

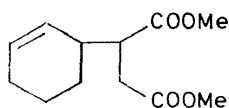
PHOTOCHEMICAL REACTIONS OF DICARBONYL COMPOUNDS

P. DE MAYO

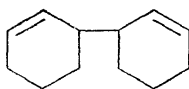
*Department of Chemistry, University of Western Ontario,
London, Ontario, Canada*

The present paper describes studies directed towards the understanding of the processes of photochemical cycloaddition¹ to alkenes. It also includes a report of experiments designed to illustrate the synthetic scope of the reaction beyond the immediate preparation of cyclobutane derivatives.

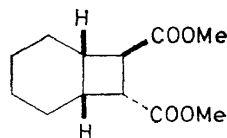
The products of the addition of dimethyl maleate to cyclohexene have been reported². They include cyclohex-2-enyl succinic ester (I) bicyclohexenyl (II) and the four cycloadditively formed saturated esters (III-VI).



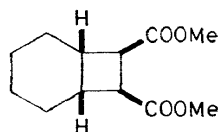
(I)



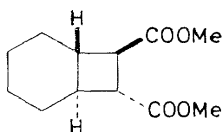
(II)



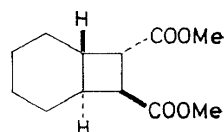
(III)



(IV)



(V)

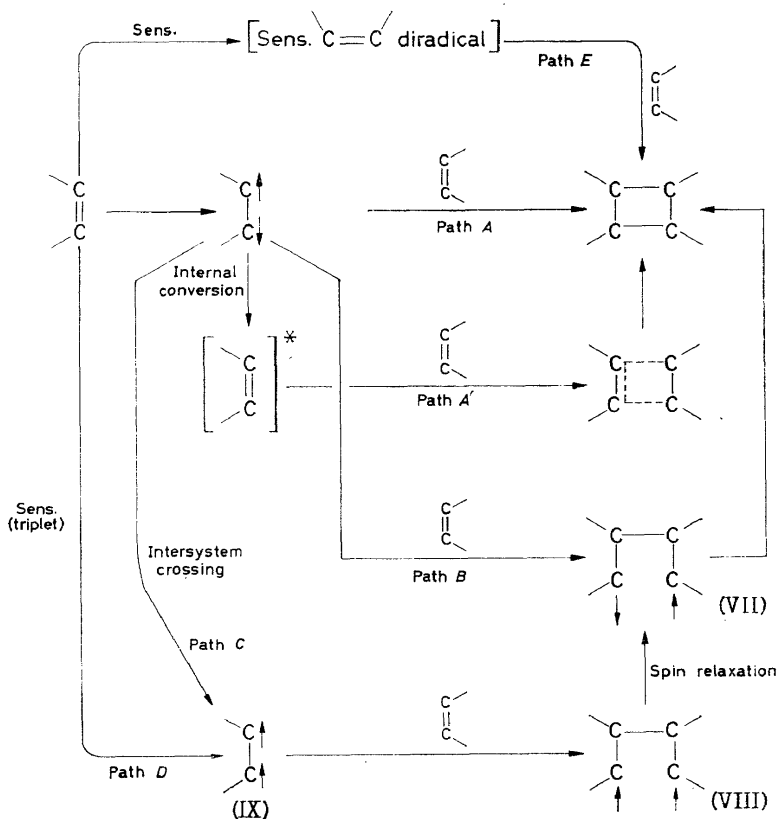


(VI)

The cycloaddition of a molecule energized by light absorption to a double bond may be envisaged as proceeding in a number of ways, each including subtler modifications. Some of these are illustrated briefly in the following Scheme. Path *A*, involving singlet addition, should imply retention of stereochemical integrity in the olefin and perhaps comparatively slight substituent effects. Internal conversion of the excited singlet to a high vibrational level of the ground state may lead to a process resembling a thermal addition (path *A'*). The addition may also proceed from the excited singlet in two steps separated by an interval sufficient for rotation (path *B*): at any rate it is not self-evident that addition of the singlet to the ethylenic linkage must be a "concerted" process as does appear to be the case in the addition of singlet methylene³.

Intersystem crossing to a triplet (path *C*), or direct excitation to a triplet by energy transfer (path *D*), represent other pathways, as does the conjectural formation of a sensitiser-addend complex (path *E*).

In such cases where a carbonyl function is conjugated with the activated bond the question arises as to whether the excited state (or states), be it in the singlet or triplet manifold, is of n,π^* or π,π^* character.



The above very approximate description ignores many considerations such as the existence of charge-transfer complexes, and the possibility of geometrically isomeric excited states⁴.

In the particular case of the addition of dimethyl maleate to cyclohexene the same quantum yield ($\Phi = 0.011$) is observed at 254 $m\mu$ and near 290 $m\mu$, and the composition of the mixture of saturated esters (III-VI) is the same. For this and other reasons it is concluded that the maleate must be the activated species[†]. The formation of the *trans*-fused products (V) and (VI), because of the spatial requirements for effective overlap, excludes paths A and A' for at least that part of the saturated ester products.

Paths B and C involve biradicals (VII) and (VIII) which could be in thermal equilibrium with their environment. The difference in the energetic requirements for cyclization might be expected to be reflected in an altered *cis*-fused:*trans*-fused ratio with varying temperature, and this has been found

[†] For various reasons the possibility of quenching of the maleate by cyclohexene followed by reaction of excited cyclohexene with ground state maleate can be ignored.

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to be the case. The variation over the range -76° to $+54^{\circ}$ is shown in *Table 1*, and a plot of $\log [cis\text{-fused}]/[trans\text{-fused}]$ against reciprocal temperature will be found in *Figure 1*. It will be noted that the ratio of *cis*-fused to *trans*-fused products changes from about 25:1 to 3:1.

Table 1. Ratio of *cis*-fused to *trans*-fused products with temperature variation

T°	% <i>cis</i> -fused	% <i>trans</i> -fused
-76	96	4
-40	91	9
-11	86	14
+34	80	20
+54	77	23

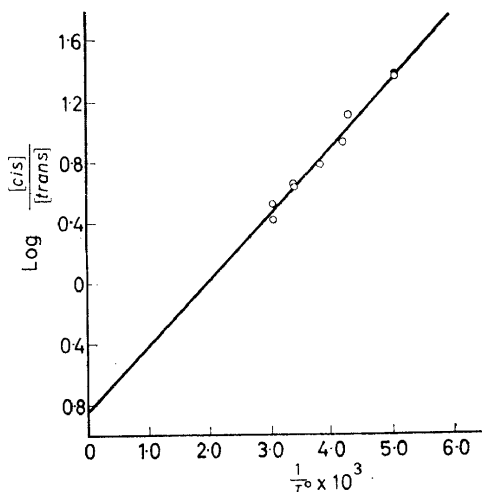


Figure 1. Plot of $\log [cis]/[trans]$ against reciprocal temperature

These results again appear to eliminate paths *A* and *A'* from further consideration for at least part of the total saturated product.

A number of cycloadditions has been induced by the agency of sensitizers, and in some of these the intermediacy of triplets, formed by direct energy transfer, has been made very probable^{5, 6}.

We have found that benzophenone, acetophenone and 4-methylacetophenone will sensitize the addition. The product analysis with the latter (see *Table 2*) is similar to (but not identical with) that formed in the direct irradiation. However, the fact of sensitization itself argues in favour, under these circumstances, of path *D* and the similarity in product analysis further suggests that the direct and indirect irradiation may proceed in part through a common intermediate. This could be the diradical (VIII) in paths *C* and *D*.

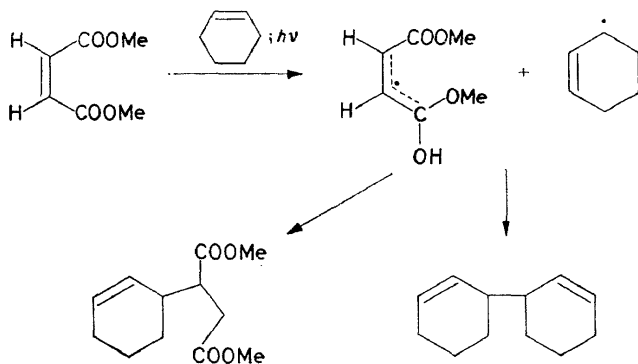
The obtention of the cyclohexenyl succinic ester (I) appears analogous,

Table 2. Composition of saturated esters obtained from dimethyl maleate and fumarate

Light	Composition (%)			
	(III)	(IV)	(V) or (VI) ^a (<i>m.p.</i> 182°)	(VI) or (V) (<i>m.p.</i> 202°)
254 m μ (Maleate)	68.1	14.6	11.6	5.7
Sensitized: 4-methylacetophenone	62.4	10.9	17.6	8.6
Sensitized: benzene	64.8	12.4	~15.1	~7.7
254 (Fumarate)	75.8	7.8	10.6	5.8

^a The allocation of specific stereochemistry to these *trans*-fused, *trans*-carboxylic acids has not been made.

for instance, to the formation of cyclohexenyl dimethyl carbinol from cyclohexene and acetone⁷, and is indicative of a hydrogen abstraction process associated with the n,π^* excited states of ketones. Such behaviour has been observed in esters though it is not so well documented^{8, 9}. In the present case this may be represented, most simply, as shown below although other

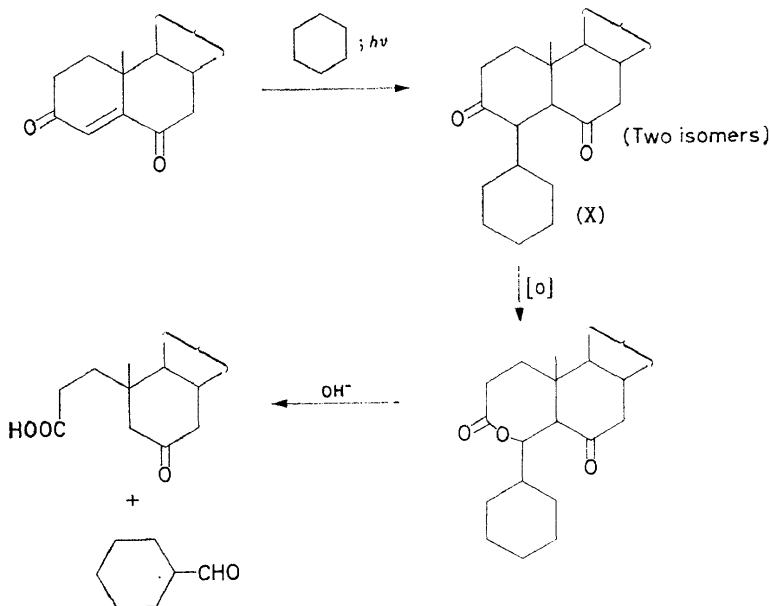


routes may be envisaged. An analogy for this is found in the efficient hydrogen abstraction by cholest-4-ene-3,6-dione from cyclohexane. From this reaction cholestane-3,6-dione and the cyclohexyl derivatives (X) (two stereoisomers) are obtained, the structure of the latter being proved by the sequence shown.

From the foregoing it would seem probable (despite extensive and necessary qualifications) that both the direct and the sensitized addition of maleate to cyclohexene proceeds through (IX) (n,π^*) and (VIII). However, were that the entire description the composition of the saturated ester mixture obtained from the sensitized and direct reaction should be precisely the same. That the difference is not due to complications from the sensitizer by-products is shown by the fact that in a solution in benzene where essentially all (98 per cent) of the light was absorbed by the benzene the products obtained by irradiation at 254 m μ were close (see Table 2) to those obtained with 4-methylacetophenone.

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Further, the composition difference between the direct and sensitized reaction cannot be attributed to fumarate formation. This can be excluded because only a small conversion was permitted, and although dimethyl fumarate forms a charge-transfer complex with cyclohexene (where dimethyl maleate does not) the absorption by fumarate would be small. In addition



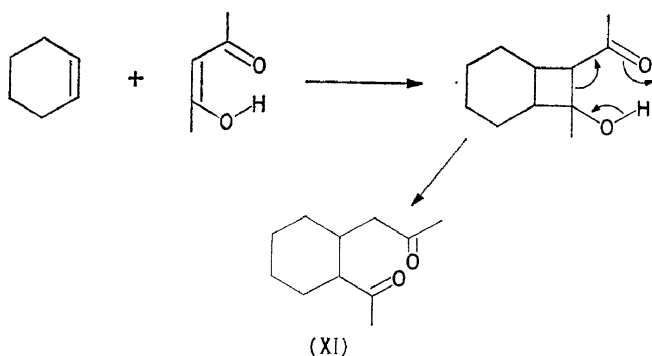
direct irradiation of dimethyl fumarate itself gave the same *cis*-fused to *trans*-fused ratio as obtained with maleate (see Table 2).

It would seem, therefore, that either the direct and sensitized reactions follow different pathways or the direct reaction follows two simultaneous pathways one of which is that, promoted by sensitization, through the triplets (IX) and (VIII). No further conclusions can be drawn at this point, but the following observations may be pertinent.

Under both conditions the ratio of the two *trans*-fused products is the same (2:1). If it is assumed that all *trans*-fused material is formed *via* the triplet pathway with some accompanying *cis*-fused products in the proportions indicated in the sensitized reactions, then approximately 2/3 of the direct process products are so accounted for. The remainder consists of *cis*-fused products in the ratio of about 3.5:1 *trans/cis* carboxyl. The same computation applied to the fumarate irradiation again leaves about 1/3 of the product to be formed in some other pathway, but in this case the material is entirely *cis*-fused, *trans* carboxyl (III).

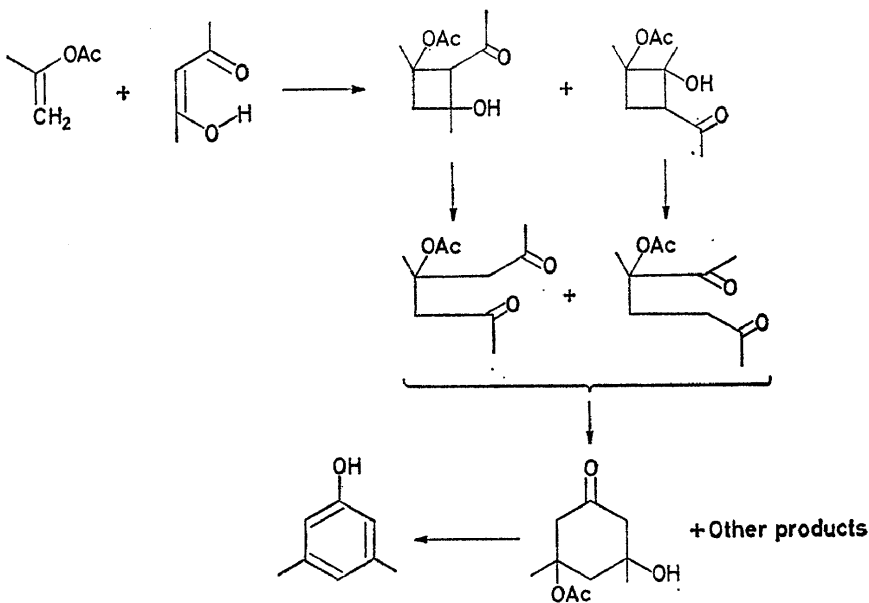
It therefore seems possible that the cycloaddition products in the direct irradiation may be formed by two pathways, and that in one of these only *cis*-fused products are formed, but in a manner such that before or after addition (but before closure of the second bond since the products are light stable) some bond rotation is permitted. Further studies are in progress.

Photochemical cycloaddition to alkenes has already found some application as a synthetic tool other than for the formation of cyclobutane derivatives^{10, 11}. Our own first attempts involved the use of acetylacetone. This, in hydrocarbon solvents such as cyclohexene, is largely enolic and constrained by hydrogen bonding. The immediate product of cycloaddition, a ketol, underwent a reverse aldol to give the 1,5-diketone (XI). This could be induced to cyclize to give derivatives of the decalin system. Amongst the other substrates employed were oct-1-ene, 1-methylcyclohexene, cyclopentene and isopropenyl acetate. In the last instance the adduct could be



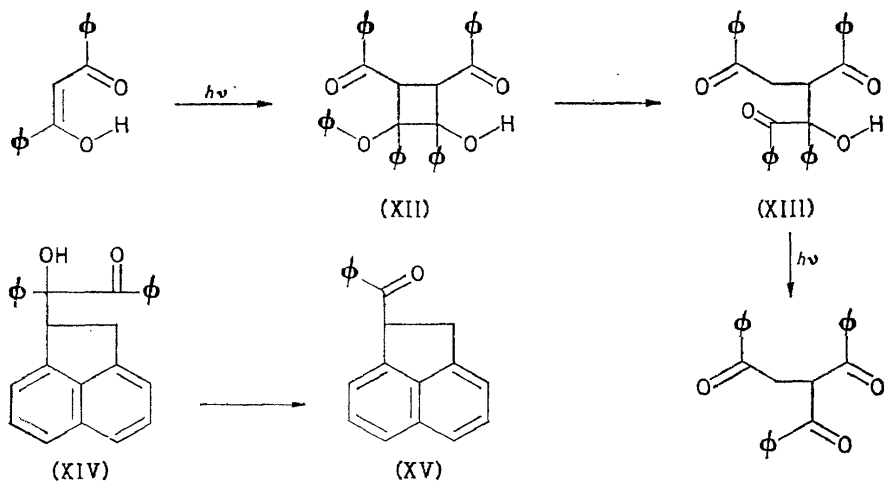
converted, by cyclization and β -elimination into a phenol. The method appears to provide a useful route to 1,5-diketones.

Using dibenzoylmethane as the addend, with a view to extending the synthesis of 1,5-diketones, a small amount of crystalline material was indeed

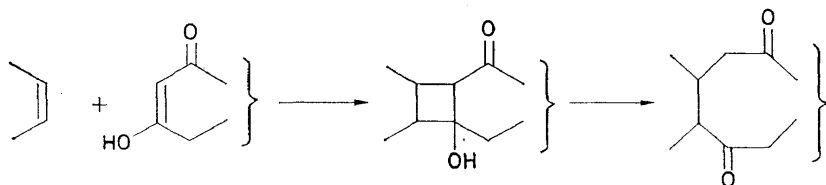


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obtained. Cyclohexene was not involved in its formation however, and the yield was markedly increased by using benzene as solvent. The product was identified as tribenzoylthane. Irradiation in more concentrated solution led to the separation of the dimer (XII) which merely on solution in any solvent was converted into (XIII). The latter, on irradiation, gave tribenzoylthane, thus defining the sequence of steps leading to its formation in more dilute solution. The cleavage of XIII has been further exemplified by the conversion of (XIV)¹² to (XV) under similar conditions, and the cleavage of benzoin to benzaldehyde.



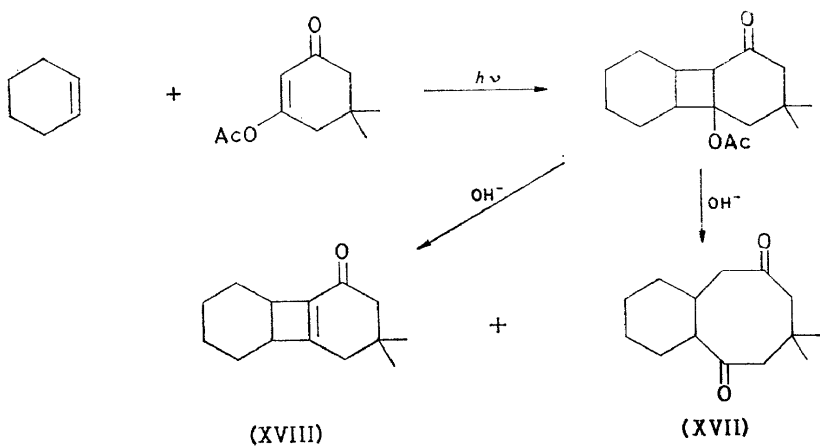
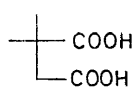
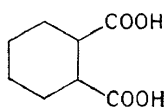
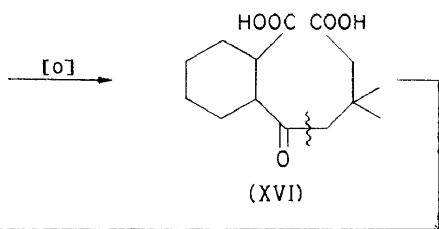
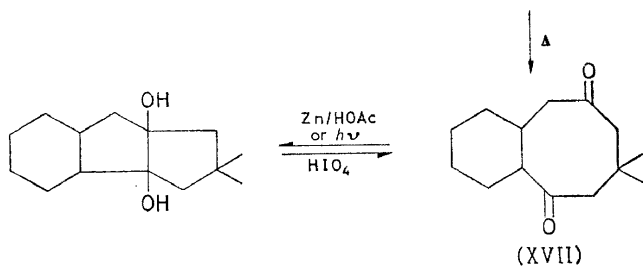
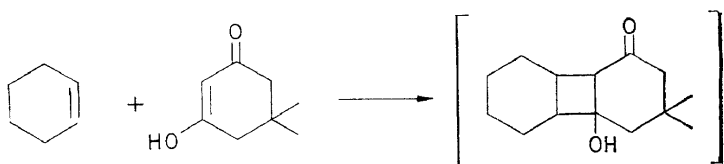
The general scheme envisaged for the further development of the synthetic utility of the cycloaddition of β -diketones may be represented as follows:



This scheme appears to provide possibilities for ring syntheses.

Irradiation of dimedone in cyclohexene gave an adduct, together with its photo-reduction product. These two substances could be inter-related chemically by periodate oxidation and zinc and acetic acid reduction.

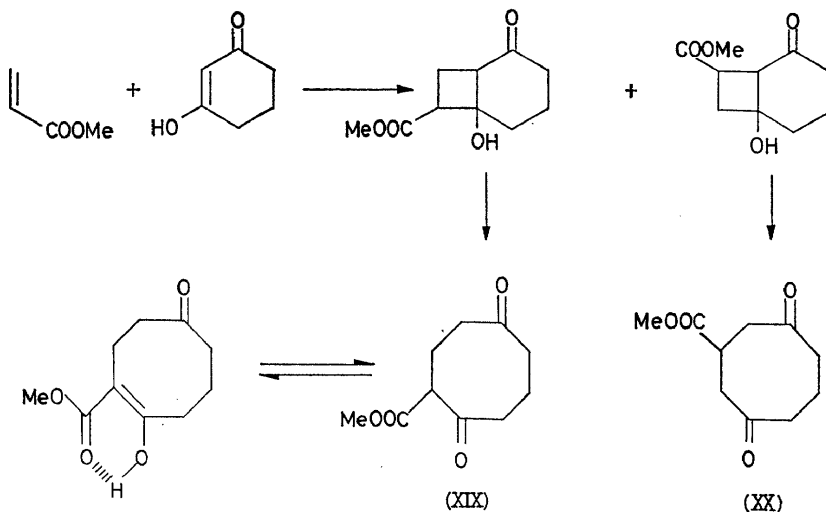
The structure of the adduct was proved by oxidation with potassium permanganate to the keto acid (XVI) and further oxidation of this with nitric acid to *trans*-cyclohexane dicarboxylic acid and *as*-dimethyl succinic acid. Use of dimedone enol acetate also led to cycloaddition and under various conditions the unsaturated ketone (XVIII) or the diketone (XVII) could be obtained by subsequent hydrolysis.



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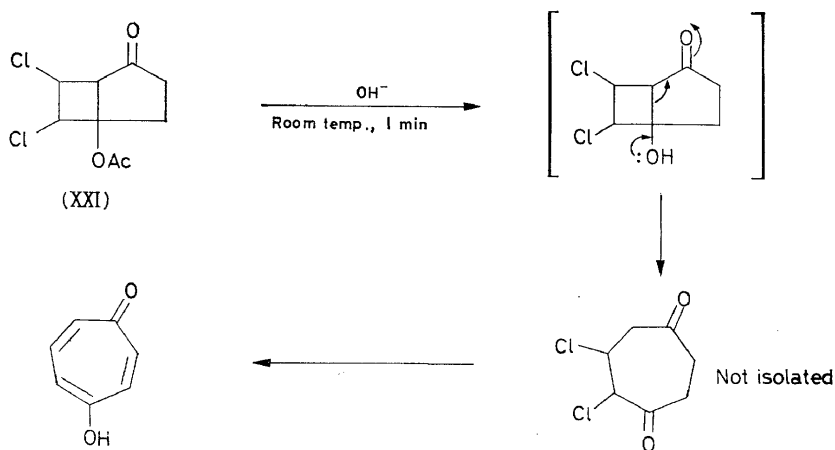
In a similar manner the enol or enol acetate of cyclopentan-1,3-dione could be added to cyclopentene. Hydrolysis, in the latter case, gave only the bicyclic diketone without any of the unsaturated ketone corresponding to (XVIII).

The cycloaddition is not limited to alkenes. Addition of methyl acrylate to the enol of cyclohexan-1,3-dione gave, two diketesters (XIX) and (XX). The former in solution was gradually transformed into the enol. This synthesis appears to be the simplest for cyclo-octane-1,5-diones.



One evident feature of photochemical cycloaddition is that both substrate and addend may be modified to contain the number of potential units of unsaturation desired in the ultimate product, without the necessity of their subsequent, and possibly difficult, introduction.

Irradiation of the enol acetate of cyclopentane-1,3-dione in ethylene dichloride led to the production of three stereoisomers. One of these (XXI),



obtained in crystalline form, on standing at room temperature in methanol containing sodium hydroxide at room temperature for one minute led to the elimination of hydrogen chloride and the formation of γ -tropolone.

It is a pleasure to acknowledge my indebtedness to Drs H. Hikino, G. Kornis and Mr R. W. Yip for ably carrying out the more recent work which their efforts have enabled me to describe.

References

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