

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

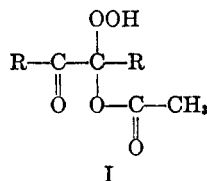
## Ozonolysis of Unsymmetrical Acetylenes

PHILIP S. BAILEY, YUN-GER CHANG, AND W. W. L. KWIE

Received August 28, 1961

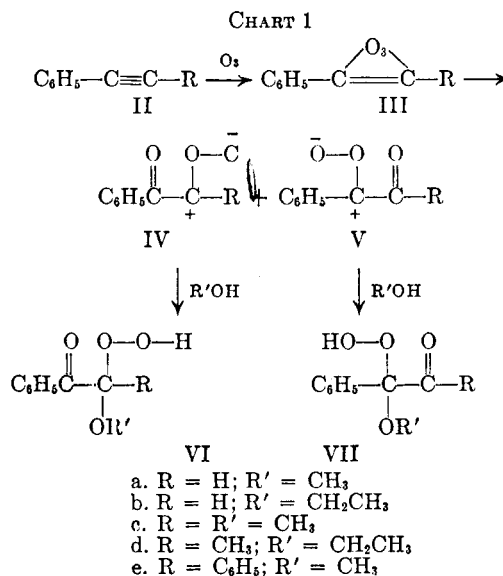
The ozonolyses of phenylacetylene and 1-phenylpropyne in methanol and ethanol were studied. Only one of the two possible hydroperoxides from each reaction could be isolated. From a quantitative study of the thermal decomposition products, however, the exact proportions of these hydroperoxides could be determined, and from this it was evident that one of the two possible Criegee zwitterions was produced predominantly in each case. The results are in agreement with predictions based on the formation of an initial five-membered ring ozone adduct with acetylenes, just as with olefins.

The ozonolysis of acetylenic compounds has been studied far less extensively than that of olefins.<sup>1</sup> The most significant study is that of Criegee and Lederer,<sup>2</sup> who showed that in acetic acid solution an acetoxy hydroperoxide (I) containing all of the atoms of the original acetylene is produced and can either be reduced to a 1,2-dicarbonyl compound or be decomposed, with rearrangement, to an anhydride and/or the corresponding acid(s). A mechanism for acetylene ozonolysis, similar to that for olefins, was suggested.<sup>1,2</sup>



The study of the ozonolysis of unsymmetrical olefins in alcohols, designed to determine which half of the molecule predominately produces the Criegee zwitterion, has given significant information concerning the nature of the attack of ozone on olefins and concerning the initial adduct.<sup>1,3,4</sup> Such a study with unsymmetrical acetylenes should also be informative in the same manner and is the subject of the present communication.

The acetylenic compounds studied were phenylacetylene (IIa) and 1-phenylpropyne (IIc). Applying the Criegee mechanism<sup>1,2</sup> to the ozonolysis of such acetylenes in alcohols, two zwitterions (IV and V) and two hydroperoxides (VI and VII) are possible, as shown in Chart 1. Ozonolyses of IIa in methanol and in ethanol gave as the only isolable hydroperoxides 25% yields of VIa and VIb, respectively. Similar ozonolyses of IIc gave no isolable hydroperoxide from methanol solvent and a 26% yield of VIc as the only isolable hydroperoxide from ethanol solvent. Hydroperoxides VII apparently are too unstable to isolate. Although it could be assumed that VII had been produced in



approximately 75% yield in each case, it seemed better to determine the actual yields of hydroperoxides VI and VII, and thus zwitterions IV and V, by decomposing the reaction mixtures, quantitatively determining the decomposition products, and relating these to the hydroperoxides from which they came.<sup>5</sup>

For this objective ozonolysis of each acetylene (IIa and IIc) was carried out in each of the solvents methanol and ethanol at about  $-65^{\circ}$ . Approximately one-mole equivalent of ozone reacted in each case. The reaction mixtures were then decomposed by refluxing for five minutes and the products were analyzed by the same procedures as described in the accompanying paper.<sup>5</sup> The data are shown in Table I. In each case the percentage yields of aromatic and of aliphatic compounds added up to only 90–91%, indicating that the total yields of the hydroperoxide mixtures (VI and VII) were only 90%. Reductions of the peroxidic reaction mixtures in two cases gave 85% isolated yields of pure reduction products (phenylglyoxal from IIa and 1-phenyl-1,2-propanedione from IIc), which is in line with the total 90% yield of hydroperoxides. From these data, then the percentage

(1) P. S. Bailey, *Chem. Revs.*, **58**, 925 (1958).  
 (2) R. Criegee and M. Lederer, *Ann.*, **583**, 29 (1953).  
 (3) P. S. Bailey and S. S. Bath, *J. Am. Chem. Soc.*, **79**, 3120 (1957).  
 (4) P. S. Bailey, S. B. Mainthia, and C. J. Abshire, *J. Am. Chem. Soc.*, **82**, 6136 (1960).

(5) P. S. Bailey and Yun-Ger Chang, *J. Org. Chem.*, **27**, 1192 (1962).

TABLE I

C <sub>6</sub> H <sub>5</sub> C≡CR Studied	R'OH Solvent	Products in Mole %			
		C <sub>6</sub> H <sub>5</sub> COOH	RCOOR'	RCOOH	C <sub>6</sub> H <sub>5</sub> COOR'
1 C <sub>6</sub> H <sub>5</sub> C≡CH	CH <sub>3</sub> OH	25.5	36.2	53.9	64.4
2 C <sub>6</sub> H <sub>5</sub> C≡CH	CH <sub>3</sub> CH <sub>2</sub> OH	25.2	36.7	54.2	65.2
3 C <sub>6</sub> H <sub>5</sub> C≡CCH <sub>3</sub>	CH <sub>3</sub> OH	29.4	32.7	57.9	60.2
4 C <sub>6</sub> H <sub>5</sub> C≡CCH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> OH	25.2	37.3	53.7	65.0

TABLE II

Starting Material	Mole Per Cent of Products			
	C <sub>6</sub> H <sub>5</sub> COOH	HCOOCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> COOCH <sub>3</sub>	HCOOH
$\begin{array}{c} \text{OOH} \\   \\ \text{C}_6\text{H}_5\text{C}-\text{C}-\text{H} \\    \quad   \\ \text{O} \quad \text{OCH}_3 \end{array}$	86 <sup>a</sup>	99 <sup>a</sup>	14 <sup>a</sup>	1 <sup>a</sup>
$\begin{array}{c} \text{OOH} \\   \\ \text{HC}-\text{C}-\text{C}_6\text{H}_5 \\    \quad   \\ \text{O} \quad \text{OCH}_3 \end{array}$	6 <sup>b</sup>	19 <sup>b</sup>	94 <sup>b</sup>	81 <sup>b</sup>
C <sub>6</sub> H <sub>5</sub> C≡C—H (90% conversion)	26 <sup>c</sup>	36 <sup>c</sup>	64 <sup>c</sup>	54 <sup>c</sup>
C <sub>6</sub> H <sub>5</sub> C≡C—H (calcd. 100% conv.)	29 <sup>d</sup>	40 <sup>d</sup>	71 <sup>d</sup>	60 <sup>d</sup>

<sup>a</sup> See ref. 5. <sup>b</sup> Based on theory shown in Chart 2. <sup>c</sup> Actual result from Table I. <sup>d</sup> Actual result divided by 0.9.

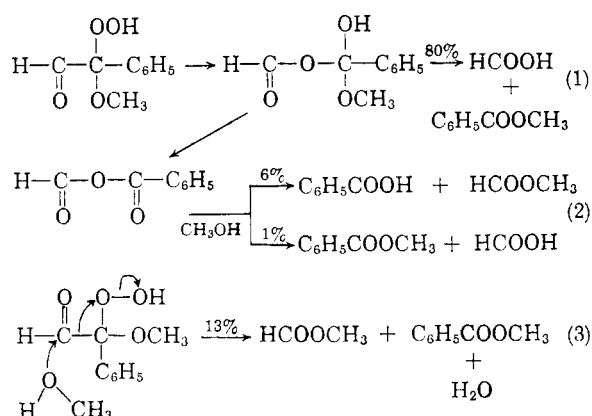
yields of the two hydroperoxides can be calculated.

Table II shows in round numbers the percentage yields, reported in the accompanying paper,<sup>5</sup> for the decomposition products of pure hydroperoxide VIa in methanol; the expected yields of these products from pure hydroperoxide VIIa, assuming that it decomposes in methanol in the same manner as does VIa (see Chart 2); the actual yields of these products from ozonolysis of phenylacetylene (IIa) in methanol and decomposition of what the latter yields would have been if a 100% rather than a 90% yield of hydroperoxides VIa and VIIa had been obtained from IIa. Table III shows the method used in calculating the actual yields of VIa and VIIa from IIa.

TABLE III

Calculation basis: Let  $x$  = yield of peroxide VIa based on 100% conversion of acetylene IIa to hydroperoxides VIa and VIIa. Then yield of VIIa =  $1 - x$ .

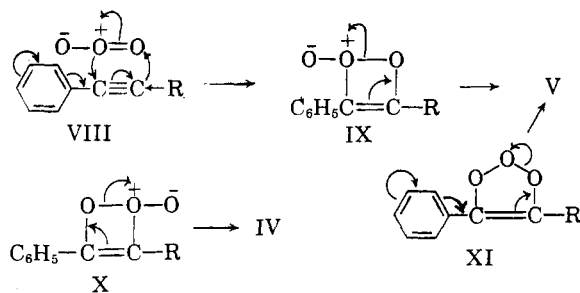
Calculation based on yields of C <sub>6</sub> H <sub>5</sub> COOH (Table II)	$0.86x + 0.06(1 - x) = 0.29$ $x = 0.29$ or 29% VIa $1 - x = 0.71$ or 71% VIIa
Calculation based on yields of HCOOCH <sub>3</sub> (Table II)	$0.99x + 0.19(1 - x) = 0.40$ $x = 0.26$ or 26% VIa $1 - x = 0.74$ or 74% VIIa
Calculation based on yields of C <sub>6</sub> H <sub>5</sub> COOCH <sub>3</sub> (Table II)	$0.14x + 0.94(1 - x) = 0.71$ $x = 0.29$ or 29% VIa $1 - x = 0.71$ or 71% VIIa
Calculation based on yields of HCOOH (Table II)	$0.01x + 0.81(1 - x) = 0.60$ $x = 0.26$ or 26% VIa $1 - x = 0.74$ or 74% VIIa
Average yields, 100% conv.	VIa = 27.5%. VIIa = 72.5%.
Yields, 90% conv.	VIa = 25%. VIIa = 65%.



The 25% calculated yield of hydroperoxide VIa agrees exactly with the actual yield isolated. The results in Tables II and III certainly show that hydroperoxide VIIa was produced in considerably higher yield than VIa, and the calculated 65% yield seems very reasonable in view of the data obtained. Similar calculations with phenylacetylene (IIa) in ethanol and with 1-phenylpropyne (IIc) in methanol and in ethanol give entirely analogous results. Thus it is evident that ozonolyses of unsymmetrical acetylenes of type II give both zwitterion possibilities with zwitterions V being predominant over zwitterions IV.

There are two possible explanations for these results. One is that ozone adds to the triple bond to give adducts with a four-membered ring as shown in VIII  $\rightarrow$  IX. As the resonance effect of the aromatic group should certainly be more powerful than the inductive effect of the alkyl group, adduct IX should certainly be produced in

greater amounts than the other possibility (X). Adduct IX would lead to zwitterion V and adduct X would give IV.



The more likely possibility, however, is that ozone adds to triple bonds in the same way that it adds to double bonds,<sup>4</sup> to give adduct XI with a five-membered ring. As in XI there is a double bond in conjugation with the aryl group (which is not true with the corresponding intermediate from a similar olefin), the resonance effect of the phenyl group should control the breakdown of the ring to give zwitterion V. In opposition to this, of course, would be the inductive and hyperconjugation effects of the methyl group (where R in XI is methyl) and this perhaps accounts for the fact that hydroperoxide VI (from zwitterion IV) is the other (minor) product. Thus, the behavior during ozonolysis of unsymmetrical alkenes<sup>4,4</sup> and acetylenes is one of the best arguments for the five-membered ring intermediate in ozonolysis. Work is in progress to compare a large number of similarly substituted unsymmetrical alkenes and alkynes in this respect.

Incidental to the present work was the study of the ozonolysis of diphenylacetylene (IIe) in methanol. The expected hydroperoxide (VIe) from the reaction apparently was too unstable to isolate. This hydroperoxide likewise was not isolable in the previous study with *cis*- and *trans*-1,2-dibenzoylstyrene.<sup>4</sup> From decomposition of the ozonolysis reaction mixture of diphenylacetylene was obtained 72% benzoic acid, 86% methyl benzoate, and 9% benzoic anhydride. These results are in line with what one would expect from decomposition of the expected hydroperoxide, in comparison to those studied in the accompanying paper.<sup>5</sup> Especially the yield of benzoic anhydride, which is much more stable than mixed anhydrides, compares favorably with the 7% yields of mixed anhydrides calculated from the study of the decompositions of hydroperoxides VI.<sup>5</sup>

#### EXPERIMENTAL<sup>6,7</sup>

*Isolation of hydroperoxides VI from ozonolysis of acetylenes II.* Forty-eight liters of an ozone-oxygen mixture was passed through a solution of 6 g. (0.0588 mole) of phenylacetylene<sup>8</sup>

in 60 ml. of anhydrous methanol at  $-30^{\circ}$ . Approximately 1 mole of ozone was absorbed. The reaction mixture was evaporated under reduced pressure to about 6 ml., cooled in an acetone-Dry Ice bath, filtered, evaporated further to 1-2 ml., cooled, and filtered again, giving a total of 2.7 g. (25% yield) of colorless VIa melting at  $79-82^{\circ}$ ; recrystallized from ethyl acetate by addition of petroleum ether (b.p.  $60-68^{\circ}$ ), m.p.  $81-81.5^{\circ}$ . Identification as  $\alpha$ -hydroperoxy- $\alpha$ -methoxyacetophenone (VIa) was by melting point and by comparison of infrared spectra with previously characterized samples.<sup>3,4</sup> In a similar fashion, ozonizing IIa in ethanol at  $-65^{\circ}$ , a 25% yield of  $\alpha$ -ethoxy- $\alpha$ -hydroperoxyacetophenone (VIb), m.p.  $77^{\circ}$ , was obtained and identified by comparison of infrared spectra with the same compound obtained by ozonolysis of 1,2-dibenzoyl ethylene in ethanol.<sup>5</sup> Likewise,  $\alpha$ -ethoxy- $\alpha$ -hydroperoxypropionophenone (VIc), m.p.  $57^{\circ}$ , was obtained in 26% yield from ozonolysis of 1-phenylpropyne (IIc)<sup>9</sup> in ethanol at  $-65^{\circ}$ . The impure hydroperoxide or solutions containing the pure or impure hydroperoxide had to be kept at temperatures well below  $0^{\circ}$ , in order to avoid decomposition, which was sometimes violent. The material was identified by analysis and by comparison of infrared spectra with the same material obtained by ozonolysis of 1,2-dibenzoylpropene in ethanol.<sup>5</sup>

*Anal.* Calcd. for  $C_{11}H_{14}O_4$ : C, 62.84; H, 6.71. Found: C, 62.51; H, 6.58.

A similar attempt to isolate  $\alpha$ -hydroperoxy- $\alpha$ -methoxyacetophenone (IIc) afforded no crystalline material.

*Ozonolyses of acetylenes (II) followed by reduction.* A solution of 1-phenylpropyne (IIc) in anhydrous methanol was ozonized as described in the preceding experiments. The cold ( $-65^{\circ}$ ) reaction mixture was poured into a cold solution of excess potassium iodide in 50:50 methanol-acetic acid. The resulting mixture was allowed to stand at room temperature for 1 hr. after which the liberated iodine was reduced with sodium thiosulfate, the colorless reaction mixture was extracted six times with ether, and the ether extract was dried and evaporated to an oily residue which gave 2.25 g. (88% yield) of 1-phenyl-1,2-propanedione. It was identified by conversion to the disemicarbazone, 4.6 g. (85% overall yield), m.p.  $215-225^{\circ}$ ; recrystallized from ethanol, it melted at  $237-238^{\circ}$ ,<sup>11</sup> with no depression in mixture melting point with a sample made from authentic 1-phenyl-1,2-propanedione.

In a similar fashion the ozonolysis reaction mixture of phenylacetylene in methanol was reduced. Phenylglyoxal was isolated as its osazone in 84% yield, m.p.  $151-153^{\circ}$  with no depression in a mixture melting point with an authentic sample.

*Ozonolysis of acetylenes (II) in methanol or ethanol followed by thermal decomposition.* Ozonolysis of phenylacetylene (IIa) and of 1-phenylpropyne (IIc) were carried out both in methanol and in ethanol (3-5 g. in 25-30 ml. of solvent at  $-65^{\circ}$ ) as described in the preceding experiments. The reaction mixtures were then carefully decomposed by refluxing for 5 min., as described for hydroperoxides VI in the accompanying paper.<sup>5</sup> Although the reaction mixtures were still slightly peroxidic after the reflux (or even after 1 hr. reflux in a separate experiment), it is obvious from the results described in the accompanying paper<sup>5</sup> that this was

(7) All melting points are corrected. Carbon and hydrogen analyses were done by The University of Texas Biochemical Institute. The ozonolysis and analytical general procedures are described in the accompanying paper.<sup>5</sup>

(8) Aldrich Chemical Co.; redistilled, b.p.  $42^{\circ}/14$  mm.;  $n_{20}^{20} 1.5483$ .

(9) Prepared in 75% yield by the method of Bergmann and Bondi<sup>10</sup>; b.p.  $67-68^{\circ}/12$  mm.

(10) E. Bergmann and A. Bondi, *Ber.*, **66**, 284 (1933).

(11) K. v. Auwers, *Ber.*, **50**, 1912 (1917), reports  $229-232^{\circ}$ . Earlier work from our laboratory,<sup>4</sup> however, found  $240-241^{\circ}$ . The differences perhaps are due to isolation of different stereoisomers or mixtures thereof.

(6) For more details see Ph. D. dissertation of Y. G. Chang, The University of Texas, June 1961.

due to some attack of ozone on the solvent rather than to the presence of hydroperoxides VI and VII. The reaction mixtures were then worked up and the products determined precisely as described for the hydroperoxide (VI) decompositions in the accompanying paper.<sup>5</sup> The results are shown in Table I.

*Ozonolysis of diphenylacetylene (IIe).* a) *Attempt to isolate a hydroperoxide.* The ozonolysis was carried out in methanol at  $-15^{\circ}$  as described for the other acetylenes. Using the procedure described earlier, no crystalline hydroperoxide could be isolated. This was also true for ozonolysis of IIe in a 1-4 methanol-carbon tetrachloride mixture at  $-20^{\circ}$ .

b) *Ozonolysis and thermal decomposition.* The ozonolysis was carried out in methanol at  $-20^{\circ}$  as described in preceding experiments. The reaction mixture was refluxed for 15 min., after which the methanol was removed under reduced pressure. The residue was treated with excess sodium bicarbonate solution and the resulting mixture was extracted six times with ether. The ether extract was evaporated under reduced pressure and the residue was distilled giving an 86% yield of methyl benzoate (b.p.  $90-95^{\circ}/15$  mm.), which was identified by gas chromatographic techniques. The remaining residue crystallized

from petroleum ether, giving a 9% yield of benzoic anhydride, m.p.  $41-42^{\circ}$ , identification by the mixture melting point method. The sodium bicarbonate extract was acidified with conc. hydrochloric acid, cooled, and filtered. The filtrate was extracted six times with ether and the ether extract was evaporated. Benzoic acid was obtained from these operations in 71% yield, m.p.  $121-122^{\circ}$ , identification by the mixture melting point method.

c) *Ozonolysis and reduction* was carried out as described in preceding experiments. Work-up as described in the immediately preceding experiment gave 16% benzoic acid and 15% methyl benzoate. The final residue was benzil (72% yield, m.p.  $95-96^{\circ}$ ). Crystalline materials were identified by the mixture melting point method and methyl benzoate by gas chromatography.

*Acknowledgment.* The authors are grateful for grants from the Robert A. Welch Foundation (F-042) and the National Science Foundation (G-7353) which made this work possible.

AUSTIN 12, TEX.

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

## Alternation Copolymerization

MICHAEL M. MARTIN AND NORMAN P. JENSEN

Received October 12, 1961

3-Phenylpropene-1, 4-phenylbutene-1, and 5-phenylpentene-1 have been found to form perfect alternating copolymers of relatively high molecular weight with maleic anhydride. An explanation for alternation copolymerization based upon interactions of dipoles in the radical and double bond is believed to be more consistent with these findings than the more generally expounded explanation which call for transition state stabilization by electron transfer.

One of the most interesting aspects of free radical chemistry is the tendency of certain monomer pairs to form alternating copolymers.<sup>1-4</sup> Styrene and maleic anhydride provide an excellent example of such a system. A copolymer is produced which is composed of equivalent amounts of each monomer, regardless of initial monomer concentrations, arranged along the chain in regularly alternating fashion. Alternating copolymers of maleic anhydride, which homopolymerizes only to a very limited degree under conditions of free radical initiation, with other monomers which readily homopolymerize, such as vinyl chloride, vinyl acetate, and isopropenyl acetate, have also been reported.<sup>5</sup>

Equally interesting is the formation of relatively high molecular weight alternating copolymers from maleic anhydride and monomers which will not

readily homopolymerize. Such terminal olefins as propylene,<sup>6,7</sup> diisobutylene,<sup>7,8</sup> octene,<sup>9</sup> dodecene,<sup>10</sup> and some allylsilanes<sup>11</sup> have been reported to copolymerize with maleic anhydride under conditions of free radical initiation, apparently to alternating copolymers. The most thorough study of such a system was by Bartlett and Nozaki.<sup>12</sup> They found that the kinetic chain length for the copolymerization of allyl acetate and maleic anhydride is 36,000, whereas for allyl acetate alone it is 36.4, for maleic anhydride alone, 29.

The failure of monomers possessing allylic hydrogens to form high molecular weight homopolymers through a free radical process is due to chain transfer with monomer. The growing polymer

(1) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, 1957, Chapt. 4.

(2) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

(3) G. M. Burnett, "Mechanism of Polymer Reactions," Interscience Publishers, Inc., New York, 1954, Chap. 8.

(4) T. Alfrey, J. J. Bohrer, and H. Mark, "Copolymerization," Interscience Publishers, Inc., New York, 1952.

(5) M. C. deWilde and G. Smets, *J. Polymer Sci.*, **5**, 253 (1950).

(6) W. E. Hanford, U. S. Patent **2,396,785**, March 19, 1946.

(7) W. E. Hanford, U. S. Patent **2,378,629**, June 19, 1945.

(8) R. M. Thomas and W. J. Sparks, U. S. Patent **2,373,067**, April 3, 1945.

(9) J. J. Gianmaria, U. S. Patent **2,698,316**, December 16, 1954.

(10) S. B. Lippencott and L. A. Mikeska, U. S. Patent **2,542,542**, February 20, 1951.

(11) Libby Owens Ford Glass Co., Brit Patent **663,770**, December 27, 1951.

(12) P. D. Bartlett and K. Nozaki, *J. Am. Chem. Soc.*, **68**, 1495 (1946).