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MECHANISTIC DICHOTOMY IN THE PHOTOREARRANGEMENT OF METHYLENE ANALOGS OF CONJUGATED CIS-BICYCLO[5.1.0]OCTENONES[1]

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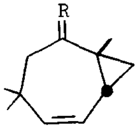
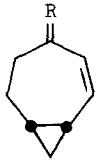
We have found that cis-bicyclo[5.1.0]octenones in which the cyclopropyl ring may be either flanked by the carbonyl group and the double bond, viz, 1a, or positioned in terminal conjugation with the enone system, viz, 2a, are subject to bond-switching rearrangements upon photolysis.[3] We describe here details of the photoreactivity of methylene analogs 1b and 2b which are particularly significant since these molecules lack n → π* excited states.

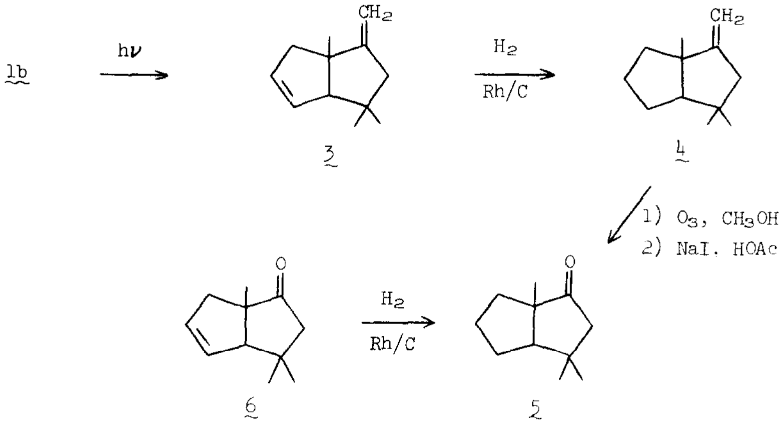


1a, R = O; b = CH$_2$

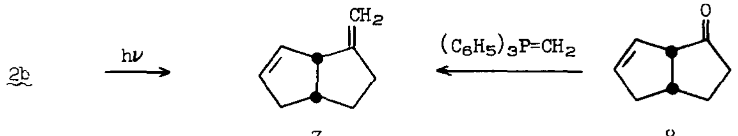


2a, R = O; b = CH$_2$

Reaction of 1,4,4-trimethyl-cis-bicyclo[5.1.0]oct-5-en-2-one (1a)[3] with methylenetriphenylphosphorane gave 1b in 50% yield as a colorless liquid:[4] bp 72-75° (1 mm); n^{24}_D 1.4887; ν_{max}^{neat} 1665, 1650, 1605, 1470, 1445, 905, 880, and 750 cm^{-1}; λ_{max}^{EtOH} strong end absorption; $\delta_{TMS}^{CDCl_3}$ 0.64-1.2 (broad multiplet, 3H, cyclopropyl protons), 0.98, 1.0, and 1.21 (singlets, 3H each, methyl groups), 2.18 (AB quartet, J_{AB} = 13 Hz, Δ_{AB} = 18 Hz, allylic methylene group), 5.00 (doublet, J = 12.0 Hz, H_5), 5.55 (doublet of doublets, J = 12.0 and 4.5 Hz, H_6), 4.82 and 5.03 (multiplets, 1H each, =CH$_2$). Direct irradiation of 1b in pentane or methanol (λ > 220 mμ, Vycor filter) yielded an isomeric hydrocarbon[4] as the major volatile photoproduct (24% and 56%, respectively, after 10 hr irradiation). There was also formed 1-3% of an unidentified product. In addition to the elemental analysis, the infrared and nmr spectra [$\delta_{TMS}^{CDCl_3}$ 0.88, 0.96, and 1.25 (singlets, 3H each, methyl groups), 2.04 (multiplet, 2H, methylene group at C_8), 2.30 (multiplet, 3H, methylene group at C_3 and methine proton at C_5)] of the primary rearrangement product were consistent with structure 3. Corroborative evidence for this formulation was ultimately derived by selective hydrogenation of 3 over 5% rhodium on carbon and ozonization of the resulting dihydro derivative 4[4] to the cyclopentanone 5 (ν_{max} 1745 cm^{-1}).[4] This compound was identical in all respects to the product of hydrogenation of ketone 6.[3] It was observed that irradiation of 1b in dilute acetone solution through either Vycor or Pyrex optics afforded only minute amounts of 3; extensive polymerization was noted. A similar result was obtained when we sought to generate the triplet of 1b by benzophenone sensitization (t-butyl alcohol solution) under conditions where the ketone absorbed over 97% of the incident radiation. The efficiency of the triplet transfer was unequivocally established in the latter series of experiments by effective quenching of benzopinacol formation by 1b when benzhydrol was added. Since 3 was independently found to be stable under these photolysis conditions, the polymerization cannot be construed as arising from the excited triplet state of 3.



In striking contrast, hydrocarbon 2b [bp 68-70° (20 mm);[4] ν_{max}^{neat} 1640, 1590, 1025, 885, 850, and 780 cm^{-1}; $\lambda_{max}^{isooctane}$ 237 mμ (ε 17,030); $\delta_{TMS}^{CCl_4}$ 0.22 (multiplet, 1H, cyclopropyl proton), 0.6-2.7 (broad absorption, 7H) 4.84 and 5.88 (singlets, 2H each, vinyl protons)], prepared in an analogous manner from cis-bicyclo[5.1.0]oct-2-en-4-one (2a),[3] was found to be transformed in high yield (95+%, vpc analysis, cyclooctane as internal standard) into a single photoproduct upon irradiation in dilute acetone solution (Pyrex). The colorless oil thus produced was readily identified as 7[4] by virtue of its spectral characteristics and unequivocal synthesis from ketone 8[5] via the Wittig reaction. When pentane was employed as solvent (Vycor filter), the process was more complex; bicyclic diene 7 was again formed as the major product (53% yield), but four additional minor components (not characterized) were also



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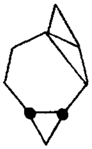
observed. A separate experiment clearly showed that these lesser products were not derived from 7 since, except for a small amount of polymer formation, the latter methylene analog was stable to the irradiation conditions. Since the triplet-sensitized process afforded only 7 and no side products, the occurrence of singlet transfer to 2b in acetone solution is very remote.

We can conclude that two fundamentally different mechanisms are operative in the photolysis of the two hydrocarbons. Thus, in the case of divinylcyclopropane 1b, there is a marked reluctance of the hydrocarbon triplet state to rearrange to 3. Since intersystem crossing of $S_1 \rightarrow T_1$ is not generally observed in olefinic systems it appears that, in the case of 1b, S_1 leads to rearrangement but the triplet only slowly polymerizes. This gross behavior in fact parallels the photochemistry of the structurally related ketone.[3] Most remarkable is the ease with which 2b rearranges to 7 under triplet conditions. This reactivity profile lies in marked contrast to the photochemical behavior which has been displayed by 1b, two conjugated methylenecyclohexenes,[6a,b] and a 1-methylene-2,5-cyclohexadiene derivative.[6c] In these latter examples, there is seen a complete absence of monomeric products in the sensitized experiments. A possible explanation for this differing behavior may be that the energy of the triplet $\pi \rightarrow \pi^*$ excitation of 2b is heavily concentrated in the conjugated diene moiety, a phenomenon which is expected to facilitate migration of the stereoelectronically favored internal cyclopropyl bond. Reaction products which are to be expected from bicyclobutane intermediate 9 were carefully sought but could not be found when 2b was irradiated directly in methanol.[7]



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Therefore, the cyclopropyl function appears to exert a significant influence on the reactivity of the transoid diene moiety in the excited states of 2b.

The highly stereoselective course of the conversion of 2b to 7 is significant and is comprehensible if rearrangement of the 1,7-bond is concerted or nearly so. The allowed symmetry of such a photoinduced sigmatropic shift of order [1,3] has been discussed earlier by Woodward and Hoffmann.[8] However, since the excited reactive species has triplet multiplicity, it may be argued that a concerted bond migration is improbable. More recently, Hoffmann[9] has reasoned that, in intramolecular rearrangements of this type, it is very likely that the orbital symmetry considerations which are operative in the excited state impose upon the molecule one set of motions which are facile and a second set of motions which are difficult. Since there exists no necessity to attain the excited state of product, the more favorable symmetry-allowed motions thus initiated could theoretically lead to the ground state product with emission of attendant radiationless energy.[10] Investigations relating to this phenomenon are continuing.

REFERENCES

(1) Appreciation is expressed to the Army Research Office (Durham) for partial financial support of this research.

(2) Ohio State University Postdoctoral Fellow, 1967-69.

(3) L. A. Paquette, G. V. Meehan, and R. F. Eizember, preceding paper.

(4) All new compounds described gave satisfactory elemental analyses ($\pm$ 0.30%).

(5) N. A. LeBel and L. A. Spurlock, Tetrahedron, 20, 215 (1964).

(6) (a) H. E. Zimmerman and G. E. Samuelson, J. Am. Chem. Soc., 89, 5971 (1967); (b) W. G. Dauben and W. A. Spitzer, ibid., 90, 802 (1968); (c) H. E. Zimmerman, P. Hackett, D. F. Juers, and B. Schröder, ibid., 89, 5973 (1967).

(7) Results in this instance were approximately the same as in pentane solution; no solvent incorporated products were seen.

(8) R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc., 87, 2511 (1965).

(9) R. Hoffmann, private communication.

(10) A very similar concept has recently been advanced in explanation of the photochemical interconversion of cis- and trans-5,6-diphenylbicyclo[3.1.0]hexan-2-ones: H. E. Zimmerman, K. G. Hancock, and G. C. Licke, J. Am. Chem. Soc., 90, 4892 (1968).