The ^{13}C spectra were determined with complete proton decoupling on the Varian DFS-60 spectrometer.[16] Several hundred scans were required to observe the ^{13}C satellites of the ^{13}C spectrum which arise from molecules whose natural abundance is only 0.02%.

(16) F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 2769 (1967).

(17) National Science Foundation Predoctoral Fellow 1965–1967.

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Base-Catalyzed Hemithioacetal Decomposition at a Diffusion-Controlled Rate[1]

Sir:

Measurements of the rate of hemithioacetal formation from acetaldehyde and thiols of differing acidity indicated that the rate of base-catalyzed hemithioacetal decomposition approaches the diffusion-controlled limit as the leaving thiol becomes more acidic.[2] The hydroxide ion catalyzed decomposition of the hemithioacetals formed by the condensation of acetaldehyde with benzenethiol, *p*-nitrobenzenethiol, and thioacetic acid has now been shown to proceed at a diffusion-controlled rate. In addition, the reaction is subject to general base catalysis with a Brønsted slope near 0.8.

The rate of hemithioacetal breakdown or formation was followed by ultraviolet spectroscopy with a stopped-flow mixing apparatus. Measurement of the equilibrium constants for thiol addition permitted calculation of both rate constants from rate measurements in either direction. The rate constants of the water and hydroxide ion catalyzed reactions were obtained over the range pH 0 to 6.5 from measurements in dilute hydrochloric acid or by extrapolation of rates obtained in buffer solutions to zero buffer concentration. Buffer catalysis was measured at two buffer ratios in most cases, and only the basic species was found to be catalytically active.

The rate constants for the hydroxide ion catalyzed breakdown of the three hemithioacetals are approximately 10^{10} M^{-1} sec^{-1}, which is in the range expected for a diffusion-controlled reaction (Table I). The value of $\Delta H^{\ddagger}$ for this reaction, from measurements at 2, 25, 30, and 40°, is approximately 2 kcal/mole.

Table I. Decomposition of Hemithioacetals Formed from Acetaldehyde and RSH at 25° and Ionic Strength 1.0 *M*

RSH	pK_a	K,[a] M^{-1}	k_{H_2O}, sec^{-1}	$k_{OH^-} \times 10^{-10}$,[b] M^{-1} sec^{-1} Obsd	Calcd
CH_3COSH	3.20	29	0.25	0.83 0.98[c]	0.83
p-$NO_2C_6H_4SH$	4.57	6.9	0.43	0.95	0.89
C_6H_5SH	6.33	29	0.010	0.68	0.69

[a] K = [hemithioacetal]/[RSH][CH_3CHO + $CH_3CH(OH)_2$]. [b] Based on hydroxide ion activity. [c] Ionic strength 0.003–0.010.

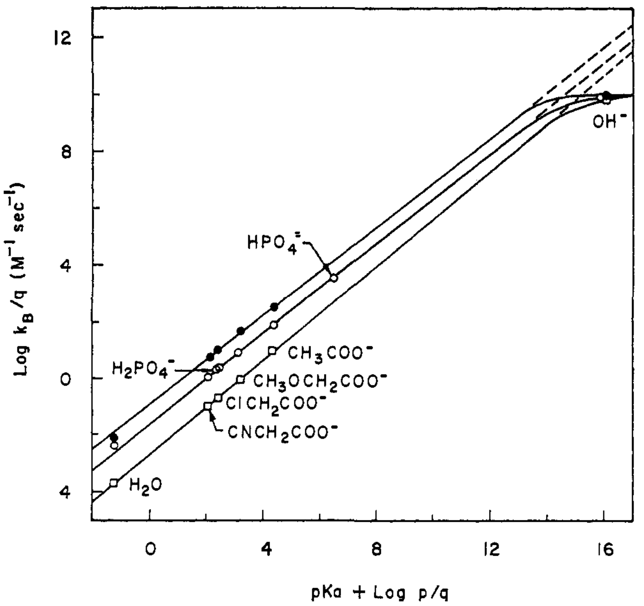
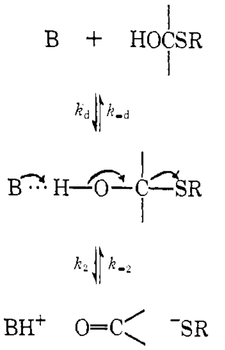


Figure 1. Brønsted plots for the decomposition of hemithioacetals formed from acetaldehyde and benzenethiol (□), thioacetic acid (○), and *p*-nitrobenzenethiol (●). Statistical corrections have been made according to R. P. Bell and P. G. Evans, *Proc. Roy. Soc.* (London), **A291**, 297 (1966).

The rate constants, k_B, for catalysis by weaker bases follow Brønsted slopes of 0.80 ± 0.03 (Figure 1). These results suggest that the reaction proceeds according to the mechanism of eq 1 and that diffusion-



(1)

controlled encounter of the reactants is largely or entirely rate determining for the hydroxide ion reaction, whereas the k_2 step becomes rate determining for weaker bases or less acidic leaving groups. Calculations based on the steady-state rate equation for this mechanism (eq 2) using values of k_dk_2/k_{-d} from the Brønsted plots

$$k_B = \frac{k_dk_2}{k_{-d} + k_2} \qquad (2)$$

and the assumption that $k_d = 0.9 \times 10^{10}$ M^{-1} sec^{-1} suggest that k_2 is partially rate limiting for the reaction of the benzenethiol compound with hydroxide ion (Table I).

An alternative mechanism in which a proton is removed in a fast step followed by general acid catalyzed expulsion of thiol is improbable for several reasons which include (1) a requirement for base catalysis of the removal of a proton from the free thiol in the reverse direction under experimental conditions in which the thiol is already 98% in the ionized form, and (2) the unlikelihood for this mechanism of similar values of

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[1] Publication No. 525. Supported by grants from the National Science Foundation and the National Institute of Child Health and Human Development of the Public Health Service (HD-01247).

[2] G. E. Lienhard and W. P. Jencks, *J. Am. Chem. Soc.*, **88**, 3982 (1966).

$k_{\mathrm{OH^-}}$ 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.

[3] M. Eigen, *Angew. Chem. Intern. Ed. Engl.*, **3**, 1 (1964).

[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.

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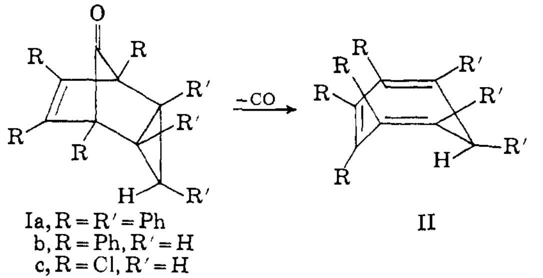
Decarbonylation Studies in the *endo*- and *exo*-Tricyclo[3.2.1.0^{2,4}]octen-8-one Series. Stereoelectronic Requirements for Cyclopropyl Participation

Sir:

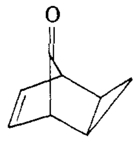
The facile decarbonylation of *endo*-tricyclo[3.2.1.0^{2,4}]octen-8-ones (I) yielding tropilidenes (II) has received but cursory examination,[1–3] while corresponding decarbonylation of an *exo* related ketone has not been previously reported. The surprising ease of decarbonylation of the heptaphenyl 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.



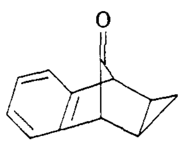
Ia, R = R′ = Ph
b, R = Ph, R′ = H
c, R = Cl, R′ = H
d, R = R′ = H

II

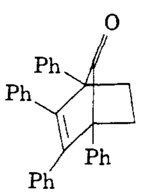
The series of compounds Ia,[1] Ib,[5] Ic,[6] Id,[2,3] IV,[7] and V[8] were synthesized by previously reported methods. The hitherto unknown *exo*-tricyclo[3.2.1.0^{2,4}]octen-8-one (III) was synthesized from 7-norbornadienol benzoate. Cuprous halide catalyzed diazomethane addition gave, in 65% yield, 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$_6$D$_6$ 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).

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[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)].