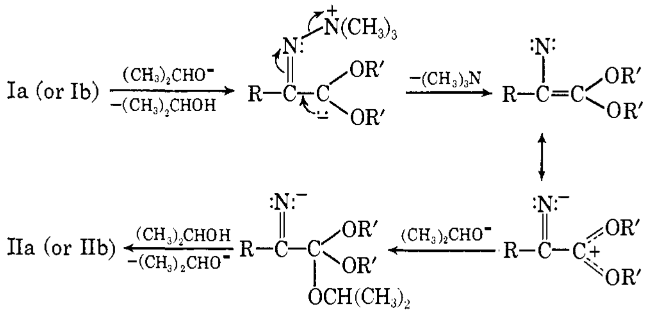
tons), 7.20 and 8.02 (5 H, broad multiplets, phenyl protons), and 9.90 ppm (1 H, broad singlet, imine proton); $\nu_{\max}^{\text{film}}$ 3260 and 1625 cm^{-1}. *Anal.* Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.67; H, 7.40; N, 6.08.

The following mechanism is proposed tentatively to explain the formation of the α-imino ortho esters IIa and IIb. In systems which undergo a Neber rearrangement, an intermediate vinylnitrene has been suggested as the immediate precursor to the azirine.[9] However, the present intermediate can be considered as a resonance hybrid in which the alkoxy groups delocalize (*i.e.*, stabilize) the adjacent positive charge. Addition of isoproproxide to such an ionized form would lead to the observed product.



Acknowledgments. This investigation was supported by a National Aeronautics and Space Administration Fellowship (to T. L. F.). The Varian A-60A spectrometer was purchased through a National Science Foundation major equipment grant (GP-3756).

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Kenneth R. Henery-Logan, Tomas L. Fridinger
Department of Chemistry, University of Maryland
College Park, Maryland 20740

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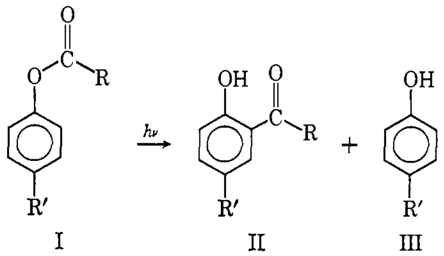
On the Mechanism of the Photo-Fries Reaction

Sir:

We wish to report some observations which bear directly on the mechanism of the photo-Fries reaction.[1] Previous workers have suggested that the rearrangement



I II III

proceeds by either a "molecular" pathway involving a bridged intermediate[2,3] or by a "radical-pair" process[4,5] in which acyl-O homolysis is followed by attack of the resulting acyl radical on the *ortho* or *para* position of the phenoxy radical. In solution the reaction is always accompanied by formation of the corresponding phenol, III.[2,4,5] The fate of the acid portion of the ester has never been generally established.[6]

Relative to this problem, we have studied the 2537-A light-induced reaction of *p*-tolyl acetate (I, R, R′ = Me) in various solvents.[7] The quantum yields of products II (R, R′ = Me) and III (R′ = Me) were measured;[8] the results are compiled in Table I. Examination of these data reveals that the quantum efficiency of the photo-Fries reaction was completely unaffected by wide variations in solvent viscosity (hence, cage participation), solvent polarity, and solvent reactivity toward radical attack. Moreover, the presence of added oxygen did not alter the yield of the rearrangement product. These results constitute compelling evidence that the photo-Fries reaction involves a *very tightly bound intermediate* which proceeds to product unaffected by its reaction environment.

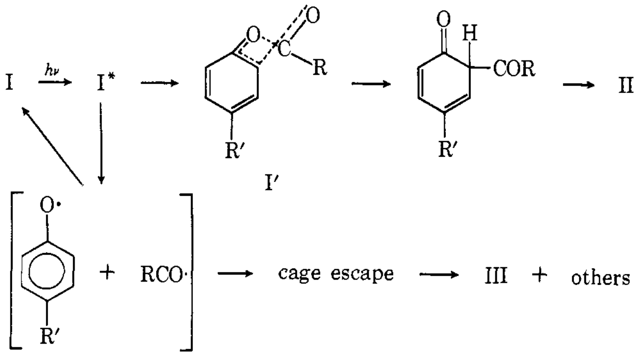
Table I. Quantum Yields[a]

Solvent[b] (viscosity[c])	Φ_{II}	Φ_{III}
EtOH (1.00)	0.17	0.45
i-PrOH (1.73)	0.17	0.09
t-BuOH (3.00)	0.18	0.07
t-BuOH, O_2	0.17	0.04
Dioxane–H_2O	0.17	0.06
Carbowax 400 (76)	0.17	0.03
Carbowax 600 (109)	0.16	0.02

[a] Determined by the method previously described.[8] Each value is an average of at least three determinations; average deviation was $\lesssim$10%. [b] Ester concentration was 0.26 ± 0.01 *M* in each run. [c] Expressed in centipoises, 30°.

This intermediate may be in the form of a photoactivated charge-transfer complex,[3] a bridged biradical with neutral charge,[2] or very tightly held radical fragments which have some brief, but finite, existence between bond breaking and bond reforming. Lacking a means to distinguish between these possibilities, we represent the intermediate or transition state as I′.

Chart I



In striking contrast, the quantum yield of III was dramatically altered by changes in solvent (Table I). *p*-Cresol formation was enhanced some 20-fold in

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(3) G. M. Coppinger and E. R. Bell, *J. Phys. Chem.*, **70**, 3479 (1966).

(4) H. Kobsa, *J. Org. Chem.*, **27**, 2393 (1962).

(5) R. A. Finnegan and J. J. Mattice, *Tetrahedron*, **21**, 1015 (1965).

(6) Recent work by E. D. A. Plank (Ph.D. Thesis, Purdue University, 1966) suggests that irradiation of 3,4-dihydrocoumarin results in the formation of a ketene intermediate.

(7) In addition to the expected Fries product (II, R, R′ = Me) and *p*-cresol (III, R′ = Me), the solvent-derived acetate was formed when the irradiation was conducted in alcoholic media. Small amounts of methane and carbon monoxide were also detected.

(8) The experimental method was previously described: D. J. Trecker, R. S. Foote, J. P. Henry, and J. E. McKeon, *J. Am. Chem. Soc.*, **88**, 3021 (1966).

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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Michael R. Sandner, David J. Trecker
Research and Development Department,
Union Carbide Corporation
Chemicals and Plastics, South Charleston, West Virginia

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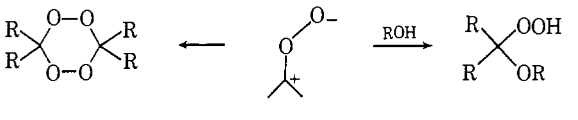
Ozonolysis. Evidence for Carbonyl Oxide Tautomerization and for 1,3-Dipolar Addition to Olefins

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]



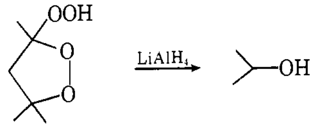
3 **1** **2**

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**) ($\sim$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



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