Like cyclobutadiene,[7] trimethylenemethane,[8] and heptafulvene,[9] pentalene should be greatly stabilized as a result of coordination to a transition metal. The recent synthesis of bis(pentalenylnickel),[10] diallyldihydropentalenylenedinickel,[11] tetraallyldihydropentalenylenedichromium,[11] and hexallyldihydropentalenylenedizirconium[11] provides support for this thesis and suggests that it may be possible to prepare additional organometallic derivatives which will serve as a source of free pentalene itself.

In this report we describe the preparation and physical properties of (octahapto-1-dimethylaminopentalene)-μ-carbonyltetracarbonyldiiron(Fe–Fe) (3), a stable transition metal π complex of dimethylaminopentalene.

3a

3b

4

5
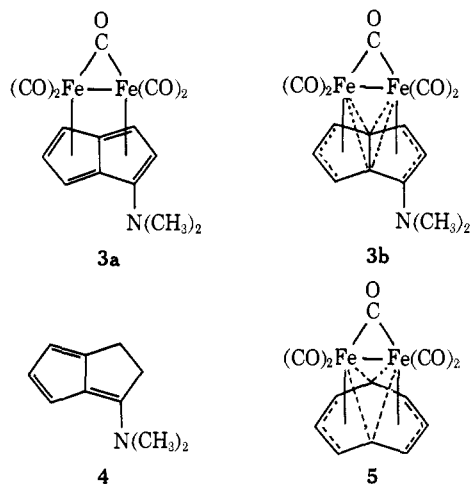
A solution containing 3-dimethylamino-1,2-dihydropentalene (4)[12] (290 mg, 2.0 mmol), iron pentacarbonyl (5 ml, 37 mmol), and 25 ml of deoxygenated methylcyclohexane was heated at 105° under nitrogen for 12 hr. The reaction mixture was then cooled, filtered, and concentrated under reduced pressure (20 mm). Preparative tlc of the residue on neutral silica gel using 9:1 benzene–acetone as the eluent afforded 85 mg (11%) of 3 as a green-black solid, mp 113–115° (N_2). Anal. Calcd for $C_{10}H_{11}NFe_2(CO)_5$: C, 45.39; H, 2.79; N, 3.53. Found: C, 45.78; H, 3.01; N, 3.47.

In the EI mass spectrum (70 eV) of 3 strong peaks corresponding to the molecular ion and fragments resulting from the successive loss of five carbonyls and two iron atoms appear at m/e 397 (11), 369 (15), 341 (16), 313 (21), 285 (64), 257 (100), 201 (29), and 145 (49). Confirmation of the molecular weight was obtained from the $CI(CH_4)$ mass spectrum[13] which shows an abundant M + 1 ion at m/e 398. The infrared spectrum (CCl_4) of 3 exhibits three bands (2025, 1987, 1957 cm^{-1}, all ±5 cm^{-1}) in the terminal CO region and one band at 1760 ± 5 cm^{-1} in the bridging CO

region. The 100-MHz nmr spectrum (acetone-d_6) of 3 shows signals at τ 4.56 (1, t, H_5), 5.24 and 6.17 (2, pair of doublets, $J_{5,6} = J_{4,5} = 2.5$ Hz, $H_{4,6}$), 5.09 (1, d, $J_{2,3} = 3$ Hz, H_3), 6.31 (1, d, H_2), and 7.29 (6, s, $(CH_3)_2N$). Assignments were confirmed by double-resonance experiments.

The above spectral data are consistent with either formulation 3a or 3b for the dimethylaminopentalene π complex and differentiation of these two possibilities must await X-ray analysis. It is interesting to note that cyclooctatetraene also forms a diiron pentacarbonyl complex[14] which has been shown to have structure 5.[15] Unlike 3, the cyclooctatetraene complex 5 exhibits fluxional behavior at room temperature.

Preliminary experiments with phenyldihydropentalene[12] and also with dihydropentalene itself[16] indicate that the procedure described above will prove to be a general method for preparing iron carbonyl complexes of pentalenes.[17] Work is presently underway to complete the characterization of several additional complexes and to explore the chemistry of the coordinated pentalene nucleus.

(14) C. E. Keller, G. F. Emerson, and R. Pettit, J. Amer. Chem. Soc., 87, 1390 (1965).

(15) E. B. Fleischer, A. L. Stone, R. B. K. Dewar, J. D. Wright, C. E. Keller, and R. Pettit, ibid., 88, 3158 (1966).

(16) J. J. Katz, M. Rosenberger, and R. K. O'Hara, ibid., 86, 249 (1964).

(17) Treatment of phenyldihydropentalene with $Fe(CO)_5$ and dihydropentalene with either $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ affords diiron pentacarbonyl complexes of phenylpentalene and pentalene as indicated by mass spectral analysis of the reaction mixtures.

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## An Inverse β-Deuterium Isotope Effect in the Solvolysis of a 1-Azabicyclo[1.1.0]butane

Sir:

We wish to report the observation that $k_H/k_D = 0.948$ for the relative rates of acid-catalyzed hydrolysis of 3-phenyl-1-azabicyclo[1.1.0]butane (1a) and its 2,2-dideuterio analog (1b). This isotope effect is consistent with a completely inductive or field transmission of the effect of β-deuterium substitution and places severe constraints on the kinds of bonding which can be present in the transition state.

1a, R = H
b, R = D

2a, R = H
b, R = D
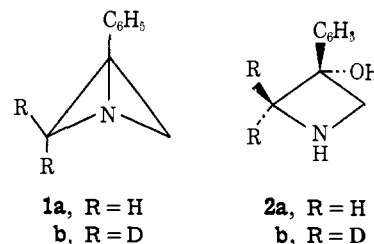
The syntheses of 1a,b have been described elsewhere.[1] The solvolysis rates were measured by the previously

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(10) T. J. Katz and N. Acton, J. Amer. Chem. Soc., 94, 3281 (1972).

(11) A. Miyake and A. Kanai, Angew. Chem., Int. Ed. Engl., 10, 801 (1971).

(12) R. Kaiser and K. Hafner, ibid., 9, 892 (1970).

(13) (a) F. H. Field, Accounts Chem. Res., 1, 42 (1968); (b) B. S. M. Munson, Anal. Chem., 43, 28A (1971).

(1) A. G. Hortmann and D. A. Robertson, J. Amer. Chem. Soc., 94, 2758 (1972); 89, 5974 (1967).

described[2] method. The buffer in all runs was 0.01 m borax, pH 9.180. Substrates 1a,b were added to the buffer as solutions in dioxane; their HCl adducts, 3a,b, were added as aqueous solutions. (It is known
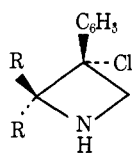
3a, R = H
b, R = D

that **3** undergoes quantitative internal displacement to generate **1** in less than 1 sec at this pH.) The observed rate constants are shown in Table I; the mean value of k_H/k_D is 0.948 $\pm$ 0.006 (95% confidence limits).

Table I. Observed Pseudo-First-Order Rate Constants[a]

Sub-strate	$10^3 k_\psi{}^H$, sec^{-1}	$10^3 k_\psi{}^D$, sec^{-1}	$k_\psi{}^H/k_\psi{}^D$ [b]
3a,b[c,d]	1.690 $\pm$ 0.002[e]	1.791 $\pm$ 0.003[e]	0.944 $\pm$ 0.002
3a,b[c,d]	1.679 $\pm$ 0.004[f]	1.770 $\pm$ 0.005[f]	0.949 $\pm$ 0.003
3a,b[g]	1.687 $\pm$ 0.006[f]	1.782 $\pm$ 0.006[f]	0.947 $\pm$ 0.004
1a,b[h]	1.558 $\pm$ 0.006[f,i]	1.634 $\pm$ 0.009[f,i]	0.953 $\pm$ 0.006

[a] Measured at 25.0₀° in 0.01 m borax buffer (pH 9.18 in absence of dioxane) using a Cary 16K spectrophotometer; temperature fluctuations in the cell were <0.1°, corresponding to <0.3% in k_ψ. [b] Calculated from $k_\psi{}^H$ and $k_\psi{}^D$ values which were measured alternately in samples of the same buffer on the same day. [c] Each substrate was freshly purified by one recrystallization. [d] These two entries differ only in being from data collected on different days. [e] Standard deviation of a set of six determinations. [f] Standard deviation of a set of four determinations. [g] Each substrate was freshly purified by two successive recrystallizations. [h] Each substrate was freshly purified by two successive distillations. [i] When determined consecutively, k_ψ values for 1a are 7.0% lower than for 3a because of the presence of 0.33% dioxane in the solvent for 1a. This is in accord with the 7.1% depression of k_ψ which is predicted from independent measurements of the solvent effect on k_ψ for 1a.

Under these conditions, **1** undergoes specific hydronium ion catalyzed hydrolysis to give the corresponding azetidinol (**2**). Evidence from the stereochemistry of the products arising from 2-exo-methyl-1a[1] and from substituent effects, $\Delta S^{\ddagger}$, and solvent isotope effects[2] implies that the mechanism is prior equilibrium protonation of the substrate followed by rate-determining cleavage of the C_3–N bond with nucleophilic participation of solvent, and that both reacting bonds in the rate-determining activated complex have covalent orders near zero (i.e., that the electronic structure of this activated complex is close to that of the corresponding carbonium ion, with a nearly vacant p orbital).

The β-deuterium isotope effects observed in solvolysis are usually consistent with a primarily hyperconjugative origin;[3,4] they show the angular dependence expected for such a transmission mechanism and range up to a maximum value of $k_H/k_D \approx 1.3$ for deuteration on a single carbon. For the one substrate previously investigated in which the β C–D bond lies in the nodal

(2) J. L. Kurz, B. K. Gillard, D. A. Robertson, and A. G. Hortmann, J. Amer. Chem. Soc., 92, 5008 (1970).
(3) (a) V. J. Shiner, Jr., and J. S. Humphrey, Jr., ibid., 85, 2416 (1963); (b) V. J. Shiner, Jr., and J. G. Jewett, ibid., 86, 945 (1964); 87, 1383 (1965); (c) V. J. Shiner, Jr., and G. S. Kriz, Jr., ibid., 86, 2643 (1964).
(4) E. R. Thorton, Annu. Rev. Phys. Chem., 17, 349 (1966).

plane of the developing p orbital, Shiner and Humphrey[3a] observed $k_H/k_D = 0.986 \pm 0.01$ for a single deuterium and interpreted that observation as a measure of the inductive contribution to β-deuterium isotope effects.

The inductive and/or field effect contribution to k_H/k_D for hydrolysis of 1a,b can be estimated from the observed difference,[5] $\Delta pK = 0.015$, for CD_3CO_2H–CH_3CO_2H, which implies $\sigma^*(CD_3) = -0.0087$ and $\sigma^*(CD_2H) = -0.0058$. Formation of the tertiary carbonium ion activated complex from 1a,b should have a ρ^* near that for protonation of a tertiary amine, for which $\rho^* = 4.29$.[6] These values of ρ^* and σ^* predict $k_H/k_D = 0.944$ in agreement with the observed value.

The observed isotope effect thus requires that there is little or no hyperconjugative overlap in the activated complex between the vacant p orbital and either C–D bond. If a factor of 1.02 is taken as the maximum hyperconjugative contribution which would be consistent with the observed value of k_H/k_D, then the correlation proposed by Shiner and Humphrey[3a] implies that the dihedral angles between both C_3–C_2–D planes and the C_2–C_3 p orbital plane must fall in the approximate range 90 $\pm$ 30°.

Such angles are possible only if the axis of the vacant p orbital lies in or near the C_2–C_3–N plane; a projection along the C_3–C_2 bond would then be similar to **4**, in which the p orbital bisects the D–C_2–D angle.

4   **5**
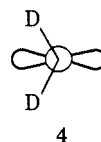
If the nuclear geometries reported for bicyclobutane[7] and for chlorocyclobutane[8] are chosen as models for the activated complex, then the corresponding p orbital C_3–C_2–D dihedral angles are 73 and 63°, which are within the allowed range. Any large tilt of the p orbital out of the C_2–C_3–N plane would cause one of those angles to decrease sufficiently to give rise to an unacceptably large hyperconjugative contribution to k_H/k_D.

This angular restriction rules out many structures which might otherwise be considered possible. For example, the geometry of the activated complex cannot be close to that expected for a nearly planar classical 1-phenylcyclobutyl cation;[9] the p orbital in such an ion should be approximately perpendicular to the plane of the cyclobutane ring, and the p orbital C_3–C_2–D angles would be near those in the projection **5**. A 127° D–C_2–D angle in **5** (by analogy to chlorocyclobutane[8]) would predict[3a] $k_H/k_D \approx 1.15$.

The structure which minimizes distortion of the natural bond angles around the carbonium ion center while keeping the p orbital in the C_2–C_3–N plane is that shown in **6**, where the nuclear configuration re-

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(6) P. R. Wells, "Linear Free Energy Relationships," Academic Press, New York, N. Y., 1968, p 38.
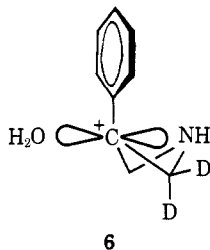(7) K. W. Cox, M. D. Harmony, B. Nelson, and K. B. Wiberg, J. Chem. Phys., 50, 1976 (1969).
(8) H. Kim and W. D. Gwinn, ibid., 44, 865 (1966).
(9) G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, J. Amer. Chem. Soc., 94, 146 (1972).

6

mains reactant-like and the p orbital lies near the C_3–N axis.[10] For ordinary solvolyses, such an orientation of the p orbital on the developing carbonium ion toward the leaving group is expected. It is perhaps surprising that, even in the present case, the interaction between the C_3^+ and the NH remains sufficiently strong in the transition state to outweigh the factors which favor a more planar configuration for the carbonium ion.

The orientation of the p orbital in **6** may be compared to that predicted by various theoretical calculations[11-14] for ground-state bicyclobutane; those predictions have varied from sharply tilted (*i.e.*, a C_1–C_3 p–π bond) to only slightly tilted (*i.e.*, a C_1–C_3 p–σ bond). Our data imply that *either* the azabicyclobutane (**1**) has a σ C_3–N bond *or* that the C_3 p orbital rotates toward the C_3–N axis during the activation process (*i.e.*, in the direction *opposite* to that required for formation of product).

Finally, since the NH is constrained to remain within covalent bonding distance of the carbon from which it is leaving in spite of the nearly complete conversion of that carbon into a carbonium ion, this activated complex provides a model for predicting the behavior of the "ion–triplet" activated complexes which must be present[15] in any nucleophilic displacement which occurs *via* the "ion-pair"[16] mechanism.

(10) Although the vacant orbital on the carbonium ion center, C_3, is termed a "p orbital" in this discussion, we do not mean to exclude the possibility that it contains some s character (as might be suggested by the bond angles around C_3). Our qualitative conclusions concerning the geometry of the activated complex should not be affected by such inclusion of a small amount of s character.

(11) J. M. Schulman and G. J. Fisanick, *J. Amer. Chem. Soc.*, **92**, 6653 (1970).

(12) O. Martensson, *Acta Chem. Scand.*, **24**, 3123 (1970).

(13) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

(14) M. Pomerantz and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **88**, 3970 (1966).

(15) J. L. Kurz and J. C. Harris, *ibid.*, **92**, 4117 (1970).

(16) R. A. Sneen and J. W. Larsen, *ibid.*, **91**, 6301 (1969), and earlier references cited therein.

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Energetics of the Cis–Trans Interconversion of a Bicyclo[5.1.0]octane System

Sir:

The synthesis[1-6] of several *trans*-bicyclo[5.1.0]octanes has been prompted by interest in the effect of strain

(1) P. G. Gassman, F. J. Williams, and J. Seter, *J. Amer. Chem. Soc.*, **90**, 6893 (1968).

(2) W. Kirmse and Ch. Hase, *Angew. Chem., Int. Ed. Engl.*, **7**, 891 (1968).

(3) K. B. Wiberg and A. de Meijere, *Tetrahedron Lett.*, 519 (1969).

(4) A. J. Ashe, III, *ibid.*, 523 (1969).

(5) P. G. Gassman, J. Seter, and F. J. Williams, *J. Amer. Chem. Soc.*, **93**, 1673 (1971).

(6) P. G. Gassman and F. J. Williams, *ibid.*, **93**, 2704 (1971).

upon reactivity. While there are estimates[7,8] of the total strain of *cis*-bicyclo[5.1.0]octane, such estimates have not been made for the trans isomer. It has been suggested,[3] however, that the strain difference between *trans*-bicyclo[6.1.0]nonane and *trans*-bicyclo[5.1.0]octane is only on the order of a few kilocalories per mole.

We herein report the synthesis of the first bicyclo[5.1.0]octane known to undergo clean, facile trans–cis equilibration (both thermal[9] and photochemical) and a direct calorimetric measurement of the ΔH of this isomerization.

The addition of singlet carbene **1** to *cis*-cycloheptene using the procedure of Koser and Pirkle[10] affords the *cis*-spiro[5.1.0]octane **2**, mp 130–131°, in 64% yield. The compound shows: ir (CCl$_4$) 1617 and 1638 cm^{-1} (conjugated carbonyl); uv (cyclohexane) λ_{max} 282 (ϵ 20,600) and 352 nm (ϵ 41); nmr (CCl$_4$) τ 3.38 (d, 1, J = 2.6 Hz, vinyl), 4.12 (d, 1.1, J = 2.6 Hz, vinyl), 7.60–8.67 (m, 12.6, cycloheptylmethylene and cyclopropylmethine), 8.70 (s, 8.8, *tert*-butyl), 8.75 (s, 8.8, *tert*-butyl).

1

2
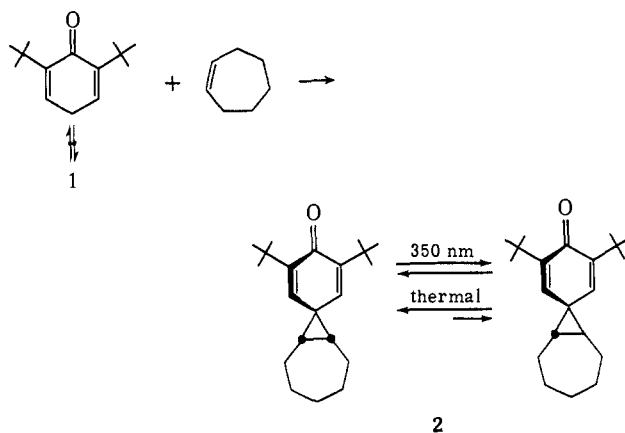
Irradiation of cyclohexane solutions of *cis*-**2** at 350 nm (Rayonet Photochemical Reactor-100) results in clean photoequilibration with the trans isomer. The position of the photostationary state is temperature dependent, principally because of a facile thermal retroreaction which may be frozen out at temperatures below −30°. At −50°, the photostationary state is 48:52 trans:cis. The nmr of this mixture shows additional singlets at τ 3.78 (vinyl) and 8.73 (*tert*-butyl) which are characteristic of the trans isomer. The infrared and ultraviolet spectra of this mixture are essentially the same as those of pure *cis*-**2**. *trans*-**2** has been further characterized chemically (while mixed with *cis*-**2**) but has not been isolated.

Of particular interest is the clean, facile thermal isomerization of *trans*-**2** to *cis*-**2**. At 22.5° this first-order reaction has a half-life of 100 min, k = 1.15 ± 0.03 × 10^{-4} sec^{-1}. Other rate constants and activation parameters are: at 35.1°, k = 4.78 ± 0.27 × 10^{-4} sec^{-1}; at 45.0°, k = 14.6 ± 1.9 × 10^{-4} sec^{-1}; $\Delta H^\ddagger$ = 20.5 kcal/mol; $\Delta S^\ddagger$ = −3.7 eu. At equi-

(7) P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *ibid.*, **92**, 2377 (1970).

(8) S. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey, and R. H. Boyd, *ibid.*, **92**, 3109 (1970).

(9) It has been reported[5] that the base-catalyzed, thermal rearrangement of *trans*-bicyclo[5.1.0]octane affords principally cyclopropane ring-opened products although 1% of the cis isomer was detected after 22% conversion.

(10) G. F. Koser and W. H. Pirkle, *J. Org. Chem.*, **32**, 1992 (1967).