6. The C_{3v} cyclononane XVII is uniquely defined for any given θ

$$\cos \omega_1 = \frac{-1 - 2 \cos \theta \sin \frac{1}{2}\theta}{2 \sin \frac{1}{2}\theta (1 + \cos \theta)}$$

7. The C_s cyclodecanes CCC (XXI), CCB (XXII), and BCB (XXIII) are analogous to the cyclooctanes (II, IV, VII) above and a unique solution requires assignment of one dihedral angle as well as θ; if ω_1 is given

$$\cos \omega_3 = \frac{1}{2} \left(\frac{\cos^2 \theta - \sin^2 \theta \cos \omega_1 - \cos \theta}{\sin \theta \sin \frac{1}{2}\theta} \right)^2 - 1$$

$$S_{DJ}^2 = 2(\cos^2 \theta - \sin^2 \theta \cos \omega_1 - 3 \cos \theta + 2) = f_{15}(\theta, \omega_1, \omega_2)$$

and solution of f_{15} for ω_2 leads to two angles corresponding to ω_2 for boat and chair subunits at the ends of the molecule.

8. The C_s cyclodecanes CBC, BBC, and BBB are similarly defined by assumption of ω_1 and $\theta(\omega_3 = 0)$

$$S_{DJ}^2 = 2(1 - \cos \theta)(\cos \theta + \cos \theta \cos \omega_1 + \cos \omega_1) = f_{15}(\theta, \omega_1, \omega_2)$$

and solution of f_{15} for ω_2 leads to two angles as in 7, above.

9. Common procedure with the more difficult rings containing only axes of symmetry has been to utilize an iterative approach to discover the true ring as may be seen in the C_2 cyclononanes which are defined by assumption of θ and one ω(here $= \omega_5$)
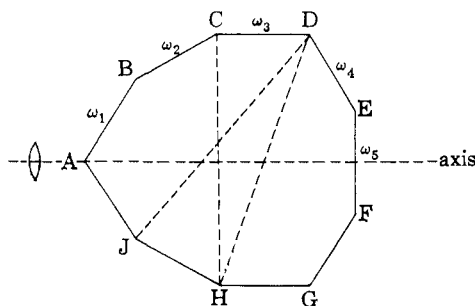
(a)   assume a value for ω_4

(b) $S_{CH} = f_{16}(\theta, \omega_4, \omega_5, \omega_4) = f_{15}(\omega_1, \omega_1)$; yields ω_1

(c) $S_{DH} = f_{15}(\theta, \omega_5, \omega_4) = f_{16}(\omega_1, \omega_1, \omega_2)$; yields ω_2

(d) $S_{DJ} = f_{15}(\theta, \omega_1, \omega_2) = f_{16}(\omega_5, \omega_4, \omega_3)$; yields ω_3

(e) $S_{HH} = f_{1-10}(\theta, \omega_1, \omega_1, \omega_2, \omega_3, \omega_4, \omega_5, \omega_4)$

(f)   vary ω_4 and repeat until $S_{HH} = 0$, a condition of a closed ring.

Strained Ring Systems. I. Peroxidation Studies with Certain Acetylenes. The Relevance of Oxirene Intermediates

By Richard N. McDonald and Peter A. Schwab[1]

Received April 1, 1964

Organic peracid oxidations of phenyl- and diphenylacetylene have led to the formation of three different types of products. Each is explicable in terms of an oxirene intermediate reacting to give products (1) of further oxidation, (2) of rearrangement, and (3) of addition, depending on the reaction conditions. Trifluoroperacetic acid treatment of diphenylacetylene gave benzil and benzoic acid. Phenylacetylene when allowed to react with trifluoroperacetic acid gave phenylacetic and benzoic acids, while with perbenzoic acid methyl and ethyl phenylacetates, methyl benzoate, benzaldehyde, and benzoic acid were produced. Peracetic acid reacted with phenylacetylene to give benzyl acetate, acetylmandelic acid, phenylacetic acid, and benzoic acid. The modes of formation of these products are discussed as is the nature of the proposed oxirene intermediates. Treatment of desyl chloride with tritylsodium gave benzilic and benzoic acids. Desyl chloride also reacted with potassium t-butoxide in dimethyl sulfoxide to give a mixture of cis- and trans-dibenzoylstilbenes.

The synthesis and chemistry of small-ring compounds has been and continues to be of interest to chemists. The simplest oxygen-containing heterocycle, oxirene (I), has not yet been fully described or characterized. It may bear some interesting relationships with two hydrocarbon small-ring compounds.

Its hydrocarbon analog, cyclopropene (II), has been reported as having various substituted derivatives, and a considerable amount is known concerning its physical and chemical behavior. Oxirene (I) may also be considered to be iso-π-electronic with cyclobutadiene (III) just as furan is to benzene. Simple molecular orbital calculations[2] predict zero delocalization energy and a singlet ground state for I, as opposed to the zero delocalization energy and triplet ground state predicted for III.[3]

An estimate of the strain energy of I is also available from its hydrocarbon counterparts. The strain energy (s.e.) of ethylene oxide, taken as the difference between the calculated and experimental heats of formation, has been found to be 13 kcal./mole.[4] Assuming the same differential in strain energy holds between cyclopropane and cyclopropene (Δs.e. $\approx$ 27 kcal./mole)[5] as in ethylene oxide and oxirene (I), we see the total s.e. of I to be ~40 kcal./mole. In addition, since the s.e. of cyclopropane is ~12 kcal./mole more than for ethylene oxide,[4] we might expect I to be more stable than II and isolable, at least on the basis of this one criterion.
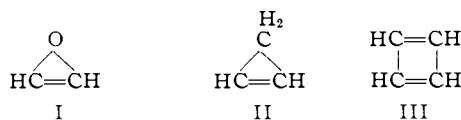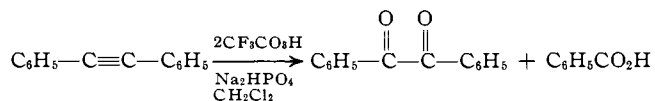
2-Methyloxirene was reported to result from the chromic anhydride oxidation of propyne.[6] This result has not been verified and appears questionable since other studies with strong oxidizing agents, e.g., $KMnO_4$,[7] SeO_2,[8] and CrO_3,[9] yield α-dicarbonyl compounds or complete fission of the triple bond to carboxylic acid products. Other investigations also appear in the literature reporting the isolation of substituted analogs of oxirene, but, in general, are followed up by a paper in subsequent years discrediting the first.[10,11]

Results and Discussion

Since an oxirene intermediate has been ruled out in the reaction of acetylene with ^3P oxygen atoms because it fails to conserve spin,[12] reaction of an acetylene with "singlet" oxygen atoms might be expected to yield this unknown class of small-ring compounds. If we consider the oxidation of carbon–carbon multiple bonds by peroxy compounds as a method of transferring "singlet" oxygen atoms to the multiple bond, such reactions appear reasonable as a possible method for obtaining oxirenes.

From the work of Franzen,[13] it was thought that the oxirene ring system may be an intermediate in the oxidation of the triple bond by an organic peracid. If this strained ring system is to be isolated, groups capable of electron delocalization might be expected to aid in its stabilization. Therefore, the organic peracid oxidations of diphenylacetylene and phenylacetylene were investigated.

Both perbenzoic acid in chloroform solution and peracetic acid in acetic acid–methylene chloride solution failed to react with diphenylacetylene under the conditions employed[14] (see Experimental). However, trifluoroperacetic acid in methylene chloride solution, with disodium hydrogen phosphate,[15] oxidized diphenylacetylene to the α-diketone, benzil, and benzoic acid. Two moles of the peracid was required to give a 76% yield of benzil and a 17% yield of benzoic acid as the only identifiable products. Benzoic acid undoubtedly arises from the complete oxidative cleavage of the triple bond via the α-diketone which undergoes further oxidation to the anhydride and is then cleaved to the observed carboxylic acid. The oxidation of diphenylacetylene

$$C_6H_5-C{\equiv}C-C_6H_5 \xrightarrow[\substack{Na_2HPO_4 \\ CH_2Cl_2}]{2CF_3CO_3H} C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-C_6H_5 + C_6H_5CO_2H$$

with ozone has been reported to give yields of 5–51% of benzil, benzoic acid being the other product.[16]

(6) M. Berthelot, Bull. soc. chim. France, 14, 113 (1870).

(7) (a) P. Piganiol, "Acetylene Homologs and Derivatives," Mapleton House, Brooklyn, N. Y., 1950, p. 113; (b) R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Academic Press, Inc., New York, N. Y., 1955, p. 31; (c) G. F. Hennion and T. F. Banigan, J. Am. Chem. Soc., 68, 1202 (1946); (d) N. A. Khan and M. S. Newman, J..Org. Chem., 17, 1063 (1952).

(8) (a) J. J. Postowsky and B. P. Lugowkin, Ber., 68, 852 (1935); (b) R. Truchet, Compt. rend., 196, 706 (1933).

(9) P. Ruggli and H. Zaeslin, Helv. Chim. Acta, 18, 845 (1935).

(10) These have been reviewed by V. Franzen, Ann., 614, 31 (1958).

(11) P. Muller and W. Schindler, U. S. Patent 2,432,118 (1947), reported the preparation of 2-chloro-3-phenyloxirene which appears quite unlikely from some similar studies by R. N. McDonald and P. A. Schwab, J. Org. Chem., 29, 2459 (1964).

(12) I. Haller and G. C. Pimentel, J. Am. Chem. Soc., 84, 2855 (1962).

(13) V. Franzen, Ber., 87, 1219, 1478 (1954).

(14) J. K. Stille and D. D. Whitehurst, J. Am. Chem. Soc., 86, 4871 (1964), report that perbenzoic acid oxidation of diphenylacetylene does take place in other solvents when allowed longer reaction times.
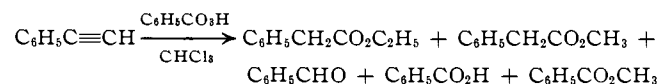
(15) W. D. Emmons and A. S. Pagano, ibid., 77, 89 (1955).

Trifluoroperacetic acid treatment of phenylacetylene gave a 25% yield of benzoic acid and a 38% yield of phenylacetic acid. The benzoic acid is again formed by complete oxidative cleavage of the triple bond. However, phenylacetic acid must arise from a rearrange-

$$C_6H_5-C{\equiv}CH \xrightarrow[\substack{Na_2HPO_4 \\ CH_2Cl_2}]{CF_3CO_3H} C_6H_5CH_2CO_2H + C_6H_5CO_2H$$
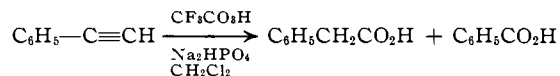
ment. It has been shown that the oxidation of phenylacetylene by nitrous oxide in ethanol gives ethyl phenylacetate, and in water phenylacetic acid is formed.[17] In inert solvents nitrous oxide reacted with phenylacetylene to give a tar from which no definite products could be isolated. However, treatment of diphenylacetylene with nitrous oxide in cyclohexane yielded diphenylketene dimer. The formation of this dimer as well as the formation of phenylacetic acid in the oxidation of phenylacetylene is consistent with the theory that a ketene is formed as an intermediate. Thus, the formation of phenylacetic acid in the peroxidation of phenylacetylene with trifluoroperacetic acid, containing at least 10% water (from its preparation by the treatment of trifluoroacetic anhydride with 90% hydrogen peroxide), is also consistent with phenylketene as an intermediate (Fig. 1).

The perbenzoic acid oxidation of phenylacetylene has been reported to yield phenylacetic acid.[18] We have found that treatment of phenylacetylene with perbenzoic acid in chloroform for 2 days gives a mixture composed of 8.1% yield of ethyl phenylacetate, 42.5% yield of methyl phenylacetate, 11.1% yield of benzaldehyde, 43.5% yield of benzoic acid, and 3.0% yield of methyl benzoate. The yield of benzoic acid is probably high since it is not known exactly how much,

$$C_6H_5C{\equiv}CH \xrightarrow[CHCl_3]{C_6H_5CO_3H} C_6H_5CH_2CO_2C_2H_5 + C_6H_5CH_2CO_2CH_3 +$$
$$C_6H_5CHO + C_6H_5CO_2H + C_6H_5CO_2CH_3$$

if any, benzoic acid is present in the chloroform solution of perbenzoic acid. Although this solution was freshly prepared, there undoubtedly still is benzoic acid present. The total yield is 108.2%, accounting for the starting material and, apparently, at least 8% of benzoic acid present in the solution of perbenzoic acid.

The formation of large amounts of methyl and ethyl phenylacetates arises from the reaction of the intermediate phenylketene with methanol and ethanol (see Fig. 1). The methyl alcohol is present in the reaction mixture from the preparation of the solution of perbenzoic acid.[19] The ethyl alcohol is present since commercial chloroform contains about 1% of this alcohol as stabilizer and no attempt was made to remove it. Of the volume of chloroform used (~520 ml.), there would be ~0.1 mole of ethanol present, more than enough to account for the amount of ethyl ester produced. The methanol would probably be in excess accounting for the considerably larger amount of methyl ester in the product.

Methyl benzoate probably arises by the methylation of benzoic acid. Benzaldehyde is possibly formed via

(16) T. L. Jacobs, ibid., 58, 2272 (1936), and R. Criegee and M. Lederer, Ann., 583, 29 (1953).

(17) G. D. Buckley and W. J. Levy, J. Chem. Soc., 3016 (1951).

(18) N. Prileschajew, J. Russ. Phys. Chem. Soc., 42, 1387 (1910); Chem. Abstr., 4, 916 (1910).

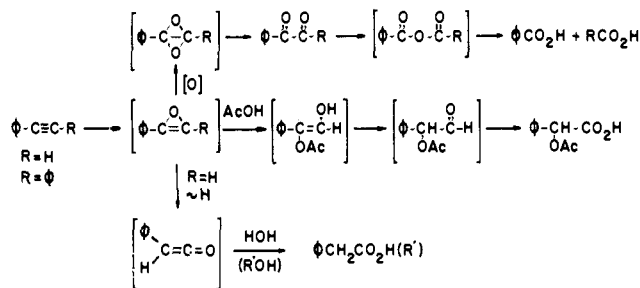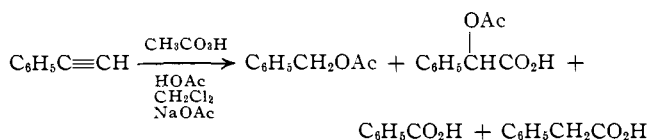(19) G. Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 431.

Figure 1.

the phenylketene intermediate. Peroxidation of the phenylketene may give an intermediate α-lactone, such as proposed by Ingold,[20] which can decarbonylate to give benzaldehyde. An alternate possibility[14] would be the Baeyer–Villiger oxidation of acetylmandelaldehyde to α-formyloxybenzyl acetate. This might then hydrolyze in the work-up to benzaldehyde.

According to Böeseken and Slooff,[21] peracetic acid had no effect on phenylacetylene. However, we have found that when 40% peracetic acid in acetic acid–methylene chloride mixture is allowed to react with this acetylene for 8 days, a mixture containing 18% yield of benzyl acetate, 39% yield of acetylmandelic acid, 23% yield of benzoic acid, and 17% yield of phenylacetic acid is obtained. The formation of benzyl acetate probably arises from the work-up of the crude reaction mix-

$$C_6H_5C{\equiv}CH \xrightarrow[\substack{HOAc \\ CH_2Cl_2 \\ NaOAc}]{CH_3CO_3H} C_6H_5CH_2OAc + C_6H_5\overset{\overset{\textstyle OAc}{\textstyle |}}{C}HCO_2H +$$
$$C_6H_5CO_2H + C_6H_5CH_2CO_2H$$

ture since the acetic acid was distilled off at a temperature of about 120°, thus causing some decarboxylation of acetylmandelic acid to give the benzyl acetate.

From our present knowledge of epoxidation reactions[22] of peracetic[23] and perbenzoic[24] acids with olefins, it appears reasonable to assume a similar electrophilic addition of "singlet" oxygen to the carbon–carbon triple bond and formation of an oxirene. This highly reactive intermediate can react further, depending
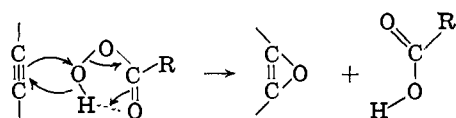
upon the reaction conditions, to give the observed products as shown in Fig. 1.

Two other structures can be considered for the intermediate produced *under these conditions;* (a) an open dipolar structure IV, and (b) an α-keto carbene V. Neither involves the strain of an oxirene (~40 kcal./mole); however, both have at least one less carbon–

IV   V

oxygen bond (~70 kcal./mole).[25] Structure IV also involves the energy of charge separation, the magnitude of which will be several kcal./mole. Also, in both IV and V, or a hybrid of the two, the carbon not bearing the oxygen is electron deficient. It is, therefore, difficult to understand the nature of further oxidation at this site by the electrophilic peracid to yield α-dicarbonyl products.

Examination of Fig. 1 shows that all of the products of the peracid oxidations of phenyl- and diphenylacetylene are economically explicable by an oxirene intermediate except possibly acetylmandelic acid. In the oxidation of phenylacetylene with peracetic acid in acetic acid, the oxirene intermediate can be attacked by acetic acid of the solvent cage or external acetate ion which explains the formation of acetylmandelic acid. However, the attack takes place at the benzylic position rather than the terminal position.

Benzylic attack by acetic acid to yield acetylmandelic acid can be rationalized in terms of either a dipolar resonance hybrid of 2-phenyloxirene (VII)[26] (or its conjugate acid), in which VI would be expected to contribute more significantly than VIII, or the ring-opened cation of the conjugate acid IX. The resulting

VI   VII   VIII

IX
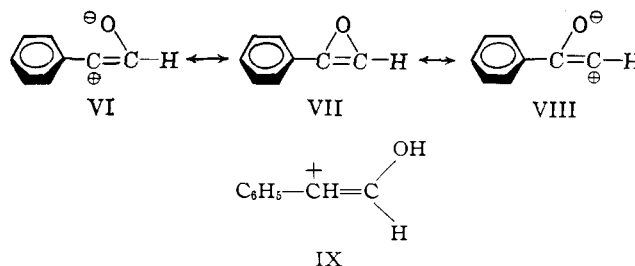
aldehyde would be expected to be readily oxidized further by excess peracetic acid to the observed acetylmandelic acid. In a relatively nonpolar and nonreactive solvent, such as chloroform or methylene chloride, opening of the strained three-membered ring with hydrogen migration occurs to give a ketene. The phenyl ring is involved in stabilizing the oxirene system (or its conjugate acid) as well as any charge buildup during migration and is, therefore, not able to migrate.

An alternate way to explain this "abnormal" ring opening would be to involve an α-lactone, formed by peroxidation of the ketene, in an A_{AL} mechanism with acetic acid. In either case the nature of the intermediates is quite interesting.

After the peroxidation of phenylacetylene with the three peracids, the crude reaction product turned red upon standing, probably owing to a small amount of polymerization of the phenylketene. This is especially true in the case of trifluoroperacetic acid since the only water present came from the 90% hydrogen peroxide or from normal work-up of the products and may account for the fact that only 63% of the material was accounted for.

(25) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

(26) The orthogonal geometry of the two rings in VII is also in keeping with the ultraviolet spectra of 2-aryloxiranes[27] in which it is found that considerable conjugation exists between the π-electron cloud of the benzene and the pseudo-π-electron cloud of the epoxide rings, the latter the result of the orbital picture of ethylene oxide proposed by A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(27) T. W. Campbell, S. Linden, S. Godshalk, and W. G. Young, *J. Am. Chem. Soc.*, **69**, 880 (1947); M. T. Rogers, *ibid.*, **69**, 2544 (1947); and N. H. Cromwell and G. V. Hudson, *ibid.*, **75**, 872 (1953).

(20) E. H. Ingold, *J. Chem. Soc.*, **125**, 1528 (1924).

(21) J. Böeseken and G. Slooff, *Rec. trav. chim.*, **49**, 95 (1930).

(22) D. Swern, *Org. Reactions*, **7**, 378 (1953).

(23) G. Levey, D. R. Campbell, J. O. Edwards, and J. Maclachlan, *J. Am. Chem. Soc.*, **79**, 1797 (1957).

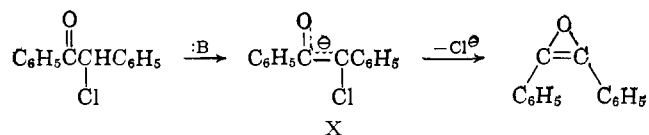(24) D. R. Campbell, J. O. Edwards, J. Maclachlan, and K. Polgar, *ibid.*, **80**, 5308 (1958).

However, in the peroxidation of diphenylacetylene, no rearrangement was observed, but instead further oxidation to the α-diketone. The migrating group here if migration were to occur must necessarily be a phenyl group. Previous studies of epoxide–carbonyl rearrangements[28] have shown that the migratory aptitude of phenyl is greater than that for hydrogen, other factors being equal. Yet in our studies with phenyl- and diphenylacetylene under the same conditions (trifluoroperacetic acid) we find rearranged products in the oxidation of phenylacetylene, but not with diphenylacetylene.

The rates of the oxidation steps will be important factors in deciding the nature of the products. The reactions of organic peracids with triple bonds have been studied and it has been shown that acetylenes react at a much slower rate than double bonds.[29] Taking the rate of reaction of peracetic acid with ethylene as unity, the rate of reaction of acetylene with this peracid is immeasurably slow, the rate of monosubstituted acetylenes is 0.1, and the rate of disubstituted acetylenes is 0.5. These authors also showed that disubstituted ethylenes are 25 times more reactive toward peracids than monosubstituted ethylenes.

2,3-Diphenyloxirene might then be expected to be removed at a very fast rate by further oxidation which may compete favorably with that of rearrangement. The product of this second oxidation, considering a normal peroxidation mechanism, may be the strained 2,4-dioxabicyclobutane,[30] which would undergo valence tautomerization to the observed α-diketone, benzil. Since the epoxidation procedure employing trifluoroperacetic acid is in the presence of a system buffered with disodium hydrogen phosphate in order to neutralize the trifluoroacetic acid as it is formed, no trifluoroacetate attack is observed.

We have also carried out the sodium tungstate catalyzed hydrogen peroxide[31] peroxidation of acetylenedicarboxylic acid monopotassium salt. After completion of the reaction, neutralization of the mixture, and work-up, a dipotassium salt was obtained which analyzed well for dipotassium oxirene-2,3-dicarboxylate, $C_4O_5K_2$. The infrared spectrum was not in disagreement with such a structure, but the ultraviolet spectrum in water showed only end absorption below 210 $m\mu$. No n.m.r. absorptions for C–H protons were observed in either water or deuterium oxide. Our efforts for the identification of this product are continuing.

In the hope of obtaining the enolate anion of desyl chloride (X) that might close to 2,3-diphenyloxirene, we have looked at the reaction of desyl chloride with

$$
\underset{\overset{|}{Cl}}{\overset{\overset{O}{\|}}{C_6H_5CCHC_6H_5}} \xrightarrow{:B} \underset{\overset{|}{Cl}}{\overset{\overset{O}{\|}\ominus}{C_6H_5C{=}CC_6H_5}} \xrightarrow{-Cl^{\ominus}} \underset{C_6H_5 \quad C_6H_5}{\overset{O}{\overset{/\backslash}{C{=}C}}}
$$

X

strong bases. The treatment of desyl chloride with tritylsodium in ether gave a 40% yield of benzoic acid and a 25% yield of benzilic acid. However, treatment with potassium t-butoxide in dimethyl sulfoxide afforded

a 24% yield of *trans*-dibenzoylstilbene and a 52% yield of *cis*-dibenzoylstilbene.. This latter reaction probably proceeds *via* a carbanion displacement mechanism of the enolate anion X attacking a molecule of desyl chloride.

Trapping experiments as well as other synthetic methods are presently under way with the goal of proving the existence of oxirenes. Some of these will be reported in the near future.

Experimental[32]

Reaction of Diphenylacetylene with Organic Peracids. 1. Trifluoroperacetic Acid.—To a stirred mixture of 35.6 g. (0.2 mole) of diphenylacetylene and 113 g. (0.8 mole) of disodium hydrogen phosphate (ground to a fine powder and dried *in vacuo* at 50° for 20 hr.) in 200 ml. of methylene chloride under reflux was added dropwise over a 2-hr. period a solution of trifluoroperacetic acid in methylene chloride. This solution was prepared by adding 7.0 ml. (0.25 mole) of 90% hydrogen peroxide to a chilled solution of 42.3 ml. (0.3 mole) of trifluoroacetic anhydride in 50 ml. of methylene chloride with stirring. After addition was complete the mixture was refluxed for an additional 2 hr., cooled, and poured into 500 ml. of water, dissolving the insoluble inorganic salts. The organic layer was separated and the aqueous layer extracted with 150 ml. of methylene chloride. The combined extracts were washed with 100 ml. of a 10% sodium bicarbonate solution and dried. The solvent was removed under reduced pressure leaving a dark yellow crystalline residue which could be recrystallized from alcohol giving a light yellow solid melting at 36–60°, and whose infrared spectrum showed it to be a mixture of starting material and a carbonyl-containing compound. This mixture was sublimed at 50–60° (0.15 mm.), the diphenylacetylene subliming leaving a yellow solid residue. After several recrystallizations from cyclohexane, the melting point remained constant at 95–96°. This light yellow solid (15 g., 36% yield) was shown to be benzil by its melting point, mixture melting point, and comparison of its infrared spectrum with that of an authentic sample. This reaction was repeated using 2 moles of trifluoroperacetic acid, giving 76% yield of benzil and 17% yield of benzoic acid.

2. Perbenzoic Acid.—To 5.0 g. (0.028 mole) of diphenylacetylene dissolved in 150 ml. of chloroform cooled to 0° was added 57 ml. of a cold 0.617 M chloroform solution of perbenzoic acid (0.029 mole). This was allowed to come to room temperature and remained there for 48 hr. The work-up was as described below for phenylacetylene; 4.6 g. of diphenylacetylene was recovered.

3. Peracetic Acid.—To a solution of 10.0 g. (0.056 mole) of diphenylacetylene in 100 ml. of methylene chloride was added at room temperature 0.61 mole of a 40% peracetic acid solution in acetic acid to which 2.0 g. of sodium acetate trihydrate had been added. After standing at room temperature for 20 hr. the reaction mixture was worked up as described for phenylacetylene; 9.0 g. of diphenylacetylene was recovered.

Reaction of Phenylacetylene with Organic Peracids. 1. Trifluoroperacetic Acid.—This reaction was run in the same manner as previously described for diphenylacetylene using the following reactants: 5.0 g. (0.05 mole) of phenylacetylene and 57 g. (0.4 mole) of disodium hydrogen phosphate in 50 ml. of methylene chloride. The trifluoroperacetic acid solution was prepared from 21 ml. (0.15 mole) of trifluoroacetic anhydride and 4 ml. (0.143 mole) of 90% hydrogen peroxide in 25 ml. of methylene chloride. Addition time was 2 hr., with an additional 0.5 hr. under reflux. The insoluble inorganic salts were filtered off and the solvent removed under reduced pressure leaving a thick red oil. This oil was distilled giving 4.0 g. of a solid, b.p. 80–85° (1 mm.), m.p. 45–51°. Its infrared spectrum showed it to consist of a mixture of benzoic and phenylacetic acids. The methyl esters were prepared by refluxing this mixture with 35 ml. of methanol, 100 ml. of ethylene chloride, and 1 ml. of concen-

(28) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

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

(30) Such a structure was proposed by K. H. Geib and P. Harteck, *Ber.*, **66**, 1815 (1933), for the product of oxygen atoms, formed from an electric discharge at a pressure of 0.5 mm., reacting with acetylene at $-180°$.

(31) G. B. Payne and P. H. Williams, *J. Org. Chem.*, **24**, 54 (1959).

(32) All melting points were taken on a Kofler hot stage and are corrected. Boiling points are uncorrected. Infrared absorption spectra were determined on a Perkin–Elmer Model 137 double beam recording spectrophotometer; n.m.r. spectra were determined on a Varian A-60 recording spectrophotometer using carbon tetrachloride as solvent (unless otherwise stated) with tetramethylsilane as the internal standard, and are singlets unless otherwise noted. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

trated sulfuric acid for 20 hr., giving 4.2 g. of a mixture of esters. Vapor phase chromatographic analysis using an F and M Model 500 linear programmed high temperature gas chromatograph with a D-C silicone oil 200 on firebrick column showed by integration of the peak areas that the mixture consisted of 38.7% of methyl benzoate, retention time 2.9 min.; and 61.3% of methyl phenylacetate, retention time 3.7 min. Thus there was 1.6 g. (24% yield based on phenylacetylene) of methyl benzoate and 2.6 g. (35% yield based on phenylacetylene) of methyl phenylacetate formed. If we assume that both benzoic and phenylacetic acids give the same yields of their corresponding methyl esters, we can conclude that the original mixture of acids consisted of 1.5 g. (25% yield) of benzoic acid and 2.5 g. (38% yield) of phenylacetic acid.

2. Perbenzoic Acid.—To 15 g. (0.15 mole) of phenylacetylene cooled to 0° was added 560 ml. of a cold 0.5 M chloroform solution of perbenzoic acid (39 g., 0.28 mole) prepared from 100 g. (0.42 mole) of benzoyl peroxide and 10.4 g. (0.44 mole) of sodium dissolved in 200 ml. of methanol according to Braun.[19] The cold reaction mixture was stirred with a magnetic stirrer and allowed to come to room temperature and remain there for 48 hr. The yellow chloroform solution was washed with two 200-ml. portions of a 10% sodium hydroxide solution followed by two 200-ml. portions of water and dried. After removal of solvent under reduced pressure, 17 g. of a crude yellow oil remained which slowly turned to a red oil upon standing. After standing several days, 1.5 g. of benzoic acid, from the air oxidation of 1.3 g. of benzaldehyde, was separated from this mixture.

Vapor phase chromatographic analysis, using the same conditions as previously mentioned (part 1 above), showed the following peaks: 0.5 min. (9%), 0.8 and 0.9 min. (11%), 2.0 min. (2%), 2.5 min. (4%), 2.9 min. (61%), and 3.5 min. (13%). This crude mixture was then separated on an Aerograph Autoprep A-700 using a 30% SE-30 on Chromosorb P column. The three high boiling fractions were collected. The main component (61%) proved to be methyl phenylacetate by comparison of its infrared and n.m.r. [2.78 (5), 6.42 (3), and 6.50 (2) τ] spectra and retention time with those of an authentic material. The component separating last (13%) was shown to be ethyl phenylacetate by comparison of its infrared and n.m.r. [2.75 (5), 5.90 (quartet, 2), 6.50 (2), and 8.79 (triplet, 3) τ] spectra and retention time with those of authentic material. The third component collected (4%) was shown to be methyl benzoate by comparison of its infrared spectrum and retention time with that of a known sample. From retention times, the 2% component was shown to be benzaldehyde. Therefore, from the v.p.c. analysis, 9.6 g. (42.5% yield) of methyl phenylacetate, 2.0 g. (8.1% yield) of ethyl phenylacetate, 0.3 g., in addition to the 1.3 g. which was oxidized to benzoic acid, (11.1% yield) of benzaldehyde, and 0.6 g. (3.0% yield) of methyl benzoate were isolated.

Acidification of the basic wash solution yielded 42.5 g. of benzoic acid. Since 39 g. of perbenzoic acid should produce 34.5 g. of benzoic acid, 8.0 g. (43.5% yield) must have been produced from the phenylacetylene assuming no benzoic acid present in the perbenzoic acid solution. The methyl ester was prepared according to Clinton and Laskowski[33] and v.p.c. analysis showed only one component, methyl benzoate.

3. Peracetic Acid.—To 30.6 g. (0.30 mole) of phenylacetylene in 300 ml. of methylene chloride at room temperature was added with stirring a cold solution of 130 ml. of 6.55 M (40%, 0.85 mole) peracetic acid in acetic acid containing 10 g. of sodium acetate trihydrate. The reaction was allowed to stir at room temperature for 8 days. The methylene chloride and acetic acid were removed by distillation. The residue was dissolved in 200 ml. of ether and washed with two 100-ml. portions of a 10% sodium carbonate solution, followed by water, and dried. The solvent was removed under reduced pressure leaving a dark yellow oil. Distillation yielded a fraction boiling at 98–99° (15 mm.) which was shown to be benzyl acetate (8 g., 19% yield, n^{20}D 1.5040). Its infrared and n.m.r. [2.71 (5), 4.48 (2), and 7.96 (3) τ] spectra were identical with an authentic sample. There was a pot residue remaining.

The combined sodium carbonate and water washings were acidified with 6 N hydrochloric acid and extracted with three 100-ml. portions of ether, washed with water, and dried. The solvent was removed under reduced pressure, leaving a mixture

of a solid and a liquid. The solid was filtered off yielding 15 g. of a crystalline material whose infrared spectrum showed it to consist of a mixture of benzoic and phenylacetic acids. Their methyl esters were prepared by refluxing them with 35 ml. of methanol, 100 ml. of ethylene chloride, and 1 ml. of concentrated sulfuric acid for 20 hr., producing 15 g. of a mixture of esters. Vapor phase chromatographic analysis (using the same conditions as previously described in part 1) showed that the mixture contained 55.5% of methyl benzoate and 44.5% of methyl phenylacetate. Thus, 8.3 g. (20% based on phenylacetylene) of methyl benzoate and 6.7 g. (15% yield based on phenylacetylene) of methyl phenylacetate were formed in the esterification reaction. Again, if we assume that the esterification of both acids gives the same yields, 8.6 g. (23% yield) of benzoic acid and 7.2 g. (17% yield) of phenylacetic acid were formed in the original peracid oxidation.

The liquid filtrate was distilled producing 22.5 g. (39% yield) of a colorless solid, b.p. 115–116° (0.05 mm.), and m.p. 53–56°. Recrystallization from benzene afforded a colorless crystalline solid with a melting point of 78–80°. Its infrared and n.m.r. [2.72 (5), 6.40 (1), and 7.93 (3) τ] spectra were identical with that of acetylmandelic acid. Treatment of this acid with diazomethane (prepared from 24 g. of potassium hydroxide in 60 ml. of water and 200 ml. of ether to which was added 20 g. (0.2 mole) of N-nitroso-N-methylurea) gave 20 g. of a liquid whose v.p.c. showed a single major component, retention time 5.2 min., methyl acetylmandelate. Its infrared spectrum was consistent with that of an authentic sample as 'was its n.m.r. [2.66 (5), 6.37 (3), 6.40 (1), and 7.92 (3) τ] spectrum.

Acetylmandelic acid was prepared according to Thayer[34]; m.p. 79–80°, 87% yield (lit.[34] m.p. 79–80°, 97–99% yield).

Methyl Acetylmandelate.—Five grams of mandelic acid was converted to its methyl ester using the same conditions outlined for the methylation of the acid products from the peracetic acid oxidation of phenylacetylene. Heating of the resulting yellow liquid ester with excess acetyl chloride for 1 hr., followed by distillation, yields 4.0 g. (59% yield) of methyl acetylmandelate, b.p. 97–98° (1 mm.). Its infrared and n.m.r. spectra and v.p.c. retention time were identical with those of the compound formed by the action of peracetic acid on phenylacetylene.

Reaction of Acetylenedicarboxylic Acid Monopotassium Salt with Hydrogen Peroxide.—The procedure employed was a modification of that used by Payne and Williams.[31] To a suspension of 152.0 g. (1.0 mole) of the monopotassium salt of acetylenedicarboxylic acid in 150 ml. of water was added a solution of 33.0 g. (0.50 mole) of potassium hydroxide in 100 ml. of water. This was warmed to 55° and 10.0 g. (0.1 mole) of sodium tungstate dihydrate was added followed by 159.0 g. (1.3 moles) of 30% hydrogen peroxide. The temperature rose to 65° and was held there for 2 hr. During the reaction a small amount of a solution of 33.0 g. (0.50 mole) of potassium hydroxide in 100 ml. of water was added to maintain the pH of the mixture at approximately 4. After standing overnight at room temperature, the remainder of the potassium hydroxide solution, except for 20 ml., was added to give the final solution a pH of 8 (on the basic side the color of the solution was a light tan). This solution was evaporated under reduced pressure at 40° to about 150 ml. total volume at which point some of the salt began crystallizing out. The resulting slurry was then poured into 1.5 l. of acetone and the resulting light tan solid was filtered, washed repeatedly with acetone, and dried in the vacuum desiccator over phosphorus pentoxide to a constant weight of 182 g. (88% yield). The infrared spectrum (in Nujol) showed bands at: 6.2 (s), 6.3 (s), 7.6 (s), 10.2 (m), 11.8 (w), 12.9 (s), and 14.9 (s) μ. The ultraviolet spectrum in water showed only end absorption below 210 mμ. No carbon-bound protons were observed in the n.m.r. spectrum in either D₂O or H₂O.

Anal. Calcd. for $C_4O_5K_2$: C, 23.29; K, 37.92. Found: C, 22.95; H, 0.70; K, 37.6.

The barium salt was prepared from the potassium salt by the addition of a solution of 100 g. (0.5 mole) of the latter to 100 g. (0.5 mole) of barium chloride dissolved in 300 ml. of hot water. The insoluble barium salt was removed by filtration and dried in a vacuum desiccator over phosphorus pentoxide to a constant weight of 84 g. (65% yield).

A suspension of the barium salt (0.32 mole) and 20 g. of anhydrous magnesium sulfate in 500 ml. of ether was stirred at 0–5°

(33) R. O. Clinton and S. C. Laskowski, *J. Am. Chem. Soc.*, **70**, 3153 (1948).

(34) F. K. Thayer, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 12.

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).

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

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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

(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. Böeseken and G. Slooff, Rec. trav. chim., **49**, 95 (1930).

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

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

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

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