passing from a viscous solvent to ethanol. Moreover, a nearly stoichiometric amount of acetone was formed when the reaction was conducted in isopropyl alcohol. We interpret this to mean that a *duality of mechanisms* is operative (Chart I). While the photo-Fries reaction itself does not involve true "free" radical intermediates, the concomitant process leading to *p*-cresol formation almost certainly does. This is in accord with recent findings on the photochemically induced decarboxylation of hindered aryl esters.[9]

The divergence in response of the two pathways to solvent change suggests that the ease of internal return of the radical pair from the solvent cage (Chart I) must be a dominant factor in determining the quantum yield of *p*-cresol formation.

Appropriate quenching experiments, with added naphthalene[10] and ferric acetylacetonate,[11] and sensitization experiments with added acetophenone,[12] demonstrated that the over-all process was unaffected by these triplet-responsive additives. This is indicative of reaction from an upper singlet state or from a triplet manifold at a rate exceeding diffusional control.

Both the role of the solvent and the fate of the acyl moiety in the phenol-forming process are now under detailed study.

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(9) R. A. Finnegan and D. Knutson, *J. Am. Chem. Soc.*, **89**, 1970 (1967).

(10) W. M. Moore and M. Ketchum, *ibid.*, 84, 1368 (1962).

(11) A. J. Fry, R. S. H. Liu, and G. S. Hammond, *ibid.*, **88**, 4781 (1966), and references therein.

(12) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

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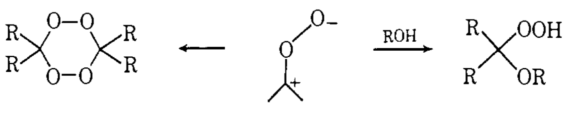
Ozonolysis. Evidence for Carbonyl Oxide Tautomerization and for 1,3-Dipolar Addition to Olefins

Sir:

Carbonyl oxides (**1**) (Criegee zwitterions) have never been isolated, but indirect evidence for their existence is abundant.[1-4] These unusual species are usually generated by ozonolysis of a suitable olefin,[1-3] although more recently evidence has been presented for their formation by reaction of a carbene with oxygen.[5] Evidence for the existence of carbonyl oxides rests principally on their reaction with alcohols to form alkoxy hydroperoxides (**2**), which have been isolated and characterized, and on the isolation and characterization of dimers (**3**).[1-4]



3 **1** **2**

Criegee[1-3] has presented sound but not unequivocal evidence which indicates that ozonides may be formed by the 1,3-dipolar addition[4] of carbonyl oxides to carbonyl compounds. We have confirmed this conclusion but further established that this reaction is probably not the most important source of ozonides.[6] Although the evidence for 1,3-dipolar addition of carbonyl oxides to aldehydes and ketones is compelling,[1-4,6,7] surprisingly no evidence exists to indicate that carbonyl oxides can add to olefins in the same way.[4] Criegee and Günther, however, have ozonized tetramethylethylene in the presence of tetracyanoethylene and obtained tetracyanoethylene oxide in 98% yield.[8] They suggested that the oxide precursor may have been the 1,3-dipolar adduct of TCNE with the dimethyl zwitterion. Kwart and Hoffman have extended the reaction to other carbonyl oxides and to norbornene.[9]

We now wish to report evidence for the *1,3-dipolar addition of a carbonyl oxide to an olefin* and, moreover, that the adducted olefin is a *vinyl hydroperoxide formed in the ozonolysis reaction by tautomerization of the carbonyl oxide.*

Ozonolysis of tetramethylethylene has been reported to yield acetone and acetone diperoxide (**5**) (~15% yield) as isolable products.[10] The reaction presumably proceeds to give acetone and the Criegee zwitterion (**4**) (carbonyl oxide) and since, apparently, disubstituted zwitterions are unreactive toward simple ketones,[1,7] no ozonide is formed. The zwitterion **4** undergoes self-condensation to yield the dimer **5** and polymeric peroxides. Usually the diperoxide is isolated by crystallization from acetone.

We have examined the crude reaction mixture by glpc from the ozonolysis of tetramethylethylene in pentane and in acetone and found it to contain at least two other products. The major one of these has been identified as the peroxy hydroperoxide **6** and is obtained in about 10% yield. Our structural assignment rests on several unequivocal pieces of evidence. *Anal.* Found: C, 48.20; H, 8.40. The infrared spectrum of **6** exhibits absorption at (cm^{-1}, CCl_4) 3565 (nonbonded, typical for hydroperoxide), 2980 (s), 1367 (s), 1161 (s), 1056 (s), 852 (m), and 867 (m). The 100-Mc nmr spectrum (CCl_4) revealed three methyl singlets at τ 8.49, 8.69, and 8.80, a two-hydrogen AB quartet at τ 6.43 ($\Delta\nu$ = 29 cps, J = 11 cps), and a broad OH at variable chemical shift. Lithium aluminum hydride reduction of **6** yielded only isopropyl alcohol, as might be expected from a retroaldol cleavage of the reduction intermediate.[11] Treatment of **6** with lead tetraacetate resulted in a vigorous release of a gas. This is taken as confirmation of the presence of the hydroperoxide

6

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

(2) R. Criegee in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p 32.

(3) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

(4) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565 (1963).

(5) P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **84**, 3408 (1962).

(6) P. R. Story, C. E. Bishop, J. R. Burgess, J. B. Olson, R. W. Murray, and R. D. Youssefyeh, presented at the International Oxidation Symposium, San Francisco, Calif., Aug 27–Sept 1, 1967, sponsored by Stanford Research Institute; to be published.

(7) R. W. Murray, P. R. Story, and L. D. Loan, *J. Am. Chem. Soc.*, **87**, 3025 (1965).

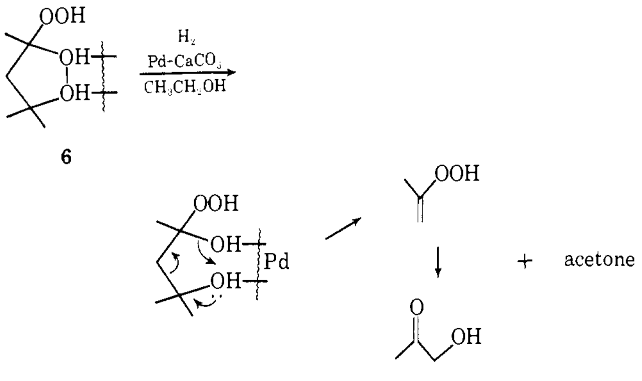
(8) R. Criegee and P. Günther, *Chem. Ber.*, **96**, 1564 (1963).

(9) H. Kwart and D. M. Hoffman, *J. Org. Chem.*, **31**, 419 (1966).

(10) R. Criegee, G. Blust, and H. Zinke, *Chem. Ber.*, **87**, 766 (1954).

(11) See, for example, N. G. Gaylord, "Reduction With Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, pp 164, 283.

function.[12] Quantitative catalytic hydrogenation resulted in the uptake of approximately 1.5 mole equiv of hydrogen to yield acetone and hydroxyacetone, as identified by nmr and infrared analysis. These products are understandable in terms of, again, a retroaldol-type cleavage of the intermediate, as illustrated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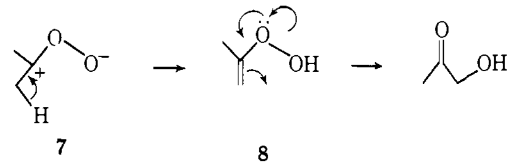
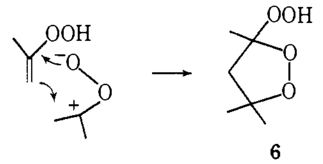
The data outlined here constitute an unequivocal structure proof for the peroxy hydroperoxide **6**. We further submit that the most reasonable interpretation of the mechanism of formation of **6** is through a 1,3-dipolar addition of the dimethyl carbonyl oxide **7** to the vinyl hydroperoxide **8** which, we propose, is formed in the reaction by tautomerization of the carbonyl oxide **7**. The vinyl hydroperoxide **8** would be expected to isomerize to hydroxyacetone, as apparently observed in hydrogenation of **6**. Therefore, if the proposed mechanistic scheme is correct, the ozonolysis reaction mixture would be expected to contain some hydroxyacetone. We have established that the other, minor product (~1% yield) isolated from the ozonolysis is indeed hydroxyacetone. Taken together, the isolation of hydroxyacetone and **6** constitutes excellent evidence for the tautomerization and subsequent rearrangement of the carbonyl oxide **7**. This work constitutes the first observation of such a rearrangement of carbonyl oxides and suggests that this type of reaction should be given serious consideration in accounting for abnormal ozonolyses. In addition, the isolation of **6** provides the first concrete evidence for a 1,3-dipolar addition of a carbonyl oxide to an olefin. An obvious extension of the observed reaction is the addition of carbonyl oxides to vinyl ethers; this investigation is in progress.


7 8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It is interesting that the zwitterion **7** is sufficiently reactive toward the vinyl hydroperoxide **8** to intercept it efficiently before isomerization to hydroxyacetone. Even though hydroxyacetone is present in the ozonolysis mixture and might be expected to yield ozonides, we have not yet detected the hydroxy ozonide which would result from its 1,3-dipolar condensation with the carbonyl oxide **7**.

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[12] R. Criegee in "Oxidation in Organic Chemistry," K. B. Wiberg' Ed., Academic Press Inc., New York, N. Y., 1965, p 302.

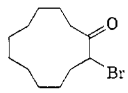
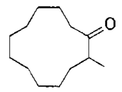
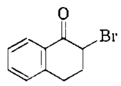
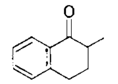
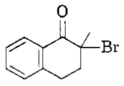
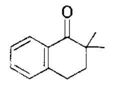
Chemistry of Enolates from Zinc Reduction of α-Bromo Ketones. A New Method of Substitution α to Carbonyl Groups

Sir:

Treatment of α-bromo ketones with zinc in 10:1 benzene–dimethyl sulfoxide generates species, presumably zinc enolates, which react with electrophiles to form carbon–carbon bonds at the original site of the bromine. This procedure, which has its origins in the classical Reformatsky reaction[1] and in zinc–acetic acid reductions,[2] represents a potentially useful alternative method for introduction of substituents at a specific position adjacent to a carbonyl group.[3]

When 0.01 mole of 2-bromocyclododecanone in 50 ml of benzene and 5 ml of dimethyl sulfoxide was treated with 0.1 g-mole of zinc powder and 0.02 mole of methyl iodide and stirred under nitrogen at room temperature for 8 hr, an essentially quantitative yield of 2-methylcyclododecanone was obtained.[4] This and other examples of methylation are given in Table I.

Table I. Methylation *via* Zinc Reduction of α-Bromo Ketones[a]

Substrate	Product	% yield[b]
		>99
		85
		57
6-Bromo-7-tridecanone	6-Methyl-7-tridecanone	66[c]
4α-Bromo-3-cholestanone	4α-Methyl-3-cholestanone	40[d]

[a] Reaction conditions like those described in the text for 2-bromocyclododecanone, unless otherwise specified. [b] Determined by vpc with calibration using an authentic sample, unless otherwise specified. [c] Run with lower concentration of bromo ketone; *cf.* Table III. [d] Determined by isolation of product. The only other compound found was 3-cholestanone (40%).

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[1] R. L. Shriner, *Org. Reactions*, **1**, 1 (1942); *cf.* W. R. Vaughan, S. C. Bernstein, and M. E. Lorber, *J. Org. Chem.*, 30, 1790 (1965), for a recent discussion of the nature of the Reformatsky reagent.

[2] *E.g.*, H. E. Zimmerman and A. Mais, *J. Am. Chem. Soc.*, **81**, 3644 (1959).

[3] H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapters 7–9, gives a general review of methods for carbon–carbon bond formation adjacent to carbonyl groups.