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CHEMICAL PROPERTIES OF THE CARBONYL n, π^* STATE.

THE PHOTOCHEMICAL PREPARATION OF OXETANES.

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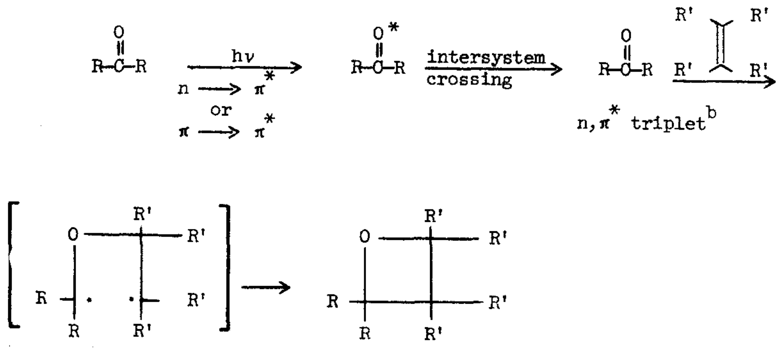
As part of our effort to understand the properties of excited states, we have investigated the mechanism of the photocycloaddition of carbonyl compounds to olefins with particular regard to the character of the excited state involved. We have found that the carbonyl n, π^* state is necessary for oxetane formation, but may not be sufficient. With this information it is now possible to define the scope and limitations of this interesting reaction (1).

In Table I reactions 1-12 deal with ketones that are reduced while entries 13-17 involve ketones that are unreactive upon irradiation in isopropyl alcohol (2). Ketones which are not reduced upon irradiation in isopropyl alcohol cannot be expected to form oxetanes in the presence of olefins. Since reduction involves hydrogen abstraction from the alcohol by the n, π^* state of the ketone (2), it is inferred that addition also requires this state. The addition of the n, π^* state to olefins completes the analogy of this state (which has an unpaired electron localized on the oxygen atom) with alkoxy radicals which are known both to abstract hydrogen from and to add to olefins (3). Thus, a competing reaction yielding carbinol (4) or pinacol may become important if the olefin bears easily abstractable hydrogen atoms. For example, we were unable to isolate an oxetane from the irradiation of benzophenone and cyclohexene, benzpinacol being the major product

Ketones in excited states other than the carbonyl n, π^* are unreactive in both reactions.[a]

Another competing reaction is energy transfer to the olefin. When benzophenone, which has a triplet energy of 70 kcals (5), was irradiated in the presence of dienes that have a triplet energy of the order of 60 kcals (5), no vinyl oxetane or dihydropyran was formed; instead, products derived from the π, π^* triplet of the diene were formed (6). In like manner, we were unable to find oxetanes when benzophenone was irradiated in the presence of the following olefins: 1,1-diphenylethylene, stilbene, methyl acrylate, and 1,2-dichloroethylene. This also accounts for the fact that the irradiation of acetone and norbornene gave norbornene dimers (7), while in the case of benzophenone and norbornene we have found by vapor phase chromatography that no norbornene dimers were formed and a fair yield of the oxetane was obtained. We conclude, therefore, that when the triplet energy of the olefin is below that of the carbonyl compound, triplet-triplet transfer may take place to the exclusion of oxetane formation.

The formation of oxetanes would then involve the sequence



Previous workers have reported only one isomeric oxetane, that expected from the more stable diradical intermediate (8,1b). We have found that the major product can be accounted for in this way; but the other oxetane may also be formed, albeit in small amounts. In the case of benzophenone and iso-

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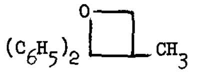
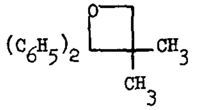
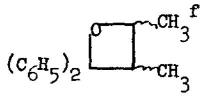
[a] Strong hydrogen donors like tri-n-butylstannane can bring about reduction of the ketone π, π^* triplet (G. S. Hammond and P. A. Leermakers, J. Am. Chem. Soc., **84**, 207 (1962); W. A. Bryce and C. H. J. Wells, Can. J. Chem., **41**, 2722 (1963)).

butylene (Table I, exp. 2), for example, the oxetane from the less stable diradical intermediate amounts to about 9% (by vapor phase chromatography and nuclear magnetic resonance) of the product.

From the examples in Table I it is evident that the photochemical method affords an excellent synthesis of oxetanes if the reactants conform to the above requirements. The value of the method is enhanced by its simplicity. In the typical experiment 200 ml. of a benzene solution, 0.1 molar in ketone and olefin was cooled to 5-10°C and irradiated with a 450 watt high-pressure mercury arc through a Pyrex filter, until the ketone had disappeared, usually one or two days.[c] The oxetanes have been characterized by elemental analysis, infrared and nuclear magnetic resonance spectra[d] and in those few cases where possible, by comparison with reported physical data.

Table I

Photocycloaddition of Ketones to Olefins

Exp.	Carbonyl Compound	Olefin	Oxetane (yield %)[e]	m.p. °C
1.	Benzophenone	Propylene	 (5)	92-95
2.	Benzophenone	Isobutylene	 (93)	88.5-90
3.	Benzophenone	*cis* or *trans*-2-Butene	 (79)	91.5-94

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b. The n, π^* singlet and triplet states both have radical character (an unpaired electron localized on oxygen) (2d). Hammond has shown that reduction of benzophenone involves the n, π^* triplet (2c); however, in some cases reaction may involve either state or both (N. K. Bridge and G. Porter, Proc. Roy. Soc., 244A, 276 (1958)).

c. In the experiments with gaseous olefins 0.1 mole of the diaryl ketone was dissolved in 150 ml. of benzene and the olefin introduced until the volume of the solution was 200 ml.

d. The infrared spectra of the oxetanes show the characteristic prominent broad band at 10.0 ± 0.3 μ that has been assigned to the asymmetrical ring stretching vibration involving the carbon-oxygen bonds (R. N. Jones and C. Sandorfy, in Weissberger, "Technique of Organic Chemistry", Vol. IX, Interscience Pub., Inc., New York (1956); p. 436). The nuclear magnetic resonance spectra of the oxetanes show the hydrogens α to oxygen at 5.0-6.0 τ while hydrogen β to oxygen on the ring occurs at 6.4-7.4 τ.

Table I (Contd.)

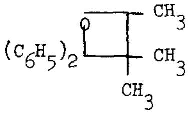
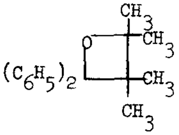
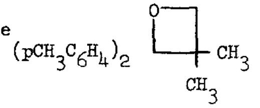
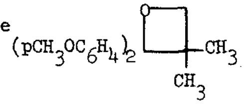
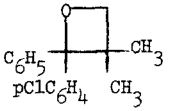
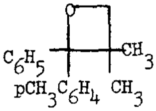
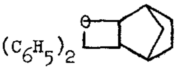
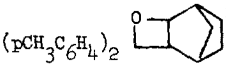
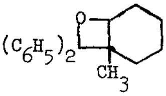
Exp.	Carbonyl Compound	Olefin	Oxetane (yield %)[a]	m.p. °C
4.	Benzophenone	2-Methyl-2-butene	 (58)	106-109[g]
5.	Benzophenone	Tetramethyl-ethylene	 (70)	123-125
6.	4,4'-Dimethyl-benzophenone	Isobutylene	 (74)	81
7.	4,4'-Dimethoxy-benzophenone	Isobutylene	 (80)	h
8.	4-Chlorobenzo-phenone	Isobutylene	 (76)	75-76
9.	4-Methylbenzo-phenone	Isobutylene	 (81)	67-68
10.	Benzophenone	Norbornene	 [i] (50)	128-129[j]
11.	4,4'-Dimethyl-benzophenone	Norbornene	 [i] (16)	117-123
12.	Benzophenone	1-Methylcyclo-hexene	 (40)	126-127
13.	4-Aminobenzo-phenone	Isobutylene	No Reaction	

Table I (Contd.)

Exp.	Carbonyl Compound	Olefin	Oxetane (yield %)^a	m.p. °C
14.	4,4'-Bis- (dimethylamino)-benzophenone	Isobutylene	"	
15.	Xanthone	Isobutylene	"	
16.	1-Naphthyl phenyl ketone	Isobutylene	"	
17.	2-Naphthyl phenyl ketone	Isobutylene	"	

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e. The yields represent pure oxetane (in some cases a mixture of isomers) realized after recrystallization. In most cases pinacol formation was the major side reaction.

f. The same oxetane was formed from both cis- and trans-2-butene. Under the condition of the experiment olefin isomerization is much more rapid than product formation. This isomerization may be the result of triplet-triplet transfer by a non-efficient process that allows both reactions to occur (J. Saltiel and G. S. Hammond, J. Am. Chem. Soc., 85, 2515 (1963); G. S. Hammond and J. Saltiel, ibid., 85, 2516 (1963)).

g. Reported m.p.: 110-111 (9a); 109-110 (9b).

h. Because of contamination by the olefin, which is formed from it readily by loss of formaldehyde, this oxetane has not as yet been crystallized.

i. The oxetane is fused exo- on the norbornene as shown by nuclear magnetic resonance.

j. Reported m.p.: 121 (7).

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