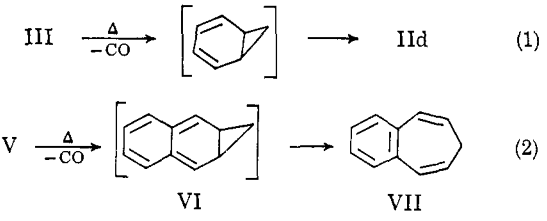
showed no parent ion but a spectrum of tropilidene superimposed over weak fragmentation of the parent ion.

The first-order rate constants for the decarbonylation of compounds Ia–d and III–V are given in Table I.[12] The rates of decarbonylation for the *endo* compounds Ia–d are markedly faster than those for the *exo* ketones III and IV or for the tetraphenylnorbornenone V. These results are explicable in terms of the geometry of the tricyclic systems and the bonding orbitals of the fused cyclopropane ring. The orbital diagram for the *endo* ketones (Figure 1) indicates that the orbitals forming the cyclopropyl "banana" bond between C$_2$ and C$_4$ are ideally situated for interaction and subsequent π-bond formation with the developing p orbitals at C$_1$ and C$_5$. Cyclopropyl participation in the decarbonylation step is thus predicted, and a concerted process involving simultaneous loss of carbon monoxide and breaking of the cyclopropyl bond can occur to form the tropilidene directly in the boat conformation.[13] The geometry of the fused cyclopropyl ring in the *exo* ketones III and IV does not allow overlap of the C$_2$–C$_4$ bond orbitals with the developing p orbitals, and cyclopropyl participation is not expected. In these cases only the C$_6$–C$_7$ π bond appears to be involved in the decarbonylation, thus giving rise to a norcaradiene intermediate directly which then opens to a tropilidene (*cf.* eq 1 and 2). That a different mechanism operates for the *exo* series of compounds is clearly indicated from the behavior of the benz derivative IV. Failure of IV to decarbonylate below 400° not only confirms the lack of cyclopropyl assistance but also supports the postulate of a norcaradiene intermediate in the decarbonylation of the *exo* ketones since loss of aromaticity in the formation of the *o*-quinoidal benznorcaradiene VI is expected to be a highly unfavored process.



The tetraphenylnorbornenone V decarbonylates seven times slower than the unsubstituted *exo* ketone III. This rate difference is found to be approximately the same between the tetraphenyl and unsubstituted *endo* ketones Ib and Id, respectively,[14] and is probably due to steric interaction between phenyls in the transition state. In any case the rate of decarbonylation of III corresponds closely to that of norbornenone derivatives, as expected for involvement of the π bond only.

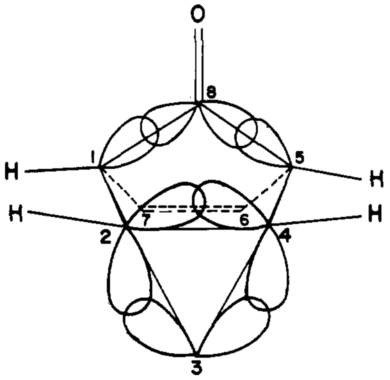


Figure 1.

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[12] Analysis was by nmr integration of the well-separated and increasing tropilidene protons against the decreasing bridgehead or cyclopropyl methylene protons in the starting material. For V the increasing singlet of the dihydrobenzene and the decreasing multiplet of the norbornenone methylenes were followed. An average of 12 integrations was taken for each point. All spectra were recorded at least 25° below the temperature at which the kinetics were determined.

[13] The skeletal geometry of the *endo*-tricyclic system less carbon monoxide very closely resembles that of tropilidene in the boat conformation.

[14] Extrapolation of the rate constant for Ib from 65 to 35° shows that Ib decarbonylates roughly five to seven times slower than Ib.

[15] Alfred P. Sloan Foundation Fellow, 1967–1969.

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Bicyclo[3.3.1]non-1-ene

Sir:

The importance of steric strain as a structure limiting factor was recognized more than 60 years ago by Bredt,[1] who noted that certain olefins with bridgehead double bonds should be incapable of existence. Prelog and his co-workers[2] systematically studied the limitations of Bredt's rule and synthesized a bicyclo[5.3.1]undecene which readily accommodated a bridgehead double bond in the three-carbon bridge. Since the analogous bicyclo[4.3.1]decene derivative showed no such tendency, they concluded that $S = 9$[3] represents the practical limit of Bredt's rule. Another $S = 9$ bridgehead olefin, bicyclo[4.4.1]undec-1-ene, has also been reported.[4,4a]

The recent findings that 2-oxobicyclo[3.3.1]nonane-1-carboxylic acid (**1**)[5] decarboxylates at 145° and bicyclo[3.3.1]nonan-2-one (**1**, R = H) exchanges its bridgehead α hydrogen at 95° in 0.1 *M* NaOD[6] suggest that bicyclo[3.3.1]non-1-enes might be isolable com-

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[1] (a) J. Bredt, J. Houben, and P. Levy, *Ber.*, **35**, 1286 (1902); (b) for a review, see F. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950).

[2] V. Prelog, V. Barman, and M. Zimmermann, *Helv. Chim. Acta*, **32**, 1284 (1949), and previous papers.

[3] For a bicyclo[$x.y.z$]compound, S (the strain number) $= x + y + z$ (x, y, and $z \neq 0$).[1b]

[4] W. G. Dauben, T. L. Westman, and F. T. Bond, 141st National Meeting of the American Chemical Society, Washington, D. C., March 28, 1962, Abstracts, p 29-O; referred to by T. L. Westman and R. D. Stevens, *Chem. Commun.*, 459 (1965).

[4a] NOTE ADDED IN PROOF. Shortly after submitting this paper we learned from Dr. W. G. Dauben that he and Dr. John Wiseman had isolated bicyclo[4.3.1]dec-1-ene some time ago in connection with some solvolysis studies. A synthesis of bicyclo[3.3.1]non-1-ene has recently been accomplished by Dr. Wiseman to whom we are grateful for spectra and a copy of a manuscript describing the work.

[5] J. P. Ferris and N. C. Miller, *J. Am. Chem. Soc.*, **88**, 3522 (1966); J. P. Ferris and N. C. Miller, *ibid.*, **85**, 1325 (1963).

[6] J. P. Schaefer and J. C. Lark, *J. Org. Chem.*, **30**, 1337 (1965).

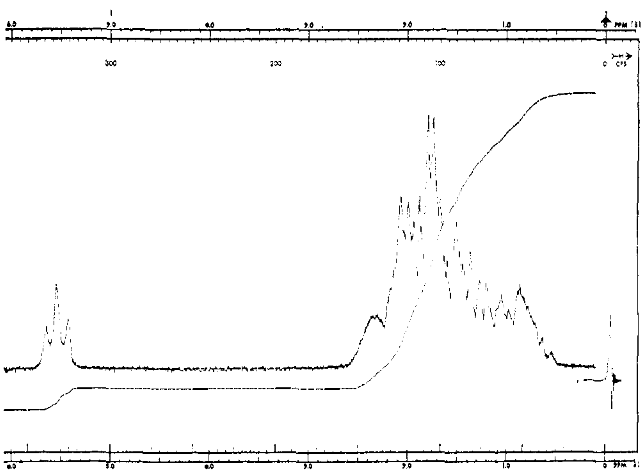
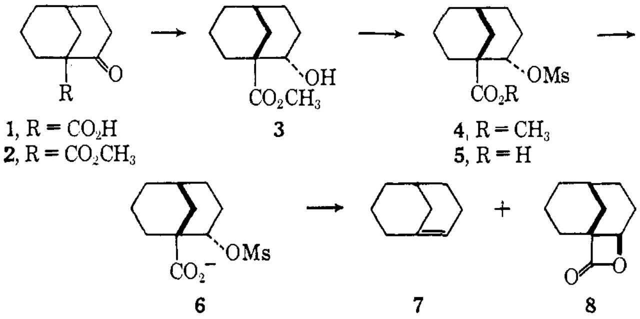


Figure 1. The 60-MHz nmr spectrum of bicyclo[3.3.1]non-1-ene (neat sample relative to external tetramethylsilane).

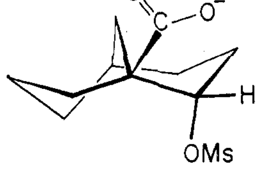
pounds, thus placing the practical limit for Bredt's rule at $S = 7$ instead of $S = 9$.[3] We have indeed found this to be the case and now report a synthesis of the most flagrant violator of Bredt's rule known to date, bicyclo-[3.3.1]non-1-ene (**7**).

Keto ester **2** [mp 70–70.5°, $\lambda_{\max}^{\mathrm{KBr}}$ 5.75 (ester CO), 5.87 (ketone CO), 8.02, 8.34, and 9.28 μ] upon hydrogenation over platinum afforded the hydroxy ester **3** [mp 39–39.5°; $\lambda_{\max}^{\mathrm{film}}$ 2.90 (OH), 5.78 (ester CO), 8.00, 9.00, 9.27, 9.48, 10.27, 11.40, 12.80, and 14.5 μ; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 3.95 (H-2, X of ABX, $J_{\mathrm{AX}} + J_{\mathrm{BX}} = 16$ Hz), 3.65 (CH_3O), 3.17 ppm (OH)]. The same hydroxy ester was obtained *via* reduction of keto ester **2** with sodium borohydride. The *endo* orientation of the hydroxyl grouping is assigned from the nmr spectrum and by analogy with the reduction of bicyclo[3.3.1]nonan-2-one (**1**, R = H) to the *endo* alcohol.[7] The mesylate derivative **4** [$\lambda_{\max}^{\mathrm{film}}$ 5.78 (ester CO), 8.49, 9.29, 9.45, 10.29, 10.82, 11.33, 11.56, and 11.95 μ; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.1 (H-2, X of ABX, $J_{\mathrm{AX}} + J_{\mathrm{BX}} = 17$ Hz), 3.66 (CH_3O), and 2.88 ppm (CH_3SO_3)] of hydroxy ester **3** afforded the acid **5** [mp 115°; $\lambda_{\max}^{\mathrm{KBr}}$ 3.0–3.8 (OH), 5.90 (CO), 8.13, 8.49, 10.6–10.8, 11.29, 11.53, 11.98, 12.70, 13.00, 13.38, 13.58, and 14.70 μ; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 12.0 (OH), 5.42 (H-2, X of ABX, $J_{\mathrm{AX}} + J_{\mathrm{BX}} = 18$ Hz), and 3.12 ppm (CH_3SO_3)] upon saponification with alcoholic potassium hydroxide followed by acidification. The acid **5** was treated with a 0.07 *M* solution of dimethylsulfinylsodium in dimethyl sulfoxide[8] containing slightly less than 1 molar equiv of the base. The mixture was stirred at 60° for 30 hr whereupon the evolution of carbon dioxide essentially ceased and, after an additional 8 hr, the neutral material was isolated by extraction with pentane–ether and chromatography on silica gel. The material eluted with pentane was distilled affording bicyclo[3.3.1]non-1-ene [15% yield, bp 60° (bath temperature) at 5 mm, $\lambda_{\max}^{\mathrm{film}}$ 3.33 (vinyl C—H), 6.15 (C=C), 8.09, 8.21, 9.06, 9.72, 9.83, 10.03, 10.30, 10.42, 11.57, 12.01, 12.32 (vinyl C–H bend), 12.60, and 14.00 μ]. The structure of this olefin is supported by its mass spectrum ($P = 122$), its nmr spectrum (Figure 1), and its rapid and nearly quantitative hydrogenation over platinum to bicyclo[3.3.1]nonane, identified by comparison with an authentic specimen.[9] Continued elution of the aforementioned chromatographic column and sublimation of the ether–pentane fractions afforded the β-lactone **8** [30% yield; mp 109–111°; $\lambda_{\max}^{\mathrm{KBr}}$ 5.50 (CO), 8.38, 8.79, 9.45, 10.83, 11.36, and 11.89 μ; $\delta_{\max}^{\mathrm{CCl_4}}$ 4.22 ppm (H-2, X of ABX, $J_{\mathrm{AX}} + J_{\mathrm{BX}} = 16$ Hz)].



1, R = CO_2H
2, R = CO_2CH_3
3
4, R = CH_3
5, R = H
6
7
8

Models reveal that the chair–chair form of the carboxylate mesylate precursor **6** of olefin **7** and β-lactone **8** cannot attain the preferred orientation for concerted β fragmentation[10] (leading to olefin **7**) or internal displacement (leading to β-lactone **8**). However, with both rings in twist-boat conformations, these groupings can adopt a nearly *anti*-periplanar orientation as illustrated in **6a**. This conformation appears to best meet the stereoelectronic requirements of the reactions leading to the observed products. We plan to examine the chemistry of these products in the near future.



6a

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(7) *Cf.* J. P. Schaefer, J. C. Lark, C. A. Flegal, and L. M. Honig, *J. Org. Chem.*, **32**, 1372 (1967).

(8) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

(9) We are grateful to Professor R. L. Burwell, Jr., and Dr. J. A. Roth for providing this sample.

(10) C. A. Grob and P. W. Schiess, *Angew. Chem. Intern. Ed. Engl.*, **6**, 1 (1967).

(11) (a) Fellow of the Alfred P. Sloan Foundation. (b) Public Health Service Fellow of the National Institute of General Medical Sciences.

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Bredt's Rule. Bicyclo[3.3.1]non-1-ene

Sir:

In the early part of this century Bredt formulated his familiar rule in a series of papers published over a period of more than 20 years.[1,2] Bredt's rule may be

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(1) J. Bredt, H. Thouet, and J. Schmitz, *Ann.*, **437**, 1 (1924), and references therein.

(2) For reviews and discussions see (a) F. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950); (b) V. Prelog, *J. Chem. Soc.*, 420 (1950); (c) R. C. Fort, Jr., and P. von R. Schleyer in "Advances in Alicyclic Chemistry," Vol. I,