

PHOTOCONDENSATION REACTIONS OF UNSATURATED KETONES¹

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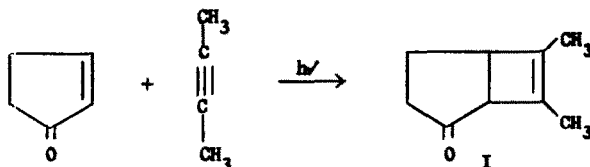
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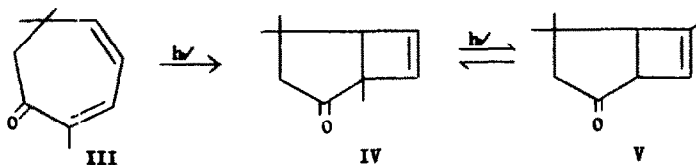
Only recently has any particular thought been given to the full characterization of the light induced condensation reactions of α,β -unsaturated, alicyclic ketones. To this end we have taken 2-cyclopentenone as a model ketone and have examined its photochemical reactions with a variety of multiple bonds. We have already reported in detail on the photodimerization of cyclopentenone and on the crossed reaction of this ketone with simple olefins.³ The latter was the first direct demonstration of the photochemical addition of unsaturated ketones to extramolecular, unactivated multiple bonds. To extend these observations, we have now considered the addition of cyclopentenone to a representative acetylene and to allene.

Mercury arc irradiation of a 10 mole per cent solution of 2-cyclopentenone in neat 2-butyne through Pyrex glass ($\lambda > 300\text{m}\mu$) gives a 60 per cent yield of a 1:1 adduct; b.p. 89-90^o/20 mm., semicarbazone m.p. 193-194^o. The infrared spectrum of the adduct contains a strong, narrow carbonyl absorption at 5.76 μ in agreement with the usual value for cyclopentanones. No double bond stretching absorptions can be seen in the 5.9-6.2 μ region, nor are any vinyl hydrogen signals detectable in the n.m.r. spectrum. There are in the resonance spectrum two vinyl methyl group absorptions centered at $\tau = 8.7$ p.p.m. These data indicate the presence of a tetra-substituted double bond; the point is confirmed by catalytic hydrogenation of the adduct to its dihydro-derivative. The n.m.r. spectrum of the reduced material shows three groups of complex absorptions centered, respectively, at $\tau = 7.2$ and 7.8 (the ring hydrogens) and 9.1 p.p.m. (methyl on saturated carbon) in the ratio of 4:4:6.

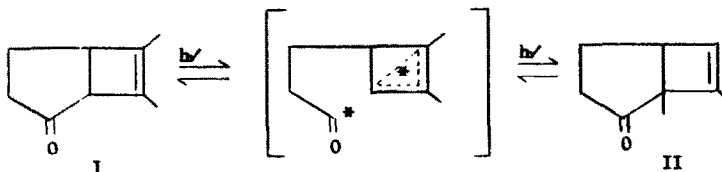
From this information we assign to the photochemical adduct the cyclobutene structure I.



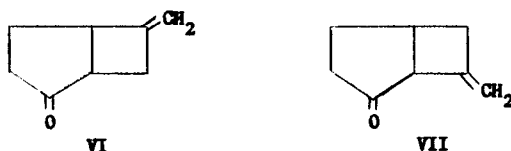
The primary photoproduct on subsequent irradiation in benzene solution is converted partially into an isomeric substance (II); b.p. 63-65°/9 mm., 2,4-dinitrophenylhydrazone m.p. 170-170.5°. In addition to the cyclopentanone-like carbonyl absorption in the infrared spectrum of II, a distinct olefinic stretching band appears at 6.05 μ . Of note in the n.m.r. spectrum of this isomer are the complex vinyl hydrogen absorptions at $\tau = 4.3$ p.p.m. (one proton), the broad vinyl methyl signal at 8.7 p.p.m., and the sharp, methyl on quaternary carbon resonance at 9.2 p.p.m. Irradiation of pure II leads to the same photochemical steady state mixture of I and II (ca. 60:40) as does irradiation of pure I. Reference to the classic work of Büchi and Burgess⁴ on the photochemical valence tautomerism of eucarvone (III) to the cyclobutene IV and the subsequent equilibration of IV with V provides the necessary analogy to complete a structural assignment for II.



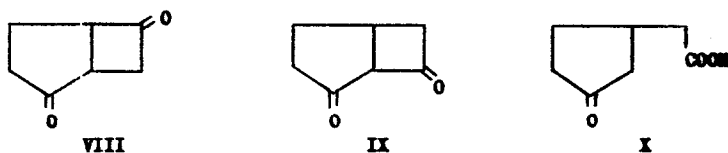
and hence



The 1:1 addition of cyclopentenone to allene, induced by ultraviolet irradiation of the ketone in benzene containing an excess of the 1,2-diene, illustrates notably the remarkable versatility of the photocondensation reaction. Vapor phase chromatographic analysis of the product (62%, b.p. 86-87°/20mm.) reveals the presence of two barely separable components, one constituting 85-90 per cent of the mixture. In addition to the cyclopentanone band at 5.74 μ , the infrared spectrum of the product contains absorptions at 3.20, 5.97 and 11.2 μ , all characteristically associated with an exocyclic methylene group. The n.m.r. spectrum has vinyl hydrogen absorption equivalent to two protons, but is completely free of any methyl group absorptions. With this information, the components of the reaction mixture are formulated as the methylene cyclobutanes VI and VII. It remains only to decide which is the major reaction product.



Ozonization of the natural mixture of VI and VII in methylene chloride at low temperature results in the rapid uptake of one molar equivalent of ozone. The infrared absorptions of the terminal methylene group are replaced by a band at 5.60 μ as anticipated for the cyclobutanones VIII and IX. In addition to this absorption and the parent band of the cyclopentanone, the ozonized material shows some additional absorption in the carbonyl region. This increases slowly with continued exposure of the product to water and apparently arises from the acid formed by reverse aldol cleavage of the β -diketone IX. Indeed, treatment of the crude ozonization mixture with warm, aqueous sodium carbonate carries this process to completion. Acidification of the reaction mixture gives 70 per cent yield of a keto-acid identical to the known 3-ketocyclopentyl acetic acid (X).⁵ Thus, as X is related to the β -diketone IX and not to the γ -diketone VIII, we conclude that the photocondensation of cyclopentenone with allene favors adduct VII.⁶



Finally, note is made of both the applicability and of the limitations of such photocyclization reactions. Much variation is possible in the choice of addend molecules. 2-Cyclohexenone and methyl acetylene are, for example, suitable choices. Simple acyclic ketones have not, in our limited trials, given satisfactory results.⁷ The same is true of sterically encumbered olefins. Yet, the reaction remains sufficiently versatile to promise diverse approaches to the synthesis of otherwise difficultly accessible compounds.

References

1. We are greatly indebted to the National Institutes of Health for a generous grant (GM-10572) made in support of this research. A part of this work was presented at the 145th Meeting of the American Chemical Society, New York, September, 1963.
2. Alfred P. Sloan Foundation Research Fellow.
3. P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 and 2454 (1962).
4. G. Buchi and E. M. Burgess, *J. Am. Chem. Soc.*, **82**, 4333 (1960).
5. J. Meinwald and E. Frauenglass, *J. Am. Chem. Soc.*, **82**, 5235 (1960).
6. This major direction of condensation is quite opposite to that which would be predicted for the corresponding thermal reaction; see, H. W. Cripps, J. K. Williams and W. H. Sharkey, *J. Am. Chem. Soc.*, **81**, 2723 (1959).
7. This point bears significantly on the mechanism of the reaction [cf. P. E. Eaton and K. Lin, *J. Am. Chem. Soc.*, **86**, 2087 (1964)]. The relation will be developed in full in a subsequent paper.