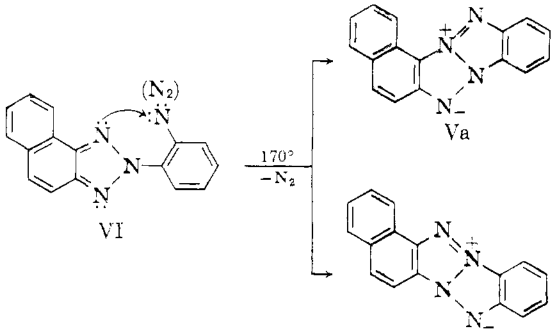
the 1- or 3-nitrogen of the triazole. Only one isolable form is possible for the tetraazacycloöctatetraene.



The evolution of one mole of nitrogen from VI proceeded smoothly at 170° in decalin to yield a yellow crystalline solid, m.p. 190–230°. The solid gave a good analysis for $C_{16}H_{10}N_4$ despite its wide melting-point range. Chromatography on Woelm non-alkaline alumina yielded two sharp-melting products, m.p. 212–213° and 243–245°. The infrared spectra of the two products showed some differences, despite their general similarity. A spectrum of a composite of the two pure isomers contained all of the peaks of the unseparated mixture.

The properties and reactions of this new system as well as some theoretical calculations will be reported in a later paper.

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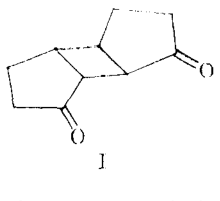
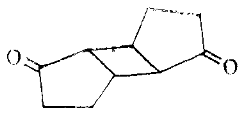
ON THE MECHANISM OF THE PHOTODIMERIZATION OF CYCLOPENTENONE

Sir:

We have shown recently that, on exposure to ultraviolet radiation, 2-cyclopentenone is converted rapidly and in high yield to the dimers I and II.[1] These are formed in approximately equal amounts; although both are sensitive to prolonged irradiation, we have found no evidence of interconversion.

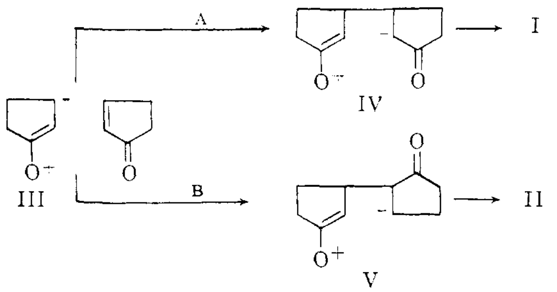


I



II

In its least sophisticated form, the mechanism of light-induced dimerization of α,β-unsaturated ketones can be represented as the attack of a photoexcited molecule on non-excited substrate. At the present time, it is not possible to describe completely the excited state of cyclopentenone. Although the initial excitation is presumably to the singlet state (N $\rightarrow$ π^* at 308 mμ), crossover to the triplet state is highly probable.[2] In either case, the charge distribution within the excited molecule at the time of reaction is not known. For the moment, the polarized form III may be taken as an adequate representation.[3] *If* the two carbon–carbon bonds to be made in the dimerization are not formed concertedly, two pathways for reaction, A and B, can be envisioned.[4]



Interaction of the negative charge with the adjacent carbonyl group should result in some stabilization of IV relative to V. Route A then appears more attractive than route B; dimer I should be the preferred product. The same conclusion can be reached by taking an uncharged diradical as the favored form of the excited state.

The non-concerted mechanism cannot be reconciled with the observation that dimers I and II are formed in similar yields unless the stabilization of the anion (or radical) in IV by the adjacent carbonyl group is inconsequential in comparison to the energies associated with IV and V. Alternatively, a one-step mechanism in which the new carbon–carbon bonds are formed concertedly may apply.

An obvious implication of either reasoning is that the carbonyl group of the non-excited partner in the photo-reaction plays an unimportant role. Indeed, we have now shown this to be true.

Irradiation of a solution of 2-cyclopentenone (0.064 mole) in cyclopentene (0.64 mole) led to rapid consumption of the unsaturated ketone. A Hanovia, 450-watt mercury arc lamp equipped with a Pyrex filter was employed as the light source. The reaction was complete within three hours. The excess olefin was removed, and the residue was fractionated through a 61-cm. spinning band column. The main fraction, b.p. 78–80° (0.7 mm.), 67% based on cyclopentenone, was shown to be homogeneous by vapor phase chromatography. The material was reduced readily under Wolff–Kishner conditions to the known hydrocarbon *cis,trans,cis*-tricyclo$[5.3.0.0^{2,6}]$ decane[1] and was therefore assigned structure VI. The small forerun from the distillation contained VI contaminated only by unreacted cyclopentenone and by an unsaturated aldehyde which arises from

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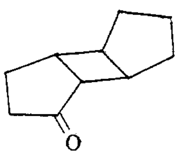
[1] P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962).

(2) We have shown that cyclopentenone sensitizes several reactions in the same fashion as does acetophenone, presumably *via* the triplet state; *cf.* G. S. Hammond, N. J. Turro and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

(3) See, for example, H. E. Zimmerman and D. I. Schuster, *ibid.*, **83**, 4486 (1961).

(4) Product decay to the ground state is assumed. If triplet states are involved, electron re-pairing can occur after the formation of the cyclobutane ring.

photolytic decomposition of the primary product.[5]



VI

Light-induced cyclobutane formation has been observed to occur *intra*molecularly between an olefin and an α,β-unsaturated ketone; for example, the isomerization of carvone to carvone-camphor,[6] and the conversions of various keto-dicyclopentadienes to the "cage" tautomers.[7] The proximity of the π systems in these examples might have special significance in that orbital overlap may contribute to the ease of reaction. No *inter*molecular analog of this photochemical reaction has been fully demonstrated previously, although such a cyclo-addition has been proposed as an intermediate step in the photochemical synthesis of 1,5-diketones.[8]

Note can now be taken of the dichotomy between the Diels–Alder reaction[9] and the observations made here. In the Diels–Alder reaction, the presence of an activating group such as carbonyl in the dienophile markedly influences the course of the reaction[10]; in addition, the *endo* stereochemistry of the major reaction product is, in most instances, predicted by the rule of maximum overlap.[11] Contrary to these specifications, a carbonyl group in the non-excited partner in the photo-addition reactions reported here is unimportant.[12] Further, the stereoselectivity of the photo-reaction is opposite to that of the Diels–Alder reaction. No products derived from the *endo* hydrocarbon *cis,cis,cis*-tricyclo[5.3.0.0^{2,6}]decane were formed in isolable amounts in either the photoreaction of cyclopentenone with itself or with cyclopentene.

Even in view of this divergence, many of the experimental approaches to elucidation of the mechanism of the Diels–Alder reaction are applicable to the study of photodimerization. Such experiments are in progress and will be reported subsequently.

Finally, attention is drawn to the potential synthetic utility of these photo-addition reactions. We have, for example, used cyclohexene and the butenes successfully as olefinic components. Presumably other α,β-unsaturated carbonyl compounds could replace cyclopentenone. The reaction therefore offers an excellent route to new ring systems.

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[5] *Cf.* C. H. Bamford and D. G. Norrish, *J. Chem. Soc.*, 1531 (1938).

[6] G. Büchi and I. M. Goldman, *J. Am. Chem. Soc.*, **79**, 4741 (1957).

[7] P. Yates and P. Eaton, *Tetrahedron Letters*, **11**, 5 (1960); R. C. Cookson, J. Hudec and R. O. Williams, *ibid.*, **22**, 29 (1960).

[8] P. de Mayo, H. Takeshita and W. A. Mueller, *Proc. Chem. Soc.*, 119 (1962).

[9] See, for example, R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[10] E. Lehman and W. Paasche, *Ber.*, **68**, 1146 (1935); K. Alder and E. Rüden, *ibid.*, **74**, 920 (1941).

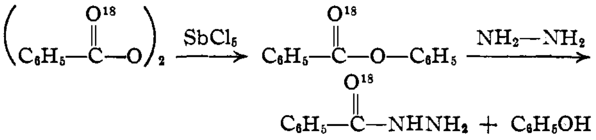
[11] The validity of this rule is now subject to some question; J. A. Berson, A. Hamlet and W. A. Mueller, *J. Am. Chem. Soc.*, **84**, 297 (1962). Reference is made to it here only as a convenient label for the factors which control the stereochemistry of the Diels–Alder reaction.

[12] The possibility exists that the mechanism of addition of cyclopentenone to cyclopentene differs significantly from that applicable to the dimerization of the ketone. It is conceivable that the former reaction proceeds *via* triplet transfer from excited ketone to olefin, followed by attack of the excited olefin on a non-excited molecule of ketone. Although such a devious reaction path cannot be excluded rigorously, it is noted that the irradiation of the ketone–olefin mixture produced none of the dimers of cyclopentene which might be expected if the excited olefin were an important reactant.

CONCERNING THE ANTIMONY PENTACHLORIDE CATALYZED DECOMPOSITION OF BENZOYL PEROXIDE AND SOME MIXED CARBONATES

Sir:

Reynhart[1] has shown that benzoyl peroxide in petroleum ether reacts at room temperature with molar amounts of antimony pentachloride to give a quantitative yield of phenyl benzoate and carbon dioxide. It has now been found that only catalytic quantities of antimony pentachloride are required to effect this conversion. The rate of the reaction is subject to profound solvent effects. For example, the reaction proceeds smoothly in petroleum ether (30–60°) at room temperature and is complete in *ca.* five hours. In toluene, under the same conditions, about three days are required. In diethyl ether very little, if any, reaction occurred after three days.



$$\left(C_6H_5-\overset{O^{18}}{\overset{\|}{C}}-O\right)_2 \xrightarrow{SbCl_5} C_6H_5-\overset{O^{18}}{\overset{\|}{C}}-O-C_6H_5 \xrightarrow{NH_2-NH_2} C_6H_5-\overset{O^{18}}{\overset{\|}{C}}-NHNH_2 + C_6H_5OH$$

Benzoyl peroxide, labeled with oxygen-18 in the carbonyl groups, was converted to phenyl benzoate which was degraded by conversion to phenol and benzoic acid hydrazide. The analytical data are collected in Table I.

TABLE I

Compound[a]	Atom % excess oxygen-18[b] Run 1	Run 2
Benzoic acid[c]	1.56	0.76
Benzoyl peroxide	1.60	0.75
Phenyl benzoate	1.59	0.72
Benzoic acid hydrazide	1.47	0.71
Phenyl phenylurethan	0.07[d]	0.00

[a] All compounds were characterized by m.p., mixed m.p., and infrared data. [b] Two runs using different samples of benzoyl peroxide were conducted. [c] Used in preparing the benzoyl peroxide. Oxygen-18 content per oxygen. [d] The analytical results in run 1 are inferior to those in run 2. The 0.07 atom % excess oxygen-18 found in the phenyl phenylurethan probably is due to a memory effect. An unlabeled sample combusted at the same time showed 0.04 atom %. The combustion apparatus was refurbished before the analyses for run 2 were conducted.

The results of this study demonstrate that the label remains in the carbonyl group during this transformation.[2] This finding eliminates from consideration a free benzoyloxy anion, cation or radical as a product forming intermediate. The tracer results coupled with the Lewis acid character

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[1] A. Reynhart, *Rec. trav. chim.*, **46**, 62 (1927).

[2] See footnote *d* of Table I for this interpretation.