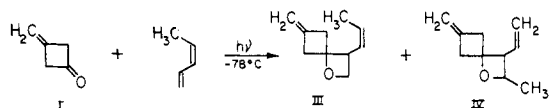


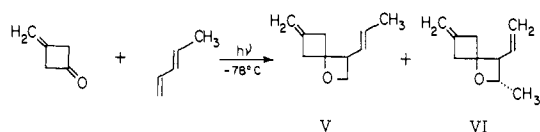
multiplet at 5.2, one-proton oxetane doublet of doublets ( $J = 5.8$  and  $7.9$  cps) at 5.4, one-proton oxetane triplet ( $J = 5.8$  cps) at 5.8,<sup>2,7</sup> one-proton allylic oxetane multiplet at 6.65, and four-proton cyclobutanone multiplet at 7.15; infrared ( $\text{CCl}_4$ ) exocyclic methylene at 5.92 and 11.3, vinyl group at 6.1, 10.25, and 10.8, and oxetane at  $10.05 \mu$ .<sup>2,8</sup> Similarly the ketone I forms an oxetane with cyclopentadiene (40%) and, as expected, with cyclopentene.

In order to show that the unusual reactivity exhibited by 3-methylene cyclobutanone (I) was not dependent upon the presence of the exocyclic methylene group, unsubstituted cyclobutanone was photolyzed in neat butadiene at  $-78^\circ$ . Here also an oxetane was isolated in 20% yield, substantially higher than the accompanying butadiene dimers (5%). Again, this observation is most striking when one notes that neither cyclopentanone nor cyclohexanone shows the least propensity for oxetane formation with butadiene under our conditions. In these cases one observes only the (expected) formation of butadiene dimers.

The solution to the problem of the anomalous behavior of the cyclobutanones came to light when piperylene was substituted for butadiene. Two oxetanes, III and IV, were formed between *cis*-piperylene and



ketone I. Similarly, *trans*-piperylene yielded a second pair of products, V and VI. The latter were easily



distinguished by nmr from those arising from *cis*-piperylene. Neither *cis*- nor *trans*-piperylene was isomerized in the course of the photolysis and there seem to be no common products between the two reactions. Moreover, that product which arises by attack on the more highly substituted double bond predominates in both cases. These two features, stereospecificity and attack on the more highly substituted double bond, clearly distinguish the reaction from that which one might expect of a triplet diradical intermediate.<sup>9</sup> Thus, we are led to the conclusion that the reactive species is the excited singlet state of the ketone.<sup>4</sup>

In studying the formation of oxetanes from cyclobutanones, we conducted most of our experiments at  $-78^\circ$ . Under these conditions, in the case of cyclobutanone, an additional component, 3-vinylcyclohexanone, was isolated.<sup>10</sup> The latter compound is not observed when the photolysis is run at  $20^\circ$  but the oxetane is still produced in comparable yield. Other products

(7) Cf. R. Srinivasan, *J. Amer. Chem. Soc.*, **82**, 775 (1960); M. Hara, Y. Odaisa, and S. Tsutsumi, *Tetrahedron Lett.*, 2981 (1967).

(8) G. M. Barrow and S. Searles, *J. Amer. Chem. Soc.*, **75**, 1175 (1953).

(9) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *ibid.*, **86**, 616 (1964); D. Arnold and A. Glick, unpublished results cited in N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *ibid.*, **89**, 3950 (1967).

(10) The formation of this product is discussed in the accompanying communication: P. Dowd, A. Gold, and K. Sachdev, *ibid.*, **92**, 5724 (1970).

produced at room temperature from cyclobutanone are acetic acid, ketene dimer, and an adduct between ketene and butadiene.

**Acknowledgment.** This work was generously supported by the National Science Foundation (Grant No. GP 6667) and the Research Corporation.

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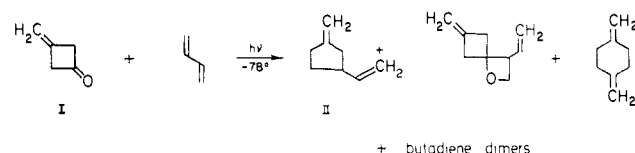
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Received May 5, 1970

### Trimethylenemethane. Trapping with Butadiene, Dimerization, and Ring Closure

Sir:

A fundamental requirement in the study of a reactive intermediate in organic chemistry is that of obtaining both spectroscopic and chemical evidence for the intermediate under conditions which, in both instances, are as closely comparable as possible. Thus, for the study of the chemical reactivity of trimethylenemethane, the conditions which were most attractive were those which have led to the spectroscopic detection of the triplet ground state: low temperature, condensed phase, and ultraviolet light.<sup>1,2</sup>

Photolysis of dilute solutions of 3-methylenecyclobutanone<sup>2</sup> (I) in liquid butadiene<sup>3</sup> at  $-78^\circ$  with a 450-W,



high-pressure mercury arc lamp through a Pyrex filter for 13 days yielded as the major product a 1,2 adduct,<sup>4</sup> 3-vinylmethylenecyclopentane (II) (23%). This product was characterized by its nmr ( $\text{CCl}_4$ ), one-proton vinyl multiplet at  $\tau$  4.3, four-proton vinyl and exocyclic methylene multiplet at 5.2, five-proton allylic multiplet at 7.7, and two-proton saturated multiplet at 8.3; ir ( $\text{CCl}_4$ ) exocyclic methylene at 6.05 and  $11.38 \mu$ , vinyl at 6.10, 10.10, and  $10.95 \mu$ ; and the mass spectrum, exact mass of molecular ion calcd for  $\text{C}_8\text{H}_{12}$ , 108.0939; found, 108.0931. Because the adduct II had the same elemental composition as the dimers of butadiene<sup>5</sup> and similar, although distinguishable,

(1) Presented in part at 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 9-13, 1968, Abstract ORGN 147; P. Dowd, *J. Amer. Chem. Soc.*, **88**, 2587 (1966).

(2) P. Dowd and K. Sachdev, *ibid.*, **89**, 715 (1967); P. Dowd, A. Gold, and K. Sachdev, *ibid.*, **90**, 2715 (1968).

(3) Cf. G. L. Closs, L. R. Kaplan, and V. I. Bendall, *ibid.*, **89**, 3376 (1967), who have trapped the 1,3-diradical precursor to benzocyclopropene under similar conditions.

(4) This is as expected for the addition of a diradical to butadiene; cf. J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962); P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Amer. Chem. Soc.*, **86**, 616 (1964), and subsequent papers in that series. The present case differs somewhat from those cited since one would expect the formation of a five-membered ring to compete very favorably with the formation of the alternative seven-membered ring compound.

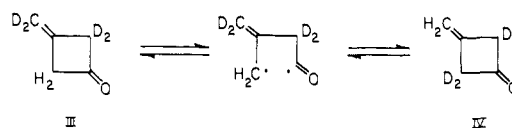
(5) Authentic samples of 4-vinylcyclohexene, *cis*-1,2-divinylcyclobutane, and *trans*-1,2-divinylcyclobutane were prepared for direct comparison according to G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963).

infrared and nmr spectra, the assigned structure was confirmed by synthesis. Thus, treatment of the known cyclopentanone-3-carboxylic acid<sup>6</sup> with 3 equiv of the Wittig reagent, methylene triphenylphosphorane, in dimethyl sulfoxide<sup>7</sup> yielded (90%)<sup>8</sup> 3-methylenecyclopentanecarboxylic acid. Lithium aluminum hydride reduction of the corresponding methyl ester afforded the corresponding alcohol (72%). Oxidation with dicyclohexylcarbodiimide-dimethyl sulfoxide<sup>10</sup> yielded the aldehyde (50%), which when treated with methylene triphenylphosphorane gave 3-vinylmethylencyclopentane (II) (65%), identical in all respects with the adduct of trimethylenemethane and butadiene.

The possibility that the adduct II might arise by energy transfer from excited ketone I to butadiene followed by attack of the excited butadiene on the exocyclic methylene of the starting ketone I was examined. It was possible to show that the ratio of the yields of the adduct II and the dimers of butadiene was sensibly constant (2:1) over a tenfold change in the concentration of starting ketone (1.0, 0.5, and 0.1 M). Further, methylenecyclobutane was not attacked when it was included in the photolysis reaction mixture. Of additional interest, the esr spectrum of trimethylenemethane was readily observed in neat *cis*-piperylene at  $-196^\circ$ . And, neither *cis*- nor *trans*-piperylene was isomerized when photolyzed in the presence of the ketone I at  $-78^\circ$ .

Although energy transfer as it is ordinarily observed appears to play a negligible role in the above reaction, the more subtle problem of energy transfer followed by immediate reaction in the solvent cage has not been eliminated. It was hoped that photolysis of ketone I specifically deuterated would shed light on this possibility as well as on the important general problem of stepwise opening of the cyclobutanone ring such that attack on the butadiene occurred after the cleavage of one carbon-carbon bond but before the loss of carbon monoxide. Photolysis of the deuterated ketone III (prepared from allene-*d*<sub>4</sub>) yielded 3-vinylmethylencyclopentane labeled with four deuterium atoms statistically scrambled among those carbons arising from trimethylenemethane. This result establishes beyond question that half of the adduct II arises from butadiene while the other half arises from the ketone I. However, on careful scrutiny, the fact that the deuterium is randomly distributed in the product proves not to be useful as proof of the presence of trimethylenemethane since the deuterium in the starting ketone III, isolated when the photolysis was run 75% to completion, is also randomly distributed among the three methylene groups of

that compound. This change presumably occurs by the mechanism shown below, III  $\rightleftharpoons$  IV.



The butadiene photolysis reaction mixture is quite complex. In addition to the photodimers of butadiene (10%) and the adduct II (23%), the mixture contained an oxetane (15%)<sup>11</sup> and the dimer of trimethylenemethane, 1,4-dimethylenecyclohexane (5%).<sup>12</sup> In inert solvents one observes a mixture of methylenecyclopropane<sup>12,13</sup> and 1,4-dimethylenecyclohexane, the ratio of which depends strongly on concentration, temperature, and the absence of a competitor for trimethylenemethane. For example, photolysis in furan at  $15^\circ$  yielded methylenecyclopropane (62%) and 1,4-dimethylenecyclohexane (1.2%). When the temperature was lowered to  $-72^\circ$  the relative yield of 1,4-dimethylenecyclohexane rose by a factor of 5. Similarly at 0.012 M starting ketone in perfluoromethylcyclohexane the dimer could not be detected whereas at 0.87 M it formed 10% of the reaction product, the remainder being methylenecyclopropane.

**Acknowledgment.** This work was generously supported by the National Science Foundation (Grant No. GP 6667) and by the Research Corporation.

(11) The structure and formation of this unexpected product are discussed in the accompanying communication: P. Dowd, A. Gold, and K. Sachdev, *ibid.*, **92**, 5725 (1970).

(12) This compound was identified by direct comparison with an authentic sample. It had also been observed by R. G. Doerr and P. S. Skell, *ibid.*, **89**, 3062, 4688 (1967), in their successful studies of the gas-phase trapping of trimethylenemethane with species presumed to be triplet cyclobutadiene and triplet methylene. See also A. C. Day and J. T. Powell, *Chem. Commun.*, 1241 (1948).

(13) R. J. Crawford and D. M. Cameron, *J. Amer. Chem. Soc.*, **88**, 2589 (1966), have observed methylenecyclopropane as the sole product in the thermal production of trimethylenemethane from 4-methylene- $\Delta$ -pyrazoline.

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## Stereospecific Photoreactions of Cyclobutanones<sup>1</sup>

Sir:

The stereochemical course of thermal (2 + 2) cycloaddition<sup>2</sup> and cycloelimination<sup>3</sup> reactions of cumulenes

(6) F. W. Kay and W. H. Perkin, Jr., *J. Chem. Soc.*, **89**, 1646 (1906); E. Hope, *ibid.*, **101**, 905 (1912); C. K. Ingold and J. F. Thorpe, *ibid.*, **119**, 501 (1921); R. Giuliano, M. Di Fonzo, and A. Ermili, *Ann. Chim. (Rome)*, **49**, 1607 (1959); R. Giuliano, M. Di Fonzo, and M. Artico, *ibid.*, **50**, 750 (1960).

(7) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

(8) The yield of this reaction is remarkable in view of the difficulty ordinarily encountered in attempted Wittig reactions on cyclopentanone rings.<sup>9</sup> As a further example the methyl ester of the above 3-methylenecyclopentanecarboxylic acid gives a low yield of impure product. It appears that the presence of the carboxylate anion suppresses enolization and/or the subsequent condensation reactions which ordinarily complicate this reaction.

(9) A. Maercker, *Org. React.*, **14**, 349 (1965). See, however, F. Sondheimer and R. Mechoulam, *J. Amer. Chem. Soc.*, **80**, 3087 (1958); **79**, 5029 (1957).

(10) K. E. Pfitzner and J. G. Moffatt, *ibid.*, **87**, 5661, 5670 (1965).

(1) Molecular Photochemistry. XXIV. Paper XXXIII: R. B. Gagosian, J. C. Dalton, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4752 (1970). The authors are pleased to acknowledge the generous support of this research by the Air Force Office of Scientific Research (Grants AFOSR 1381 and 1848).

(2) R. Huisgen, L. A. Feiler, and G. Benisch, *Chem. Ber.*, **102**, 3460 (1969), and previous papers in this series; T. DoMinh and O. P. Strausz, *J. Amer. Chem. Soc.*, **92**, 1766 (1970); R. Montaigne and L. Ghosez, *Angew. Chem.*, **80**, 194 (1968); W. T. Brady, E. F. Hoff, R. Roc, Jr., and F. H. Parry, Jr., *J. Amer. Chem. Soc.*, **91**, 5679 (1969); W. T. Brady and E. F. Hoff, *ibid.*, **90**, 6256 (1968); E. P. Kiefer and M. Y. Okamura, *ibid.*, **90**, 4187 (1968); J. E. Baldwin and U. V. Roy, *Chem. Commun.*, 1225 (1969); E. J. Moriconi and J. F. Kelly, *Tetrahedron Lett.*, 1435 (1968); H. Bestian, H. Biener, K. Clauss, and H. Heyn, *Justus Liebigs Ann. Chem.*, **718**, 94 (1968).

(3) L. A. Paquette, M. J. Wyvrat, and G. A. Allen, Jr., *J. Amer. Chem. Soc.*, **92**, 1736 (1970); J. E. Baldwin and P. W. Ford, *ibid.*, **91**, 7192 (1969).