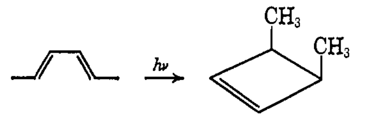
The third and fourth isomers which were formed in 1-2% yield were identified as *trans*- and *cis*-1,4-hexadienes, respectively, by comparing their ir and nmr spectra with those of authentic material.

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).

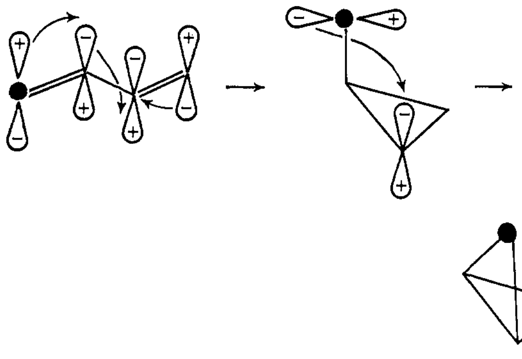


(3)

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).

R. Srinivasan
IBM Watson Research Center
Yorktown Heights, New York 10598

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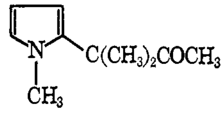
Cyclopropanones. X. Reaction of 2,2-Dimethylcyclopropanone and N-Methylpyrrole. A New Entry into the Tropinone Series[1]

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]



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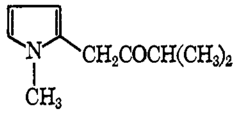

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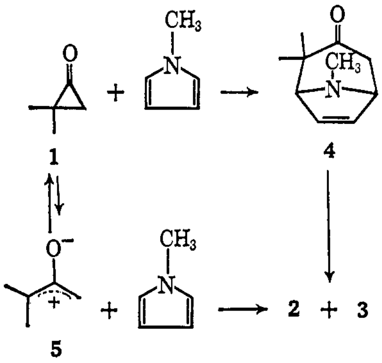
Scheme I



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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).

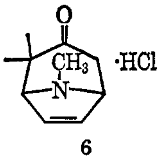
[4] The synthesis reported here appears to be the simplest known for preparing 2,2-dialkylated tropine derivatives.

Treatment of **1** with purified N-methylpyrrole resulted in the formation of **4** in approximately 50% yield (nmr). Extraction with 1% aqueous HCl followed by neutralization resulted in the isolation of **4**, purity approximately 90%; nmr (neat), δ 0.87 (s, 3 H), 1.23 (s, 3 H), 2.24 (s, 3 H), 2.37 (AB, 2 H, $\Delta\nu_{AB}$ = 34.8 Hz, J_{AB} = 16 Hz, high-field half split further, J = 2 Hz, low-field half split further, J = 4.5 Hz), 3.16 (m, 1 H), 3.50–3.70 (m, 1 H), 5.97–6.25 (m, 2 H) (integration approximate due to impurities); ir, $\lambda_{max}^{CCl_4}$ 3.27, 3.61, and 5.86 μ; mass spectrum (75 eV), *m/e* (relative intensity) 165 (10.7 M^+), 123 (0.75), 122 (6.2), 95 (36.9), 94 (100). The nmr of **4** is very similar to that of the previously reported **1**–furan adduct.[5]

Treatment of **4** with methanolic HCl was followed by the isolation of the hydrochloride **6**: nmr ($CDCl_3$), δ 1.16 (s, 3 H), 1.79 (s, 3 H), 2.65 (d of d, 1 H, J = 18 Hz, J = 2 Hz), 3.17 (s, 3 H), 4.05 (d of d, 1 H, J = 18 Hz, J = 4 Hz), 4.38 (s, 1 H), 4.53–4.75 (m, 1 H), 6.51 (m, 2 H), 11.23–13.06 (1 H); ir, λ_{max}^{KBr} 5.82 μ; mass spectrum (75 eV), *m/e* (relative intensity) 165 (4.0, M^+), 123 (0.67), 122 (3.6), 95 (27.8), 94 (100). *Anal.* Calcd for $C_{10}H_{16}NOCl$: C, 59.55; H, 8.00; N, 6.95; Cl, 17.58. Found: C, 59.31; H, 8.08; N, 6.75; Cl, 17.61.

Compound **4** was subjected to preparative vpc workup under the same conditions used previously.[2] This procedure resulted in the collection of a mixture of **2** and **3** in the ratio **3**:**2** = 6:1 (nmr). The uncorrected vpc yield of **2** and **3** was approximately 50%.

Reduction of **4** (H_2–Pd–C) followed by preparative vpc led to the isolation of 336 mg (31%) of **7**: nmr[6] ($CDCl_3$), δ 1.00 (s, 3 H), 1.29 (s, 3 H), 1.35–2.24 (m, 5 H), 2.35 (s 3 H), 2.58–3.07 (m, 2 H), 3.17–3.48 (m, 1 H); ir, λ_{max}^{neat} 3.60 μ, 5.86; mass spectrum[7] (75 ev), *m/e* (relative intensity) 167 (19.6, M^+), 82 (100). *Anal.* Calcd for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.38. Found: C, 71.61; H, 10.38; N, 8.54.



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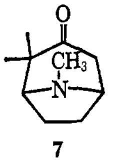

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(5) W. B. Hammond and N. J. Turro, *J. Am. Chem. Soc.*, **88**, 2880 (1966); W. B. Hammond, Ph.D. Dissertation, Columbia University, 1967.

(6) These values are consistent with the values for tropinone: R. J. Bishop, G. Fodor, A. R. Katritzky, F. Soti, L. E. Sutton, and F. J. Swinbourne, *J. Chem. Soc., C*, 74 (1966).

(7) This spectrum correlates with that of tropinone: H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 92.

(8) Alfred P. Sloan Fellow, 1966–1970.

(9) National Science Foundation Predoctoral Trainee, 1965–1966; National Science Foundation Predoctoral Fellow, 1966–present.

Nicholas J. Turro,[8] Simon S. Edelson[9]
Chemistry Department, Columbia University
New York, New York 10027

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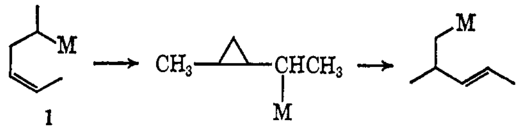
Coordination-Catalyzed Skeletal Rearrangement of *cis*- and *trans*-2-Methylvinylcyclopropanes

Sir:

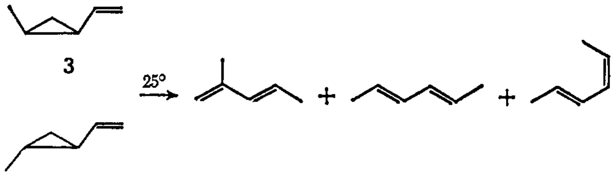
We recently reported the skeletal rearrangement of *cis*-1,4-hexadiene to *trans*-2-methyl-1,3-pentadiene by a nickel-based coordination catalyst.[1,2] One possible reaction path for this transformation would involve the intervention of a cyclopropylcarbinylnickel derivative, **2**, derived from rearrangement of **1**.[3] Interaction of



cis- and *trans*-2-methylvinylcyclopropanes (**3** and **4**) with the catalyst would be expected to generate the respective *cis* and *trans* isomers of **2** if the catalyst is capable of transferring the elements of nickel hydride to olefinic bonds.[1,5] With this in mind, we have examined the behavior of **3** and **4** in the presence of the catalyst.

The methylvinylcyclopropanes were prepared by thermolysis of a 1:1 mixture of *trans*- and *cis*-3-methyl-5-vinylpyrazolines, prepared by reaction of butadiene with diazoethane, using the general procedure reported by Crawford.[6] The resulting 1:1 mixture of *trans*- and *cis*-2-methylvinylcyclopropanes was resolved, and the compounds were collected *via* preparative glpc. Structure assignments were confirmed by comparison of the nmr and infrared spectra with those reported by Roth and König,[7] who synthesized the compounds by a different route.

Addition of diisobutylaluminum chloride to toluene solutions containing *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II) and either **3** or **4** (olefin:Al:Ni, 18:-4.5:1) at 25° results in the formation of *trans*-2-methyl-1,3-pentadiene and *trans,trans*- and *trans,cis*-2,4-hexadienes. *trans*-2-Methyl-1,3-pentadiene is the major isomeric product in each case. At −22°, **3** and **4** remained essentially unchanged during a 3-hr period (<2% conversion) in the presence of the catalyst components. However, the addition of ethylene to the reaction mixtures at −22° has a remarkable effect on the rate of formation of isomeric products. Thus, **3** was converted quantitatively into products within *ca.* 5 min when the above olefin:Al:Ni ratio was employed. The dimerization of ethylene also occurred.



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(1) R. G. Miller, *J. Am. Chem. Soc.*, **89**, 2785 (1967).

(2) Subsequent experiments by Mr. Dennis Baker have uncovered the related conversion of 1,4-pentadiene into 2-methyl-1,3-butadiene and *trans*- and *cis*-1,3-pentadienes.

(3) A large body of evidence supporting the participation of a cyclopropylcarbinyl Grignard reagent in the interconversion of allylcarbinyl Grignards has been obtained by Roberts and coworkers.[4]

(4) (a) M. S. Silver, P. A. Shafer, J. E. Nordlander, C. Rüchardt, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 2646 (1960); (b) D. J. Patel, C. L. Hamilton, and J. D. Roberts, *ibid.*, **87**, 5144 (1965); M. E. H. Howden, A. Maercker, J. Burdon, and J. D. Roberts, *ibid.*, **88**, 1732 (1966).

(5) R. G. Miller, T. J. Kealy, and A. L Barney, *ibid.*, **89**, 3756 (1967).

(6) R. J. Crawford and D. M. Cameron, *Can. J. Chem.*, **45**, 691 (1967).

(7) W. R. Roth and J. König, *Ann. Chem.*, **688**, 28 (1965). The compounds were first reported by R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 5578 (1964).