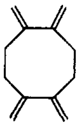
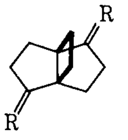
suggesting that the product was, in fact, **2**, formed by a 1,5-transannular photo-ring closure.[5]

The structure **2** was confirmed by ozonolysis to the crystalline diketone **3**[7] (mp 75–76°). The ir of the diketone showed a sharp absorption at 5.75 μ, indicating that both carbonyls were contained in five-membered rings. The rather complex nmr spectrum of the diketone could be greatly simplified by stirring a CCl_4 solution with D_2O containing Na_2CO_3. This resulted in the exchange of four protons (mass spectrum) and caused the nmr spectrum to collapse to an A_2B_2 pattern (4 H) centered at δ 2.27 and a broad singlet (4 H) at δ 2.00. The diketone underwent smooth Wolff–Kishner reduction to give the parent [3.3.2]propellane (**4**), whose nmr spectrum displayed a sharp singlet at δ 1.63 for the four equivalent cyclobutyl protons.



1



2, $R = CH_2$
3, $R = O$
4, $R = H_2$

The geometry of **2**, which causes the orbitals of the central single bond to lie in a plane almost orthogonal to the π lobes of the methylene groups, confers on this compound a reasonable degree of thermal stability. We have used this fact to develop a scheme which allows separation of **2** from the by-products in the photolysis of **1**, all of which contain a cyclobutene ring which can be reopened by pyrolysis in a flow system under conditions where **2** is stable. The mixture of **2** and conjugated dienes which is obtained from pyrolysis of the crude photolysate is allowed to react with maleic anhydride in refluxing $CHCl_3$. Since **2** does not react, it can be separated from the Diels–Alder adducts by simple column chromatography and thus obtained essentially pure without the necessity of tedious vpc collection.[8]

We are currently exploring ring contraction reactions in the diketone **3**, which would lead to [2.2.2]propellane.[1,3,8a]

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(5) For a review of 1,5-transannular reactions in cyclooctane derivatives, see A. C. Cope, *Quart. Rev. Chem. Soc.*, **20**, 119 (1966). Our expectation that the structure of **1** would dispose it favorably toward such a reaction was based in part on the fact that the 1,3,5,7 isomer of **1** undergoes a 1,5 transannular cycloaddition reaction with tetracyanoethylene.[6]

(6) J. K. Williams and R. E. Benson, *J. Amer. Chem. Soc.*, **84**, 1257 (1962).

(7) All compounds gave elemental analyses and mass spectra in accord with the proposed formulas.

(8) This scheme also allows the use in the photolysis of unpurified **1**, which contains an isomer that is converted by photolysis to a product containing a cyclobutene ring.[4] Thus, **2** can be obtained from 1,2-dimethylenecyclobutane in three steps without purification of any of the intermediates.[4]

(8a) Note Added in Proof. Professor Cargill has kindly provided us with the ir and nmr spectra of [3.3.2]propellane prepared in his laboratory by a route different from ours;[2] these proved to be indistinguishable from those obtained from **4**. Preliminary experiments in our laboratory indicate unusual reactivity of the central C-C single bond in this molecule toward free-radical addition.

(9) NIH Postdoctoral Fellow, 1969–1970.

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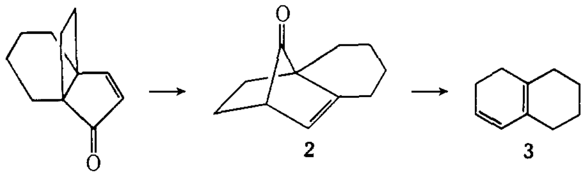
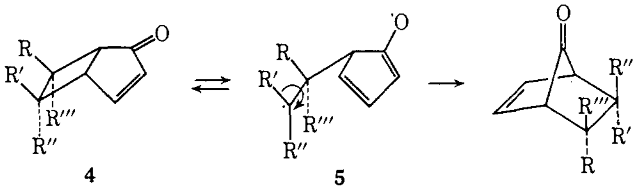
Stereochemistry of a Photochemical Allylic Rearrangement[1]

Sir:

Irradiation of tricyclo[4.3.2.0^{1,6}]undec-3-en-2-one (**1**) in methylene chloride (0.83 *M*) with the output from ten "blacklights" (General Electric F15-T8-BL) through Pyrex yielded only ketone **2** (crude yield, 95%). Similar irradiation of bicyclo[3.2.0]hept-3-en-2-one (**4a**) in pentane (0.014 *M*) gave 7-ketonorbornene (**6a**) in 10–20% yield along with one or more dimers, mp 174–177°, in 60–70% yield. These photoisomerizations, as well as the analogous verbenone–chrysanthenone rearrangement,[2a,b] represent photochemical allylic shifts in which the migrating atom is carbon,[2] and which are restricted by the geometry of the substrates to being suprafacial. If these reactions proceed with simultaneous bonding of the migrating carbon to the α and γ positions (concerted reactions), we may expect, based on consideration of the symmetry of the first antibonding MO (ψ_3) of the allyl radical,[3] that the stereochemistry of the migrating carbon will be retained.[4] A nonconcerted, or "diradical," process should result in randomization of configuration, provided the diradical is relatively long-lived. We have investigated the stereochemistry of the **4** → **6** change and we report our findings here.



1 **2** **3**



4 **5** **6**

a, R = R′ = R″ = R‴ = H
b, R = R′ = D; R″ = R‴ = H
c, R = R″ = D; R′ = R‴ = H
d, R = R′ = H; R″ = R‴ = D

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(1) Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank the National Science Foundation for a grant toward the purchase of the mass spectrometer used in this work.

(2) (a) J. J. Hurst and G. W. Whitham, *J. Chem. Soc.*, 2464 (1960); (b) W. F. Erman, *J. Amer. Chem. Soc.*, **89**, 3828 (1967). See also (c) H. E. Zimmerman and D. J. Sam, *ibid.*, **88**, 4905 (1966); (d) H. E. Zimmerman and R. L. Morse, *ibid.*, **90**, 964 (1968); (e) R. F. C. Brown, R. C. Cookson, and J. Hudec, *Chem. Commun.*, 823 (1967); (f) R. C. Cookson and D. C. Warrell, *J. Chem. Soc., C*, 1391 (1967); (g) R. C. Cookson, *Quart. Rev. Chem. Soc.*, **22**, 423 (1968); (h) L. A. Paquette, G. V. Meehan, and R. F. Eizember, *Tetrahedron Lett.*, 995, 999 (1969); (i) H. Prinzbach, H. Hagemann, J. H. Hartenstein, and R. Kitzing, *Chem. Ber.*, **98**, 2201 (1965); and (j) P. J. Kropp, *J. Amer. Chem. Soc.*, **89**, 1126 (1967).

(3) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969). The constructive comments of Professor Hoffmann are greatly appreciated.

(4) Retention is expected if the rearrangement occurs in an excited state; however, if the change occurs in a vibrationally excited, electronic ground state inversion of configuration is predicted. An excellent discussion of thermal 1,3-sigmatropic reactions obviates the necessity of further elaboration here: J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

Ketone **4a** was prepared from 2-cyclopentenone by photocycloaddition with 1,2-dichloroethylene, ketalization, dehalogenation, hydrogenation, bromination, dehydrobromination, and hydrolysis[5] in an overall yield of 47%.[6] 7-Ketonorbornene, **6a**, was identified by comparison of infrared and nmr spectra with those of authentic material.[7,8] The synthesis of *exo*-6,7-bisdeuteriobicyclo[3.2.0]hept-3-en-2-one, **4b**, was accomplished as outlined above except that reduction with deuteriodiimide[10] was substituted for the hydrogenation step. Irradiation of **4b** as above gave 5,6-bisdeuterio-7-ketonorbornene.

Because of the simplicity of the nmr spectra of 7-ketonorbornenes,[11] determination of the stereochemistry of the allylic rearrangement is simply a matter of measuring the ratio of *endo* and *exo* protons in the dideuterated product.[12] The nmr spectrum of labeled 7-ketonorbornene obtained from irradiation of **4b** exhibits signals at δ 1.90 and 1.13 corresponding to the *exo* and *endo* protons, respectively, on C-5 and C-6. The integrated area of the lower field signal is 2.5 times that of the upfield one, indicating that the photochemical isomerization, **4** → **6**, proceeds with complete loss of stereochemistry at the migrating carbon.[13]

In order to eliminate loss of stereochemical integrity in ketone **4** *via* rapid equilibration with diradical **5** followed by a slower concerted isomerization of **4** to **6** as a possible course of events, we determined the stereochemistry of product and of recovered starting ketone both after *ca.* 70 and 25% disappearance of starting ketone **4**. The stereochemistry of product ketone, **6**, as determined by the nmr analysis outlined above, was invariant with reaction progress. Starting ketone, **4b**, underwent loss of stereochemistry at one of the labeled carbons, presumably C-6, relatively slowly; the stereomutation was *ca.* 50% complete at 25% reaction.

In a final control experiment, irradiation of *cis-exo*-5,6-dideuterio-7-ketonorbornene, **6d**,[14] under the conditions of the isomerization (0.040 *M* in pentane) gave only recovered material with no loss of stereochemistry, nor was decarbonylation observed.[15]

The experimental results outlined above clearly demonstrate the nonconcerted nature of the isomerization, **4** → **6**, and imply that the verbenone–chrysanthenone isomerization is likewise nonconcerted. The intermediacy of diradical **5** is strongly indicated.[16]

That the isomerizations reported here are nonconcerted does not detract from the theory of orbital symmetry conservation in concerted reactions, but serves to emphasize that relaxation of electronically excited species to ground-state diradicals is often the major path in photochemical reactions.

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[5] This sequence is a combination of methods first described by H. O. House and T. H. Cronin, *J. Org. Chem.*, **30**, 1061 (1965), and E. W. Garbish, *ibid.*, 30, 2109 (1965).

[6] Satisfactory combustion analyses as well as nmr, ir, and uv spectra of all new compounds and/or suitable derivatives thereof have been obtained.

[7] We thank Professor R. S. Bly for this comparison.

[8] The synthesis of **1** was similar to that of **4a**. See also R. L. Cargill, A. C. Miller, D. M. Pond, P. deMayo, M. F. Tchir, K. R. Neuberger, and J. Saltiel, *Mol. Photochem.*, **1**, 301 (1969). The structure of **2** rests on the spectral data, $\lambda_{\max}^{\mathrm{EtOH}}$ 270 nm (ϵ 21), $\bar{\nu}_{\max}^{\mathrm{CCl_4}}$ 1665 and 1785 cm^{-1}. The nmr spectrum exhibits a signal at 6.00 ppm (single vinyl hydrogen). Thermal decarbonylation to the known diene, **3**,[9] completes the structure proof.

[9] R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Amer. Chem. Soc.*, **85**, 3030 (1963). We thank Professor Bates for comparing the spectra of our diene with those of his sample.

[10] Exclusive *exo* deuteration was established by analysis of the 60- and 100-MHz nmr spectra of **4b**. The deuterium content of **4b** was determined by nmr and mass spectrometry to be 87% d_2, 10% d_1, and 3% d_0. We thank Professor P. G. Gassman for his advice concerning the deuteriodiimide reduction.

[11] The nmr spectra of norbornenes are discussed by A. P. Marchand and J. E. Rose, *J. Amer. Chem. Soc.*, **90**, 3724 (1968), and by B. Franzus, W. C. Baird, N. F. Chamberlain, T. Hines, and E. I. Snyder, *ibid.*, **90**, 3721 (1968), and references cited therein. A complete analysis of our spectra will be presented in the full paper.

[12] Given the deuterium analysis of **4b**, see ref 10, and making the reasonable assumption that in the monodeuterated species C-6 and C-7 are equally deuterated (*exo*), we may calculate the ratio of *exo* to *endo* protons in the product, **6**, for each of three limiting cases. For rearrangement occurring with complete retention of configuration at the migrating carbon, this ratio will be 12; for migration with complete inversion, 1.0; and for migration with complete loss of stereochemistry, 2.5. It is assumed in these calculations that the stereochemical integrity of C-7 is retained.

[13] From analysis of the deuterium-decoupled 100-MHz nmr spectrum of labeled photoproduct **6**, it is possible to rule out the presence of *cis-exo*-5,6-bisdeuterio-7-ketonorobornene (**6d**). A mechanism for isomerization of 4 involving dissociation into ethylene and cyclopentadienone followed by recombination in a Diels–Alder reaction is thereby excluded.

[14] This ketone was prepared from the corresponding alcohol, B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.*, **87**, 3423 (1965), by the method of R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963).

[15] The photodecarbonylation of **6** and related ketones is discussed by (a) D. I. Schuster, F-T. H. Lee, A. Padwa, and P. G. Gassman, *ibid.*, 30, 2262 (1965); (b) L. D. Hess, Ph.D. Dissertation, University of California, Riverside, Calif., 1965; quoted in J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 407; and (c) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966).

[16] It has been noted (ref 2f,g) that when the migrating carbon bears certain substituents, thermal and photochemical allylic shifts occur with loss of stereochemistry. Possible substituent effects on the photochemical isomerizations reported here are eliminated; therefore our results show that the nonconcerted path is the less energetic one for this type rearrangement.

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Reaction of Atomic Oxygen with Aromatic Hydrocarbons[1]

Sir:

Reactions of oxygen atoms with organic molecules have been reported by a number of investigators;[2,3] however, reactions with saturated hydrocarbons and aromatic compounds have received little attention, possibly due to the decreased reactivity of these compounds. Using the mercury photosensitized decomposition of nitrous oxide, Cvetanović[4] studied benzene and toluene in a circulating system. Benzene gave phenol while toluene gave three to four times as much *o*-cresol as *p*-cresol and less than 5% *m*-cresol in the volatile addition products.

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[2] (a) E. Murad and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **81**, 6405 (1959); (b) I. Haller and G. C. Pimentel, *ibid.*, **84**, 2855 (1962); (c) D. Saunders and J. Heicklen, *ibid.*, **87**, 2088 (1965).

[3] R. J. Cvetanović, *Advan. Photochem.*, **1**, 115 (1963).

[4] G. Boocock and R. J. Cvetanović, *Can. J. Chem.*, **39**, 2436 (1961); G. R. H. Jones and R. J. Cvetanović, *ibid.*, **39**, 2444 (1961).