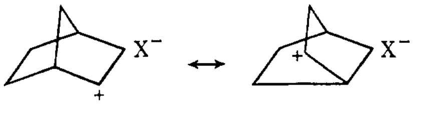
mides indicates that there is a fundamental electronic difference in the transition states that are involved. In view of the fact that this difference is in the direction that one would expect if participation during the ionization step occurred, we are forced to conclude that our findings provide compelling support for Winstein's[4] suggestion that the transition states for the solvolysis of simple *exo*-norbornyl compounds are nonclassical.[8]

This conclusion is based on the following argument. For a classical norbornyl cation that arises from the solvolysis of an *exo*-oriented exiphile, the secondary isotope effect (k_H/k_D) is approximately 1.18 ± 0.02 for two deuterium atoms. If the charge at C_2 is delocalized between C_1 and C_2 in the transition state, the magnitude of the effect would be diminished by a factor of $(1.18)^n$, where n is the fraction of the charge associated with C_2. For a transition state in which the resonance forms are equal contributors, only one-half of the electronic charge would reside on C_2. The isotope effect that would be associated with a transition state approximating this situation would therefore be $(1.18)^{1/2}$ or 1.085; this value corresponds exactly to what was observed for the solvolysis of *exo*-norbornyl bromide.[1,10]



[8] Brown[9] has argued that, because parallels exist between the solvolysis rates of compounds that lead to classical norbornyl cations, the stereochemical fate of these cations, and the behavior of the parent norbornyl systems, these data cannot logically be used as a foundation for postulating nonclassical behavior for the parent system. Unfortunately, the perturbations that result from the conversion of a secondary system to a tertiary system introduces additional factors (*e.g.*, new steric effects) that cloud the interpretation of data and cast doubt upon the validity of arguments based upon the analogous behavior of secondary and tertiary systems. The difference in secondary isotope effects for these two systems clearly demonstrates that tertiary norbornyl systems should not be used as models for the norbornyl cation.

[9] A summary of H. C. Brown's arguments along with numerous references to his papers can be found in *Chem. Eng. News*, **45**, 86 (Feb 13, 1967).

[10] It would be erroneous to conclude that the excellent agreement between the observed isotope effect and that calculated on the basis of the above model requires that in the transition state for solvolysis of simple *exo*-norbornyl derivatives the norbornyl fragment must be completely symmetrical. A transition state in which bridging was only one-third complete could not be distinguished from the above model due to the experimental uncertainties that are involved in the isotope effects.

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Received April 26, 1968

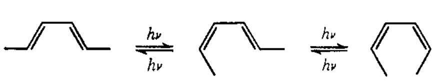
Mechanism of the Photochemical Valence Tautomerization of 1,3-Butadienes

Sir:

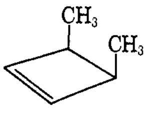
Irradiation of 1,3-butadiene is known to give rise to cyclobutene (1a) and bicyclo[1.1.0]butane (1b), the former being the major product.[1] While the experimental evidence strongly suggests that both processes occur from the excited singlet state of 1,3-butadiene,[2a] the difference between the two reaction pathways has never been satisfactorily explained. On the basis of a study of the photoisomerization of the stereoisomers of 2,4-hexadiene, we propose that (1a) is a concerted process, while (1b) is most probably a stepwise reaction.[2b]

(1)

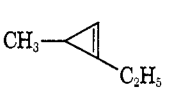
The photoisomerizations of *trans,trans*-, *cis,trans*-, and *cis,cis*-2,4-hexadienes were studied in ether solution at 2537 Å. The stereoisomerizations indicated by (2) rapidly led to a photostationary state in which the concentrations corresponded to *trans,trans* 35.7%; *cis,trans* 30.5%; *cis,cis* 33.7%. At the same time, four other isomers (mol wt by mass spectrometry = 82) were also formed more slowly. The most important of these amounted to 33% of the hexadiene that disappeared. Its ir (strong absorptions at 727, 2950, and 3020 cm^{-1}) and nmr spectra (τ 3.98 (2 H), singlet; ~7.1 (2 H), multiplet; 9.02 (6 H), doublet (J = 7 cps) with fine structure) when considered together with the fact that it isomerized cleanly at 180° to give *cis,-trans*-2,4-hexadiene showed that it was *cis*-3,4-dimethylcyclobutene (I). The stereochemistry of the thermal decomposition of this molecule has already been demonstrated by Winter[3] to be conrotatory.



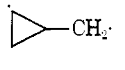
(2)



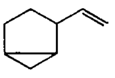
I



II



III



IV

The second isomer which accounted for about 5% of the hexadiene that disappeared had infrared absorptions at 1775 and 1725 cm^{-1} (m) as well as at 1375 and 1360 cm^{-1} (m). The nmr spectrum consisted of a broad (half-width 4 cps) absorption (1 H) at τ 3.45, an octet at 7.5 (2 H), and a complex absorption from 8.5 to 9.1 (7 H). In the 100-Mc spectrum,[4] the last absorption could be resolved into an octet (1 H) at τ 8.6, a symmetric triplet at 8.86 (3 H), and a doublet at 8.99 (3 H). Decoupling experiments showed that the absorptions at τ 7.5 and 8.86 could be attributed to the CH_2 and CH_3 of an ethyl group while the proton at τ 8.6 and the three protons at 8.99 could be due to a $>CHCH_3$ group. The lone proton at τ 3.45 was coupled to all of these protons with coupling constants which ranged from 1.8 cps for the CH proton to 1.0 cps for the CH_3 of the ethyl group. The presence of an ethyl and a methyl group left only three carbons to account for. Two of these presumably formed the ends of an olefinic group while the third carbon was not olefinic. The infrared absorption at 1775 cm^{-1} is quite close to the C=C stretching frequency in 1,3-dimethylcyclopropene[5] of 1773 cm^{-1}. The structure which would fit all of these data is that of 1-ethyl-3-methylcyclopropene (II).

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[1] R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 4045 (1963).

[2] (a) R. Srinivasan, *Advan. Photochem.*, **4**, 113 (1966). (b) It is assumed that the same mechanism is operative in the valence tautomerization of all linear 1,3-dienes.

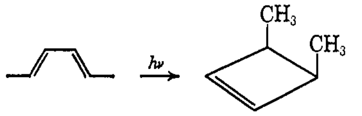
[3] R. E. K. Winter, *Tetrahedron Letters*, 1207 (1965). We thank Dr. Winter for supplying us with the spectral data for I for comparison.

[4] We thank Dr. C. S. Yannoni of this laboratory for these spectra.

[5] G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 74 (1966).

The third and fourth isomers which were formed in 1-2% yield were identified as *trans*- and *cis*-1,4-hexadienes, respectively, by comparing their ir and nmr spectra with those of authentic material.

Rate studies which were carried out separately on the three 2,4-hexadiene isomers at conversions (to all other isomers) of less than 10% showed that the rate of formation of *cis*-3,4-dimethylcyclobutene (I) was detectable only when pure *trans,trans*-2,4-hexadiene was used. From the other two 2,4-hexadiene isomers the formation of I was observed only when more than 25% *trans,trans*-2,4-hexadiene had accumulated in the system. This leaves no doubt that I is formed exclusively by the photoisomerization of *trans,trans*-2,4-hexadiene (eq 3).

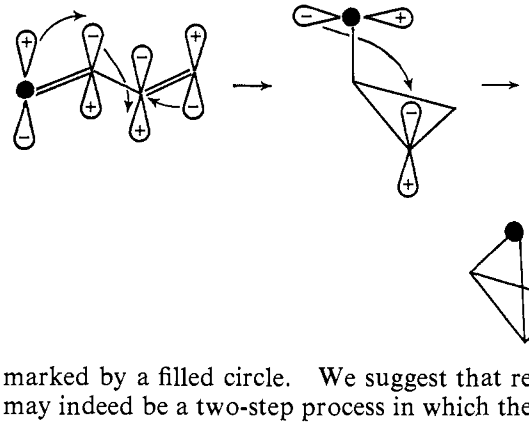


(3)

The quantum yield for this reaction was less than 0.01.

The application of the rules proposed by Woodward and Hoffmann[6] to the valence tautomerization of 2,4-hexadiene would predict that closure to a cyclobutene in the electronically excited state be disrotatory. This is clearly verified by reaction 3. While there are other examples in the literature[7a] of the photochemical closure of 1,3-dienes by a disrotatory process, this is believed to be the first example in which (i) the stereochemistry of the reactant is established and (ii) the diene is linear so that it does not have any constraints on its mode of closure.

The formation of bicyclo[1.1.0]butane by (1b) if it were a smooth concerted process in accordance with orbital symmetry would lead to a *trans*-fused bicyclic system.[7b] Alternatively, the reaction can proceed as in (4) which involves a stepwise motion of the carbon marked by a filled circle. We suggest that reaction 1b may indeed be a two-step process in which the diradical III is a definite intermediate. This would explain (i) the formation of the cyclopropene II from III by a hydrogen migration; (ii) the observed formation of the dimer IV as the major dimeric product in the direct irradiation of 1,3-butadiene[8] (this product can be viewed as the adduct of the diradical III to butadiene); and (iii) the ready rearrangement of 1,3-butadiene to a methyl and a C_3H_3 radical in gas-phase photolysis and the additional fact that deuterium labeling shows a wide degree of scrambling of the H atoms among all four carbon atoms.[9]



(4)

It is reasonable to expect that the initial step in (4) is reversible since an activation energy must exist for the closure of the second three-membered ring. This would explain the preponderance of cyclobutene (which is formed by a symmetry-allowed concerted process) to bicyclobutane in the valence tautomerization of 1,3-butadiene even though in its ground state butadiene is predominantly transoid in geometry and not favorably disposed toward (1a).

Acknowledgment. It is a pleasure to acknowledge the able technical assistance given by Mrs. Jane M. Picone.

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[6] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), and earlier references therein.

[7] (a) K. J. Crowley, *Tetrahedron*, **21**, 1001 (1965); W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *J. Am. Chem. Soc.*, **88**, 2742 (1966). (b) Such a process would involve the rotation of the lobes at all four carbon atoms in the same sense when viewed along a line parallel to the double bands in the transoid form of 1,2-butadiene.

[8] R. Srinivasan and F. I. Sonntag, *J. Am. Chem. Soc.*, **87**, 3778 (1965).

[9] I. Haller and R. Srinivasan, *ibid.*, **88**, 3694 (1966).

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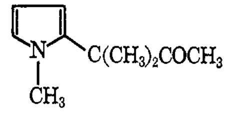
Received June 6, 1968

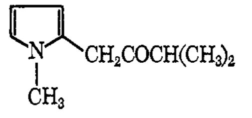
Cyclopropanones. X. Reaction of 2,2-Dimethylcyclopropanone and N-Methylpyrrole. A New Entry into the Tropinone Series[1]

Sir:

Treatment of 2,2-dimethylcyclopropanone (**1**) with N-methylpyrrole followed by concentration and preparative vpc results in isolation of **2** and **3**.[2] Two mechanisms were proposed[2] to explain these results. One involved the rearrangement of the intermediate tropine **4**, and the second involves the proposed attack of the zwitterion[3] **5** on N-methylpyrrole (Scheme I). We wish to report evidence for the former mechanism and point out a new entry into the tropine family of alkaloids.[4]

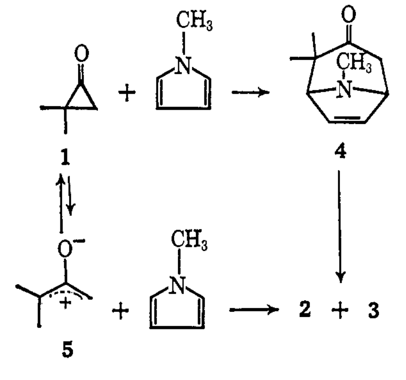


2



3

Scheme I



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[1] (a) This research was supported by the Air Force Office of Scientific Research (Grant AFOSR-68-1381). A generous gift from the Upjohn Co. is also gratefully acknowledged. (b) Paper IX: N. J. Turro and W. B. Hammond, *Tetrahedron*, in press.

[2] N. J. Turro, S. S. Edelson, J. R. Williams, and T. R. Darling, *J. Am. Chem. Soc.*, 90, 1926 (1968).

[3] J. G. Burr and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954).

[4] The synthesis reported here appears to be the simplest known for preparing 2,2-dialkylated tropine derivatives.