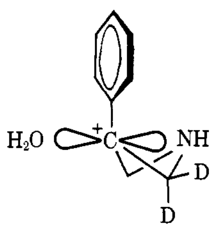

6

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.

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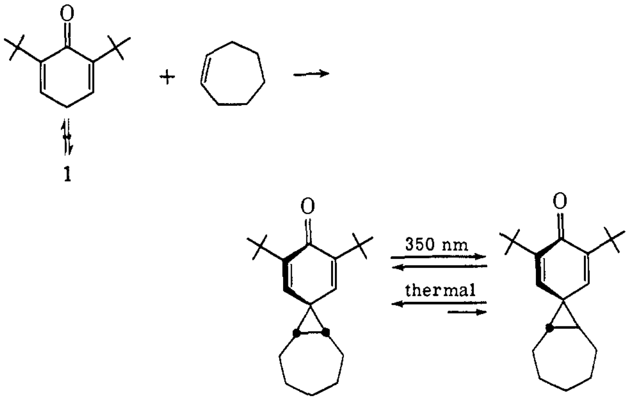
Energetics of the Cis–Trans Interconversion of a Bicyclo[5.1.0]octane System

Sir:

The synthesis[1–6] of several *trans*-bicyclo[5.1.0]octanes has been prompted by interest in the effect of strain 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, $k = 1.15 \pm 0.03 \times 10^{-4}$ sec^{-1}. Other rate constants and activation parameters are: at 35.1°, $k = 4.78 \pm 0.27 \times 10^{-4}$ sec^{-1}; at 45.0°, $k = 14.6 \pm 1.9 \times 10^{-4}$ sec^{-1}; $\Delta H^{\ddagger} = 20.5$ kcal/mol; $\Delta S^{\ddagger} = -3.7$ eu. At equi-

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

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

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(9) It has been reported[2] 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).

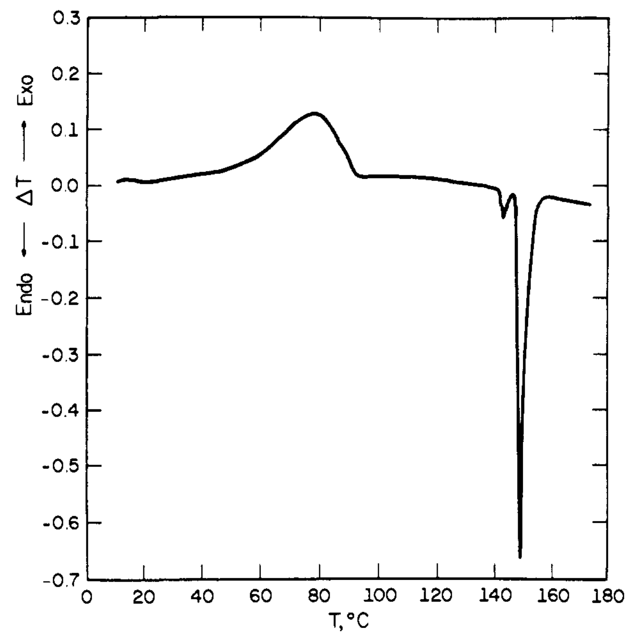

Figure 1. Thermogram of 0.98 mg of *trans*-**2** and 3.68 mg of *cis*-**2** in 10.42 mg of Dow-Corning 704 silicon oil. For calibration, 1.22 mg of 50:32:18 Sn-Pb-Cd eutectic has been included. The exotherm at *ca.* 77° arises from the isomerization; the endotherm at 148° arises from fusion of the eutectic.

librium, too little *trans*-**2** is present to allow direct determination of K_{eq} (and hence ΔG) by nmr.

Direct determinations of ΔH of isomerization have been made *via* differential scanning calorimetry using a DuPont 900 thermal analyzer. Although neat mixtures of *cis*- and *trans*-**2** can be obtained by irradiation in (and subsequent evaporation of) liquid butane, these mixtures were semicrystalline and the phase changes (*i.e.*, crystallization and melting) which attended the trans–cis isomerization during thermal analysis complicate data interpretation. These problems were circumvented by conducting the isomerization in a nonvolatile inert solvent. Irradiation and analysis were performed in Dow-Corning 704 silicon diffusion pump oil. To circumvent calibration difficulties which might attend the use of the silicon oil, a weighed sample of 50:32:18 tin–lead–cadmium eutectic,[11] mp 148°, was included in each run as an internal standard. The ΔH_{fus} of the alloy was predetermined. A sample thermogram is shown in Figure 1. By this technique, a ΔH value of -9.0 ± 1.0 kcal/mol has been obtained for the trans–cis isomerization. Assuming negligible differences between the ΔH values for solution and vaporization of the two isomers, this value is approximately $\Delta H_g°$.

Efforts to obtain similar thermal data for the analogous bicyclo[6.1.0]nonane isomers have been forestalled by extraneous reactions which occur at the higher temperature required for trans–cis isomerization. In this instance, ΔG can be obtained directly *via* equilibration and is -2.9 kcal/mol at 158° in cyclohexane, a value in close accord with that reported for bicyclo[6.1.0]nonan-2-one.[3,12]

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[11] C. D. Hodgman, Ed., "Handbook of Chemistry and Physics," 44th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1962–1963, p 1536.

[12] K. B. Wiberg and A. de Meijere, *Tetrahedron Lett.*, 59 (1969).

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[13] Alfred P. Sloan Foundation Research Fellow, 1970–1972.

[14] National Science Foundation Trainee, 1969–1972.

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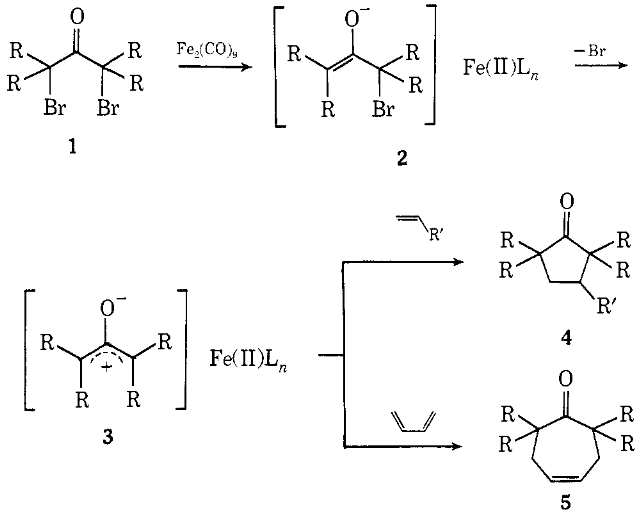
Mechanistic Aspects of the Reaction of α,α'-Dibromo Ketones and Iron Carbonyl. Reductive Rearrangements of Dibromo Ketones[1]

Sir:

We have recently reported the iron carbonyl assisted coupling of α,α'-dibromo ketones with unsaturated substrates which serves as a highly versatile method for the construction of a carbocyclic framework.[1,2] This paper presents evidence that the overall transformation proceeds by the route outlined in Scheme I:

Scheme I



initial reduction of the dibromide **1** with $Fe_2(CO)_9$ produces the iron enolate **2** (L = Br^-, CO, and solvent, etc.), which eliminates bromide ion to form the key oxyallyl–Fe(II) intermediate **3**; subsequent cyclocoupling with nucleophilic olefins or conjugated dienes yields the five- or seven-membered carbocycles **4** and **5**, respectively.

Formation of enolate species with α-bromo ketones was demonstrated by the reduction of 3-*endo*-bromocamphor with $Fe_2(CO)_9$[3] in dimethylformamide (DMF) containing 5% D_2O (60°, 17 hr) to give 3-*exo*-deuteriocamphor (87% d_1 and 13% d_0) in quantitative yield.[4] Dibromo ketones of type **1**, as usual, underwent successive debromination in moist solvent to produce the parent dialkyl ketones.

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[1] Carbon–Carbon Bond Formations Promoted by Transition Metal Carbonyls. III. Part II: R. Noyori, K. Yokoyama, S. Makino, and Y. Hayakawa, *J. Amer. Chem. Soc.*, 94, 1772 (1972).

[2] R. Noyori, S. Makino, and H. Takaya, *ibid.*, 93, 1272 (1971).

[3] Reaction was performed under a nitrogen atmosphere using the bromide (or dibromide) and $Fe_2(CO)_9$ in a mole ratio of 1:1.2. Iron pentacarbonyl was much less effective as a reducing agent. All new compounds gave correct elemental analyses and/or molecular peaks in exact mass spectra. Ir and nmr (with and without added $Eu(fod)_3$) were consistent with the structures assigned.

[4] *Cf.* R. R. Sauers and C. K. Hu, *J. Org. Chem.*, 36, 1153 (1971).