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TETRAMETHYL CYCLOBUTADIENE VIA IRRADIATION OF HEXAMETHYL DEWAR BENZENE MONO-OZONIDE

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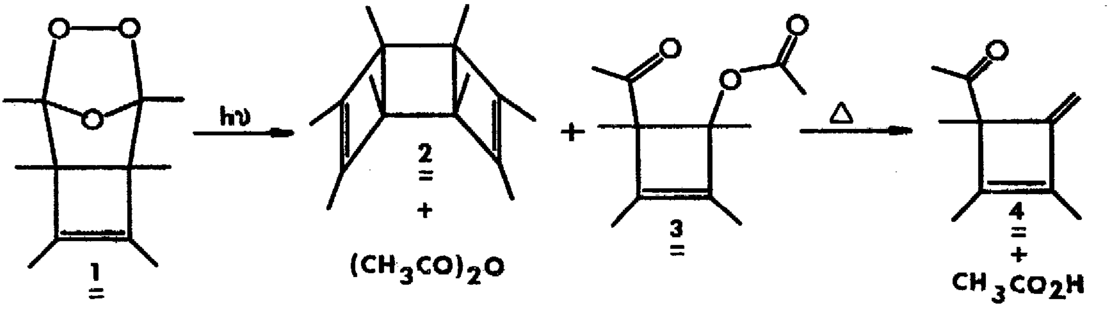
The structure of cyclobutadiene has been a topic of considerable interest. Theoretical calculations have predicted a singlet ground state with D_{2h} symmetry [2] and experimental results have generally been consistent with this structure. [3] Recently, however, strong evidence has been presented which indicates cyclobutadiene has D_{4h} symmetry. [4] We report here our results on tetramethyl cyclobutadiene (TMCB) which suggest that this compound has a singlet ground state.

Direct irradiation of hexamethyl Dewar benzene mono-ozonide, (1), [5] produced syn dimer 2 and 3 in 40 and 49 percent yields respectively. [6] Compound 3 undergoes slow thermal decomposition at room temperature to give 4, the previously reported primary photoproduct. [5] Irradiation of 1 in the presence of diethyl maleate or fumarate gave 3 in 48 percent yield and a 41 percent yield of the respective stereospecific Diels-Alder adduct of TMCB and maleate or fumarate. [6] Dimer 2 was not observed. These results coupled with the observation that diphenylethylene, a more efficient free radical scavenger than maleate [7], failed to affect the reaction in any way is consistent with the presence of a free



1

2 + $(CH_3CO)_2O$

3

4 + CH_3CO_2H

TMCB rather than a radical type intermediate.

Irradiation of 1 was then carried out at 77°K in EPA. The solution was cooled such that the glass formed a thin layer on the walls of a pyrex vessel which was immersed in liquid nitrogen. After photolysis, a solution of EPA containing a 50 fold molar excess of diethyl fumarate at room temperature was added and the mixture stirred thoroughly until the glass was melted. Analysis revealed the presence of roughly equal amounts of dimer 2 and the stereospecific TMCB/fumarate adduct. The results were duplicated when the fumarate was added to the glass one full hour after irradiation, indicating that 2 was formed not in the glass but rather during work-up following addition of fumarate. These results are again consistent with a free TMCB, stable at 77°K, rather than a radical type species.

Irradiation of 1 using a triplet sensitizer produced significant changes in the product distribution depending on the sensitizer, Table I. Trapping experiments with maleate and fumarate were carried out on the benzophenone, 2-acetonaphthone and triphenylene sensitized photolyses as described earlier in solution; and in all cases dimer 2 was not formed, the yield of 3 was unchanged, and stereospecific trapping adducts were observed in yields equivalent to the yields of 2 shown in Table I. Low temperature trapping following sensitized photolysis gave results which were identical to the direct photolysis. Again, these observations seem best explained by free TMCB as opposed to a free radical stepwise mechanism.

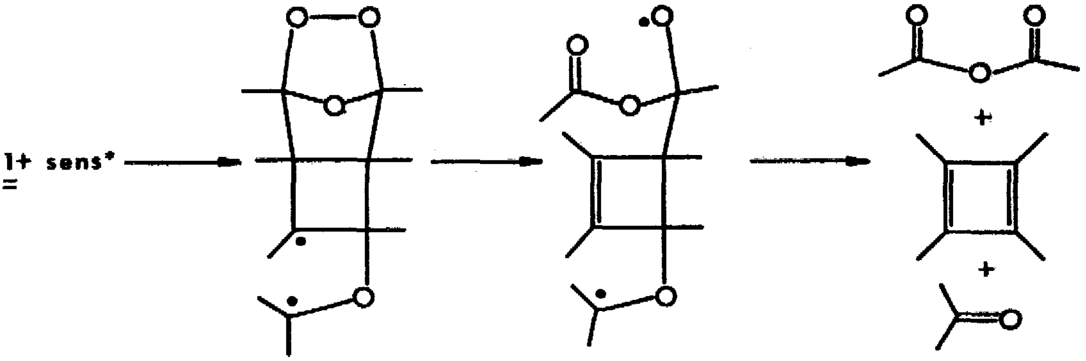
Table I Sensitized Photolysis of 1 in Benzene

Sensitizer	Transition	E_t	%2	%3
Xanthone	π,π^*	74.2	57	32
Acetophenone	n,π^*	73.6	78	7
Benzophenone	n,π^*	68.5	82	8
Fluorene	π,π^*	67.6	58	30
Triphenylene	π,π^*	66.6	50	24
2-Acetonaphthone	π,π^*	59.3	86	6
Benzil	n,π^*	53.7	82	10
Fluorenone	π,π^*	53.3	88	8
	-	-	40	49

When 2-acetonaphthone sensitized photolysis was performed at 77°K for 1 hr., the glass matrix turned yellow upon irradiation (λmax, 386 nm) and faded upon warming. Maier and Schneider generated TMCB via an alternate route at 77°K in

EPA and observed an absorption maximum at 375 nm.[8] While irradiation of pure EPA for 8 hrs. produced no new absorption band, irradiation of 2-acetonaphthone or benzophenone alone for 6 hrs. produced a strong absorption in the visible region of very similar shape to the ozonide containing sample. It is very likely then, that the absorbing species is not TMCB but is rather some free radical species, generated slowly by sensitizer and much faster by decomposing ozonide. That free radicals are indeed present was demonstrated by the presence of an intense line in esr spectrum (g=2). Since no absorption in the visible region was observed attributable to TMCB and calculations for cyclobutadiene had predicted allowed absorptions for the triplet in this region,[2a] we conclude that TMCB possesses a singlet configuration. This is further supported by the lack of any esr signal attributable to a triplet or biradical species in the glass. Based on the initial ozonide concentration and the quantity consumed during irradiation, a 0.0027M concentration of TMCB was present in the glass, more than sufficient to have been observed.

Finally, regarding the unusual effect of sensitizer on the product distribution, we believe that the results are best explained by the reaction of excited ketone sensitizer with the cyclobutene double bond to form a biradical which breaks up to form TMCB as the predominant product. Evidence for this mechanism comes from the fact that with the exception of 2-acetonaphthone, the sensitizers producing high yields of 2 are known either to undergo cycloaddition to olefins or cause cis-trans isomerization.[9] Furthermore, the rate constant for the ozonide quenching of benzophenone triplets is 9.54×10^6 M^{-1} sec^{-1} and 1.45×10^5 M^{-1} sec^{-1} for fluorenone triplets. These rates are similar to the rates Yang measured for the quenching of benzophenone triplets by 3-methyl-2-pentene



and is well below typical diffusional energy transfer processes.[9a] The fact that oxetane products were not observed is not unexpected since it involves the incorporation of a high degree of strain in the product. That the high yields (78-88%) of 2 were due to quenching of the triplet state sensitizer while the low yields (50-58%) were due to quenching of the singlet state sensitizer was ruled out since a study of the product distribution from the benzophenone, fluorene and triphenylene sensitized reactions over a 50 fold ozonide concentration revealed no changes. Had singlet quenching been competitive with intersystem crossing, one would have expected a change in the product distribution toward higher yields of 2 at lower concentrations of ozonide. Furthermore, the low rates of quenching are not consistent with the high reactivity of the sensitizer singlet states.

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