k_{OH^-} near 10^{10} M^{-1} sec^{-1} for hemithioacetals formed from thiols of differing leaving ability.

Figure 1 represents a modification of the type of curve described by Eigen for proton-transfer reactions.[3,4] The experimental points require that the break at the diffusion-controlled limit be sharp and that the Brønsted slope be nearly constant over a large range of basicity. The solid lines in the figure are calculated from the Brønsted relationship and eq 2. A simple proton-transfer reaction should exhibit a Brønsted slope or 0 or 1.0.[3] The slope of 0.80 ± 0.03 for this reaction requires that the k_2 step be concerted in the sense that both movement of the proton and changes in bonding at the central carbon atom have occurred when the transition state is reached. Either diffusion-controlled encounter or the k_2 step is rate limiting; the range in which both steps are partially rate determining is small. There is evidence that proton transfer may be kinetically significant in the oxygen exchange reaction of substituted methyl benzoates[5] and it is probable that other carbonyl and acyl group reactions will be found to proceed through a rate-determining diffusion-controlled encounter which may be preceded by unfavorable equilibrium steps to give a relatively slow over-all rate.

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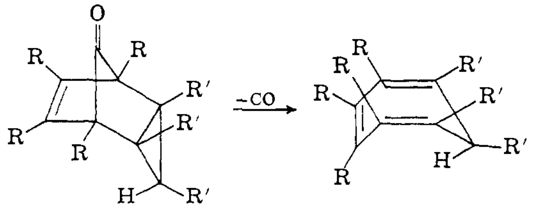
(4) M. Eigen, *Discussions Faraday Soc.*, 39, 7 (1965).
(5) M. L. Bender and R. J. Thomas, *J. Am. Chem. Soc.*, 83, 4189 (1961).
(6) National Science Foundation Predoctoral Fellow, 1965-1967.

R. Barnett,[6] **W. P. Jencks**
Graduate Department of Biochemistry
Brandeis University, Waltham, Massachusetts 02154
Received August 4, 1967

Decarbonylation Studies in the *endo*- and *exo*-Tricyclo[3.2.1.0^{2,4}]octen-8-one Series. Stereoelectronic Requirements for Cyclopropyl Participation

Sir:

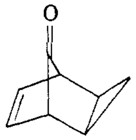
The facile decarbonylation of *endo*-tricyclo[3.2.1.0^{2,4}]-octen-8-ones (I) yielding tropilidenes (II) has received but cursory examination,[1-3] while corresponding decarbonylation of an *exo* related ketone has not been previously reported. The surprising ease of decarbonylation of the heptaphenyl compound Ia, briefly described several years ago by one of us,[1] prompted a more complete study of the *endo* and *exo* series since decarbonylation of bicyclo[2.2.1]hepten-7-ones is generally of consequence only above 150°.[4] We now report striking evidence for different pathways in the decarbonylation of the *endo*- and *exo*-tricyclic ketones with cyclopropyl participation occurring only in the *endo* series.



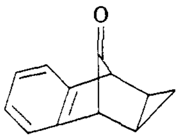
Ia, R = R′ = Ph
b, R = Ph, R′ = H
c, R = Cl, R′ = H
d, R = R′ = H

II

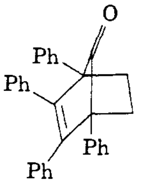
The series of compounds Ia,[1] Ib,[5] Ic,[6] Id,[2,3] IV,[7] and V[8] were synthesized by previously reported methods. The hitherto unknown *exo*-tricyclo[3.2.1.0^{2,4}]-octen-8-one (III) was synthesized from 7-norbornadienol benzoate. Cuprous halide catalyzed diazomethane addition gave, in 65% yield, a 5:1 mixture of *exo*,-*syn*-8- and *endo*,*syn*-8-tricyclo[3.2.1.0^{2,4}]octenyl benzoate.[9] Addition of methyl Grignard afforded the corresponding tricyclic alcohols and dimethylphenylcarbinol. Chromic acid oxidation followed by glpc[10] separation (7% Carbowax 20 M; 115°) gave the *exo* ketone III free of the *endo* ketone Id which decarbonylated to tropilidene under the conditions employed (see Table I). The bridged *exo* structure III is assigned on the basis of the nmr (CCl_4) spectrum [τ 3.20, triplet, J = 3 cps (2 H); 7.07, multiplet (2 H); 8.77, multiplet (2 H); 9.00, multiplet (2 H)][11] and infrared carbonyl absorption at 1780 cm^{-1}. The mass spectrum of III



III



IV



V

Table I. Decarbonylation Rate Data for Bridged Ketones

Compd	Temp, °C	10^4k, sec^{-1}	$t_{1/2}$, min
Ia	70.0	0.15[a,b]	770
Ib	65.0	1.84 ± 0.07[a]	63
Ic	50.0	2.55 ± 0.07[a]	45
Id	35.0	1.30 ± 0.07[a]	89[c]
III	150.0	1.41 ± 0.09[d]	82
IV	*Ca.* 400	37% yield of 3,4-benztropilidene (VII)	
V	150.0	0.198 ± 0.007[d]	585

[a] C_6D_6 as solvent. [b] Approximate rate since retro-Diels–Alder competes favorably with decarbonylation. A complete study of this compound is underway. [c] Tanida, *et al.*,[2] report a half-life of 130 min (36°), and Clarke and Johnson[3] *ca.* 10 min (30°) for this process. [d] PhOPh as solvent.

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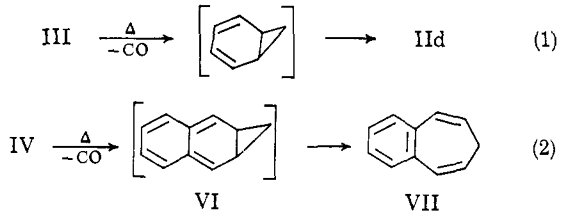
(1) M. A. Battiste, *Chem. Ind.* (London), 550 (1961).
(2) H. Tanida, T. Tsuji, and T. Irie, *J. Am. Chem. Soc.*, 89, 1953 (1967).
(3) S. C. Clarke and B. L. Johnson, *Tetrahedron Letters*, 617 (1967).
(4) C. F. H. Allen, *Chem. Rev.*, **37**, 209 (1945); **62**, 653 (1962).
(5) T. J. Barton, Ph.D. Thesis, University of Florida, 1966.
(6) M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *J. Am. Chem. Soc.*, 89, 1954 (1967).
(7) (a) M. E. Brennan, M.S. Thesis, University of Florida, 1965; (b) M. A. Battiste and M. E. Brennan, *Tetrahedron Letters*, 5857 (1966); (c) M. E. Brennan, Ph.D. Thesis, University of Florida, 1967.
(8) C. F. H. Allen, R. W. Ryan, Jr., and J. A. VanAllan, *J. Org. Chem.*, **27**, 778 (1962).
(9) This result is consistent with that of Pincock, *et al.*, for the addition of diazomethane to 7-norbornadienol acetate: J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966).
(10) A third component was isolated in small quantity and shown to be identical with the bis adduct ketone previously obtained by Brennan from the cuprous halide catalyzed addition of diazomethane to 7-norbornadienol followed by chromic acid oxidation.[7a,c]
(11) There is a striking similarity of this spectrum to that of the benz derivative IV [nmr ($CDCl_3$) τ 2.81, multiplet (4 H); 6.57, singlet (2 H); 8.61, multiplet (2 H); 8.83, multiplet (2 H)] and no correlation with that of the *endo* ketone Id [nmr (CCl_4) τ 4.03, triplet, J = 3 cps (2 H); 6.95, multiplet (2 H); 8.55, multiplet (2 H); 9.38, doublet of triplets (1 H); 9.93, doublet of triplets (1 H)].

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.

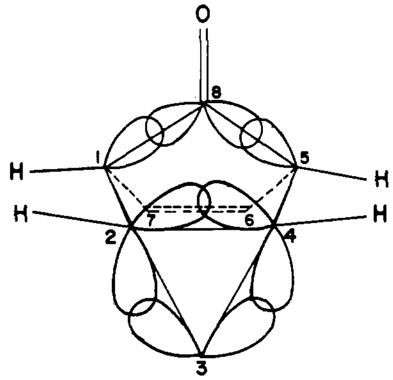


Figure 1.

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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.

Brian Halton, Merle A. Battiste[15]
Rolf Rehberg, Cynthia L. Deyrup, Michael E. Brennan
Department of Chemistry, University of Florida
Gainesville, Florida 32601

Received September 5, 1967

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.

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