The mercuric trifluoroacetate promoted[19] allylic carbamate equilibrium is notable for the mildness of the reaction conditions and the high isolated yields. Unwanted skeletal isomerizations would appear precluded since allylic carbonium ions are not intermediates. The method reported here for contrathermodynamic allylic isomer enrichment is limited to the conversion of carbamic esters of 2-alken-1-ols, which contain a disubstituted double bond, to the correspondinng 1-alken-3-ol derivatives. Although this method represents a general approach for achieving contrathermodynamic allylic isomerizations, the reaction conditions we have thus far investigated do not specifically afford only the contrathermodynamic isomer. One can imagine, however, that similar catalysts, which have even higher selectivities for binding specifically the terminal alkene isomer, may overcome this limitation.

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Supplementary Material Available. Experimental procedure (2 pages). Ordering information is given on any current masthead page.

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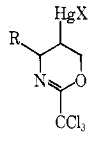
(8) Since in this case Y contains a protic hydrogen, the ion pair **2** would be in equilibrium with HX and the neutral adduct i.



i

(9) A mechanism similar to that shown in eq 1 has been suggested for the palladium(II)-catalyzed isomerization of allylic esters: P. M. Henry, *J. Am. Chem. Soc.*, **94,** 5200 (1972).

(10) Equilibration of the butenyl acetates in acetic acid by treatment with *p*-toluenesulfonic acid (0.3 M, 60 °C, 9–16 days)[2b] or perchloric acid (8.3 mM, 75 °C, 3–5 h)[11b] has been reported.[11] Recoveries varied from 30 to 84% and the equilibrium composition[11b] was 38.2% α-methylallyl acetate, 51.4% *trans*-crotyl acetate, and 10.4% *cis*-crotyl acetate.

(11) (a) Z. Rappoport, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, **94,** 2320 (1972); (b) H. E. Green, Ph.D. Thesis, University of California, Los Angeles, Calif., 1965.

(12) E. S. Lewis, J. T. Hill, and E. R. Newman, *J. Am. Chem. Soc.*, **90,** 662 (1968).

(13) At 25 °C in THF the rate constant for the catalyzed conversion of **4a** to **5a** was measured by the initial rate method: $k_{cat} = 4 \pm 3 \times 10^{-3}$ mol l.$^{-1}$ s^{-1} (five determinations). The extent of reaction ranged from 3 to 30% and the equivalent of catalyst varied from 0.05 to 1.0.[14] The corresponding rate constant for the thermal, gas phase, isomerization was estimated by extrapolating rate constants[12] for the conversion of $CH_3CH{=}CHCH_2O$-$(C{=}O)Z$ to $CH_3CHO(C{=}O)ZCH{=}CH_2$ (Z = CF_3, CH_3, and OCH_3) from 325 to 25 °C, plotting the logarithm of these extrapolated rate constants vs. σ_m (correlation coefficient, 1.00), and estimating $K_{thermal}$ for the conversion of **4a** to **5a** from this plot using the σ_m constant for the $N(CH_3)_2$ group; $k_{thermal} = 3 \times 10^{-17}$ s^{-1}.

(14) Details will be reported in the subsequent full paper and the Ph.D. thesis of C. B. Campbell.

(15) H. C. Brown and M.-H. Rei, *J. Chem. Soc., Chem. Commun.*, 1296 (1969).

(16) H. C. Brown, M.-H. Rei, and K.-T. Liu, *J. Am. Chem. Soc.*, **92,** 1760 (1970).

(17) A variety of structures would appear possible for these postulated covalent adducts. This aspect is under investigation.

(18) This result is not unexpected. The equilibrium constant for the formation of the mercuric trifluoroacetate complex of 3,3-dimethyl-1-butene is nine times less than that of 1-hexene.[15] A competing oxidation reaction also becomes important here at long reaction times.

(19) Winstein and coworkers[11a] have reported that the crotyl and α-methyl allyl acetates may be equilibrated by treatment at 75 °C for 23 h with 1.1–1.3 equiv of mercuric acetate in acetic acid. Less than 48% of the allylic esters were recovered from this treatment. An intermolecular acetoxymercuration–deactoxymercuration mechanism was suggested for this process.

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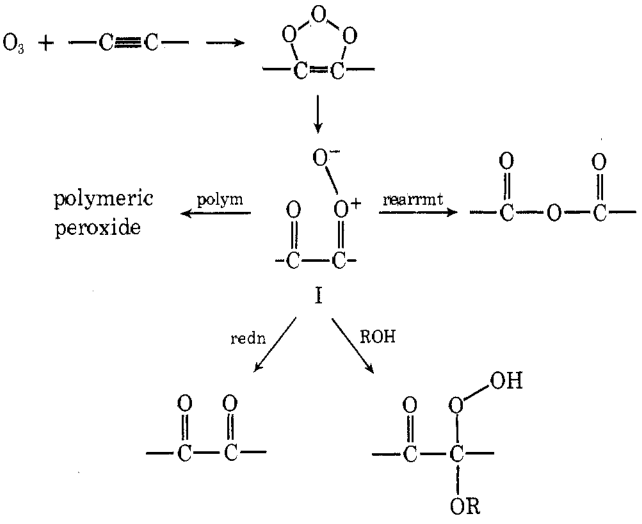
Reductive Trapping in the Ozonolysis of Diphenylacetylene

Summary: Evidence is presented that establishes the existence of a relatively stable (half-life ~35 min, −42 °C) reducible intermediate in the ozonolysis of diphenylacetylene.

Sir: The reaction of ozone with alkenes has been the subject of extensive study.[1] By comparison the number of mechanistic studies of the ozonolysis of alkynes has been relatively small, although recently there has been renewed interest.[2-10] The mechanism suggested by Criegee and Lederer is analogous to that for alkenes and a slightly modified version is depicted in Scheme I.[5]

Scheme I



The intermediacy of I, an α-carbonyl carbonyl oxide, is supported by solvent trapping,[5,6] reductive trapping,[8,9] and spectroscopic work.[7] The stability of I, whether it is a long-lived intermediate, and its mode of rearrangement to the anhydride products are open questions. In this work the reaction of diphenylacetylene and ozone has been studied in an effort to answer some of those questions.

Previous work has shown the products of the reaction of diphenylacetylene and ozone to be benzil, benzoic anhydride,

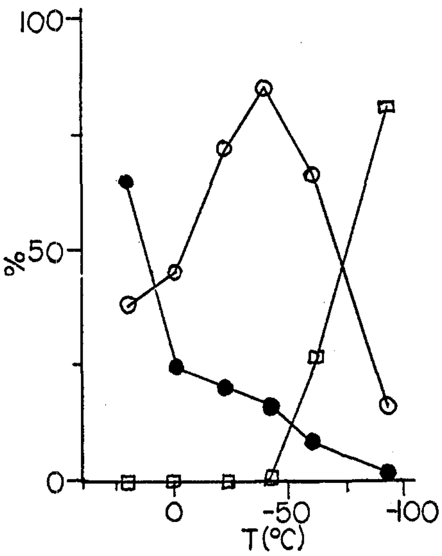


Figure 1. Plot of product mixture composition vs. temperature for O_3 + DPA with subsequent addition of Ph_2S: DPA (□), $(PhCO)_2O$ + $PhCO_2H$ (●), and $(Ph-CO)_2$ (○).

and benzoic acid.[2-4,8] In addition Yang and Libman have shown that ozonolysis of diphenylacetylene in the presence of TCNE at low temperature (−78 °C) in ethyl acetate gives rise to TCNE epoxide and benzil.[8] Our results confirm the earlier work with yields of benzoic anhydride/benzoic acid in the range of 70–80%. Solvents used include diethyl ether, acetone, and methycyclohexane. The ozonolyses, whether carried out at ambient temperatures or performed at low temperatures (−93, −42 °C) and then warmed, yield approximately the same product mixtures (see Table I).

Table I. Product Compositions of O_3 + Diphenylacetylene Reaction in Acetone

Expt	*T*, °C	Benzil, %	Benzoic anhydride, %[a]
1	20	26	45
2	−42	18	43
3	−93	27	35

[a] Benzoic acid present but not determined quantitatively.

In the low temperature reduction experiments using either Ph_3P or Ph_2S as reductant (both of which are known to efficiently reduce peroxides), varying amounts of benzoic anhydride, benzil, and diphenylacetylene were recovered, depending on either the temperature of the reaction or the time before addition of the reducing agent.[11,12] The product mixtures were independent of the amount of reducing agent added in excess of molar ratios of 1:1.

Figure 1 is a plot of the product mixture content vs. temperature in those experiments in which reducing agent (Ph_2S) was added after a fixed period of time (2 min) after ozone addition (~30 min). The plot indicates the production of benzil reached a maximum (~85%) at −42 °C. At lower temperatures increasing amounts of diphenylacetylene were recovered, indicating insufficient time for the completion of reaction of ozone with the acetylene, and at higher temperatures increasing amounts of benzoic anhydride are isolated. The reactions of ozone with alkynes are known to be significantly slower than ozone's reactions with alkenes.[10] The lack of reaction at the lowest temperature is therefore not surprising. The increasing benzil/benzoic anhydride ratios with decreasing temperature (see Table II) can only be explained by the trapping (by reduction) of some thermally unstable species. Reasonably stable at −42 °C, it is, on warming or carrying out the reaction at higher temperatures, converted to benzoic anhydride.

Table II. Ratio of Benzil to Benzoic Anhydride Acid on Addition of Ph_2S 2 Min after Ozonolysis

T, °C	Benzil/ benzoic anhydride acid	*T*, °C	Benzil/ benzoic anhydride acid
+20	0.59	−42	5.7
0	1.8	−62	8.1
−23	3.8	−93	16.

Product trapping by reduction as a function of time at a fixed temperature was performed. Addition of ozone to a solution of diphenylacetylene in acetone kept at −42 ± 2°C, with subsequent periodic withdrawals of aliquots of solution, was carried out. The aliquots were added to individual solutions of diphenyl sulfide in acetone at −42 °C. Workup and analysis of the quenched (by reduction) aliquots showed decreasing amounts of benzil and increasing amounts of benzoic anhydride as shown in Table III. If it is assumed that at −42 °C the ozone and diphenylacetylene reacted rapidly to give a thermally unstable species, and that the yield of benzil produced by reduction represents the concentration of that thermally unstable species, then the rate constant for disappearance of the unstable precursor can be obtained from a plot of the log of the benzil yield vs. time. Such a plot is linear (see supplementary material) and the slope gives a rate constant of $3.3 \pm 0.8 \times 10^{-4}\ s^{-1}$ and a half-life of ~35 ± 10 min at −42 °C.

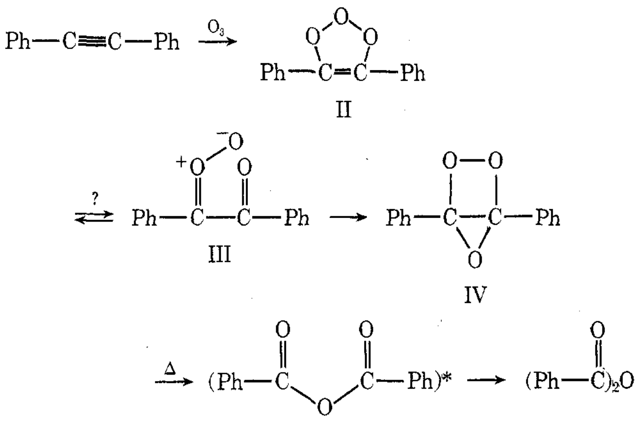
Table III. Percent Yield of Benzil on Addition of Ph_2S after Varying Periods of Time after Ozonolysis

Time, min	% yield of benzil (−42 °C)
0	79
15	59
30	55
45	31
60	25

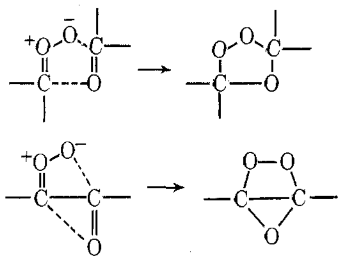
The nature of the transformation of this precursor species to benzoic anhydride has been further probed using energy acceptors capable of fluorescence. A solution of the precursor was prepared in acetone at −42 °C; excess or unreacted ozone was swept out by passing a stream of dry cooled nitrogen through the solution. To these solutions was added 9,10-diphenylanthracene, a known singlet energy acceptor.[13] On warming, the solutions were observed to chemiluminesce with the characteristic yellow-green color of the 9,10-diphenylanthracene fluorescence. Control experiments indicated the necessary presence of the benzoic anhydride precursor and the fluorescer to observe chemiluminescence.

Scheme II summarizes the suggested mechanism for the reaction. It is constructed in analogy with the well-studied reactions of alkenes, as well as solvent trapping and product study work done by others (already mentioned) on alkyne–ozone reactions. Species II, a 1,2,3-trioxolene, is just the 1,3-dipolar cycloaddition product of ozone and the alkyne and is analogous to the 1,2,3-trioxolane product from the addition of ozone to an alkene. Species III is an α-carbonyl carbonyl oxide. It is not clear whether II and III are in fact in equilibrium as suggested by Keay and Hamilton, and are the precursor to the benzoic anhydride.[9]

Scheme II



It is also possible species IV is the relatively stable benzoic anhydride precursor. Its formation is analogous to the addition of the carbonyl oxide to ketones and aldehydes in alkene ozonolyses to produce 1,2,4-trioxolanes (secondary ozonides) as shown below. Also the rate constant for transformation of



a species like IV to products would be relatively insensitive to polar substituent and solvent effects, a characteristic found for simple alkynes.[10] The exceptional stability (considering their strain and peroxidic nature) of dioxetanes (for cis-diethoxydioxetane $t_{1/2}$ = 10 min at 50 °C) also lends support for the possible existence of IV.[13] In addition, the observation of chemiluminescence on decomposition of the precursor in the presence of fluorescers serves as a direct indication of the presence of IV, even if only as a fleeting species.

It should be noted that the scheme presented in speculative. Other possibilities also present themselves. As noted by a referee species III may be a direct precursor to the chemiluminescence and the benzoic anhydride, although there is little precedent for the reaction. Also homolytic cleavage of species II to give a diradical is a possibility. This type of cleavage is suggested in gas phase ozone reactions.[14]

In conclusion the evidence presented lends supports for the existence of the relatively stable precursor $t_{1/2}$ = 35 min, −42 °C) to the isolable products from the ozonolysis of diphenylacetylene.

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Supplementary Material Available. Plot of the log of the benzil yield vs. time to addition of Ph_2S and experimental precedures (3 pages). Ordering information is given on any current masthead.

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