groups: a CF doublet at ϕ +170.8, J_{HF} = 48 cps, due to nitrile XII, an NF doublet at ϕ −53.0, J_{HF} = about 66 cps, and a CF doublet, J_{HF} = 48 cps, of triplets, J_{HF} = 4 cps, at ϕ +183.7 due to fluorimine XI, and a doublet, J_{HNF} = 24 cps, at ϕ −44.8 due to the dibromo(difluoramino)phenylethane. With time, the 53.0 and ϕ +183.7 peaks disappeared and the ϕ +170.8 peak grew. Chromatography of the crude residue on silica gel packed with pentane gave, in the pentane–methylene chloride (10:1) eluent, the dibromodifluoraminophenylethane whose F^{19} nmr spectrum is described above. It was a colorless liquid.

Anal. Calcd for $C_8H_6BrNF_2$: C, 30.50; H, 2.24; N, 4.44. Found: C, 30.39; H, 2.30; N, 4.47.

From the pentane–methylene chloride (2:1) eluent was obtained α-fluorophenylacetonitrile, a colorless liquid, F^{19} nmr discussed above.

Anal. Calcd for C_8H_6NF: C, 71.10; H, 4.48; N, 10.36. Found: C, 71.46; H, 4.59; N, 10.59.

1,2-Dicyano-1-fluoro-1-propene.—A solution of 2 g of 1-fluorimino-4-difluoramino-2-fluoro-3-methyl-2-butene in 20 ml of methylene chloride was cooled in an ice bath while 5 ml of triethylamine in 20 ml of methylene chloride was added dropwise. After 1 hr at 20°, the solution was washed with water, 10% aqueous hydrochloric acid, and water. The methylene chloride solution was distilled *in vacuo* through traps cooled to 0 and −80°. The 0° trap retained the 1,2-dicyano-1-fluoro-1-propene; two peaks (*cis,trans* isomers) were present in glpc on a 5-ft G.E. SF-96 silicon on Chromosorb column at 96°.

Anal. Calcd for $C_5H_3N_2F$: C, 54.55; H, 2.75; N, 25.45. C, 54.9; H, 2.88; N, 26.05.

The F^{19} spectrum of the sample had peaks, each a quartet, J_{HF} = 4 cps, at ϕ +102.7 and +105.4. The proton nmr spectrum exhibited two methyl peaks, each as doublet (J_{HF} = 4 cps) at δ 2.11 and 2.20. Observing the proton spectrum while irradiating F^{19} at 23,836 cps LSB collapsed one methyl doublet to a singlet; at 23,936 cps LSB, crystal frequency 37.617 Mc, the other methyl doublet became a singlet.

Registry No.—II, 10036-38-1; IV, 10039-65-3; i, 10036-39-2; V, 10036-40-5; *cis* VI, 10036-41-6; *trans* VI, 10036-42-7; XII, 10036-43-8; XI, 10036-44-9; *cis*-1,2-dicyano-1-fluoro-1-propene, 367-07-7; *trans*-1,2-dicyano-1-fluoro-1-propene, 367–08-8; tetrafluorohydrazine, 10036-47-2.

Direction of Cleavage of Primary Ozonides in the Methanolic Ozonolyses of Styrene, Propenylbenzene, and 2-Methylpropenylbenzene

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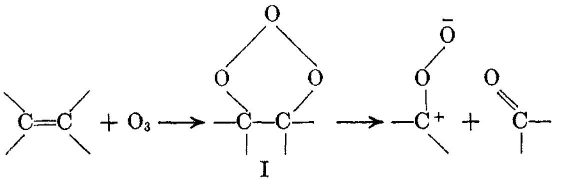
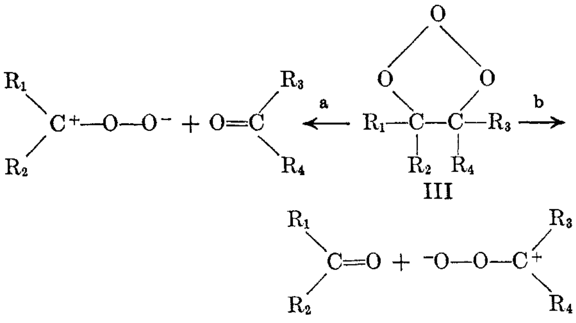
Received October 25, 1966

The carbonyl component/methoxyhydroperoxide ratios resulting from ozonolysis of the title olefins in methanol have been determined at −65 to −70°. A rationale for these observations has been offered in terms of the direction of cleavage of the primary ozonides. Some properties of the hydroperoxidic products are discussed.

It has proved possible to rationalize many of the facts associated with the ozonolysis of olefins on the basis that a "primary ozonide" I[1] is first formed, and that this undergoes heterolysis according to a proposal by Criegee,[8] as shown in eq 1. With a primary ozonide such as III, derived from an unsymmetrical olefin, alternate modes of cleavage are possible (eq 2).



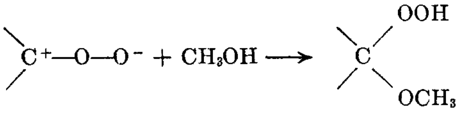
(1)



(2)

The present study has dealt with the ozonolysis of unsymmetrical olefins, with a view toward gaining an insight into the factors which determine the relative importance of cleavage paths a and b. The compounds which have been ozonized at *ca.* −70° are styrene (IV), *trans*-propenylbenzene (V), and 2-methylpropenylbenzene (VI). The "participating" solvent methanol was employed in order to intercept the zwitterions and convert them to isolable α-methoxyhydroperoxides (eq 3).

$C_6H_5CH{=}CH_2$	$C_6H_5CH\overset{t}{=}CHCH_3$	$C_6H_5CH{=}C(CH_3)_2$
IV	V	VI



(3)

The products expected from these reactions are outlined in Scheme I. All these were indeed obtained,

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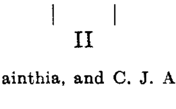
[1] Structure I presently enjoys rather universal acceptance as most accurately representing the initial ozone–olefin addition compound,[2–5] the "molozonide" II[6,7] having been generally superseded.



II

(2) P. S. Bailey, S. B. Mainthia, and C. J. Abshire, *J. Am. Chem. Soc.*, **82**, 6136 (1960).

(3) R. Huisgen, *Angew. Chem. Intl. Ed. Engl.*, **2**, 565 (1963).

(4) (a) F. L. Greenwood, *J. Org. Chem.*, **29**, 1321 (1964); (b) F. L. Greenwood and B. J. Haske, *Tetrahedron Letters*, 631 (1965).

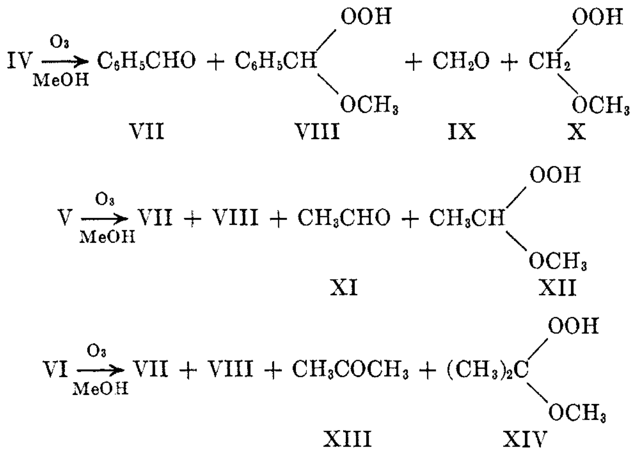
(5) P. S. Bailey, J. A. Thompson, and B. A. Shoulders, *J. Am. Chem. Soc.*, **88**, 4098 (1966).

(6) H. Staudinger, *Ber.*, **58**, 1088 (1925).

(7) P. S. Bailey and S. S. Bath, *J. Am. Chem. Soc.*, **79**, 3120 (1957).

(8) R. Criegee, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **18**, 111 (1957).

SCHEME I



$$\mathrm{IV} \xrightarrow[\text{MeOH}]{O_3} \underset{\text{VII}}{C_6H_5CHO} + \underset{\text{VIII}}{C_6H_5CH(OOH)(OCH_3)} + \underset{\text{IX}}{CH_2O} + \underset{\text{X}}{CH_2(OOH)(OCH_3)}$$

$$\mathrm{V} \xrightarrow[\text{MeOH}]{O_3} \mathrm{VII} + \mathrm{VIII} + \underset{\text{XI}}{CH_3CHO} + \underset{\text{XII}}{CH_3CH(OOH)(OCH_3)}$$

$$\mathrm{VI} \xrightarrow[\text{MeOH}]{O_3} \mathrm{VII} + \mathrm{VIII} + \underset{\text{XIII}}{CH_3COCH_3} + \underset{\text{XIV}}{(CH_3)_2C(OOH)(OCH_3)}$$

and were sufficiently stable and separable so that their respective yields could be established.[9] Repeated experiments demonstrated ready reproducibility, and material balances were always around 90%. The results are summarized in Table I. Normalized product ratios are given in Scheme II.

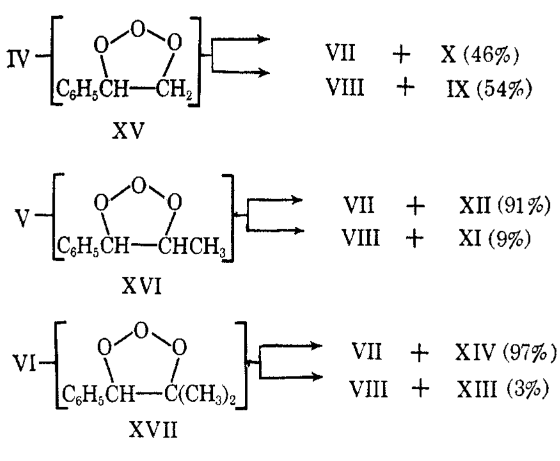
TABLE I

PRODUCT DISTRIBUTION IN VARIOUS OZONOLYSES

	Methanol distillate	Water layer	Pentane extract	Ether extract	Total	% yield
		Styrene[a]				
Active oxygen	3.1[b]	14.9	5.5	30.3	53.8	89.7
VII	3.9[c]		13.6[d]	8.7	26.2	43.7
IX	11.4	16.2[e]			27.6	46.0
VIII			4.7	26.4	31.1	51.8
X	3.1[f]	14.9[g]	0.8	4.7	23.5	39.2
		trans-Propenylbenzene[a]				
Active oxygen	4.8	30.1	4.3	17.1	56.3	93.8
VII	6.3[c]		42.4	3.4	52.1	86.8
XI[h]					...	...
VIII			2.4	2.6	5.0	8.3
XII	4.8	30.1	1.9	15.1	51.9	86.5
		2-Methylpropenylbenzene[i]				
Active oxygen	1.9	27.5	1.6	7.3	38.3	95.7
VII	4.7[c]		30.9	1.9	37.5	93.7
XIII[h]					...	...
VIII			0	1.0	1.0	2.5
XIV	1.9	27.5	1.6	6.3	37.3	93.2

[a] Concentration, 60 mmoles in 90 ml of methanol. [b] All values expressed in millimoles. [c] DNPH derivatives of benzaldehyde and the other carbonyl product were readily separable by fractional recrystallization. [d] All values derived from distillative work-up of the organic extracts were corrected for the amount previously removed for active oxygen determination. [e] By DNPH assay. [f] Hydroperoxide VIII was not distillable under the conditions used to remove this solvent. [g] Hydroperoxide VIII was not hydrolyzed to any appreciable extent by the extraction procedure. [h] No attempt was made to assay for this product with DNPH, because of the ready hydrolysis of the corresponding hydroperoxide under acid conditions. [i] Concentration, 40 mmoles in 75 ml of methanol.

SCHEME II



It is indeed striking that whereas heterolysis of XV exhibited little directional specificity,[10] with XVI and XVII a marked preference for one cleavage path over the other was found.

Discussion

The assumption that breakdown of XV–XVII favors the aldehyde–zwitterion pairs having the lower total energy[13] would intuitively lead one to predict as major products of methanolic ozonolysis those which are formed only in small amounts (except for the case of XV, where the two possible cleavage paths were of almost equal significance). The most thermodynamically significant factor in these heterolyses would be expected to be the relative stabilities of the high-energy zwitterions. While data are not available for this species, enthalpy values have clearly demonstrated the order of carbonium ion stability to be methyl < ethyl < isopropyl < benzyl.[14] The resonance stabilization associated with a phenyl group adjacent to an electron-deficient center then plays a generally insignificant role in the product-determining stage of these reactions.[15] Transition states involved in highly exothermic processes such as primary ozonide decomposition[19] are understood[20] to closely resemble the reactants (in this case, III) rather than the products, so that (in Hammond's words) "there should be no regular tendency for the most stable products to be produced the most rapidly in competitive reactions."

The reported greater instability of primary ozonides bearing *cis* substituents,[4] and the already stated possibility that such reactions could proceed directly to the

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(9) Hydroperoxides VIII, X, and XII, as well as peroxide XVIII encountered later, have not to our knowledge been previously isolated. Their spectral characteristics are compiled in Table II.

(10) It is of some interest that Briner[11] upon ozonizing styrene in carbon tetrachloride (a nonparticipating solvent), estimated by means of infrared spectra of the resulting solutions that VII and IX were produced in roughly equivalent amounts, albeit in low yields accompanied by peroxidic material. In a note published after completion of this manuscript, Fliszar[12] has ozonized styrene in carbon tetrachloride–methanol at 15–35° and has determined by quantitative infrared spectroscopy that 41% (average value) of the reacted olefin goes to VII.

(11) (a) E. Briner, S. Fliszar, and M. Ricca, *Helv. Chim. Acta*, **42**, 749 (1959); (b) E. Briner, C. Christol, H. Christol, S. Fliszar, and G. Rossetti, *ibid.*, **46**, 2249 (1963).

(12) S. Fliszar, *Can. J. Chem.*, **44**, 2351 (1966).

(13) A. Maggiolo, "Organic Ozone Reactions and Techniques," 4th ed, Welsbach Corp., Philadelphia, Pa., 1962.

(14) D. Bethell and V. Gold, *Quart. Rev.* (London), **12**, 173 (1958).

(15) Structure II, by the same reasoning, should also be eliminated from any consideration as the primary ozonide, since initial attack by the electrophilic terminal atom of ozone would involve the β carbon (relative to phenyl) in order to satisfy the Markovnikoff convention,[16] and the intermediates resulting from ring closure would upon directionally predetermined breakdown give the aliphatic aldehyde or ketone and the benzylic zwitterion. (This conclusion has been previously reached by Maggiolo[13] in connection with the results of Briner.[11])

(16) Polar addition of halogen acids to IV[17] and V[18] gave the respective 1-halo-1-phenylalkanes as the sole products.

(17) A. A. Dolnick and H. Naidus, U. S. Patent 2,573,695 (1951); *Chem. Abstr.*, **46**, 5072*f* (1952).

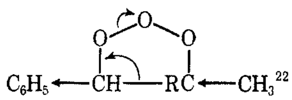
(18) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 3645 (1963).

(19) R. Criegee and G. Schroder [*Ber.*, **93**, 689 (1960)] calorimetrically determined the heat of decomposition of the primary ozonide of *trans*-1,2-di-*t*-butylethylene as being about 40 kcal/mole.

(20) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

most stable cleavage products without the intermediacy of I^2 did not appear to be a factor here. The similarity of results from V and VI (whose proposed initial adduct XVII would have a phenyl and a methyl group in a *cis* relationship) is indicative of the same reaction pathway. In addition, ozonolysis of *cis*-propenylbenzene[21] gave a 9:1 ratio of VII to XI, virtually the same value as obtained with the *trans* isomer V.

One may conclude, as did Bailey for a series of 1-substituted 1,2-dibenzoylethylenes,[2] that polarization due to the combined inductive effects of the substituents controlled the direction of cleavage of XV–XVII. In the case of XV, where only the weak negative inductive effect of phenyl is operable, the breakdown approached being nonselective; the small but definite preference for VIII and IX might reflect some influence from relative product stabilities, and perhaps a slightly longer lifetime for the initial adduct itself. With XVI and XVII, where the electrostatic effects of the substituents are codirectional, the predominance of the inductive influence was unequivocal.



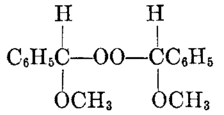
XVI′, R = H
XVII′, R = CH_3

Speculation such as the foregoing on the factors determining the course of heterolysis in these particular cases has assumed the validity of the Criegee mechanism (eq 1 and 3). Very recent research[23] has indicated dependence of ozonide stereochemistry on olefin geometry and thereby casts doubt on the universality of this mechanism, at least in nonparticipating solvent systems. The Criegee approach, however, does seem to better explain the products obtained in participating solvents such as methanol. A more perplexing question is the influence, if any, of methanol upon the direction of cleavage. If this relatively polar solvent does participate in the decomposition of I^{24} (thus circumventing the intermediacy of the Criegee zwitterion in the formation of methoxyhydroperoxides[2]), the ratio of products may indeed be solvent dependent.[25]

Bernatek, Kolsaker, and Ledaal[27] have attempted to rationalize their results from the "anomalous" ozonolysis of a series of 2-substituted 1,4-naphthoquinones by developing a Hammett-type relationship, assuming a primary ozonide with decided sp^2 character, and utilizing conformationally and experimentally modified σ_p values (which by definition include inductive and resonance contributions) to explain the effect of substituents on the ratio of products. According to this hypothesis, zwitterion formation predominates at the carbon atom having the higher value for the arithmetic sum of the σ_p constants for its substituents. Extension of this relationship to XV–XVII would predict that VIII should be the major product in the ozonolyses of V and VI. This is in direct variance with the results actually obtained, indicating again the negligible part played by resonance factors in the cleavage of these primary ozonides.[28]

Some Properties of the Methoxy Hydroperoxides

As a means of securing purer samples of VIII and of checking the workup procedure used for the unsymmetrical olefins IV–VI, the ozonolysis of *trans*-stilbene was also investigated. Because of the poor solubility of this olefin in methanol at low temperatures, a mixed solvent incorporating methylene chloride was used. After work-up it was found that only low yields of VII were procurable upon distillation, and that the still pot residue (which possessed a very weak ν_{OH} in the infrared region and weighed a good deal more than the anticipated quantitative yield of VIII[30]) appeared to consist mainly of a condensation product involving VII and VIII. Spectral examination of the distillate from the pentane extract of one such run revealed the presence of a significant amount of the dimethyl acetal of VII. Extended refrigeration of the still pot residue from a similar experiment resulted in the precipitation of a low-melting solid whose spectral properties (see Table II) appeared to indicate the structure α,α'-dimethoxybenzyl peroxide (XVIII). Corroboration of the assigned structure was obtained when a sample in methanol was treated with a deficiency of triethylamine. Product determination through vapor phase chromatography (vpc), infrared spectra, and 2,4-dinitrophenylhydrazine (DNPH) derivatization showed that the peroxide had completely reacted to give virtually quantitative yields of VII and methyl benzoate. The course of the base-catalyzed decomposition of XVIII is readily explicable by α-proton removal and stabilization of the transient carbanion.



$$C_6H_5\overset{H}{\underset{OCH_3}{C}}-OO-\overset{H}{\underset{OCH_3}{C}}C_6H_5$$

XVIII

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[21] This isomer was prepared following the directions of ref 18, and ozonized in the same fashion as IV–VI.

[22] This representation is identical with structure XXXIV in ref 2.

[23] (a) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Am. Chem. Soc.*, **88**, 3143, 3144 (1966); (b) F. L. Greenwood, *ibid.*, **88**, 3146 (1966).

[24] Addition of cold methanol to a solution of *trans*-1,2-di-*t*-butylethylene primary ozonide in freon 11 gave the methoxy hydroperoxide in good yield.[5]

[25] However, as a referee has kindly pointed out, bimolecular solvolysis should occur preferentially at the benzylic carbon (benzyl derivatives undergo SN2 reactions more readily than corresponding alkyl compounds[26]), leading to the formation of large amounts of VIII, particularly from XVI and XVII, where steric effects of the methyl substituents should reinforce this selectivity. This was not observed.

[26] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 282.

[27] E. Bernatek, P. Kolsaker, and T. Ledaal, *Tetrahedron Letters*, 1317 (1963).

[28] A later contribution from the Oslo group[29] has proposed a somewhat different rationale for sp^3-hybridized primary ozonides, in which zwitterion formation predominates at the carbon atom with the lower value of $\Sigma\sigma C_i$.

[29] T. Ledaal, *Tetrahedron Letters*, 3861 (1966).

[30] Characterization of the key product VIII was based on infrared and nmr spectra (see Table II), hydrolysis to VII in high yield under conditions of steam distillation,[31] reduction to VII in high yield with dimethyl sulfide,[32] a positive lead tetracetate test (for hydroperoxides),[33] good microanalytical and active oxygen assay values, independent synthesis through the autoxidation of benzyl methyl ether,[34] and vpc results (*cf.* Experimental Section).

[31] α-Methoxybenzylic hydroperoxides give excellent yields of the corresponding benzaldehydes when subjected to steam distillation: L. A. Subluskey, G. C. Harris, A. Maggiolo, and A. L. Tumulo, Advances in Chemistry Series, Vol. 21, John Wiley and Sons, Inc., New York, N. Y., 1959, p 149.

[32] J. J. Pappas, W. P. Keaveney, E. Gancher, and M. G. Berger, *Tetrahedron Letters*, 4273 (1966).

[33] R. Criegee, H. Pilz, and H. Flygare, *Ber.*, **72**, 1799 (1939).

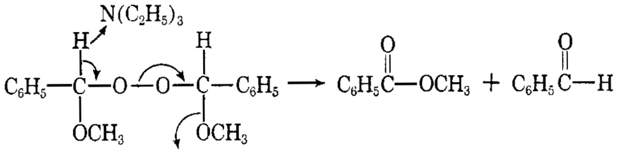
[34] D. B. Sharp and T. M. Patrick, *J. Org. Chem.*, **26**, 1389 (1961).

TABLE II

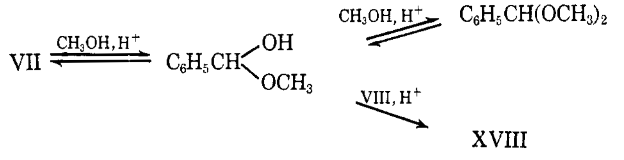
INFRARED AND NMR SPECTRAL DATA ON METHOXY PEROXIDES

Compound	Strongest infrared bands, μ^a	Chemical shift, δ^b	Rel peak areas
α-Methoxybenzyl hydroperoxide (VIII)	2.95, 6.83, 8.22, 9.1, 9.27, 13.15, 14.25	10.0 (s)[c]	1
		7.1–7.5 (m)	5.6
		5.63 (s)	1
		3.43 (s)	3
Methoxymethyl hydroperoxide (X)[d]	2.95, 8.65, 9.3, 10.2	8–10 (s)	1
		4.89 (s)	2
		3.41 (s)	3
1-Methoxyethyl hydroperoxide (XII)	2.95, 7.2, 8.7, 9.05, 9.65	9.6 (s)	1
		4.88 (q), J = 11 cps	1
		3.44 (s)	3
		1.28 (d), J = 11 cps	3
1-Methoxy-1-methylethyl hydroperoxide (XIV)[d]	2.95, 7.2–7.3 (d), 8.25, 8.6, 9.35	9.6 (s)	1
		3.25 (s)	3
		1.33 (s)	6
α,α′-Dimethoxybenzyl peroxide (XVIII)	Basically same as that of VIII, save that bands at 2.95, 11.9, and 12.3 are missing here	7.1–7.6 (m)	5
		5.69 (s)	1
		3.53, with smaller companion peak at 3.45	3

[a] Spectra were determined by means of a Perkin-Elmer 137 spectrophotometer, with bands recorded to the nearest 0.05 μ. Neat samples were used, except in the spectrum of XVIII which was taken as a dilute solution in chloroform. [b] Spectra were obtained as 20% solutions in carbon tetrachloride on a Varian A-60A spectrometer. The tabulated chemical shifts (parts per million downfield from tetramethylsilane) were taken at 0°, except for those of X and XII which were recorded at 40°. s = singlet, d = doublet, q = quartet, m = multiplet. [c] The hydroperoxy proton signal of all the hydroperoxides was quite broad. [d] The sample used to determine the spectra of this compound was a mixture with benzaldehyde.



Although at least one example of facile intermolecular condensation between methoxy hydroperoxides and aldehydes has been reported,[35] the products from the ozonolyses of IV–VI did not interact to any appreciable extent under the neutral conditions used.[36] The isolation of an acetal among the products of stilbene ozonolysis indicated the intervention of acid catalysis. That methylene chloride is attacked to some extent by ozone has previously been demonstrated,[37] and the generation of hydrogen chloride by such a process would be likely. (Indeed, Bailey[38] has postulated this acid evolution as a possible reason for different yields of anthraquinone from anthracene ozonation in methylene chloride and in carbon tetrachloride.) Thus, one may account for the observed products by assuming as the pivotal intermediate the hemiacetal, capable of reacting with the solvent to form the acetal or with the more nucleophilic hydroperoxide to produce XVIII.



When stilbene was ozonized in methanol alone, it was discovered that VII and VIII were indeed the major products; although no acetal was observed in the distillate, XVIII was formed in *ca.* 15% yield. Even this greatly reduced amount of the peroxide may have been accountable to the presence of benzoic acid: the solubility of the olefin was so low (at −60 to −70°) that the solvent was saturated with ozone throughout (as evidenced by the persistent blue color of the solution), which may have led to some oxidation of VII during ozone addition.[39] Benzoic acid was indeed among the products, although, admittedly, low levels of this material were often encountered as a result of air oxidation of VII during handling.

Hydrolytic stability of these hydroperoxides at ambient temperatures was also found to be quite reasonable. Maggiolo and co-workers[31] have shown that aliphatic alkoxyhydroperoxides are less susceptible to hydrolysis than the corresponding aromatic compounds. Thus X and XII could be recovered intact (by ether extraction) from the aqueous extracts of the respective ozonolysis residues, even after several days' standing. On the other hand, XIV[40] was more readily hydrolyzable; in an ozonolysis of VI performed prior to the experiment reported in Table I, almost no XIV was found in the ether extract. This was presumably due to the fact that since the extraction sequence was performed in a more leisurely fashion than in the tabulated experiment, the water-soluble peroxide had practically all decomposed before some of it could be removed by the ether. Despite the phenyl substituent, VIII was sufficiently resistant to hydrolysis to assure that the extraction procedure used in the reaction work-up did not significantly alter the product ratio. This fact was demonstrated at different times by vpc, infrared spectra, and nuclear magnetic resonance (nmr) spectra. For example, 2.3 g of a material found by nmr to be VIII containing 13.4 mole % VII[41] was taken up in 25 ml of ether, shaken vigorously for 15 min with 25 ml of water, separated, and dried. The resulting ether solution gave virtually the same spectrum, with the relative content of VII now at 14.2%, which was probably within experimental error.

No systematic investigation was made regarding thermal and mechanical stability of these materials, but from an empirical point of view their handling posed no serious problems. At pressures around 1 mm, heating a sample of VIII to 100–120° resulted in slow decomposition to methyl benzoate. Using lower pressure (less than 100 μ) and temperature (50–70°), this product was distilled intact. The aliphatic hydroperoxides were distilled from the ozonolysis ether extracts, accompanied by VII, at 30–40° and 1–3 mm. As an indication of the care required in handling these compounds, however, a 1-μl sample of almost pure XII detonated upon being injected into a vpc unit (injector temperature, 225°), destroying the syringe. Since

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[35] P. S. Bailey, *J. Org. Chem.*, **22**, 1548 (1957).

[36] Small amounts of XVIII (less than 5% of total aromatic product) were occasionally encountered in the still pot residues of pentane extracts from the ozonolysis of styrene.

[37] C. R. Dick and R. F. Hanna, *J. Org. Chem.*, **29**, 1218 (1964).

[38] P. S. Bailey, P. Kolsaker, B. Sinha, J. B. Ashton, F. Dobinson, and J. E. Batterbee, *ibid.*, **29**, 1400 (1964).

[39] In the absence of more reactive components, benzaldehyde has been reported to react almost quantitatively with ozone at temperatures as low as −20°. H. M. White and P. S. Bailey, *ibid.*, **30**, 3037 (1965).

[40] R. Criegee and G. Lohaus [*Ann.*, **583**, 6 (1953)] synthesized this substance through the methanolic ozonolysis of tetramethylethylene.

[41] This value was determined by comparing relative signal areas of the formyl proton of VII vs. the tertiary or "acetal" proton of VIII.

another sample of the same material had been uneventfully chromatographed a few minutes earlier, the explosion may have been due to shock sensitivity, that is, from a too severe depression of the plunger.

Experimental Section

(**Caution**.—Although no serious incidents occurred during the course of this work, these hydroperoxides, particularly those of lower molecular weight, are potentially explosive and precautions such as adequate shielding were exercised thoughout.)

The ozone source was a Welsbach T-816 laboratory ozonator, using Air Products' pure dry oxygen as the feed gas. Ozone concentration at a gas flow rate of 1.0 l./min was around 5.3 wt % and was determined iodimetrically. The reactor used in the ozonolyses was "Mini-Lab" assembly no. 10104 (Ace Glass). The reagent grade methanol used as solvent was distilled over magnesium immediately before use. Stabilized styrene (Eastman) was used directly (and the small amount of polystyrene removed from solution), since predistillation resulted in slightly lower yields. Propenylbenzene (Columbia Organic Chemicals, overwhelmingly *trans* isomer) was distilled before use. Anhydrous sodium sulfate served as drying agent for the organic extracts. The gas chromatographic work was done at 150° (injector temperature, 225°) on a Wilkens A-90-P instrument employing helium gas flow and a 5-ft column containing 20% SF-96 on 60–80 firebrick. Infrared and nmr spectra were obtained as cited in footnotes to Table II. Microanalyses were performed by Mrs. Barbara Artman of these laboratories.

2-Methylpropenylbenzene (VI).—To 38.9 g (0.1 mole) of benzyltriphenylphosphonium chloride in 250 ml of dry tetrahydrofuran was added (under nitrogen) 65 ml of *n*-butyllithium in hexane (Foote Mineral Co., equivalent to 0.1 mole). When the red-burgundy solution had cooled to room temperature, 11.5 ml (0.15 mole) of pure, freshly distilled acetone was added in one portion. After 93 hr the solvent was stripped at atmospheric pressure and the residue was triturated with three successive portions of 75 ml of pentane–25 ml of ether. The combined extract was dried and distilled to give a forerun (1.05 g) consisting mainly of mesityl oxide, and a main cut [bp 55° (4–5 mm), lit.[42] bp 70.5–71.5° (12 mm)] consisting of 6.60 g (50%) of VI. Characterization was by means of infrared spectra ($\nu_{\max}^{\text{neat}}$ 5.97, 6.2, 6.67, 6.9, 7.23, 13.5, and 14.3 μ), nmr spectra (five-proton multiplet centered at δ 7.17, one-proton multiplet centered at 6.24, adjacent three-proton doublets, $J = 2$ and <2 cps, respectively, at 1.85 and 1.80), infrared spectra [$\lambda_{\max}^{\text{CH}_3\text{OH}}$ 244 mμ (ε 13,930), lit.[43] $\lambda_{\max}^{\text{isooctane}}$ 245 mμ (ε 12,400)], and independent synthesis through the alternate Wittig reaction of isopropylidenetriphenylphosphorane and benzaldehyde.

Ozonolysis Procedure.—The olefin (60 mmoles) in methanol (90 ml) was maintained at −70 to −65° by a Dry Ice–acetone bath, while a stoichiometric amount of ozone was added until appearance of a blue color. The contents were swept free of ozone with a nitrogen stream, allowed to warm to *ca.* 10°, and the solvent was stripped at 10–20° and 10–25 mm into a Dry Ice–acetone-cooled receiver. The clear liquid residue was shaken with 75 ml of pentane and 65 ml of distilled water. The pentane layer was separated and the remainder was extracted with 55 ml of ether. The two extracts, the water layer, and the methanolic distillate were separately diluted to exactly 100 ml with the respective solvents; 5-ml aliquots were withdrawn from each; and active oxygen content was determined by the technique of Wagner.[44] The low volatility and water solubility of VIII, plus its resistance toward hydrolysis, permitted assignment of total active oxygen in both methanolic distillate and water layer to the aliphatic hydroperoxides.

The methanolic solution (10 ml) was added to a solution prepared from 1.5 g (7.5 mmoles) of DNPH, 100 ml of hot water, and 17 ml of concentrated hydrochloric acid. The instantly formed precipitate was collected soon thereafter and recrystallized from ethanol–ethyl acetate–nitromethane to give pure (by infrared spectra and mixture melting point) benzaldehyde dinitrophenylhydrazone; solvent evaporation from the filtrate and recrystallization from ethanol gave the pure derivative of the aliphatic carbonyl compound. The formaldehyde content of the water layer from the ozonolysis of IV was gravimetrically determined in the same fashion. (Addition of a sample of X containing some VII to a DNPH solution precipitated VII-DNPH, contaminated by only a trade of IX–DNPH; we therefore assumed that the dinitrophenylhydrazone of IX obtained from the ozonolysis of IV originated not from acid hydrolysis of X but from the primary presence of IX. However, similar treatment of a mixture of XII and VII formed the derivatives of both VII and XI, and ready hydrolysis of XIV, likewise, prevented determination of acetone by this technique. The relatively great difference in volatility between VII and VIII led to the conclusion that virtually no VIII was present in the methanolic distillate, and that all the VII-DNPH secured from this source was necessarily derived from free VII.)

The two organic extracts were dried and flash distilled; the residues were vacuum distilled. The pentane extracts gave largely VII [bp 35° (*ca.* 3 mm)] accompanied by lesser quantities of VIII (nondistillable at a water bath temperature of 55° and pressures around 1 mm) and the aliphatic hydroperoxide (codistillable with VII). The ether extracts yielded the bulk of total VIII, most of the aliphatic hydroperoxide not in the methanol or water phases, and small amounts of VII. Invariably a little VII was retained in the pot even after extended distillation, but the relative amounts of VII and VIII were accessible through examination of the nmr spectrum.[41] The presence of both VII and the aliphatic hydroperoxide (X, XII, or XIV) in the distillates, qualitatively detectable by infrared spectra, was quantitatively determinable through vpc (benzaldehyde peak area *vs.* total area of the several volatile constituents resulting from hydroperoxide pyrolysis), active oxygen assay, and nmr. Results of representative experiments are listed in Table I. The product ratios in Scheme II were based on [VII]:[VIII]; the total quantity of the aliphatic hydroperoxide, or the actual aliphatic product ratio in the case of styrene, was invariably in virtual agreement with these values.

Spectral data for the hydroperoxides are in Table II. Compound X could not be obtained in sufficient purity for elemental analysis. However, active oxygen assay of a mixture of VII and X, assigning total activity to a peroxide of molecular weight 78, demonstrated the material to be about 39% X, in agreement with an nmr integration of the same sample. Active oxygen assay of pure XII in refluxing isopropyl alcohol[44] indicated at least 91% purity (based on molecular weight 92).[45]

Anal. Calcd for $C_3H_8O_3$: C, 39.12; H, 8.75. Found: C, 39.25; H, 9.09.

The structure of XIV was based solely on its spectra.

It was discovered while taking nmr spectra that VIII was capable of slow but measurable decomposition to XVIII, in a process not involving VII. (Hydroperoxides containing strongly electron-releasing groups are known to disproportionate under acid conditions to hydrogen peroxide and the symmetrical dialkyl peroxide.)[46] Hydroperoxide VIII was stabilized by using spectral grade carbon tetrachloride distilled from calcium hydride, and by taking the spectra at 0 rather than 40°. After treatment with sodium iodide in refluxing isopropyl alcohol, pot residues containing predominantly VIII required amounts of standard thiosulfate solution equivalent to 85–91% of this hydroperoxide (mol wt, 154).[45] Crude VIII was distilled at 45–90 μ (Pirani gauge) and a bath temperature of 50–70°.

Anal. Calcd for $C_8H_{10}O_3$: C, 62.32; H, 6.58. Found: C, 62.23; H, 6.47.

α-Methoxybenzyl Hydroperoxide (VIII) by Autoxidation.[34]—Benzyl methyl ether (Eastman) was consecutively washed with two volumes of 10% aqueous Girard reagent T and 10% aqueous sodium bicarbonate, then the organic layer was dried and distilled, bp 80–81° (37–38 mm). This material (24 g) was oxidized, using the procedure of Sharp and Patrick, for 2.5 hr at a flow rate of 0.5 l./min. The oxygenated, decanted ether weighed 20.25 g and active oxygen assay indicated the equivalent of 4.3% VIII. The total material was distilled to remove the unreacted ether, bp 33° (2 mm), no $\nu_{\text{C=O}}$ in the infrared region.

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[42] C. Ruchardt, *Ber.*, **94**, 2599 (1961).

[43] W. H. Urry and M. S. Kharasch, *J. Am. Chem. Soc.*, **66**, 1438 (1944).

[44] C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).

[45] This value was probably a trifle low, since slight thermal decomposition of the hydroperoxide prior to iodide addition would not be unexpected.

[46] A. G. Davies, "Organic Peroxides," Butterworth and Co., Ltd., London, 1961, p 43. The occasionally observed slow evolution of bubbles in the nmr sample tube could have been due to hydrogen peroxide.

The residue (0.82 g) was spectrally identical with ozonolysis-derived VIII, and was somewhat purer than comparable ozonolysis residues.

Vpc Analysis. Neat residual samples of VIII (secured from different sources and contaminated with VII) gave chromatograms consisting of four substances with retention time less than 1 min, plus VII and methyl benzoate in about a 35:65 molar ratio. Previous investigation of the methanolic ozonolysis of *trans*-stilbene[47] indicated that gas chromatography of VIII at 150° did not give methyl benzoate as the exclusive aromatic degradative product, but a significant amount of VII as well. Apparently the hydroperoxide undergoes hydrolytic as well as thermal decomposition.

The different VII:VIII ratios resulting from ozonolyses of IV and V were reflected in vpc data obtained from injection of the respective reaction mixtures. The peak area of VII relative to that of methyl benzoate was found to be, in the single experiments performed, 50:50 in the case of IV and 88:12 for V. Calculations assuming the retention of the 35:65 ratio mentioned above from component VIII of each mixture[48] gave the following approximations for molar proportions of VII:VIII in these reactions: IV, 34:66; V, 85:15. Although these ratios were not in quantitative agreement with those based on direct isolation, they at least faithfully mirrored the degree of difference between the systems.

α,α'-Dimethoxybenzyl Peroxide (XVIII). Ozonolysis of *trans*-Stilbene.—*trans*-Stilbene (3.61 g, 20 mmoles), in 45 ml each of methanol and reagent grade methylene chloride, was ozonated at −66 to −69°, to the appearance of a blue color. A work-up similar to that used in the styrene series was carried out, except that no active oxygen determinations were performed. The distilled reaction solvent contained 2.1 mmoles of VII (DNPH assay). The vacuum distillate from the pentane extract weighed only 0.97 g; infrared analysis revealed it to be VII accompanied by a larger amount of an extraneous material having strong ν_{CO} absorption (9.05 and 9.5 mμ). Independent synthesis[49] and nmr spectra proved this new compound to be the dimethyl acetal of VII. The pot residue from this same extract weighed 2.91 g; infrared and nmr spectra showed very little VIII, mostly a structurally similar, nonhydroxylic condensation product later shown to be XVIII (see next paragraph). The ether extract gave virtually no vacuum distillate (*ca.* 0.03 g), and a pot residue weighing 1.09 g which was VIII containing a little XVIII.

Extended refrigeration of the pentane pot residue gave a low-melting (below 40°) solid which proved to be pure XVIII. This peroxide, whose spectra (Table II) coincided with the assigned structure, was almost inert to sodium iodide in refluxing isopropyl alcohol.

Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.04; H, 6.63; mol wt, 274. Found: C, 70.12; H, 6.22; mol wt (vapor pressure osmometry), 258.

Reaction of XVIII with Triethylamine.—An ice-cooled solution of 0.65 g (2.4 mmoles) of XVIII in 2 ml of methanol was treated with 2 drops of triethylamine. After overnight standing, infrared spectra showed that bands characteristic of both VII and methyl benzoate were in evidence, and that absorption due to XVIII (notably the very strong ν_{CO} at 9.05 μ) had completely disappeared. Exactly one-third by weight of the total solution was added to an excess of DNPH test solution; filtration and drying left 0.225 g of the benzaldehyde derivative, equivalent to 0.8 mmole. The yield of VII in the total solution was therefore quantitiative. Vpc analysis of the balance showed that the yield of methyl benzoate, by comparison of its peak area with that due to VII, was about 92%.

Registry No.—IV, 100-42-5; V, 873-66-5; VI, 768-49-0; VII, 100-52-7; VIII, 10027-71-1; X, 10027-72-2; XII, 10027-73-3; IX, 50-00-0; XI, 75-07-0; XIV, 10027-74-4; XVIII, 10027-75-5.

Acknowledgments.—We wish to thank Dr. A. M. Fusco and Mr. W. M. Arnheim for determining and aiding in the interpretation of the nmr spectra, and Professor N. Kornblum for a number of helpful discussions.

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[47] C. D. Johnson and P. S. Bailey, *J. Org. Chem.*, **29**, 703 (1964). (*Cf.* Table II in this paper.)

[48] We concur with a referee's statement that such an assumption is quantitatively invalid. The obvious great difference in aldehyde/ester ratios, however, agreed sufficiently well with what one would expect from our other results that this vpc data was felt to be worthy of inclusion.

[49] T. Langvad, *Acta Chem. Scand.*, **8**, 336 (1954); *Chem. Abstr.*, **49**, 5277c (1955).

Reactions of 2,3-Dichlorotetrafluoropropene with Nucleophiles Containing Phosphorus[1]

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Received November 7, 1966

A series of novel 2-chlorotetrafluoroallylphosphorus compounds has been prepared by reaction between 2,3-dichlorotetrafluoropropene and nucleophiles containing phosphorus, including phosphites, phosphinide ions, and phosphines. The spectral properties of these compounds are discussed.

The chemistry of polyfluoroalkyl derivatives of phosphorus is of considerable interest, in that the strongly electron-withdrawing polyfluoroalkyl groups profoundly modify the normal chemical behavior of the phosphorus atom and attached groups. This area of chemistry has been the subject of some attention in recent years.[2] However one restriction on the types of molecules available for study in this area has been the fact that the main preparative routes have been free-radical reactions either of polyfluoroalkyl iodides,[3,4] *e.g.*, as in eq 1, or of fluoro olefins,[5,6] *e.g.*, as in eq 2.

$$CF_3I + P \longrightarrow CF_3PI_2 + (CF_3)_2PI + (CF_3)_3P \qquad (1)$$

$$CF_2{:}CF_2 + PH_3 \longrightarrow CHF_2CF_2PH_2 + (CHF_2CF_2)_2PH + H_2PCF_2CF_2PH_2 \qquad (2)$$

In the present work a new approach to the synthesis of phosphorus compounds bearing an unsaturated polyfluoroalkyl group has been developed. This depends on the susceptibility of a polyfluoroallylic chloride to nucleophilic attack.

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[1] This work was supported by Grant GP-3887 from the National Science Foundation.

[2] For a review, see R. E. Banks and R. N. Haszeldine in *Advan. Inorg. Chem. Radiochem.*, **3**, 367 (1961).

[3] F. W. Bennett, H. J. Emeleus, and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).

[4] H. J. Emeleus and J. D. Smith, *ibid.*, 375 (1959).

[5] G. W. Parshall, D. C. England, and R. V. Lindsey, *J. Am. Chem. Soc.*, **81**, 4801 (1959).

[6] G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J. Chem. Soc.*, 1083 (1963).