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2-METHYLENEBICYCLO[2.1.1]HEXANES: A NON-STEREOSPECIFIC, PHOTOSENSITIZED, CYCLIZATION REACTION OF TRIENES

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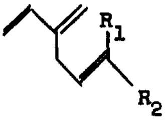
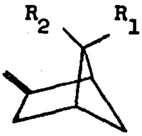
The photochemical synthesis of 2-methylenebicyclo-[2.1.1]hexane has recently been reported by de Mayo et al. (1) We wish to communicate here results of our independent studies on related systems and discuss their mechanistic implications.

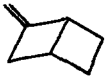
In agreement with de Mayo's report, we observed that irradiation of $\leq$ 2% solution of 3-methylene-1,5-hexadiene, Ia, in an inert solvent (n-hexane, benzene, or ether) in the presence of a photosensitizer (β-acetonaphthone, triphenylene, benzophenone, or fluorenone) led to quantitative conversion of the triene to a new hydrocarbon. We have also assigned the photoproduct the structure 2-methylenebicyclo[2.1.1]hexane, IIa, mainly based on analysis (calculated for C_7H_{10}: C, 89.28; H, 10.72. Found: C, 88.87; H, 10.66), molecular weight (94 by mass spectroscopy) and n.m.r. spectrum. The spectrum is shown in Fig. I. The high field quartet, centered at 1.15 p.p.m. and of relative area 2.0, is assigned to the endo methylene protons (H_2) (2), and the multiplets centered at 1.80, 2.17 p.p.m. of relative area 2.0 each to exo-methylene and allylic



I



II



III

a: $R_1 = R_2 = H$

b: $R_1 = H$ $R_2 = CH_3$

c: $R_1 = CH_3$ $R_2 = H$

d: $R_1 = CH_3$ $R_2 = CH_3$

protons respectively. The two multiplets, centered at 2.54 and 2.89 p.p.m. with relative area of 1.0 each, have a gross feature of two doublets with a coupling constant of 7.0 c.p.s. These are due to the bridgehead protons H_1 and H_4. The magnitude of the coupling constant is somewhat surprising, although not unreasonable, in view of the reported large

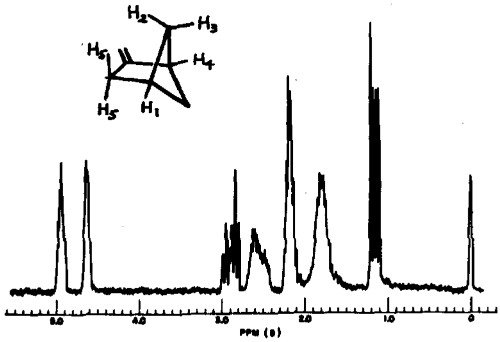


FIG. I

N.m.r. Spectrum of IIa in CCl_4 (TMSi as internal standard) coupling constant (J = 18 c.p.s.) between the bridgehead protons in bicyclo[1.1.1]pentane. (3) The lower-field doublet is further split into two triplets, indicating the signal must be due to H_4. (4) The alternative structure of 2-methylene-bicyclo[2.2.0]hexane, III, cannot account for all the features in the n.m.r. spectrum. None of the protons in III should give signals at an unusually high field of 1.15 p.p.m., (5) a smaller coupling constant between the tertiary protons would be expected, and because of lack of symmetry, a more complicated spectrum would be expected. Furthermore, on oxidative ozonization, a ketone was obtained which shows identical carbonyl absorption (1755 cm.^{-1}) to that reported by de Mayo.

Similarly, irradiation of Id gave one product only. Its n.m.r. spectrum shows singlets at 0.78, 1.28 p.p.m. (3 protons each), a doublet (1 proton) centered at 0.99 p.p.m., a multiplet between 1.93-2.62 p.p.m. (5 protons), and two low-field multiplets centered at 4.64 and 4.87 p.p.m. (1 proton each). It is consistent with structure IId. However, irradiation of either a solution of Ib or Ic gave an identical product mixture of two products in a ratio of 5.8 to 1. By comparison of their n.m.r. spectra with those of IIa and IId, we have assigned structure IIb to the major product and IIc to the minor. We have observed that throughout the reaction the relative amounts of the two products remained the same regardless of the composition of the triene mixture, while at the same time the relative amounts of the starting materials were found unchanged (see Table).

TABLE

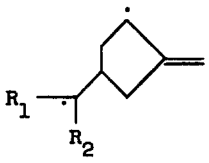
Relative Amounts of Reactants and Products During Irradiation[a]

	Percentage of		Percentage of	
Conversion	Ib	Ic	IIb	IIc
0	97	2.9	-	-
45%	98	2.4	86	14
84%	[b]		85	15
100%	-	-	86	14
0	13	87	-	-
50	13	87	85	15
54	13	87	85	15
100	-	-	86	14

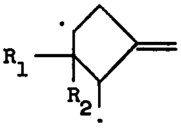
[a] Degassed MeOH solution of 2% trienes with triphenylene as sensitizer, irradiated with AH-3 lamp with Pyrex vessels.

[b] Concentration of Ic too low for accurate measurement.

We believe that these results clearly indicate the presence of long lived intermediates in these reactions, a point assumed in mechanistic discussions of previous studies of sensitized reaction of dienes (6). The identity of the product mixtures in the cases of IIb and IIc suggests either the presence of a common intermediate or different but rapidly equilibrating intermediates. The rotational isomers of a diradical intermediate are probably initially formed and equilibrate rapidly prior to ring closure to the final products. Structures IV and V are the two internally cyclized diradicals which could lead to the correct products. However, only IV can exist in two rotational isomeric forms. Further, on the grounds of energy considerations, V is an unlikely intermediate in these reactions. (7) The long lifetime of diradical IV is probably due to the inherited triplet spin multiplicity. This result is particularly interesting in



IV



V

view of the observation that the rate of spin inversion of triplet trimethylene diradical, formed by addition of triplet carbene to olefin, is comparable to the rate of rotation around a single bond (8). Extending the separation of the unpaired electrons apparently increases the lifetime of the diradicals. Our results also indicate that energy transfer to the isolated double bond has not occurred and that the diradical intermediates once formed do not revert back to the starting material.*

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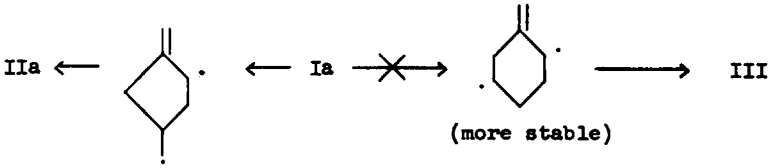
*It has been pointed out by a referee that the nature of the product cannot be explained in terms of relative stabilities of the diradical intermediates:



This is in direct contrast with the myrcene photoproduct. (2) Presently we cannot offer an attractive explanation. The problem is still under consideration.

It is interesting to compare the above results with those of direct irradiation of Ib and Ic. We have found that with dilute solutions of the trienes, two major products, which are different from IIb and IIc, are formed, and together they account for 85% of the product mixtures. These products have not yet been isolated and identified. Based on known chemistry of dienes under direct irradiation, (9) we believe that the products are the corresponding cyclobutenes. Among the four minor products, we have found (by comparison of v.p.c. retention times) that IIb and IIc are also formed under these conditions. However, starting with a triene mixture of 97% Ib and 3% Ic, IIb and IIc were obtained in a relative ratio of 2.3:1.0, while a mixture of 13% Ib and 87% Ic gave a ratio of 1.4:1.0. These ratios are also invariant throughout the reactions. Unfortunately, due to the complexity of the reactions under such conditions, mechanistic implications are not as clear. We can safely assert, however, that if formation of these products also involves step-wise mechanisms, the intermediates must be different from those in the sensitized reactions. Among other possible explanations, the difference can be attributed to the difference in spin multiplicities, *i.e.*, singlet diradical intermediates are involved under these conditions.

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* Contribution No. 1192

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3. K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler and J. Lavanish, Tetrahedron, 21, 2749 (1965).
4. (a) The assignment is in agreement with Wiberg's[4b] finding that in bicyclo[2.1.1]hexanes (Fig. I) $|J_{3,4}| = 2.6\text{-}3.3$ c.p.s. and $|J_{2,4}| \sim 0$ c.p.s.
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