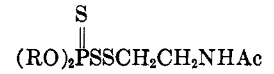
TABLE I



$(RO)_2P(=S)SSCH_2CH_2NHAc$

R	Yield, %	$n^{25}D$	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found	P, % Calcd	P, % Found	S, % Calcd	S, % Found
C_3H_7	22	1.5420	36.24	36.11	6.69	6.77	4.23	4.16	9.34	9.13	29.02	28.83
i-C_3H_7	27	1.5375[a]	36.24	35.95	6.69	6.67	4.23	4.47	9.34	9.16	29.02	29.06
C_4H_9	39	1.5345	40.09	39.84	7.28	7.39	3.89	3.73	8.61	8.09	26.55	26.55

[a] Solidified upon standing, recrystallized from benzene–petroleum ether (mp 40–42°).

pressure to give a pasty solid. This crude product was mixed with 25 ml of cyclohexane–benzene 1:1 mixture, filtered, and washed with more solvent to separate out the remaining sulfinic acid. The solvent was removed from the combined filtrates to give an amber oil. This oil was chromatographed on an 18 in. × 1 in. column filled with 125 g of 200 mesh Florisil. The sample was put on and then developed with 400 ml of cyclohexane–benzene 1:1, 200 ml of benzene, and then 400 ml of chloroform. The cyclohexane–benzene fraction contained the alkylthioperoxyphosphorothionates.[12]

The benzene and chloroform fractions were rechromatographed as before. The benzene and chloroform fractions were combined, and the solvents were removed under high vacuum on a rotary evaporator to give the SS-2-acetaminoethyl-O,O-dialkyl thioperoxymonophosphorothionates.

Registry No.—2 (R = propyl), 15790-97-3; 2 (R = isopropyl), 15790-98-4; 2 (R = butyl), 15790-99-5.

[12] In cases where R = i-C_3H_7, the thioperoxy compound was a solid, mp 90–91° [lit. 90–91°, N. I. Zimbyanksii, O. A. Prib, and B. S. Dreck, *Zh. Obshch. Khim.*, **31**, 880 (1961)]. *Anal.* Calcd for $C_{12}H_{28}O_4P_2S_4$: C, 33.79; H, 6.62. Found: C, 33.79; H, 6.58.

Kinetics of Hydrolysis of the Tetramethyl Ketal of *p*-Benzoquinone[1]

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One of the more interesting features of the kinetics of hydrolysis of ortho esters is the lack of parallelism between substrate reactivity and stability of the corresponding carbonium ions which are evidently formed as the products of the rate-determining step.[3] Thus, ethyl orthocarbonate is less reactive than ethyl orthobenzoate which is less reactive than ethyl orthoformate.[4] In fact, ortho esters are generally less reactive than ketals. Thus, reactivities are inversely related to the expected carbonium ion stabilities within this series. This behavior has been suggested to result from considerations regarding substrate basicity,[4,5] substrate stabilization through double-bond–no-bond resonance,[6] and saturation effects.[7] In contrast, the rates of hydrolysis of acetals and ketals appear to be correlated well, for the most part, with stabilities of the derived carbonium ions.[8,9] However, Kreevoy and Taft have observed that the rates of hydrolysis of diethyl ketals derived from benzophenone and fluorenone are substantially less than would have been predicted on the basis of expected resonance stabilization of the corresponding carbonium ions.[10,11] This behavior was rationalized on the basis that as the transition state became increasingly stable relative to starting material it would be reached progressively earlier and, hence, would possess less carbonium ion character and be less susceptible to stabilization by resonance.[12] A related argument has been applied to the kinetics of hydrolysis of ortho esters.[13] While such arguments certainly will have validity in some cases, there seems to be a reasonable limitation to their applicability. *Thus, a change in substrate structure which would impart additional stabilization to the transition state relative to the ground state will not alter the transition state structure to such an extent that the structural change actually results in a less reactive substrate.*

We now wish to report an additional apparent lack of correlation between carbonium-ion stability and substrate reactivity for ketal hydrolysis.

Acid-catalyzed hydrolysis of the tetramethyl ketal of *p*-benzoquinone(3,3,6,6-tetramethoxy-1,4-cyclohexadiene) proceeds in two distinct steps, the first reaction being about 300 times more rapid than the second. The intermediate exhibits a shoulder in the ultraviolet spectrum near 235 mμ and is almost certainly the monoketal (6,6-dimethoxy-1,4-cyclohexadien-3-one). The product is *p*-benzoquinone as evidenced by its absorption spectrum and by direct isolation.[14] First-order rate constants for both the hydrolysis and decomposition of the intermediate in aqueous solution at 25° and ionic strength 0.50 are collected as a function of pH in Table I. Both reactions are seen to be first order in hydrogen ion activity: formation of the monoketal has a second-order rate constant of 650 M^{-1} sec^{-1} and the hydrolysis of this species a corresponding value of 2.1 M^{-1} sec^{-1}. The greater reactivity of the diketal is certainly expected since the electron-withdrawing properties of the carbonyl function present in the monoketal should destabilize the carbonium ion formed from the latter species with respect to that derived from the former. What is surprising is that the diketal is about an order of magnitude less reactive than 2,2-dimethoxy-

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[2] Career Development Awardee of the National Institutes of Health.

[3] For a discussion of this and related points, see E. H. Cordes, *Progr. Phys. Org. Chem.*, **4**, 1 (1967).

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TABLE I

FIRST-ORDER RATE CONSTANTS FOR HYDROLYSIS OF THE TETRAMETHYL KETAL OF *p*-BENZOQUINONE IN AQUEOUS SOLUTION AT 25° AS A FUNCTION OF pH[a]

Formation of intermediate		Decomposition of intermediate	
pH	$10^3 k_{obsd}$, sec^{-1}	pH	$10^3 k_{obsd}$, sec^{-1}
5.60	1.83	3.36	0.987
5.56	1.925	3.36	0.917
5.45	2.52	3.02	2.18
5.12	5.13	2.80	3.47
4.94	7.53	2.79	3.27
4.90	6.30	2.61	4.13
4.77	10.66	2.43	6.86
4.56	15.06	2.42	9.47

[a] Dilute acetate, and chloroacetate buffers employed in appropriate ranges of pH. The formation of the intermediate was followed at 280 mμ, its decomposition at 245 mμ.

propane.[8,15] The cross-conjugated carbonium ion derived from the diketal of *p*-benzoquinone should certainly be a great deal more stable than that derived from 2,2-dimethoxypropane and, hence, one might well have expected the former species to be very much the more reactive. The explanation for the opposite result is not clear. This observation does suggest that those factors which account for the related behavior observed with ortho esters may be important for the determination of reactivities of at least some ketals as well.

Experimental Section

We are indebted to Dr. Bernard Belleau for providing a sample of *p*-benzoquinone tetramethyl ketal.[14] The sample provided was recrystallized twice from petroleum ether (bp 60–80) prior to use in kinetic measurements, mp 44°. Kinetic measurements were performed spectrophotometrically with the aid of a Zeiss PMQ II spectrophotometer equipped with a thermostated cell holder through which water from a thermostated bath was continuously circulated. Formation of the reaction intermediate was followed at 280 and its decomposition at 245 mμ. All reactions were carried out at 25°, ionic strength 0.50, in aqueous solution containing 3% acetonitrile. First-order rate constants were calculated in the usual fashion and second-order rate constants by dividing the first-order constants by the activity of hydrogen ions. Values of pH were obtained with the aid of a Radiometer PHM 4c pH meter. Distilled water was employed throughout.

Registry No.—Tetramethyl ketal of *p*-benzylquinone 1579-103-4.

(15) The data for comparison, obtained by Kreevoy and Taft[9] refer to 50% dioxane solutions. Previous work in this laboratory (K. Koehler, unpublished observations) indicates that rates for reactions of the type of interest here are slowed by about an order of magnitude in 50% aqueous dioxane compared with water. This factor has been employed in arriving at the indicated rate ratio.

The Photocycloaddition of Diphenylacetylene to 2,3-Dihydropyran

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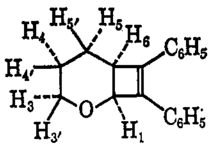
Cyclobutanes are frequently generated in photochemical reactions between olefins. Numerous examples of self-addition as well as cycloaddition between unlike olefins are encountered.[1-3] Reports of cyclobutene formation in the analogous reactions between acetylenes and olefins are confined almost exclusively to the cycloaddition of alkynes to α,β-unsaturated carbonyl compounds,[4-10] most of which require sensitization, although the photocycloaddition reaction between dimethylacetylene dicarboxylate and norbornene has recently been reported.[11] Reports of the participation of arylacetylenes in the photochemical synthesis of cyclobutenes are rare.[10,12]

During the course of our investigation of the photochemical behavior of acetylenes, we found that diphenylacetylene reacted smoothly with an excess of 2,3-dihydropyran to yield a 1:1 addition product upon irradiation at 2537 Å.



I

The product was characterized as the cyclobutene addition product (I), 7,8-diphenyl-2-oxabicyclo[4.2.0]-oct-7-ene, on the basis of spectral evidence presented in the Experimental Section.

An interesting feature of the nmr spectrum was the quartet at τ 6.90 instead of the expected octet. Based on a molecular model, we interpret this to reflect a 90° dihedral angle between H_6–C_6 and H_5–C_5.

In an attempt to gain information regarding the reactive excited species involved in the reaction between diphenylacetylene and 2,3-dihydropyran, quenching and sensitization experiments were performed. It was found that pyrene (triplet energy 48.7 kcal/mol[13]) inhibited the reaction between diphenylacetylene (triplet energy 51 kcal/mol[14]) and 2,3-dihydropyran. Equimolar concentrations of diphenylacetylene and quencher were used. Since their molar extinction coefficients are approximately equal at the excitation wavelength (log ε 4.1 at 2537 Å) the quenching effect was due to triplet energy transfer rather than absorption of the exciting light by pyrene. On the other hand, the reaction conducted in a pyrex vessel and irradiated at 3400 Å was successfully sensitized by triphenylene (triplet energy 66.6 kcal/mol[13]). The unsensitized reaction does not occur upon photolysis at this wavelength. We conclude that the reaction

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