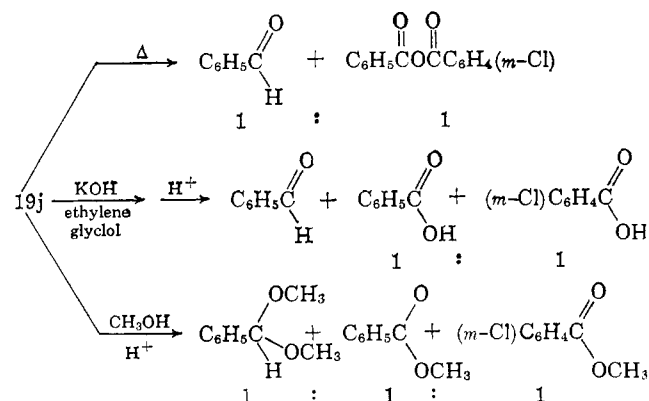
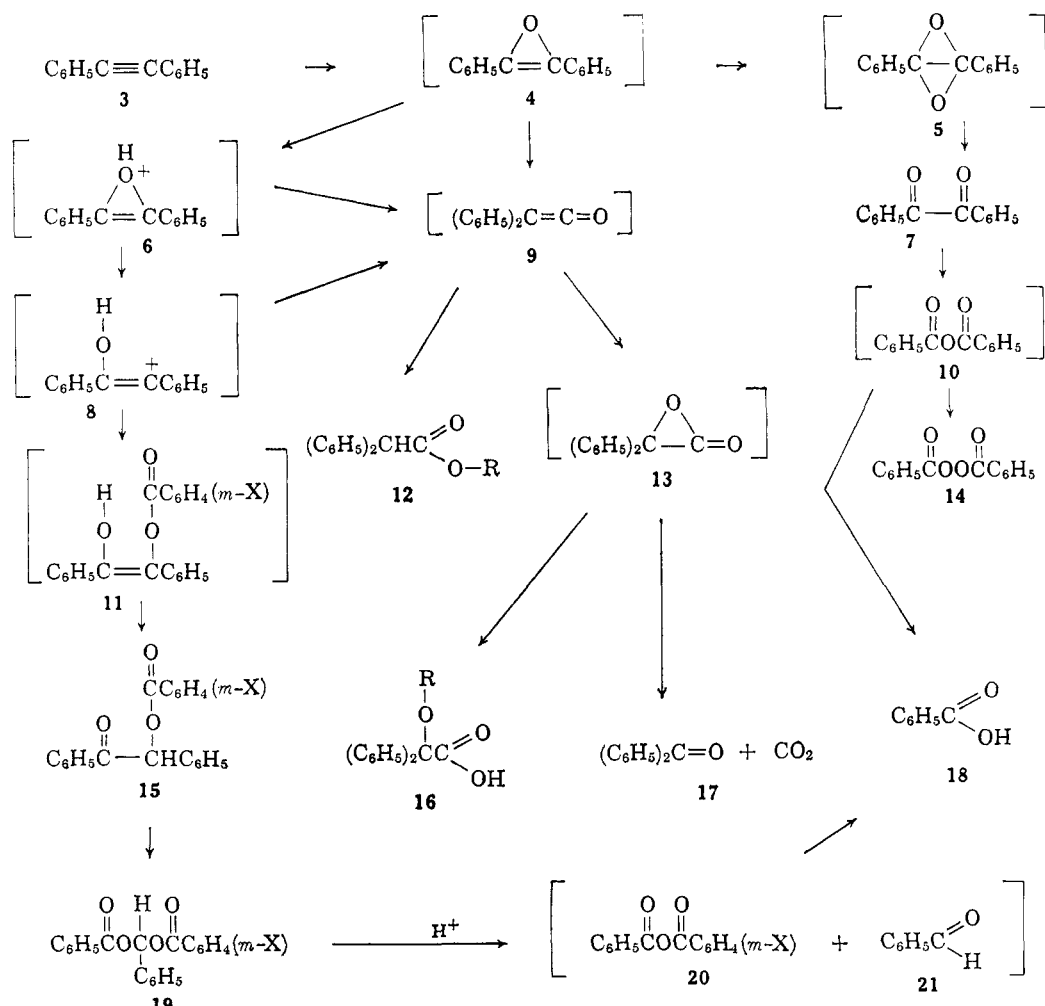(8) R. Adams and E. Vollweiler, J. Am. Chem. Soc., 40, 1732 (1918).

Figure 1.

The nuclear magnetic resonance spectrum of 19j showed the tertiary proton at 1.72 τ, a shift which may be rationalized by the fact that the three strong electron-withdrawing groups are attached to the tertiary carbon atom.

Purification of compound 19 was extremely difficult as heat decomposed it to benzaldehyde and an anhydride; column chromatography on either alumina or silicic acid also produced benzaldehyde. Vapor phase chromatography of 19j decomposed it quantitatively to benzaldehyde and this was used as an aid in yield determination.

Discussion

Apparently, the rate-controlling step for the formation of all products is the addition of the first mole of oxygen to the acetylenic bond. This is indicated by the fact that in most instances large amounts of starting material were recovered and in general the products isolated required at least 2 moles of active oxygen for their production. Of primary concern is this first intermediate (4). A concerted mechanism similar to that described by Swern[2] and others[9-11] seems to be the most logical for its production.

All of the oxidations conducted indicate that three distinct types of products are isolable from the reaction. These are produced via addition, rearrangement, or

cleavage of the intermediates. The general reaction scheme is shown in Fig. 1 which depicts the formation of the products from the oxidation of diphenylacetylene (3) with m-chloroperoxybenzoic acid.

It has been shown[12] that epoxidation of olefins, which leads to strained epoxides, gives high yields of aldehydes and ketones as rearrangement products. It has also been reported[13] that, in special instances, addition to the epoxide may also occur yielding α-hydroxy esters. It is not unreasonable, therefore, to expect that oxidation of acetylenes would give similar results.

Addition.—One of the dominant pathways toward product formation is that of addition to the oxirene (4). As shown in Fig. 1, protonation of the oxirene would produce 6. The formation of cation 6 would be expected to be favorable since the acid produced from the epoxidation would be immediately available to the newly formed oxirene. Although the delocalization energy of oxirene is predicted to be zero and presumably ring opening would be facile without the aid of acid, the delocalization energy of protonated oxirene may be substantial.[14] Oxirene can be predicted to be a strong base. Immediately after the transfer of oxygen by peracid to the acetylene, the corresponding acid is available to the oxirene base, and inside the solvent

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(11) A. Darby, H. Henbest, and J. McClenaghan, Chem. Ind. (London), 462 (1962).

(12) J. Traynham and W. Baird, Jr., J. Org. Chem., 27, 3189 (1962).

(13) R. Filler, B. Camara, and S. Naqvi, J. Am. Chem. Soc., 81, 658 (1959).

(14) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1962. Chapter 5.

cage. Thus immediate protonation of the oxirene would be expected to take place in most circumstances, even in the presence of added base. Addition of the benzoate ion to protonated oxirene produced 11, isolated as the α-keto ester (15). Product 19 is formed from 15 *via* a Baeyer-Villiger type oxidation as demonstrated by the fact that, in a separate experiment, peroxidation of 15 afforded 19. Baeyer-Villiger oxidation of dicarbonyl compounds has been shown[15] to be catalyzed by base, and 19 was isolated in the greatest yield when solid sodium carbonate was present in the reaction mixture.

Rearrangement.—It has been shown[6,7,16,17] that, in the oxidation of acetylenes, rearrangement is one of the dominant features. Ketene production was reported in each instance but different intermediates were postulated for its formation.
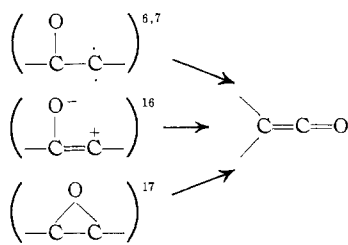
The products of rearrangement, isolated from the oxidation of 3 with peroxy acids, also indicate a ketene intermediate (9). Considering the reaction conditions, two routes are plausible for ketene production. One route is phenyl migration in 4 by a concerted mechanism that could yield 9 directly. The alternate route to the ketene intermediate could arise from phenyl migration in carbonium ion 8 or from a concerted rearrangement in the protonated oxirene 6, both followed by proton elimination. Since rearrangement occurs most readily in polar solvents and since 6 is predicted to be formed in the presence of acid, the latter route is favored. Rearrangement of the oxirene *via* a carbene is doubtful as α-keto carbenes are known to produce by-products of α-keto ethers when they are generated in alcohol solutions.[18] No α-keto ethers were found in the reaction mixture of the oxidation of diphenylacetylene with *m*-chloroperoxybenzoic acid in ethanol.

The ketene, once produced, can react with alcohol or water to form derivatives of diphenylacetic acid (12). When 3 was oxidized with *m*-chloroperoxybenzoic acid in 80% benzene–20% diethyl ether solution, ethyl diphenylacetate was isolated from the reaction in a moderate yield. The product of ethanol necessary for ester formation is explained by the fact that decomposition of peroxyacids in ether solutions produces the alcohol of the corresponding ether.[19]

The ketene 9 also suffers further oxidation to produce an α-lactone (13) which may react with protonic solvents to yield derivatives of benzilic acid (16). Complete oxidation of 9 forms benzophenone (17) and carbon dioxide. Oxidation of diphenylketene by *m*-

chloroperoxybenzoic acid was in fact shown in a separate experiment to produce rapidly benzophenone and carbon dioxide.

Cleavage.—The oxirene intermediate 4 on further oxidation may produce 2,4-diphenyl-1,3-dioxabicyclo-[1.1.0]butane (5). This intermediate, on isomerization, would lead to benzil (7), although benzil may be produced by the oxidation of benzoin formed by the attack of water on 6 or 8. Benzoin will oxidize to benzil under these conditions. The production of glyoxal by the oxidation of acetylene with monoatomic oxygen in a discharge tube at −190° has been postulated[20] to proceed through the initial formation of 1,3-dioxabicyclo-[1.1.0]butane.

Products 10, 14, and 18 may be explained by the oxidation of benzil (7). Baeyer–Villiger oxidation of α-diketones is known to yield anhydrides.[15] It was also shown in a separate experiment that benzoic anhydride (10) is converted to benzoyl peroxide (14) and benzoic acid (18) by oxidation with *m*-chloroperoxybenzoic acid. Presumably, this oxidation also proceeds by a Baeyer–Villiger type mechanism.

An alternate route to the formation of 18 is the decomposition of 19 by acid catalysis to the anhydride 20 and benzaldehyde (21) followed by oxidation. This latter mechanism could be responsible for the major portion of benzoic acid production as oxidation of 3 in presence of base produced no benzoic acid and in acid solution benzoic acid was the major product. Oxidation of 4 in acid solution would probably proceed through a protonated oxirene, 6. This cation should be quite inert to electrophilic attack by peracid, and thus cleavage *via* intermediate 5 should be hindered in acid solutions. However, in the presence of sodium carbonate, no benzil was produced, but this is not unreasonable in consideration of the fact that acid would be immediately available to the oxirene even in the presence of base. Also it was found that oxidation of benzil occurred at a slower rate than oxidation of diphenylacetylene under similar reaction conditions.

Although the oxirene 4 was not isolated, the products of the oxidation can be most conveniently accounted for as arising from this intermediate.

Experimental

(15) C. Hassall, "Organic Reactions," Vol. 9, John Wiley and Sons, Inc., New York, N. Y., 1960, p. 73.

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(17) J. Haller and G. Pimentel, *J. Am. Chem. Soc.*, **84**, 2855 (1962).

(18) G. Schröter, *Ber.*, **42**, 2345 (1909).

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(24) I. Kolthoff, T. Lee, and M. Mairs, *J. Polymer Sci.*, **2**, 199 (1947).

(25) Phosphate buffer solutions of this type have been shown to quantitatively remove carboxylic acids from peroxy acids: N. Vilhas, *Bull. Soc. Chim. France*, 1401 (1959).

through a column of Molecular Sieve to remove the last traces of water and methanol.[26]

Oxidation of 3 with Peroxybenzoic Acid in 80% Benzene–20% Diethyl Ether.—To 1 l. of 0.642 M peroxybenzoic acid in 80% benzene–20% diethyl ether was added 100 g. (0.562 mole) of diphenylacetylene. The reaction was allowed to proceed at room temperature in the dark until a negative test with acidified potassium iodide was achieved.

Rate Studies on the Oxidation of Diphenylacetylene with Peroxybenzoic Acid.—To a solution of 90% chloroform–10% benzene, containing 1.00168 g. (0.00562 mole) of diphenylacetylene, was added 13.90 ml. of 0.432 M (0.00562 mole) peroxybenzoic acid in 90% chloroform–10% benzene and the total volume of the solution was raised to 100.0 ml. by the addition of more solvent. The reaction was maintained at a constant temperature of 25°. Oxidation was followed by periodically titrating a 1.00-ml. aliquot of the reaction solution with standardized sodium thiosulfate solution and noting the disappearance of active oxygen. A blank, containing the same initial concentration of peroxybenzoic acid in 90% chloroform–10% benzene, was run simultaneously with the oxidation under the same conditions, and was also titrated periodically to allow compensation for the decomposition of peroxybenzoic acid by solvent. Rate studies using 1:2, 2:1, and 3:1 mole ratios of peroxybenzoic acid to diphenylacetylene were conducted in a similar manner. When $\log a(b - x)/b(a - x)$ was plotted against time, a straight line was produced for all oxidations, with $k = 5 \times 10^{-5}$ sec.$^{-1}$.

Oxidation of 3 with m-Chloroperoxybenzoic Acid in Benzene with Sodium Carbonate as an Insoluble Base.—To a solution of 41.8 g. (0.235 mole) of diphenylacetylene in 600 ml. of benzene was added 95.6 g. (0.352 mole)[27] of m-chloroperoxybenzoic acid[28] and 70 g. of sodium carbonate. The reaction was stirred and protected from light. After 1 hr. the reaction had warmed to about 50° and began to evolve carbon dioxide and oxygen. Evolution of gases ceased after 8 hr., the reaction mixture gelled, and the reaction was essentially complete.

Separation and Analysis of Products. A. Acids.—The acids produced in the oxidations were easily separated from the neutral products by partitioning the reaction solution between ether and 2 N sodium hydroxide or 5% sodium carbonate solutions. The basic aqueous layer was then acidified and the insoluble acids removed by suction filtration. The dried acids were esterified by dissolving them in acidified methanol and heating the solution to the reflux temperature for 6 hr. The esters were obtained by evaporation of the methanol, partitioning between 2 N sodium hydroxide solution and ether, drying over sodium sulfate, and evaporation of the ether. Analysis of the percentage composition and product identification was achieved by means of gas chromatography.

B. Neutral Compounds.—The neutral portion in ether solution was dried and the ether was removed under reduced pressure. The best separation without product decomposition was achieved by chromatography on a column of silica gel eluting with continual gradient addition from pentane through carbon tetrachloride, chloroform, ether, ethyl acetate, and finally methanol. Weight distribution plots were then constructed and the peaks analyzed by infrared spectrophotometry. Similar peaks were combined and rechromatographed using slower eluent polarity change. Similar peaks were again combined and pure products were obtained by low-temperature crystallization techniques. Analyses were achieved by comparison of the infrared spectra, proton magnetic resonance spectra, molecular weights, and melting points of the products with those of authentic samples.

Oxidation of Diphenylketene.—A solution of 1.1 g. (0.0057 mole) of freshly prepared[29,30] diphenylketene was added to a stirred solution of 2.0 g. (0.010 mole)[27] of m-chloroperoxybenzoic

acid and 3.0 g. of sodium carbonate in 35 ml. of benzene. Carbon dioxide was immediately evolved. The reaction was stirred for 3 hr. Extraction of the resultant solution with 2 N sodium hydroxide solution and evaporation of the benzene gave 0.8 g. (77%) of benzophenone. Acidification of the basic extract gave m-chlorobenzoic acid as the only acidic component from the oxidation.

Oxidation of Benzoic Anhydride.—A solution of 1 g. (0.0044 mole) of benzoic anhydride[31] and 1 g. (0.0052 mole)[27] of m-chloroperoxybenzoic acid in 20 ml. of benzene was allowed to react at room temperature for 2 weeks. The reaction mixture was extracted with phosphate buffer solution and the neutral portion was dried over sodium sulfate. Evaporation of the solvent and infrared analysis of the neutral components revealed them to be a mixture of peroxides. The peroxides were purified by crystallization from ether at −78°, and were subsequently decomposed by treatment with 20 ml. of a solution of 1 g. of sodium dissolved in methanol. The solution was then acidified and partitioned between ether and a solution of sodium thiosulfate. After washing the ether solution with water and drying, the ether was removed. The resulting mixture was esterified with methanol and analyzed by gas chromatography. The mixture was found to be composed of 27% methyl benzoate and 69% methyl m-chlorobenzoate.[28]

The acid portion from the original oxidation was obtained by acidifying the phosphate buffer solution and extracting with ether. The ether layer was washed with water, dried, and the ether was removed. The resultant acid mixture was found to be composed of 71% methyl benzoate and 24% methyl m-chlorobenzoate.[28]

Oxidation of O-(m-chlorobenzoyl)benzoin with Peroxybenzoic Acid.—To a stirred suspension of 2 g. of sodium carbonate and 15.5 ml. of 0.375 M (0.00582 mole) peroxybenzoic acid in 90% benzene–10% carbon tetrachloride was added 2.00 g. of O-(m-chlorobenzoyl)benzoin and 5 ml. of benzene. The reaction was allowed to proceed for 13 hr. at room temperature. The products were obtained by partitioning the reaction mixture between water and ether. The ether layer contained 1.95 g. (94%) of O-benzoyl-O′-(m-chlorobenzoyl)dihydroxyphenylmethane (19j). Acidification of the aqueous layer, extraction with ether, esterification with methanol, and analysis by vapor phase chromatography showed benzoic acid to be the only acidic component in the reaction mixture.

O-Benzoylbenzoin (15e).—Esterification of benzoin was achieved by dissolving benzoyl chloride in pyridine and adding an equimolar amount of benzoin. Product isolation was accomplished by partitioning the reaction mixture between water and benzene and washing the benzene alternately with dilute hydrochloric acid, dilute sodium hydroxide, and water. The benzene solution was dried and benzene was removed. The product was purified by recrystallization from ethanol. The yield in this reaction was usually greater than 70%, m.p. 123–124°, lit.[32] m.p. 124–125°.

O-Acetylbenzoin (15g) and O-(m-chlorobenzoyl)benzoin (15f) were synthesized using procedures identical with that of **15e** with comparable yields. O-Acetylbenzoin, m.p. 82–83°, lit.[33] m.p. 83°. The infrared and proton magnetic resonance spectra of O-(m-chlorobenzoyl)benzoin were consistent with a compound of this structure, m.p. 104.5–105°.

O-Benzoyl-O′-(m-chlorobenzoyl)dihydroxyphenylmethane (19j).—A convenient method for the preparation of this type of compound has been reported.[8] Equimolar amounts of benzaldehyde and benzoyl bromide were mixed and allowed to react at room temperature until the entire reaction mixture solidified (about 8 hr.). The addition compound was triturated with pentane and recrystallized from hexane. The yield was nearly quantitative. To a stirred suspension of 2.5 g. (0.011 mole) of silver m-chlorobenzoate in diethyl ether, 2.9 g. (0.010 mole) of the addition compound was added in one portion. The reaction was stirred for 1 hr. and allowed to stand overnight at room temperature. The reaction mixture was filtered and the filtrate was partitioned between 2 N sodium hydroxide and additional ether. The ether layer was dried and the ether removed by evaporation *in vacuo*. The crude oily product was purified by crystallization from pentane at −78° and a yield of 2.2 g. (60%) was obtained. The pure product was a light yellow

(26) Titration of the peroxyacid solution with a standardized solution of sodium thiosulfate showed no loss of active oxygen on passing through the column.

(27) Assuming that commercial m-chloroperoxybenzoic acid contains 85% active oxygen.

(28) m-Chloroperoxybenzoic acid was purchased from FMC Corp., Carteret, N. J., and used without further purification. This commercial peroxyacid was found to contain up to 5% impurity of some acid of lower molecular weight than m-chlorobenzoic acid by reduction with sodium thiosulfate and esterification with methanol followed by gas chromatographic analysis. This impurity was not benzoic acid and corrections had to be made in order to evaluate the true yield of benzoic acid from the oxidations.

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-oil at room temperature and had infrared and proton magnetic resonance spectra consistent with a compound of this structure.

Anal. Calcd. for $C_{21}H_{15}O_4Cl$: C, 68.76; H, 4.09; mol. wt., 366.5. Found: C, 68.42; H, 4.06; mol. wt., 366.4. The molecular weight was determined on the Mechrolab Model 301 vapor pressure osmometer using chloroform as the solvent.

O,O'-Dibenzoyldihydroxyphenylmethane (19i) was synthesized using a procedure identical with that of 19j with comparable yields, m.p. 61.5–62.5°, lit.[8] m.p. 62–63°.

The Reaction of the Cyclooctatetraenyl Dianion with *gem*-Dihalides. The Addition of Alkyl Carbenes to Cyclooctatetraene
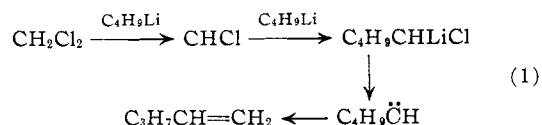
BY THOMAS J. KATZ AND PETER J. GARRATT

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Dipotassium or dilithium cyclooctatetraenide reacts with 1,1-dichloroethane to yield *syn*-9-methylbicyclo-[6.1.0]nonatriene (II) and with 1,1,1-trichloroethane to yield 9-chloro-9-methylbicyclo[6.1.0]nonatriene. A mixture of cyclooctatetraene and methylene chloride reacts with methyllithium containing lithium iodide to give II in low yield and with methyllithium containing lithium bromide to give some II, but mainly *syn*-and *anti*-9-chlorobicyclo[6.1.0]nonatriene (Ia and b). (The predominant *syn* isomer, Ia, is isolated.)

Introduction

Mixtures of methylene chloride, methyl- or *n*-butyllithium in ether, and any of a number of olefins react to form chlorocyclopropanes,[1] apparently through the intermediate divalent carbon species[2] chlorocarbene, which adds to the olefin to yield the observed product. Accompanying this reaction is a side reaction in which *n*-butyllithium, for example, combines with methylene chloride to yield 1-pentene, apparently through the intermediacy of an alkyl carbene (eq. 1).[3]

$$CH_2Cl_2 \xrightarrow{C_4H_9Li} CHCl \xrightarrow{C_4H_9Li} C_4H_9CHLiCl$$

$$C_3H_7CH{=}CH_2 \longleftarrow C_4H_9\ddot{C}H \qquad (1)$$

However, one product normally not observed is the alkylcyclopropane that would form if the alkylcarbene added to the olefin. Presumably this reaction cannot compete with others that the alkylcarbenes might undergo, such as intramolecular rearrangement to yield olefins or internal insertion to yield cyclopropanes. It is observed that olefins and. cyclopropanes form in numerous reactions that appear to proceed through the intermediacy of alkylcarbenes[2]— the reaction of alkyllithiums with methylene chloride,[3] the thermal decomposition of salts of toluenesulfonylhydrazones,[4] the thermolysis or photolysis of diazoalkanes,[5] the dehydrohalogenation of alkyl halides,[6] and the reduction of *gem*-dihalides[7]— in a reaction that is rapid, for the lifetime of ethylidene formed in the vapor-phase photolysis

of diazoethane is very short.[5b] Two exceptional reactions of methylene chloride and methyllithium are with benzene, which yields 1-methylcycloheptatriene,[8] and with dimethylacetylene, which yields trimethylcyclopropene,[9] but these undoubtedly proceed through the formation of the expected chlorocarbene adducts, followed by their dissociation to the tropylium and dimethylcyclopropenium cations, which, in turn, are alkylated by the methyllithium. There are some cases reported in which alkylcarbenes undergo intermolecular reaction. These include reactions of ethylidene in the vapor phase, even with propylene, to yield some dimethylcyclopropanes (but not with *cis*- or *trans*-2-butene to yield trimethylcyclopropanes)[5b] and in ether solution with phenylsilane to yield phenylethylsilane.[10] Another reaction that may be of this kind, reported after the completion of our work, is that of styrene with methylene chloride and methyllithium, which yields 1-phenyl-2-methylcyclopropane.[11]

Considering these results, the reaction of cyclooctatetraene with methylene chloride and methyllithium is surprising. The 9-chlorobicyclo[6.1.0]nonatriene (Ia or b), the expected product of the reaction, was sought as an intermediate for the synthesis of the cyclononatetraenyl anion,[12,13] but initial experiments yielded none of this material. Instead, there was discovered in low yield (*ca.* 3%) *syn*-9-methylbicyclo[6.1.0]nonatriene (II). This reaction and the reaction of dipotassium cyclooctatetraenide with *gem*-dihalides, a more felicitous procedure for adding alkylcarbene fragments to cyclooctatetraene, are reported below.

Ia   Ib   II
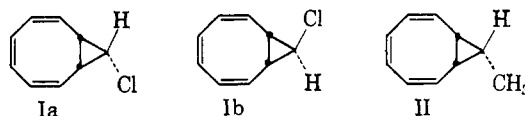
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