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REACTION OF DIPHENYLCYCLOBUTENEDIONE WITH METHYL PHOSPHITES(1a)

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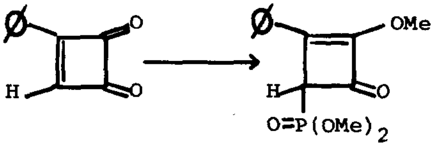
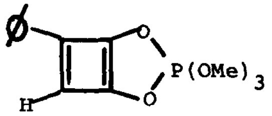
The reaction of phenylcyclobutenedione (I) with trimethylphosphite has recently been reported to give the adduct (II).(2) Not surprisingly products derived from the cyclobutadiene structure (III) were not observed, although such an intermediate would be analogous to the products obtained with simpler diketones.(3) The lack of reaction of diphenylcyclobutenedione (IV) with trimethylphosphite is noted in this same publication.



I II



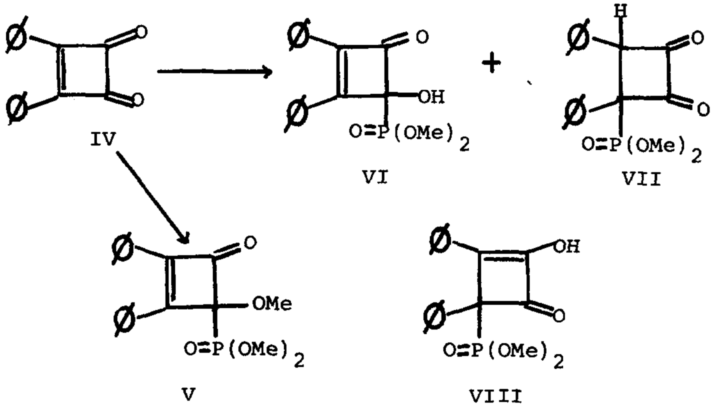
III

In the course of investigating condensation reactions of cyclobutenediones we have studied the thermal and photolytic reactions of diphenylcyclobutenedione with trimethyl- and dimethylphosphite. In contrast to the earlier work,(2) we have observed addition reactions with both reagents.

A solution of diphenylcyclobutenedione (IV)(4) in neat trimethylphosphite on standing three days at room temperature gave the adduct (V) in 91% yield. This same 1,2-adduct was obtained in 72% yield on heating the solution two hours at 80 °C. It was essential that the trimethylphosphite be freshly distilled from sodium, since impure material severely reduced the yield of

(V) and caused the formation of several byproducts.

The reaction of diphenylcyclobutenedione with neat dimethylphosphite at 80° C. led to the formation of two adducts in approximately 40% yield each. These have been identified as the 1,2-adduct (VI) and the 1,4-adduct (VII).



The structural assignments cited above are based on complete spectral and analytical data as well as the fact that the product(VI) is converted quantitatively to (V) on warming with trimethylphosphite. The nuclear magnetic resonance and ultraviolet data are given in Table 1. The infrared, mass spectrometric, and analytical results are not shown but are in full accord with the proposed structures.

Structures analogous to (II) for the adducts (V) and (VI) are eliminated by the difference in the ultraviolet spectra of (VI) and (VII) in basic solution. If (VI) were in fact a 1,4-adduct such as (VIII) it would merely be the enol tautomer of (VII) and should therefore give a similar ultraviolet spectrum in basic solution.

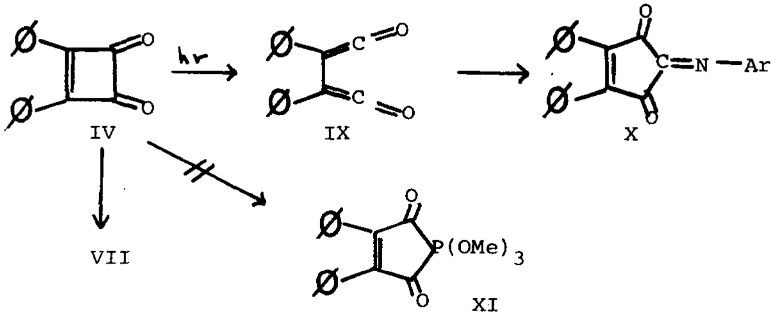
It has recently been demonstrated that on irradiation with a high pressure lamp, diphenylcyclobutenedione is efficiently converted to the diketene (IX) which in the presence of an isonitrile gives the adduct (X). Analogous attempts in our laboratory to trap the diketene with trimethylphosphite in hopes of obtaining products such as (XI) were unsuccesful. Rather, irradiation

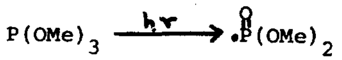
TABLE 1

	V (mp 111°C)	VI (mp 173-4°C)	VII (oil)
UV (neutral * solution)	219 mu (4.19)	220 mu (4.18)	222 mu (4.26)
	324 mu (4.28)	326 mu (4.13)	285 mu (4.05)
UV (basic solution)	-	225 mu (4.20)	decomposes
		362 mu (4.18)	
NMR **	7.97 (2H)	7.82 (2H)	7.38 (10H)
	7.53 (2H)	7.36 (8H)	
	7.30 (6H)		
	4.15 (3H)		5.72 (1H) +
	3.74 (3H) ++	3.62 (3H) ++	3.77 (3H) ++
	3.68 (3H) ++	3.56 (3H) ++	3.44 (3H) ++

* in ethanol, intensity as log ** in $CDCl_3$, except VI (DMSO), signal positions in ppm + doublet, J_{PH} 15 cps ++ doublet J_{PH} 11 cps

of a benzene or tetrahydrofuran solution of diphenylcyclobutenedione and trimethylphosphite (ratio 1:25) afforded adduct (VII) in quantitative yield. This reaction can be rationalized as resulting from the initial photolytic generation of the dialkyl phosphite radical (XII) (6,7) which then adds to the cyclobutenedione (or diketene) moiety. Proton abstraction (or cyclization-proton abstraction) leads to the observed product. An obvious manner to eliminate this competing reaction is to preform the diketene (IX) by low temperature irradiation followed by addition of the trimethylphosphite trapping reagent. Such experiments are now planned.





$$P(OMe)_3 \xrightarrow{h\nu} \cdot\overset{O}{\overset{\|}{P}}(OMe)_2 \qquad (XII)$$

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