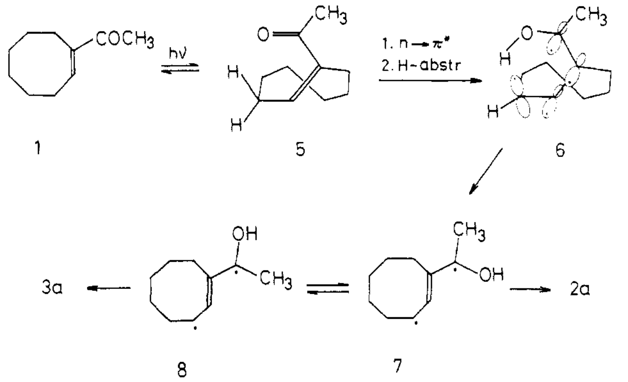
along with the enone **4** (40%). The acetates were independently synthesized by the reaction of **1** and acetic anhydride in the presence of *p*-toluenesulfonic acid.[11] The stereochemistry of **2b** and **3b** was confirmed on the basis of nuclear Overhauser effects (NOE) (100 MHz, 10% $CDCl_3$ solution).[12] 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.

* Address correspondence to this author.

R. Noyori,* H. Inoue, M. Katô
Department of Chemistry, Nagoya University
Nagoya, Japan

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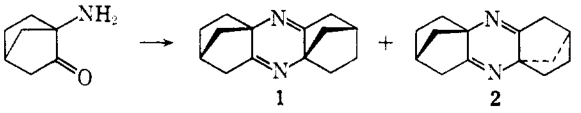
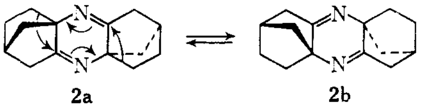
The Photochemical Racemization of 1,2,3,4,4a,6,7,8,9,9a-Decahydro-*syn*-2,4a,7,9a-dimethanophenazine. A Synchronous Pair of Sigmatropic Shifts

Sir:

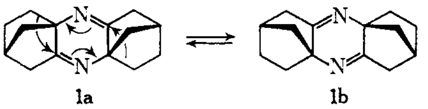
In the course of another study, we have accidentally discovered that free 1-amino-2-norbornanone[1] rapidly self-condenses to form a mixture of two diastereoisomeric dihydropyrazines **1** and **2** (95% yield).[2]



1 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**.



(1)



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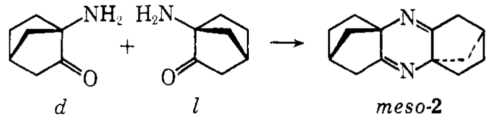
(1) A. Nickon, T. Nishida, and Y. Lin, *J. Amer. Chem. Soc.*, **91**, 6860 (1969).

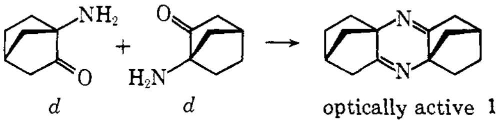
(2) D. E. Applequist and J. P. Kliuman, *J. Org. Chem.*, 26, 2178 (1961); J. Meinwald and D. E. Putzig, *ibid.*, 35, 1891 (1970).

pure samples of **1** (mp 160–170°) whose spectral properties were almost identical with those of the mixture. *Anal.* Found: C, 78.53; H, 8.46; N, 13.01.

Fortunately, the problem of isomer separation could be largely avoided by generating compound **1** from optically active amino ketone. Examination of eq 3 shows the unwanted *meso*-**2** can only arise from the combination of one *d* and one *l* form of the amino ketone. On the other hand, **1** results when a *d* reacts with another *d*, or an *l* with an *l* (eq 4). Consequently, if one enatiomer is present in excess, optically active **1** is formed.



(3)



(4)

The amino ketone was resolved as its *d*-10-camphorsulfonic acid salt.[3] The two diastereomeric salts were fractionally recrystallized from acetone to constant rotation. The salt with the lower rotation, mp 208–209°, $[\alpha]_{578}$ +23.9° (MeOH), $[\alpha]_{365}$ +173°, was treated with dilute aqueous base and the product sublimed to yield optically active dihydropyrazine **1**, $[\alpha]_{578}$ −106.8° (CH_3OH), $[\alpha]_{365}$ −353°, apparently still containing some meso compound (mp 160–167°, sealed tube).

Dilute solutions of optically active **1** (50–90 mg (100 ml)) in methanol were prepared. These were irradiated through quartz under a positive pressure of nitrogen at 25°, 1.5 in. from a Hanovia 200-W mercury lamp. After 30 hr, racemization was greater than 90% complete ($[\alpha]_{365}$ −25°). No racemization occurred when Pyrex or Vycor filters were used.

Loss of optical activity by photoreactions other than racemization has been ruled out by continuously monitoring the shape and intensity of the characteristic ultraviolet spectrum of **1** (λ_{max} 208, ϵ 2.2 × 10^3; 250, ϵ 2.5 × 10^2) and observing that no changes take place. In addition, partially racemized dihydropyrazine with an optical rotation identical with that of the solution and other properties identical with the starting material could be recovered in 50% yield[4] by sublimation after 60–70% racemization. Rearrangement of **1** catalyzed by other photoproducts generated during the reaction might also account for our observations. However, we reject this hypothesis since photolysis was cleanly first order in starting material over four half-lives.

So far **1** does not appear to racemize thermally or in the presence of toluenesulfonic acid. It easily survived routine sublimation at 110–130°, and solutions in heptane were indefinitely stable at 25° and did not lose any optical activity after 4 days in a nitrogen-filled sealed tube at 110°. Longer periods of heating resulted in slow decomposition to a brown tar. The presence of magnesium oxide as an acid scavenger retarded but did not halt this process. The optical rotation of solutions in ethylene dichloride *ca.* 5 m*M* in **1** and 5–10 m*M* in toluenesulfonic acid gave a small initial loss of optical activity at 50°, then remained unchanged. The initial loss of optical activity was greater when less care was taken to exclude water from the system and was probably due to acid-catalyzed hydrolysis of **1**.

The thermal stability and photolability of **1** are in accord with the orbital symmetry considerations of Woodward and Hoffmann.[5] If the synchronous rearrangement of **1** proceeds with retention of configuration at both migrating centers, then, using Woodward–Hoffmann notation,[5] it must be a $[\sigma^2s + \pi^2s + \sigma^2a + \pi^2a]$ or entirely suprafacial or entirely antarafacial process, hence photochemically allowed and thermally forbidden, as observed. The thermally allowed process would require inversion at one center and retention at the other, very likely an energetically unfavorable process.

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(3) The camphor-10-sulfonic acid salt could be prepared by evaporation of an aqueous solution of 1 equiv of the amine hydrochloride and 1 equiv of camphor-10-sulfonic acid, and crystallization of the residue from acetone.

(4) The low recovery yield can be ascribed to the small quantity of material (<10 mg), the partial decomposition occurring during photolysis, and the partial decomposition which always accompanied sublimation of dihydropyrazine 1.

(5) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

* Address correspondence to this author.

Donald G. Farnum,* Glenn R. Carlson
Department of Chemistry, Michigan State University
East Lansing, Michigan 48823

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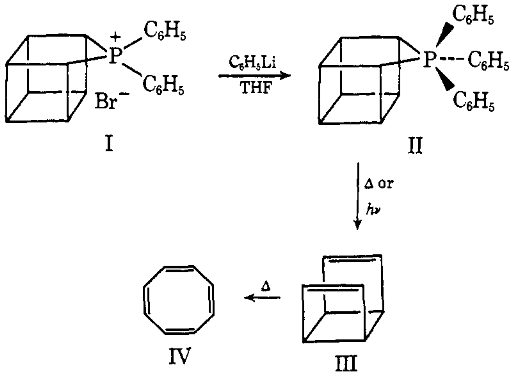
Stable Cycloalkyl Pentavalent Phosphoranes

Sir:

Tetraarylphosphonium salts react with phenyllithium to give pentaarylphosphoranes,[1] but phosphonium salts that have hydrogen atoms attached to one of the carbons bonded to phosphorus give ylides instead.[1b,2] We are reporting below that the phosphonium salt I, although it has hydrogen atoms attached to carbons bonded to phosphorus, reacts with phenyllithium to give not the ylide, but the corresponding pentavalent phosphorane, II. We are also reporting that when



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(1) (a) G. Wittig and M. Rieber, *Justus Liebigs Ann. Chem.*, **562**, 187 (1949); (b) G. Wittig and G. Geissler, *ibid.*, **580**, 44 (1953).

(2) (a) D. Seyferth, W. B. Hughes, and J. K. Heeren, *J. Amer. Chem. Soc.*, **87**, 2847 (1965) (b) A. Maercker, *Org. React.*, **14**, 270 (1965).