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THE PHOTOCHEMISTRY OF CONJUGATED ACETYLENIC OLEFINS AND CARBONYL DERIVATIVES

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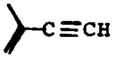
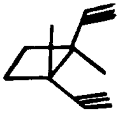
The photochemistry of conjugated olefins has already been studied in great detail and important information on photochemical processes in general has resulted from these investigations(1). In contrast, similar studies on acetylenic analogs have received only minimal attention and their photochemical reactivity has remained unclear. We wish to report herein, results which have an important bearing on this subject.

The sensitized photolysis of 2-methyl-1-butene-3-yne (I) led to the formation of two significant products in a ratio of 8:1 and a number of minor products. The major product, b.p. 58-59°/40 min., has been identified as trans-1,2-diethynyl-1,2-dimethylcyclobutane (II). The assignment of structure II follows from the n.m.r. spectrum, which shows singlets at 1.51 (area 3) and 2.32 (area 1) and an AA'BB' pattern centered at 2.08 δ (area 2). Dimer II



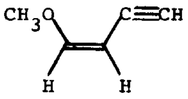
I



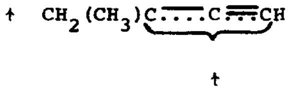
II

was further hydrogenated (96% theoretical uptake of hydrogen) to the corresponding saturated compound and this was found to be identical in every respect with trans-1,2-diethyl-1,2-dimethylcyclobutane$^{(2)}$. The second major product has not been conclusively identified, however from its n.m.r. spectrum which shows singlets at 1.33 and 2.38 δ and an AA'BB' pattern, it is most logically the cis isomer of II.

Similarly, the sensitized photolysis of vinylacetylene afforded trans-1,2-diethynylcyclobutane, b.p. 50-52°/50 mm. along with five unidentified minor products. In contrast, photolysis of cis-1-methoxy-1-buten-3-yne (III) causes only isomerization to the trans-isomer without the formation of dimers. A similar result was obtained with the olefinic analog 1-methoxybutadiene, which on photolysis underwent isomerization without dimer formation.



III



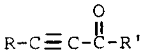
$$\uparrow\ CH_2(CH_3)\underbrace{C\overset{\text{—}}{\cdots\cdot}C\overset{=}{\cdots}CH}_{\uparrow}$$

IV

The dimerization of I and the isomerization of III has been sensitized by acetophenone, benzophenone, 4,4'-bis(dimethylamino) benzophenone and 2-acetonaphthone (E_T = 59 kcal/mole). However, when 1-acetonaphthone (E_t = 56.4 kcal/mole) and other lower energy sensitizers were employed, the efficiency of the dimerization decreased drastically. This result indicates that the triplet energy of conjugated acetylenic olefins probably lies in the range of 57-59 kcal/mole. This triplet energy range is comparable to triplet energies of butadiene and isoprene (E_T = 59.6 and 60.0 kcal/mole respectively)$^{(1,3)}$ and indicates that stabilization via an allenic triplet such as IV must be involved.

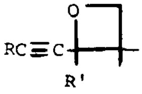
The quantum yield for the dimerization of I has not been measured, but it is very low. In spite of this, the selectivity of the reaction should make it synthetically interesting. In one example, photolysis of an ether solution 5M in I and 0.4M in benzophenone for 60 hr. using a 450 W medium pressure mercury arc lamp and a vycor filter afforded a 6% yield of both major products, 96% pure after distillation.

The photochemistry of acetylenic aldehydes and ketones was also studied. The direct photolysis of propynal V (R = R' = H), phenylpropynal V R = C_6H_5 ; R' = H) or 3-butyn-2-one V (R = H ; R' = CH_3) in solution using a 450 W medium pressure mercury arc lamp and a vycor filter resulted in the formation of high molecular weight, undefined products. However, in the presence of an olefin such as isobutylene, oxetane formation was observed. For example, photolysis of a 0.5M solution of propynal in 1:1 isobutylene-pentane for three hours afforded a 30% yield of three products in a ratio of 10:3.4:1, plus unreacted starting material. The two major products were identified as oxetanes VI and VII (R = H; R' = H) respectively. Irradiation of a

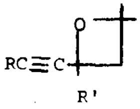


$R{-}C{\equiv}C{-}\overset{O}{\overset{\|}{C}}{-}R'$

V



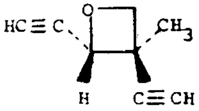
VI



VII

0.2 M solution of phenylpropynal in isobutylene-pentane for 12 hr. afforded a 70% yield of four products in the ratio 9:4:1:1. The major product has been identified as VI (R = C_6H_5; R' = H). Similarly, 3-butyn-2-one gave three major products in the ratio 10:8:1, the major products being assigned structures IX and X (R = H ; R' = CH_3). During the course of this investigation a preliminary communication on the photoaddition of acetylenic ketones to olefins appeared$^{(4)}$. The reported results are in agreement with our findings.

An experiment was also performed to determine the triplet energy of propynal relative to 2-methyl-1-butene-3-yne (I). A pentane solution containing I and V in a ratio of 10:1 was photolyzed directly to give a complex mixture of products which did not contain the dimers of I, but did contain as the major product VIII. The n.m.r. spectrum ($CDCl_3$) of VIII showed singlets at 1.61 (area 3) and 2.32 (area 1) and doublets at 2.75 (J = 2, area 1), 4.14 (J = 5, area 1), 4.62 (J = 5, area 1) and 5.27δ (J = 2, area 1). This suggests that



VIII

propynal probably possesses a triplet energy level lower than that of 2-methyl-1-butene-3-yne since cycloaddition rather than energy transfer takes place.

Oxetane formation is a reaction characteristic of saturated and aromatic aldehydes and ketones which possess low lying $\eta \rightarrow \pi^*$ triplet states(5). The analogous reaction mode observed for the acetylenic carbonyl compounds indicates that they also possess low lying $\eta \rightarrow \pi^*$ triplet states.

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