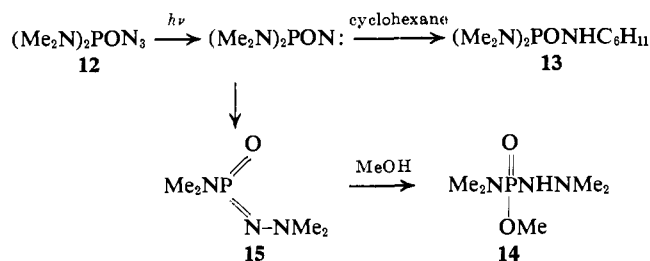


double bonds, but this factor is not dominant in all situations. It is reported that pyrolysis of diphenylphosphinyl azide^{8a} leads to phenyl migration, and migration of saturated carbon has also been observed.^{8b} We find that a dimethylamino group attached to phosphorus also migrates readily in the corresponding nitrene. Thus, photolysis of bis(dimethylamino)phosphoryl azide (**12**)^{7c} in cyclohexane afforded only a 7% yield of the product (**13**)^{12,13} of insertion into the solvent. The remaining high molecular weight residue could not be directly identified, but its nature is indicated by the results of a photolysis of **12** in methanol. Again, the product did not involve direct attack of the nitrene on the solvent, but instead a product (**14**)¹⁶ was obtained from trapping of a reactive rearrangement product by the methanol solvent. The intermediate metaphosphate derivative (**15**) would be expected to give high molecular weight material in the absence of such a trapping reagent.



That dimethylamino, alkyl, or phenyl groups are able to migrate in situations in which alkoxy and phenoxy groups do not is not surprising, but it does suggest the limitations in the classes of compounds which can be utilized to afford nonrearranging highly reactive nitrene insertion reagents. Within this class of phosphorylnitrenes, however, are materials with particularly attractive potential for functionalizations utilizing proximity effects.

Acknowledgment. This work was supported by the National Institutes of Health.

(16) An authentic sample¹³ of **14** was obtained by stepwise reaction of methylchlorophosphate with dimethylamine and unsymmetrical dimethylhydrazine.

(17) NIH Postdoctoral Fellow, 1972–1974.

R. Breslow,* A. Feiring,¹⁷ F. Herman
 Department of Chemistry, Columbia University
 New York, New York 10027
 Received May 23, 1974

Automerization of 6-Methylenebicyclo[3.2.1]oct-2-ene¹

Sir:

As part of a study of the sigmatropic rearrangements of some biallylic systems,² we have examined the pyrolysis of 6-methylenebicyclo[3.2.1]oct-2-ene. During the course of this work, Hasselmann³ reported a closely related thermal rearrangement of 6-methylenebicyclo-

(1) This work was supported in part by the National Science Foundation (GP-33909X), the National Institute of General Medical Sciences (GM-16962), and the Hoffmann-LaRoche Foundation. We are grateful to Ms. Linda Gardiner for participation in the early stages of this work.

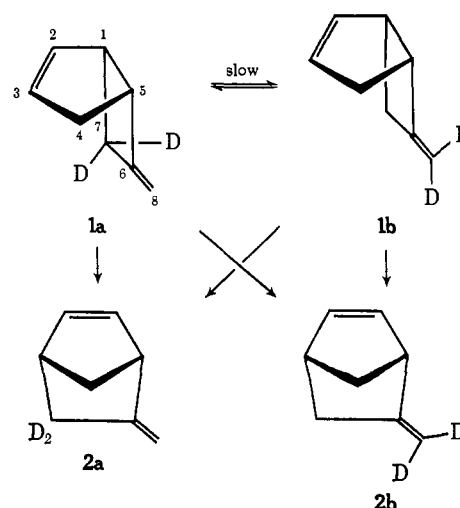
(2) (a) J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, **95**, 267, 269 (1973), and references cited there; (b) J. A. Berson, T. Miyashi, and G. Jones, II, *ibid.*, **96**, 3468 (1974).

(3) D. Hasselmann, *Tetrahedron Lett.*, (a) 3465 (1972); (b) 3739 (1973).

[3.2.0]hept-2-ene, deuterated either at C₇ (**1a**) or C₈ (**1b**), to 2-methylenebicyclo[2.2.1]hept-5-ene, **2a** and **2b**. In each case, the product of formal [1,3]-sigmatropic rearrangement predominated slightly (**1a** → 56% **2a** and 44% **2b**; **1b** → 60% **2b** and 40% **2a**).

Three interpretations of these results were considered (Scheme I)^{3b}: (1) a nearly equal competition between

Scheme I



a [3,3]-sigmatropic (Cope) rearrangement (**1a** → **2b**) and a [1,3]-sigmatropic rearrangement (**1a** → **2a**); (2) a competition between a [1,3]-sigmatropic rearrangement and a diradical mechanism involving C₁–C₇ bond cleavage to give a freely rotating intermediate, with the sigmatropic rate constant about one-seventh (from **1a**) or one-fifth (from **1b**) as large as the diradical-forming rate constant; (3) cleavage of the C₁–C₇ bond to give a “not completely equilibrated” diradical, which for steric reasons cyclized preferentially at C₃–C₇ rather than at C₃–C₈.

The substrate in our work is 6-methylenebicyclo[3.2.1]oct-2-ene-3,9,9-*d*₃ (**3a**), which can be synthesized with 0.91 D at C₃ and >1.96 D at C₉ in eight steps⁴ from norborn-5-en-2-one. Molecule **3a** is conceptually related to Hasselmann's **1a–b** system by the insertion of a methylene group into the bridge bond (C₁–C₅ of **1a–b**). This introduces diagnostically useful symmetry properties into the several conceivable automerization pathways.

Heating a neat, degassed sample of **3a** at 308.6° causes the C₃ deuterium to become distributed between C₃ and C₁, while the C₉ deuterium becomes distributed between C₉ and C₇. The reaction is monitored by integration of the magnetic resonance signals of the protons at C₂ (δ 6.04), C₃ (δ 5.48), and C₉ (δ 5.05) with a Jeol 100-MHz spectrometer. After six half-lives, the C₃ and C₉ proton signals, corrected for incomplete deuteration in **3a**, have intensities of 50 ± 3% and 52 ± 3% of one and two protons, respectively. Aside from a minor side reaction which produces 1–10% of the endocyclic isomer of **3a**, 6-methylbicyclo[3.2.1]octa-2,6-diene,⁵ there are no other changes in the system.

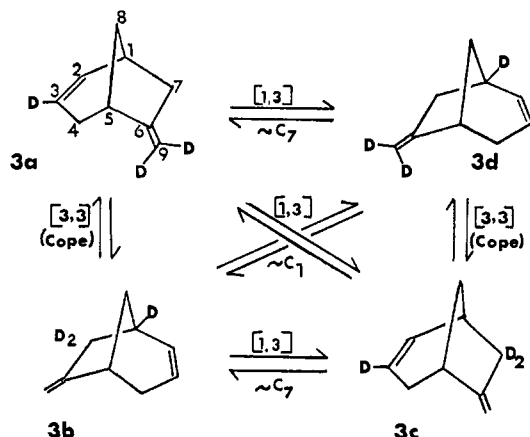
(4) Via bicyclo[3.2.1]oct-2-en-6-one: S. A. Monti and S. Yuan, *J. Org. Chem.*, **36**, 3350 (1971).

(5) Formation of this diene does not interfere with the automerization. In particular, it does not provide a mechanism for mixing C₉ deuterons with C₇ protons, since heating a mixture of 80% C₉-deuterated **3a** and 20% of 6-trideuteriomethylbicyclo[3.2.1]octa-2,6-diene for three automerization half-lives gives recovered 6-methylenebicyclo[3.2.1]oct-2-ene with no deuterium at C₉.

To follow the automerizations, which may be visualized *a priori* as interconversions of **3a**, **3b**, **3c**, and **3d** by any or all of the formal mechanisms shown, we note that the proton counts at C₁, C₃, C₇, and C₉ respectively (corrected for full deuteration) in **3a** are 1, 0, 2, and 0, in **3b** are 0, 1, 0, and 2, in **3c** are 1, 0, 0, and 2, and in **3d** are 0, 1, 2, and 0. The rearrangements of the label at C₃ and at C₉ both are clean first-order reactions with rate constants⁶ for approach to the equilibrium distribution, respectively, $k_3 = (1.82 \pm 0.08) \times 10^{-5} \text{ sec}^{-1}$ and $k_9 = (1.77 \pm 0.12) \times 10^{-5} \text{ sec}^{-1}$.

If these rate constants are taken to be identical, only three formal mechanisms are possible (Scheme II):

Scheme II

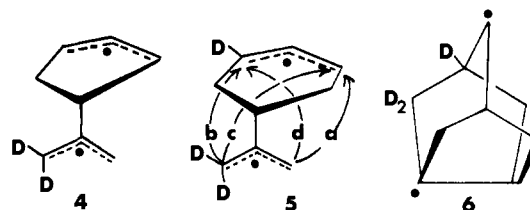


(4) **3a** \rightleftharpoons **3b** only (pure Cope rearrangement); (5) **3a** \rightleftharpoons equal amounts of **3c** + **3d** only; (6) any mixture of these two mechanisms. Category 6 includes as a special case the mixture one-third (4) and two-thirds (5), which is indistinguishable from a common randomized diradical intermediate. This species could arise from cleavage at C₁-C₇ of **3a** and would recycle with equal rates to **3a**, **3b**, **3c**, and **3d**.

Alternatively, on the (unjustified) assumption that the observed rate constant ratio of 1.03 ± 0.08 is different from unity, k_3/k_9 can be related to the rate constants for a mechanism involving competitive independent [1,3]-sigmatropy of C₇ (**3a** \rightarrow **3d**, k_8) and randomized diradical formation (k_R) by the equation $1.03 = k_3/k_9 = 2(k_8/k_R) + 1$, from which it may be calculated that $k_8/k_R = 0.015$. Thus, [1,3]-sigmatropy, if present at all, contributes only about one part in 70 to the overall rearrangement. The competitive mechanisms (1 and 2) above, which were compatible with the results in the **1a-b** system, cannot be important here.

What causes the apparent difference in behavior between **3a** and **1a-b**? It is conceivable that this merely reflects a shift, for some not very obvious reason, in the relative magnitudes of the competing rate constants in mechanisms 1 and 2. However, another formal possibility derives from mechanism 3, involving an "incompletely equilibrated" diradical. These species, **4**³ from **1b** and **5** from **3a**, each are hypothetically derived by cleavage of the C₁-C₇ bond and rotation of the exo-methylene group toward the underside of the remaining ring. Diradical **5** has a mirror plane, which

(6) Calculated using a nonweighted least-squares program kindly supplied by Professor K. B. Wiberg. An iterative procedure which varies the infinity value to give the best fit to the data gives values of 1.67×10^{-5} and $1.65 \times 10^{-5} \text{ sec}^{-1}$, respectively, for the two scrambling rate constants. The rates are not affected by glass wool.



requires two pairwise equivalences of the ring-closure rate constants, $k_a = k_b$ and $k_c = k_d$. The pure Cope rearrangement of **3a**, mechanism 4, also might involve an intermediate 1,4-diradical⁷ (**6**), which again would have C₈ symmetry. Either **5** or **6** necessarily would produce the equivalence of k_3 and k_9 observed here experimentally.

Distinctions among the mechanisms involving pure Cope rearrangement, randomized diradical, and symmetrical but "incompletely equilibrated" diradical are possible in principle in the **3a** system. One experimental approach involves optically active **3a**.

(7) Cf. (a) W. v. E. Doering, V. G. Toscano, and G. H. Beasley, *Tetrahedron*, **27**, 5299 (1971); (b) M. J. S. Dewar and L. E. Wade, *J. Amer. Chem. Soc.*, **95**, 290 (1973); (c) J. J. Gajewski, L. K. Hoffman, and C. N. Shih, *ibid.*, **96**, 3705 (1974).

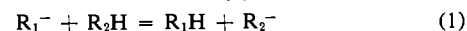
Jerome A. Berson,* John M. Janusz
Department of Chemistry, Yale University
New Haven, Connecticut 06520
Received June 14, 1974

Intrinsic Acidities of Carbon Acids, RH, Bond Dissociation Energies of R-H, and Electron Affinities of R from Gas Phase Proton Transfer Equilibrium Measurements

Sir:

In recent years studies of gas phase acidities and basicities of organic compounds have led to valuable insights for the separation of intrinsic and solvent induced substituent effects.¹⁻⁴ The present study deals with carbon acids—a group which has been little investigated to date. Brauman¹ has observed that the acidity of toluene is comparable to methanol and ethanol. Bohme, *et al.*,⁵ have ordered the acidities of 18 carbon acids between methane and nitromethane and revealed many interesting trends. However, since the compounds cover an energy range of 70 kcal/mol, little quantitative information may be extracted.

The acidities of 11 selected carbon acids, RH, measured in the present work are shown in Tables I and II. The data were obtained from measurement of the equilibrium constants K_1 for the reaction (1) at 600°K. Using



$\Delta G^\circ_1 = -RT(\ln K_1)$ it was assumed that $\Delta G^\circ_1 = \Delta H^\circ_1$ such that

$$\Delta G^\circ_1 = \Delta H^\circ_1 = D(R_2-H) - EA(R_2) - D(R_1-H) + EA(R_1)$$

(1) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **92**, 5986 (1970).

(2) J. P. Briggs, R. Yamdagni, and P. Kebarle, *J. Amer. Chem. Soc.*, **94**, 5128 (1972).

(3) M. Taagepera, W. G. Henderson, R. T. Brownlee, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 1369 (1972).

(4) R. Yamdagni, T. B. McMahon, and P. Kebarle, *J. Amer. Chem. Soc.*, **96**, 4035 (1974).

(5) D. K. Bohme, E. Lee Ruff, and L. B. Young, *J. Amer. Chem. Soc.*, **94**, 5153 (1972).