infrared and nmr spectra, the assigned structure was confirmed by synthesis. Thus, treatment of the known cyclopentanone-3-carboxylic acid[6] with 3 equiv of the Wittig reagent, methylene triphenylphosphorane, in dimethyl sulfoxide[7] yielded (90%)[8] 3-methylenecyclopentanecarboxylic acid. Lithium aluminum hydride reduction of the corresponding methyl ester afforded the corresponding alcohol (72%). Oxidation with dicyclohexylcarbodiimide–dimethyl sulfoxide[10] yielded the aldehyde (50%), which when treated with methylene triphenylphosphorane gave 3-vinylmethylenecyclopentane (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 $-196°$. And, neither cis- nor trans-piperylene was isomerized when photolyzed in the presence of the ketone I at $-78°$.

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_4) yielded 3-vinylmethylenecyclopentane 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.
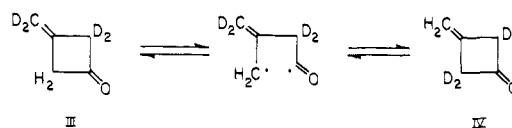
The butadiene photolysis reaction mixture is quite complex. In addition to the photodimers of butadiene (10%) and the adduct II (23%), the mixture contained an oxetane (15%)[11] and the dimer of trimethylenemethane, 1,4-dimethylenecyclohexane (5%).[12] In inert solvents one observes a mixture of methylenecyclopropane[12,13] 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° yielded methylenecyclopropane (62%) and 1,4-dimethylenecyclohexane (1.2%). When the temperature was lowered to $-72°$ 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 methylenecyclopane.

(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 gasphase 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-Δ-pyrazoline.

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Stereospecific Photoreactions of Cyclobutanones[1]

Sir:

The stereochemical course of thermal (2 + 2) cycloaddition[2] and cycloelimination[3] 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.[9] 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. Roe, 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. Wyvratt, and G. A. Allen, Jr., J. Amer. Chem. Soc., 92, 1736 (1970); J. E. Baldwin and P. W. Ford, ibid., 91, 7192 (1969).

has received considerable attention recently, in part due to a general interest in testing the predictions of orbital symmetry arguments.[4] In particular, ketenes are expected to serve as ideal substrates for concerted (π_s^2 + π_a^2) thermal cycloadditions to olefins.[4b] Indeed, detailed study of the cycloaddition of ketenes to olefins[5] has revealed that this class of reactions possesses important characteristics which are diagnostic for concerted cycloadditions, i.e., a high degree of stereospecificity,[5,6] a large negative entropy of activation,[6] and modest response of reaction rate to large changes in solvent polarity.[6a] Many cases are known[4] for which the rules for conservation of orbital symmetry predict a concerted thermal process to be allowed while the corresponding concerted photochemical process is predicted to be forbidden (and vice versa).

We report here that irradiation of methanolic solutions of cyclobutanones 1c (Scheme I) and 1t (Scheme II)

Scheme I
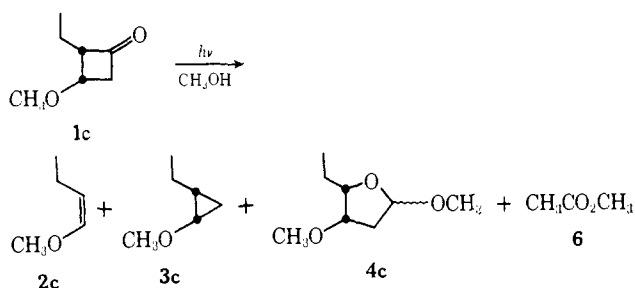
Scheme II
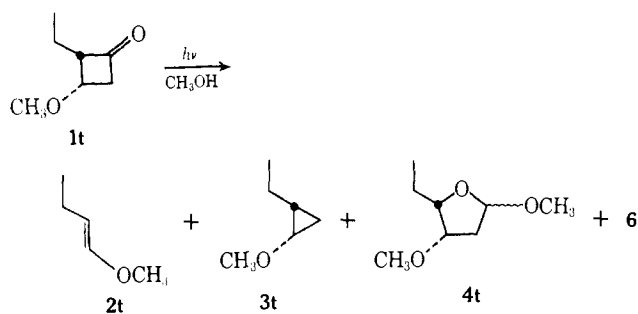
results in three different stereoselective reactions, two of which are also stereospecific. The results of our quantitative study of the photolyses of 1c and 1t in methanol and benzene are summarized in Table I.

The ketenes 1c and 1t were prepared by standard stereospecific thermal cycloadditions.[6,7] The cyclopropanes 3c and 3t were prepared by cyclopropylation[8]

Table I.[a-c] Quantum Yields for Product Formation

	2c	2t	3c	3t	4c	4t	6
			Irradiation in Methanol				
1c	0.11	0.004	0.01	0.001	0.03	<0.001	0.09
1t	0.004	0.10	0.002	0.03	<0.001	0.06	0.09
			Irradiation in Benzene				
1c	0.08	0.005	0.01	0.002			
1t	0.004	0.10	0.002	0.06			

[a] Irradiation in methanol and benzene, 313 nm, approximately 1 M in cyclobutanone, with cyclopentanone actinometry. These values represent lower limits, error limits ∼20%. [b] No interconversion of 1c and 1t could be found even after extended irradiation. [c] No quenching of any product could be detected in solutions containing 1 M piperylene.

of olefins 2c and 2t, respectively. The structures of 4c and 4t were established by Jones oxidation[9] to the lactones 5c and 5t, which were prepared by Baeyer–Villiger oxidation[10] of 1c and 1t, respectively. Since the latter reaction is known to proceed stereospecifically with retention of configuration,[10] the identical stereochemistry of the ethyl and methoxy functions within the series of cis compounds, 1c–5c, and within the series of trans compounds, 1t–5t, is established.

Scheme III
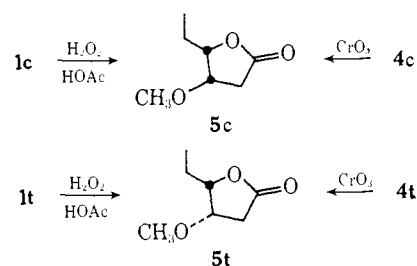
The salient features of our data are that the three characteristic solution photoreactions of cyclobutanones,[11a] i.e., decarboxylation, (2 + 2) cycloelimination, and (in methanol) ring expansion are all significantly stereoselective and the former two photoreactions are stereospecific. Quinkert, et al., have reported a photolysis of epimeric steroidal cyclobutanones which resulted in stereospecific ring expansion in methanol, but which did not display stereoselectivity for both epimers. Our results contrast sharply with published work[12] on cyclopentanones and cyclohexanones, both of which exhibit photochemical behavior that suggests the occurrence of intermediates capable of scrambling (a) initial ketone stereochemistry and (b) product stereo-

(4) (a) R. B. Woodward and R. Hoffmann, Angew. Chem., Int. Ed. Engl., 8, 781 (1969); (b) R. B. Woodward and R. Hoffmann, ibid., 8, 847 (1969).

(5) (a) R. H. Hask, P. G. Gott, and J. C. Martin, J. Org. Chem., 29, 1239 (1964); (b) J. C. Martin, V. W. Goodlett, and R. D. Burpitt, ibid., 30, 4309 (1965); (c) T. DoMinh and O. D. Strausz, J. Amer. Chem. Soc., 92, 1766 (1970); (d) F. E. Luknitskii and B. A. Vovsi, Russ. Chem. Rev., 38, 487 (1969); (e) M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, Helv. Chim. Acta, 53, 417 (1970).

(6) (a) R. Huisgen, L. A. Feiler, and P. Otto, Chem. Ber., 102, 3444 (1969); (b) R. Huisgen, L. A. Feiler, and G. Binsch, ibid., 102, 3474 (1969).

(7) The 1 M olefin (2c or 2t) in CH_2Cl_2 is continuously saturated with ketene. The reaction is followed by glc (10 ft × ¼ in. 20% Carbowax 20M at 120°). When about 95% of the olefin has reacted, the solution is distilled to yield cyclobutanones 1c or 1t contaminated with ketene dimer. Final separation is by glc (conditions as above). Preparation of olefins 2c and 2t and their reaction with ketene is similar to that described in ref 5b.

(8) To a solution of 0.05 mol of olefins 2c and 2t and 0.038 mol of Et_2Zn in 40 ml of Et_2O was added 0.063 mol of CH_2I_2 dropwise with

stirring under a nitrogen atmosphere. The mixture was stirred overnight and then added to 100 ml of 2% HCl (aqueous). The organic layer was separated, and washed with 5% $NaHCO_3$ (aqueous) with water, and then dried over $MgSO_4$. Distillation and glc separation (10 ft × ¼ in., 20% XF 1150 at 80°) gave 3c and 3t. See J. Furukawa, N. Kawabata, and J. Nishimura, Tetrahedron, 24, 53 (1968).

(9) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, J. Chem. Soc., 2548 (1953); (b) W. C. Agosta and D. K. Herron, J. Amer. Chem. Soc., 90, 7025 (1968).

(10) (a) C. H. Halsall, Org. React., 9, 73 (1957); (b) J. B. Lee and B. C. Uff, Quart. Rev. Chem. Soc., 21, 449 (1967); (c) P. deMayo, Ed., "Molecular Rearrangements," Vol. 1, Wiley, New York, N. Y., 1963, p 577.

(11) (a) N. J. Turro and R. M. Southam, Tetrahedron Lett., 545 (1967); D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, J. Amer. Chem. Soc., 92, 4349 (1970); (b) G. Quinkert, G. Cimbollek, and G. Buhr, Tetrahedron Lett., 4573 (1966).

(12) (a) J. A. Barltrop and J. D. Coyle, Chem. Commun., 1081 (1969); (b) C. C. Badcock, M. J. Perona, G. O. Pritchard, and B. Rickborn, J. Amer. Chem. Soc., 91, 543 (1969); (c) H. M. Frey, Chem. Ind. (London), 947 (1966).

chemistry. Especially interesting is the stereospecificity in the formation of **3** since published work indicates that in the vapor, cyclobutanones lose CO *via* a triplet mechanism.[13]

The lack of total stereospecificity in the products from irradiation of ketones **1c** and **1t** can be accounted for entirely as the result of contamination of solutions of **1c** with **1t** and *vice versa*. The most satisfactory separation of ketones **1c** and **1t** (by gas–liquid chromatography) leads to a few per cent of cis–trans isomerization under our conditions.

The photoreactions of cyclobutanones cannot be quenched by 1,3-dienes, a result which argues for the intermediacy of either an excited singlet or very rapidly decomposing (unquenchable) triplet.[14] The lack of scrambling of stereochemistry in the photoreactions reported in Tables I and II rules out any intermediate capable of surviving long enough to undergo bond rotations. Since the triplet states of **1c** and **1t** are not expected to undergo concerted rearrangements,[15] any triplet intermediate would be expected to suffer substantial loss of stereochemistry.[16] We conclude, therefore, that the excited singlet ketone is probably a precursor of the photoproducts.[17]

One can envision either (1) a set of competing concerted reactions occurring from the excited singlets of **1c** and **1t**, or (2) a set of competing reactions from a singlet biradical **7** generated from the excited singlet states of **1c** and **1t** (or some combination of these two). Although these possibilities are quite similar conceptually we feel that the singlet biradical hypothesis is more attractive because it readily (a) explains the stereoselectivity of formation of **2** and **4**, (b) allows rationalization of the three kinds of reactions observed

7
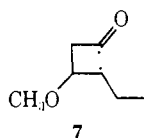
from **1** on the basis of one intermediate, and (c) allows rationalization of the reaction inefficiency on the basis of cyclization of **7** to **1**. The latter piece of evidence is quite convincing, since the net inefficiency of the reactions is unlikely to be attributable to an intersystem crossing from S_1 to produce an unreactive triplet.[18] Finally, the trapping by butadiene, of an intermediate whose structure probably resembles **7**, adds further support to the singlet biradical hypothesis.[17]

(13) (a) N. E. Lee and E. K. C. Lee, *J. Chem. Phys.*, 50, 2094 (1969). (b) NOTE ADDED IN PROOF. Recent results reported by N. E. Lee, H. A. J. Carless, and E. K. C. Lee (*J. Amer. Chem. Soc.*, 92, 4482 (1970)) demonstrated that loss of CO from 2,3-dimethylcyclobutanone is not stereospecific, but that cycloelimination is moderately stereospecific (vapor photolysis).

(14) A singlet-state decomposition has been previously suggested for cyclobutanones: N. J. Turro and D. M. McDaniel, *Mol. Photochem.*, 2, 39 (1970); H. O. Denschlag and E. K. C. Lee, *J. Amer. Chem. Soc.*, 90, 3628 (1968).

(15) Because the singlet excited state of ketene is energetically below that of cyclobutanone 1, it is possible that ketene produced from cycloelimination is in an electronically excited state.

(16) N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, 92, 320 (1970).

(17) P. Dowd, A. Gold, and K. Sachdev, *ibid.*, 92, 5724 (1970).

(18) (a) For example, singlet biradicals, believed to be produced by type II abstraction,[18b] do not possess a lifetime sufficient to allow racemization, whereas the related triplet biradicals are significantly racemized during its lifetime. (b) N. C. Yang and S. P. Elliott, *J. Amer. Chem. Soc.*, 91, 7751 (1969).

Recent evidence has been put forth supporting the proposition that singlet 1,4 biradicals can undergo stereospecific cyclization and hydrogen reversion.[18b] The data reported here indicate that stereospecificity, *per se*, may not be a firm diagnostic test for the concertedness of cycloeliminations and (invoking microscopic reversibility) cycloadditions.

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Solvent Assistance in the Solvolysis of Secondary Substrates. The Use of Added Azide Ion as a Mechanistic Probe

Sir:

Recent work has revealed a striking difference in the solvolytic behavior between simple secondary (*e.g.*, isopropyl) and 2-adamantyl tosylates.[1] This behavior has been interpreted to indicate that considerable nucleophilic solvent assistance to ionization, ordinarily present in simple secondary substrates, is absent or is sharply reduced in the solvolysis of 2-adamantyl tosylate. The lessened role of solvent assistance in 2-adamantyl solvolysis is attributed to steric hindrance which would be present in a pentacovalent transition state. In order to test this conclusion further we have studied the solvolysis of 2-adamantyl tosylate in the presence of azide ion, a strong nucleophile.

The classic studies of Hughes and Ingold[2] introduced the technique of adding strong nucleophiles (lyate ion, azide ion) to a solvolysis medium in order to determine the susceptibility of a given substrate to direct displacement (SN2) reactions. When such a strong nucleophile produces a marked rate enhancement and a quantitatively corresponding alteration in the product composition (when this can be determined), a bimolecular substitution process is implicated.

Added azide ion has been used in another way: to trap carbonium ions.[3] For solvolyses proceeding *via* a carbonium-ion (k_c)[4] pathway, the degree of azide incorporation increases with the stability of the carbonium ion, as measured by the solvolysis rate.[5] As is often found, the selectivity of an intermediate increases with its stability.[6]

(1) (a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 92, 2538 (1970); (b) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, 92, 2540 (1970); (c) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, 92, 2542 (1970); (d) M. L. Sinnott, H. J. Storesund, and M. C. Whiting, *Chem. Commun.*, 1000 (1969); (e) J. A. Bone and M. C. Whiting, *ibid.*, 115 (1970): (f) D. Lendir and P. v. R. Schleyer, *ibid.*, 941 (1970).

(2) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969; (b) L. C. Batemen, K. A. Cooper, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 925 (1940).

(3) D. Bethell and V. Gold, "Carbonium Ions," Academic Press, New York, N. Y., 1967, pp 37–38.

(4) For definition and discussion of these terms see ref 1a.

(5) R. A. Sneen, J. V. Carter, and P. S. Kay, *J. Amer. Chem. Soc.*, 88, 2594 (1966).

(6) (a) Z. Majerski, S. Borcić. and D. E. Sunko, *Tetrahedron*, 25, 301 (1969); (b) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 22; (c) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 155.