The results obtained with the β-lactams, when compared with those for the azetines, serve to emphasize that the carbonyl compounds have available to them a reaction path which is inaccessible to **5** and **6**. Although direct comparisons of reaction rates in the two different systems cannot be made in this instance, it is quite possible that such behavior is the result of two distinctly different concerted processes: $[{}_{\sigma}2_{s} + {}_{\sigma}2_{a}]$ retrogression in the case of **1** and **2** and conrotatory opening in the case of **5** and **6**.

Acknowledgment. We thank the National Science Foundation, Eli Lilly and Co., and Lederle Laboratories, American Cyanamid Co., for support of this research.

(14) (a) National Science Foundation Undergraduate Research Participant, Summers 1968, 1969; (b) Senior Education Awardee, American Cyanamid Company, 1969-1970.

Leo A. Paquette, M. J. Wyvratt,[14a] George R. Allen, Jr.[14b]
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

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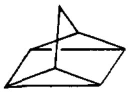
The Tricyclo[4.1.0.0^{2,5}]hept-3-ene to Quadricyclane Rearrangement. Intramolecular Trapping of a 1,3 Diradical by a Remote Cyclobutene Ring

Sir:

Because the total strain energy in the quadricyclane ring system (**1**) is extremely high (95 kcal/mol),[1] the preparation of such molecules by customary ground-state reactions has not proven feasible, even when symmetry-allowedness is favorable.[2] Instead, the photorearrangement of norbornadiene derivatives has been frequently utilized as the synthetic entry to quadricyclanes.[3] At this time, we wish to report on an exceptionally facile approach to the *trans*-tricyclo[4.1.0.0^{2,5}]hept-3-ene nucleus (**2**) and also to exemplify the thermal rearrangement of such alicyclic structures to quadricyclane derivatives. The driving force behind such a novel transformation, the result of intramolecular trapping of a 1,3 diradical by a remote cyclobutene ring, is very likely derived from the presence in **2** of strain energy greater than 100 kcal/mol.



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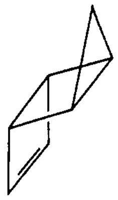

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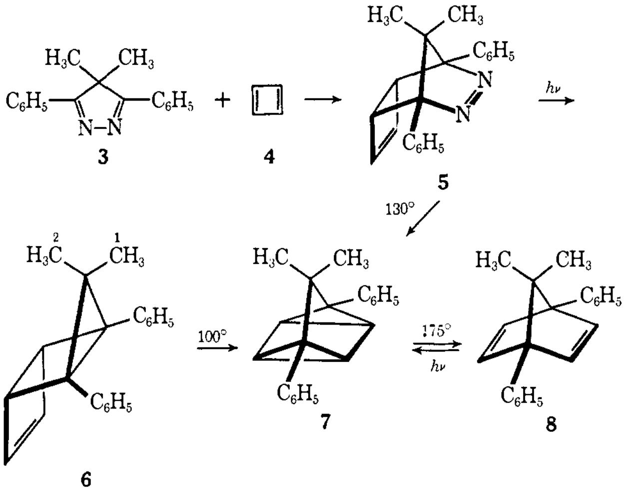
Exposure of isopyrazole **3**[4] to cyclobutadiene (**4**), generated *in situ* from ceric ion oxidation of cyclobutadieneiron tricarbonyl,[5] afforded in 65% yield the tricyclic azo compound **5**, mp 153–154°;[6] $\lambda_{\max}^{C_2H_5OH}$ 343 (ε 64) and 353 nm (ε 64); $\delta_{TMS}^{CDCl_3}$ 0.28 (s, 3, $-CH_3$), 1.04 (s, 3, $-CH_3$), 3.88 (s, 2, allylic), 6.05 (s, 2, vinyl), and 7.32–7.80 (m, 10, aryl). Irradiation of **5** in ether solution with a 200-W Hanovia lamp (Pyrex filter) for 3 hr produced **6** in quantitative yield: mp 65.5–67°;[6] $\delta_{TMS}^{CDCl_3}$ 0.88 (s, 3, 1–CH_3), 1.44 (s, 3, 2-CH_3), 3.36 (d, J = 1.5 Hz, 2, allylic), 6.41 (d, J = 1.5 Hz, 2, vinyl), and 7.22 (m, 10, aryl). The *trans* stereochemistry of **6** and the spatial relationships of the two methyl groups were established experimentally by application of nuclear Overhauser effects.[7] Thus, of the two methyl groups, that labeled 1-CH_3 is sufficiently distant from the allylic and vinyl hydrogens that it should not contribute to the relaxation of either proton type. In line with this consideration, double irradiation of the δ 0.88 singlet did not result in any significant intensity change of either the 3.36 or 6.41 signals. Saturation of the δ 1.44 methyl singlet, however, reproducibly gave evidence of a 7% intensity enhancement in the 3.36 absorption. Accordingly, the 2-CH_3 group and the allylic hydrogens must be proximal, an observation which requires the spatial relationship embodied uniquely in the *trans* isomer. The relatively small NOE effect is due to the mutual relaxation of the two allylic hydrogens such that outside protons contribute less by comparison.



Although nitrogen elimination from **5** has apparently proceeded with retention of configuration, no definite stereochemical conclusions should be drawn at this time in the absence of low-temperature studies (now in progress) which may shed light on the possible intervention of the ephemeral *cis* isomer.[8]

Thermolysis of **6** in tetrachloroethylene solution at 100° could be conveniently monitored by nmr spectroscopy. After approximately 4 hr, quantitative conversion to quadricyclane **7** was observed. Evaporation of the solvent and recrystallization of the residue from ethanol gave long white needles, mp 136.5–

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(1) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968).

(2) N. Rieber, J. Alberts, J. A. Lipsky, and D. M. Lemal, *ibid.*, **91**, 5668 (1969).

(3) See, for example: (a) S. J. Cristol and R. L. Snell, *ibid.*, **80**, 1950 (1958); (b) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961); (c) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Amer. Chem. Soc.*, **83**, 4674 (1961); (d) P. G. Gassman, D. H. Aue, and D. S. Patton, *ibid.*, **90**, 7271 (1968); (e) J. R. Edman, *ibid.*, **91**, 7103 (1969), and pertinent references cited therein.

(4) A. B. Evnin and D. R. Arnold, *ibid.*, **90**, 5330 (1968).

(5) (a) L. A. Paquette and L. D. Wise, *ibid.*, **89**, 6659 (1967); (b) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965).

(6) Satisfactory elemental analyses (±0.3%) were obtained for all new compounds.

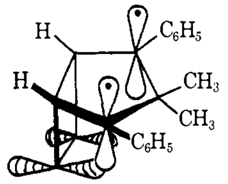
(7) For a recent review, see G. Moreau, *Bull. Soc. Chim. Fr.*, 1770 (1969). The stereochemistry of **5** was established in a comparable NOE study.

(8) Exceptionally rapid stereomutation of the *cis* isomer can be expected if it does intervene. Compare the ease of equilibration of bicyclo[2.1.0]pentane derivatives: M. J. Jorgenson, R. J. Clark, and J. Corn, *J. Amer. Chem. Soc.*, **90**, 7020 (1968); C. Mackenzie, W. P. Lay, J. R. Telford, and D. L. Williams-Smith, *Chem. Commun.*, 761 (1969).

138° (60% isolated yield);[6] $\lambda_{\max}^{\text{isooctane}}$ 234 nm (ϵ 8900); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 1.03 (s, 6, $-CH_3$), 2.02 (s, 4, cyclopropyl), and 7.29 (s, 10, aryl). The identical substance was isolated from the thermal decomposition of **5** at 135° in $Cl_2C{=}CCl_2$. When the thermolysis of this azo compound at different temperatures was monitored by nmr spectroscopy, it was noted that nitrogen evolution and quadricyclane production were quite slow at 125°. At 135°, however, the conversion was complete after several hours.

Assignment of the quadricyclane structure to **7** follows from its ultraviolet absorption[9] and the highly symmetrical nature of its nmr spectrum. In particular, the absence of vinyl protons demands that the molecule be tetracyclic. Chemical substantiation of the quadricyclane formulation was derived by thermal rearrangement of **7** ($Cl_2C{=}CCl_2$ solution) at 175°. At this temperature, **7** was converted cleanly to the norbornadiene derivative **8**: mp 188–190°;[6] $\lambda_{\max}^{\text{isooctane}}$ 253 (ϵ 670), 258 (ϵ 695), and 266 nm (ϵ 485); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 0.83 (s, 6, $-CH_3$), 7.07 (s, 4, vinyl), and 7.40 (s, 10, aryl). Irradiation of **8** in hexane solution through quartz optics resulted in reconversion to **7**.

Since the thermal rearrangement of **6** to **7** is the formal result of a $_{\sigma}2_s + {}_{\pi}2_s$ cycloaddition, a concerted rebonding process is intrinsically orbital-symmetry forbidden.[10] Rather, the C_2–C_5 bond almost certainly suffers homolytic rupture with formation of 1,3-diradical **9**.[11] Intramolecular trapping of the diradical appears to occur to the exclusion of other possible reactions, in contrast with earlier attempts to trap other 1,3-diradicals on an intermolecular basis with such simple olefins as isobutylene.[12] Because the thermal decomposition of azo compound **5** requires temperatures (135°) in excess of those required for the **6** → **7** rearrangement (100°), no firm conclusions regarding the mechanism of this fragmentation can be drawn at the present time. However, one might expect that, if the required $_{\sigma}2_s + {}_{\sigma}2_s + {}_{\pi}2_s$ transformation were concerted, a more ready fragmentation would be encountered. Since the cost of symmetry forbiddenness is necessarily a function of the reaction under study, a firm answer must await the synthesis of the *exo* isomer of **5** and a comparison of the two rates of decomposition.



9

The ready availability of *trans*-tricyclo[4.1.0.0^{2,5}]hept-3-enes by means of this direct and apparently general synthesis[13] now causes these alicyclic molecules to became an attractive focus of further synthetic and mechanistic study. Those aspects of this research presently under active investigation will be reported in subsequent papers.

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[14] National Institutes of Health Predoctoral Fellow, 1969–present.

Leo A. Paquette, Louis M. Leichter[14]
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

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Cycloaddition of Ethoxyketene to Olefins

Sir:

We wish to report the preparation and subsequent cycloaddition of the elusive ethoxyketene intermediate to a series of simple olefins. An interesting facet of these cycloadditions is their unusual stereoselectivity[1] which appears to show a gratifying correlation with the Woodward–Hoffmann orbital symmetry conservation rule.

Ethoxyketene was prepared *in situ* by two independent methods, the photochemical Wolff rearrangement of ethyl diazoacetate[2] and the dehydrochlorination of ethoxyacetyl chloride with triethylamine in anhydrous media.

We have found that the photolysis of ethyl diazoacetate (**1**) in olefinic solvents affords, in addition to products attributed to insertion and addition reactions of carbethoxymethylene, substantial yields (up to 18%) of products which can only be rationalized in terms of a Wolff rearrangement of the carbethoxymethylene[3] followed by cycloaddition of the resulting ethoxyketene to the olefin. These products have apparently been overlooked in earlier studies.

The ketene produced by the classical method was generally allowed to react *in situ* with the olefin with or without a solvent. At −78° it appears to be rather stable. At room temperature it slowly forms a polymeric material and some ketene dimer can be isolated. Cycloaddition readily occurs at 80–100° to give cyclobutanones in moderate to good yields.

A typical experiment with vinyl ethyl ether consists of mixing equimolar olefinic solutions of ethoxyacetyl chloride and triethylamine at Dry Ice–acetone temperature. The reaction mixture is carefully sealed in a

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[9] The ultraviolet spectrum of phenylcyclopropane serves as a rough analogy: M. T. Rogers, *J. Amer. Chem. Soc.*, **69**, 2544 (1947).

[10] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem. Intern. Ed. Engl.*, **8**, 781 (1969).

[11] Obviously, it is not known whether C_2 and C_5 in **9** are formally sp^2-hybridized and therefore planar. For a summary of those reactions in which 1,3-diradicals are presumed to occur, see D. R. Arnold, A. B. Evnin, and P. H. Kasai, *J. Amer. Chem. Soc.*, **91**, 784 (1969), ref 1.

[12] G. L. Closs, L. R. Kaplan, and V. I. Bendall, *ibid.*, **89**, 3376 (1967).

[13] L. M. Leichter, unpublished observations.

[1] Stereospecific cycloadditions of ketoketenes to double bonds are well established: R. Montaigne and L. Ghosez, *Angew. Chem.*, **80**, 194 (1968); T. Huisgen, L. A. Feiler, and P. Otto, *Tetrahedron Lett.*, 4485 (1969); R. Huisgen and P. Otto, *ibid.*, 4491 (1968); W. T. Brady and H. R. O'Neal, *J. Org. Chem.*, **32**, 612 (1967); W. T. Brady and E. F. Hoff, *J. Amer. Chem. Soc.*, **90**, 6256 (1968). After the present article had been submitted a brief communication by W. T. Brady, E. F. Hoff, R. Roe, Jr., and F. H. Parry, Jr. (*ibid.*, **91**, 5679 (1969)), appeared describing somewhat similar observations on the stereospecific aspect of the cycloaddition of monohalo- and monomethylketene to cyclopentadiene as those found in this work.

[2] J. Shafer, P. Barnowsky, R. Laursen, P. Finn, and F. H. Westheimer, *J. Biol. Chem.*, **241**, 421 (1966); O. P. Strausz, Th. DoMinh, and H. E. Gunning, *J. Amer. Chem. Soc.*, **90**, 1660 (1968); H. Chaimovich, R. J. Vaughan, and F. H. Westheimer, *ibid.*, **90**, 4088 (1968); D. E. Thornton, R. K. Gosavi, and O. P. Strausz, *ibid.*, **92**, 1768 (1970).

[3] Ketene formation was observed only in direct photolysis; triplet benzophenone sensitization of **1** afforded triplet carbene which adds nonstereospecifically to olefins and abstracts hydrogen to yield ethyl acetate. Thermolysis of **1** (at 140°) produced singlet carbene, probably in the lowest lying excited singlet state which adds stereospecifically to olefins without giving ethoxyketene.