

terium on equilibration with aqueous base. A second equilibration resulted in no further loss of deuterium.¹¹ This result was further confirmed by photolysis of 2,2,4,4-tetradeuteriocyclobutanone in butadiene. The 3-vinylcyclohexanone-*d*₄ (IV) produced exchanged two, and only two, deuterium atoms on treatment with aqueous base.¹¹ These findings strictly limit the mode of opening of the cyclobutanone ring to cleavage of the α carbon-carbon bond as shown in V. Thus the diradical V is tentatively proposed as the central reactive intermediate leading to the production of 3-vinylcyclohexanone (I). The possible intermediacy of a diradical such as V is further supported by the recent studies of Turro and McDaniel.^{12a}



The orientation of addition^{12b} of V¹³ to butadiene is most interesting. It indicates that acyl radicals may be more reactive than alkyl radicals toward addition to butadiene. An estimate¹⁴ of the enthalpy of addition of alkyl and acyl radicals to ethylene places them only 4 kcal apart with the latter being the less exothermic of the two. Although this number clearly favors the production of 2-vinylcyclohexanone, it is somewhat uncertain and only one of several factors which govern the relative reactivities of these free radicals, as Walling has pointed out.¹⁴ Experimental determination of the relative reactivities of acyl and alkyl radicals has not been reported. Indeed, part of the importance of the present work stems from the fact that this may possibly be the first direct comparison of the relative reactivities of alkyl and acyl radicals toward conjugated olefins.

Acknowledgment. It is a pleasure to acknowledge discussions with Dr. Paul Engel. This work was generously supported by the National Science Foundation (Grant No. GP 6667) and the Research Corporation.

(11) It was possible to assign the positions of the remaining deuterium atoms using nmr and especially mass spectrometry.

(12) (a) N. J. Turro and D. McDaniel, *J. Amer. Chem. Soc.*, **92**, 0000 (1970). (b) It is quite possible that mixture of 3-vinylcyclohexanone and 2-vinylcyclohexanone is formed in this reaction. An authentic sample of 2-vinylcyclohexanone has been prepared according to J. K. Crandall, J. P. Arrington, and J. Hen, *ibid.*, **89**, 6208 (1967). It would not have been detected under our photolysis reaction conditions (400-hr irradiation at -78° of a 10% solution of the substrate in butadiene as solvent with a 450-W Hanovia high-pressure mercury lamp using Pyrex as filter) since it is completely destroyed in a relatively short time. Except for the great difference in temperature, this might have been inferred from the work of Crandall, *et al.* On the other hand, we have established that the observed products, 3-vinylcyclohexanone and oxetane, are stable under our conditions.

(13) It has been assumed here that cyclobutanone reacts with butadiene in the open, diradical form. Clearly an addition reaction which occurs through a closed excited state of the ketone has not been eliminated. In the latter case one might expect initial bond formation to occur at oxygen rather than at carbon; see, however, J. A. Baltrop and H. A. Carless, *Tetrahedron Lett.*, 3901 (1968), for examples in which the opposite conclusion might possibly be reached.

(14) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 240-243.

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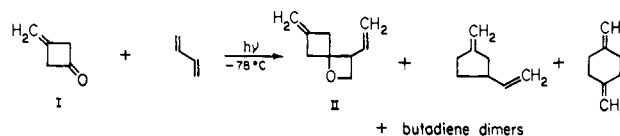
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Oxetane Formation in the Photochemical Reaction of Cyclobutanones with Butadiene, Cyclopentadiene, and Piperylene

Sir:

The elucidation of the rules which govern intermolecular energy transfer in solution is one of the most pressing and fascinating problems in modern organic photochemistry. A rule of considerable importance is that which governs the outcome of the Paterno-Buchi reaction,¹ the formation of oxetanes from n, π^* triplet ketones and olefins. For oxetane formation to occur, the triplet energy of the olefin must be higher than that of the ketone in order that energy transfer not dominate the reaction.² Thus, conjugated dienes with cis and trans triplet energies of approximately 54 and 60 kcal, respectively, are expected to be poor substrates in oxetane formation with simple aliphatic ketones whose triplet energies are generally expected to be greater than 70 kcal.^{2,3} We have discovered a most interesting seeming exception to this rule in the case of cyclobutanone. This is only an apparent exception since we have shown (*vide infra*) that cyclobutanone reacts with dienes through its excited singlet state. Since cyclohexanone and cyclopentanone behave in a completely normal fashion in the presence of dienes, this is the first case in which the effects of ground-state ring strain have appeared as controlling factors in oxetane formation—more generally stated—in the relative rates of intersystem crossing and photochemical reaction. In this sense, the present case complements those recently studied in which it is demonstrated⁴ that singlet excited ketones may be efficiently trapped by electron-deficient olefins but where the structure of the ketone was not a controlling factor.

When 3-methylenecyclobutanone⁵ (I) was photolyzed in liquid butadiene at -78° the oxetane II was formed



in 17% yield.⁶ The structural assignment is based on the mass spectrum: exact mass of molecular ion calcd for C₉H₁₂O, 136,0888; found, 136,0883; nmr (CCl₄) one-proton vinyl multiplet at τ 3.7-4.3, two-proton vinyl multiplet at 4.9, two-proton exocyclic methylene

(1) E. Paterno and G. Chieffi, *Gazz. Chim. Ital.*, **39**, 341 (1909); G. Buchi, C. G. Inman, and E. S. Lipinsky, *J. Amer. Chem. Soc.*, **76**, 4327 (1954); D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

(2) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964).

(3) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

(4) J. J. Beereboom and M. S. von Wittenau, *J. Org. Chem.*, **30**, 1231 (1965); N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *J. Amer. Chem. Soc.*, **89**, 3950 (1967); J. A. Baltrop and H. A. J. Carless, *Tetrahedron Lett.*, 3901 (1968). The importance of the excited singlet state to the understanding of the solution photochemistry of cyclobutanone is further demonstrated by the recent studies of N. J. Turro and D. McDaniel, *J. Amer. Chem. Soc.*, **92**, 5727 (1970).

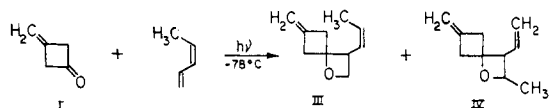
(5) P. Dowd and K. Sachdev, *ibid.*, **89**, 715 (1967).

(6) A 10% solution of the ketone in butadiene as solvent was maintained at -78° while irradiation was carried out using a 450-W Hanovia high-pressure mercury lamp. A Pyrex filter was used. The products were isolated by vapor phase chromatography on TCEP. Other products formed in this reaction are discussed in the preceding communication: P. Dowd, G. Sengupta, and K. Sachdev, *J. Amer. Chem. Soc.*, **92**, 5726 (1970).

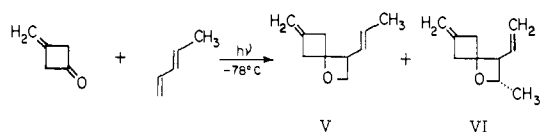
multiplet at 5.2, one-proton oxetane doublet of doublets ($J = 5.8$ and 7.9 cps) at 5.4, one-proton oxetane triplet ($J = 5.8$ cps) at 5.8,^{2,7} one-proton allylic oxetane multiplet at 6.65, and four-proton cyclobutanone multiplet at 7.15; infrared (CCl_4) exocyclic methylene at 5.92 and 11.3, vinyl group at 6.1, 10.25, and 10.8, and oxetane at 10.05μ .^{2,8} 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° . 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.⁹ Thus, we are led to the conclusion that the reactive species is the excited singlet state of the ketone.⁴

In studying the formation of oxetanes from cyclobutanones, we conducted most of our experiments at -78° . Under these conditions, in the case of cyclobutanone, an additional component, 3-vinylcyclohexanone, was isolated.¹⁰ The latter compound is not observed when the photolysis is run at 20° 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.

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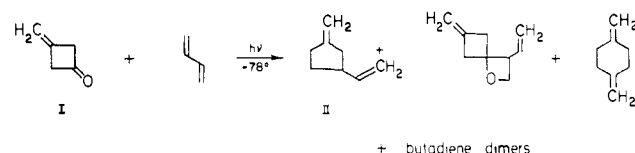
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Trimethylenemethane. Trapping with Butadiene, Dimerization, and Ring Closure

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.^{1,2}

Photolysis of dilute solutions of 3-methylenecyclobutanone² (I) in liquid butadiene³ at -78° 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,⁴ 3-vinylmethylenecyclopentane (II) (23%). This product was characterized by its nmr (CCl_4), one-proton vinyl multiplet at τ 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 (CCl_4) exocyclic methylene at 6.05 and 11.38μ , vinyl at 6.10, 10.10, and 10.95μ ; and the mass spectrum, exact mass of molecular ion calcd for C_8H_{12} , 108.0939; found, 108.0931. Because the adduct II had the same elemental composition as the dimers of butadiene⁵ 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).