developed positive charge the reduction of hyperconjugation on replacing hydrogen with deuterium may be counterbalanced by an increase in the electron releasing inductive effect of deuterium compared to hydrogen, and thus no isotope effect observed.

The bond angles of ammonia and trimethylamine suggest that the energy required for rehybridization on protonation is small; for phosphine the rehybridization energy may be large, while for trimethylphosphine it should be intermediate. The precise magnitude of the rehybridization energy has not been evaluated.

It is probable that the reversal in gas-phase basicity on methylating ammonia and phosphine is due to a composite of the above factors and possibly some further unrecognized factors.

Acknowledgment. We wish to thank Dr. Fred Kaplan for his helpful instruction in the early stages of our ion cyclotron resonance spectroscopy investigations.

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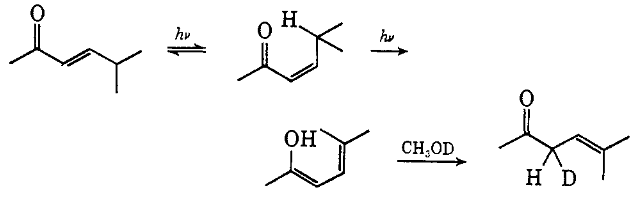
Photolysis of 1-Acetylcyclooctene. Direct Observation of Dienol Intermediate in Photochemical Deconjugation of α,β-Unsaturated Ketone

Sir:

The photochemical deconjugation of open-chain[1] and some cyclic α,β-unsaturated ketones[2] which bear γ-hydrogen atom(s) is well known. The intermediacy of a 1,3-dienol arising from a 1,5-hydrogen shift has been suggested since photolysis of 5-methyl-3-hexen-2-one in CH_3OD affords 5-methyl-4-hexen-2-one-3-*d* (Scheme I).[3] We wish to report the direct observation of 1,3-dienol formed in the photochemical reaction of 1-acetylcyclooctene (**1**).

Scheme I



A solution of **1** in carefully deoxygenated acetonitrile (*ca.* 5%) was irradiated using light of wavelength longer than 350 nm (aqueous $CuSO_4$ as a filter) at room temperature. The course of the reaction was monitored spectrometrically. After irradiation for 10 hr, **1** was consumed completely, and highly air-sensitive compounds (two components, *vide infra*) were obtained in 80% yield. The infrared spectrum showed no carbonyl absorption, but characteristic bands at 3450 (OH), 1656 (C=C), and 1191 cm^{-1} (C–O). The ultraviolet absorption exhibited a maximum at 255 nm (log ε *ca.* 4.0). The nmr signals due to the olefinic protons (Figure 1) are compatible only with a mixture of dienols **2a** and **3b** in a 5:1 ratio.[4,5] Appearance of the H_a signal at lower field than that of $H_{a'}$ is ascribed to the anisotropic effect of the enol oxygen. The hydroxyl signal at δ 5.68 disappeared upon addition of CH_3OD.[6] The assignments were ascertained by double resonance techniques.

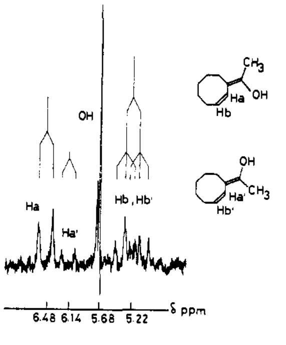
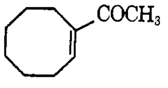
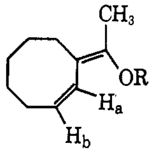


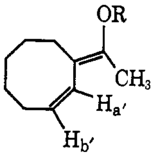
Figure 1. The nmr spectrum of the photolysate of **1** (5% CH_3CN solution, 60 MHz, TMS).



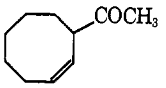
1



2a, R = H
b, R = $COCH_3$



3a, R = H
b, R = $COCH_3$



4

These new isomers in acetonitrile were fairly stable in the dark, and remained practically unchanged for 3 days at room temperature. Heating at 100° for 2 hr gave a mixture of 3-acetylcyclooctene (**4**)[7,8] and the starting enone **1** (83:17 ratio). Addition of a trace amount of sulfuric acid at room temperature caused instantaneous conversion to a mixture of ketones **4** and **1** (75:25), while exposure to potassium *tert*-butoxide in *tert*-butyl alcohol afforded **4** exclusively. Treatment with acetic anhydride–pyridine at −20° furnished the dienol acetates **2b**[9] and **3b**[10] (60% yield, 5:1 ratio)

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(1) For a review see N. C. Yang in "Reactivities of the Photoexcited Molecule," Interscience, New York, N. Y., 1967, p 145.

(2) (a) H. Nozaki, T. Mori, and R. Noyori, *Tetrahedron*, **22**, 1207 (1966); (b) R. G. Carlson and J. H. Bateman, *Tetrahedron Lett.*, 4151 (1967).

(3) N. C. Yang and M. J. Jorgenson, *ibid.*, 1203 (1974).

(4) Silylation with *N,O*-bis(trimethylsilyl)acetamide followed by glpc analysis gave the same isomeric ratio.

(5) The splitting patterns show a close resemblance to those of 3-methylenecyclooctene prepared from 2-cyclooctenone and methylenetriphenylphosphrane: $J_{H_a-H_b} = J_{H_{a'}-H_{b'}} = 12$ Hz and $J_{H_b-CH_2} = J_{H_{b'}-CH_2} = 8$ Hz.

(6) The spectrum at higher field (in CD_3CN) is rather complicated by overlapping with signals of high molecular weight by-products (<20%) and CHD_2CN, but exhibits distinct singlets at δ 1.88 and 1.82 arising from methyl groups of **2a** and **3a**, respectively.

(7) All stable new compounds gave correct elemental analyses and molecular peaks in mass spectra.

(8) E. J. Corey and L. S. Hegedus, unpublished data; L. S. Hegedus, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1970.

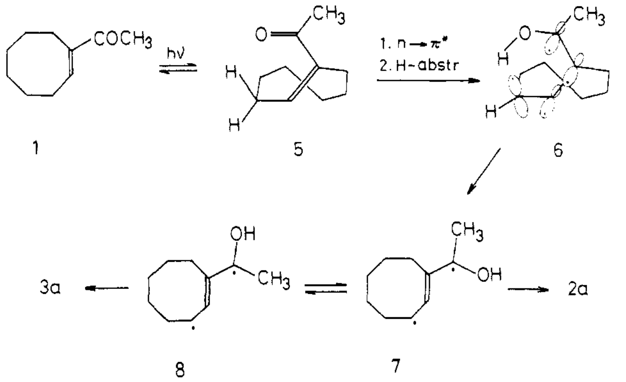
(9) Spectral characteristics for **2b** are: uv (95% C_2H_5OH) 241 nm (log ε 4.15); ir (neat) 1755 and 1207 cm^{-1} (acetate); nmr (CCl_4, TMS) δ 1.59 (m, 6, CH_2), 1.87 (s, 3, $=C(OCOCH_3)CH_3$), 2.07 (s, 3, $COCH_3$),

along with the enone **4** (40%). The acetates were independently synthesized by the reaction of **1** and acetic anhydride in the presence of *p*-toluenesulfonic acid.[11] The stereochemistry of **2b** and **3b** was confirmed on the basis of nuclear Overhauser effects (NOE) (100 MHz, 10% $CDCl_3$ solution).[12] When the allylic methyl protons in **3b** were saturated by double irradiation, the $H_{a'}$ signal showed a 19 ± 1% increase in integrated area. On the other hand, irradiation of the allylic methyl group of **2b** caused no significant change in the signal intensity of H_a (0 ± 1%).

The photolysate of **1** formed in CH_3OD exhibited practically the same nmr spectrum as that obtained in an acetonitrile solution except for the OH signal, and on standing at 25° for 4 days gave 3-acetylcyclooctene-3-*d* (95% pure by nmr).

The photochemical enone–dienol conversion is well accounted for by Scheme II. Photolysis of the enone **1** has recently been reported to cause cis–trans isomerization, establishing an equilibrium between **1** and **5**.[13] As shown above, however, prolonged exposure to light of >350 nm, where the trans enone **5** absorbs the photoenergy more efficiently than the cis isomer **1**,[13] induces further transformation. Inspection of the Dreiding models indicates that the γ-hydrogen abstraction by the n,π* triplet carbonyl group through a cyclic transition state is feasible only with the trans enone **5**. The twisted triplet species **6** thus formed would be stabilized by changing the geometry to form the sterically less constrained biradical **7**. Subsequent decay to the ground state affords the dienol **2a**. The lifetime of **7** would conceivably be long enough to allow isomerization to **8**, which leads to formation of **3a**, the minor product.[14]

Scheme II



The existence of the simple dienols (**2a** and **3a**) as long-lived species seems rather unusual.[15] Their high stability could arise from the fairly rigid s-trans diene structure. The dienol intermediate ordinarily involved in the photoisomerization has a flexible diene structure (*cf.* Scheme I), and readily ketonizes with loss of conjugation. The favoring of sp^2 configuration in eight-membered rings over sp^3 configuration might be added to the stabilization factors.[16]

Acknowledgment. We wish to thank to Drs. T. Nishida and I. Miura of NET-Varian Co., Ltd. for the measurement of nuclear Overhauser effects.

2.2–2.6 (m, 4, allylic CH_2), 5.44 (dt, 1, J = 12 and 7 Hz, H_b), and 6.11 (d, 1, J = 12 Hz, H_a).

[10] Spectral characteristics for **3b** are: uv (95% C_2H_5OH) 239 nm (log ε 3.98); ir (neat) 1753 and 1206 cm^{-1} (acetate); nmr (CCl_4, TMS δ 1.55 (m, 6, CH_2), 1.87 (s, 3, $=C(OCOCH_3)CH_3$), 2.07 (s, 3, $COCH_3$), 2.2–2.5 (m, 4, allylic CH_2), 5.60 (dt, 1, J = 12 and 7 Hz, $H_{b'}$), and 6.07 (d, 1, J = 12 Hz, $H_{a'}$).

[11] *Cf.* D. H. R. Barton, R. M. Evans, J. C. Hamlet, P. G. Jones, and T. Walker, *J. Chem. Soc.*, 747 (1954).

[12] F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5250 (1965).

[13] P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968).

[14] Detection of enol crotonaldehyde in the vapor phase by ir was recorded. See J. W. Coomber, J. N. Pitts, Jr., and R. R. Schrock, *Chem. Commun.*, 190 (1968).

[15] Transformation of certain photochromic ketones to dienols stable at low temperature has been redorded; for example, see K. R. Huffman, M. Loy, and E. F. Ullman, *J. Amer. Chem. Soc.*, 87, 5417 (1965); W. A. Henderson, Jr., and E. F. Ullman, *ibid.*, **87**, 5424 (1965).

[16] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 267.

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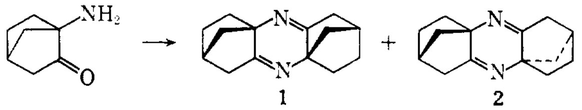
The Photochemical Racemization of 1,2,3,4,4a,6,7,8,9,9a-Decahydro-*syn*-2,4a,7,9a-dimethanophenazine. A Synchronous Pair of Sigmatropic Shifts

Sir:

In the course of another study, we have accidentally discovered that free 1-amino-2-norbornanone[1] rapidly self-condenses to form a mixture of two diastereoisomeric dihydropyrazines **1** and **2** (95% yield).[2]



1 **2**

1 and **2** are the first members of a general class of compounds capable of undergoing two simultaneous Wagner–Meerwein type shifts (eq 1 and 2). In the case of *meso*-**2** this rearrangement would be totally degenerate (**2a** ≡ **2b**). However, a similar rearrangement in chiral **1**, while being structurally degenerate, leads to complete racemization (**1a** and **1b** are mirror images). At this time, we wish to report the photochemically induced racemization of optically active **1**.

2a **2b** (1)

1a **1b** (2)

A mixture of **1** and **2** [ir (Nujol) 1680 cm^{-1}, weak (no C=O or NH); nmr τ (CCl_4) 7.5–8.8 (18 H, complex multiplet); mass spectrum *m/e* 214] could be obtained by treatment of the amino ketone hydrochloride with 10% aqueous sodium hydroxide. Fractional sublimation (110–130° at 760 mm) led to pure meso compound **2** (mp 190–192° in a sealed tube. *Anal.* Found: C, 78.57; H, 8.42; N, 13.01) as the minor more volatile component. Further sublimation resulted in less

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[1] A. Nickon, T. Nishida, and Y. Lin, *J. Amer. Chem. Soc.*, **91**, 6860 (1969).

[2] D. E. Applequist and J. P. Klieman, *J. Org. Chem.*, 26, 2178 (1961); J. Meinwald and D. E. Putzig, *ibid.*, **35**, 1891 (1970).