

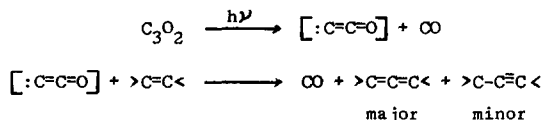
PHOTOLYSIS OF CARBON SUBOXIDE IN 1,2-DIMETHYLCYCLOPROPENE*

Hai Won Chang, Ann Lautzenheiser and Alfred P. Wolf
Chemistry Department, Brookhaven National Laboratory,
Upton, New York 11973

(Received 31 August 1966; in revised form 20 October 1966)

The photolysis of carbon suboxide in the presence of open chain olefins with 2537 Å light has been reported in several publications (1,2). Baker, *et al.* (3) reported on the relative reactivities of a number of olefins towards photolysis in the presence of C₃O₂. Willis and Bayes (4) have reported on a very detailed study of C₃O₂-olefin and C₃O₂-olefin-inert moderator photolyses and find a set of relative reactivities opposite to those of Baker, *et al.* (3).

The net effect of carbon suboxide photolysis in the presence of olefins is the insertion of a single carbon atom, the products being a mixture of an allene and an alkyne, presumably formed by reaction between the intermediate keto-carbene (1,2,4) and the olefin. The central carbon atom of the carbon suboxide appears in the products (2).



A study of this reaction with cyclic olefins could shed light on the nature of the intermediates of the reaction and it could conceivably lead to new and interesting products. Accordingly one of the reaction mixtures studied was C₃O₂ in the presence of 1,2-dimethylcyclopropene(I). We obtained 2-methyl-1-pentene-3-yne(II) as a major product of the

*Work done under the auspices of the U. S. Atomic Energy Commission.

photolysis, and 2-pentyne(III), a rearrangement product of the starting olefin, as one of the minor products.

Experimental

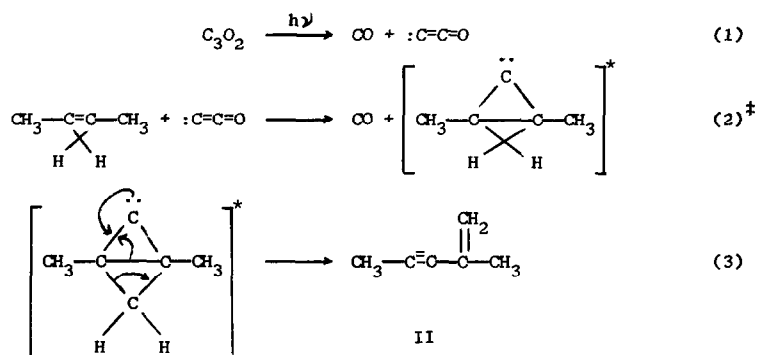
The carbon suboxide was prepared in 42% yield by pyrolyzing diacetyl-tartaric anhydride (5) at $700^{\circ} \pm 10^{\circ}\text{C}$. The compound was purified by distillation, followed by preparative glpc on an SE-30 silicone column. It is essential that a thermistor detector be used, as a hot wire detector will decompose a sufficient amount of the C_3O_2 to introduce detectable impurities in the product C_3O_2 . 1,2-Dimethylcyclopropene was prepared according to the method of Doering and Mole (6), by the photolysis of diazomethane in the presence of 2-butyne. It was purified by glpc on a di-decylphthalate column. The identity of the product, I, was checked by taking its NMR spectrum. The photolysis of C_3O_2 and I in ratios of 1:6 was carried out in a cylindrical quartz cell, 5.8 cm in diameter and 33 cm long. The cell was placed inside a coiled Hanovia low pressure Hg lamp (120 m.a.), and the reaction was conducted in a refrigerated room ($3^{\circ}\text{-}4^{\circ}\text{C}$) to minimize thermal polymerization of both starting materials. The photolysis was allowed to proceed for six hours. An external blower was used at the bottom of the reaction cell to provide circulation of the cold air around the cell.

After irradiation, the mixture was separated into fractions by glpc on a di-2-ethylhexylsebacate column operated at 30°C . Repeated runs were made to collect product sufficient for subsequent analytical procedures. The major product (II) was obtained in 13.8% yield, based on the amount of C_3O_2 present at time zero, and in ca. 41% yield, based on the amount of carbon monoxide evolved.

The identity of the product (II) was determined on the basis of its mass spectrum (parent $m/e = 80$), IR spectrum and NMR spectrum. The IR showed characteristic bands at 795 cm^{-1} ($>\text{C}=\text{CH}-$), 895 cm^{-1} (s terminal methylene), 1624 cm^{-1} ($>\text{C}=\text{C}<$), and 2245 cm^{-1} ($\text{RC}\equiv\text{C-R}$). The NMR showed a

poorly resolved triplet with a very small coupling constant, $\bar{\zeta}$ 1 cps, at $\delta = 1.81$ ppm. A singlet at 1.90 ppm and a broad singlet at 5.06 ppm also appeared. The peak areas were in the ratio 3:3:2. Additional confirmation of the structure was obtained by finding that three moles of hydrogen were absorbed when II was hydrogenated in acetic acid using a Pt catalyst. The product of reduction was identified as 2-methylpentane by comparison of its mass spectrum, its IR and NMR spectra and glpc retention times with those of an authentic sample.

A mechanism, involving an unstable bicyclic carbene intermediate which rearranges under the conditions of the reaction can be postulated to account for the formation of the product (II), eqs. 1 (4), 2 and 3.



It should be noted that the intermediate, eq. 2, could in principle undergo intramolecular insertion to give dimethyltetrahydrene. A facile electronic rearrangement is preferred instead, to give the open chain compound. The lack of intramolecular insertion may have been due to a

[‡]Equation 2 does not mean to imply that the carbene is formed in a concerted manner. It may indeed be a two step reaction involving the initial addition of the keto carbene followed by decomposition to the carbene with concomitant loss of CO. It is also possible that the keto carbene adduct can decompose to the product (II), in a concerted reaction. Our results do not allow differentiation of these pathways.

number of factors including the lack of adequate deexcitation of the excited intermediate. Conceivably a liquid or solid phase experiment would alter the product spectrum.

2-pentyne (III) was also formed during the photolysis. The mass spectrum, IR and NMR spectra were identical with those of the authentic material. A blank run of I without carbon suboxide present also gives III. This compound is probably formed by the photochemical cleavage of an isomer of the starting material (I).[‡]

Minor products formed in the photolysis have as yet not been identified. The interesting products resulting from the net addition of a carbon atom in gas phase C_3O_2 photolyses in the presence of olefins are undergoing further study.

REFERENCES

1. K. D. Bayes, J. Amer. Chem. Soc. 83, 3712 (1961); ibid. 84, 4077 (1962); ibid. 85, 1730 (1963).
2. R. T. Mullen and A. P. Wolf, J. Amer. Chem. Soc. 84, 3214 (1962).
3. R. T. K. Baker, J. A. Kerr, and A. F. Trotman-Dickenson, Chem. Comm. 358 (1965).
4. C. Willis and K. D. Bayes, J. Amer. Chem. Soc. 88, 3203 (1966).
5. C. D. Hurd and F. D. Pilgrim, J. Amer. Chem. Soc. 55, 757 (1933).
6. W. von E. Doering and T. Mole, Tetrahedron 10, 65 (1960).
7. H. H. Stechl, Angew. Chem. 75, 1176 (1963).

[‡]One can speculate that production of III from I occurs via the singlet state of I rather than the triplet state, since Stechl (7) has shown that the benzophenone sensitized photolysis of 1,3,3-trimethylcyclopropene gave a tricyclic dimer as the major product.