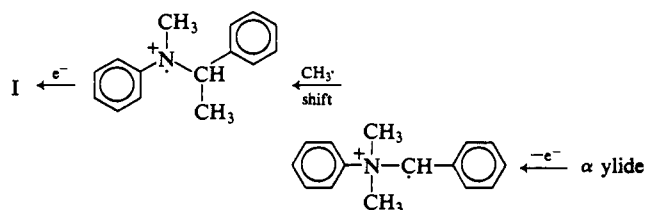


electron from the ylide gives a radical cation which methyl radical shift (methyl carbonium ion shift requires a one-electron C-C bond in the final intermediate) converts to an anilinylium cation. An electron must then be regained to reach I. If nuclear polarization is to be observed in this case, the last two steps must be much faster than the nuclear spin relaxation time¹³ or a strong polarization of the group adjacent to the final unpaired electron site is required. But extended CIDNP has only been observed during intense polarization activity.¹⁴ Furthermore the bimolecularity and less extensive resonance interactions for intermediates along this rearrangement route decrease its viability.



The intensity of the observed pmr effect requires that a free-radical intermediate be a direct product precursor. In addition, the particular form of the observed spectrum indicates that the major variations in spin state populations are for the most probable transitions.¹⁵ Thus a closely associated and short-lived free-radical pair as in Scheme I may be reasonable.

(13) K. H. Hausser and D. Stehlik, *Advan. Magnetic Resonance*, **3**, 79 (1967).

(14) A. R. Lepley, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract PHYS-109.

(15) A -1:-1:1:1 pattern might otherwise be anticipated.¹⁴

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On the Mechanism of the Thermal Reorganization of Bicyclo[6.1.0]nona-2,4,6-trienes to 8,9-Dihydroindenes

Sir:

Since the first report of the title reaction 8 years ago, many additional examples have been published.^{1,2} A number of workers have considered possible mechanisms, the greatest amount of attention having been focused on the hypothetical intermediacy of 1,3,5,7-cyclononatetraene or derivatives thereof.^{1a-d,f,h,3} The problem which

(1) (a) E. Vogel and H. Kiefer, *Angew. Chem.*, **73**, 548 (1961); (b) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Lett.*, 673 (1963); (c) K. F. Bangert and V. Boekelheide, *Chem. Ind. (London)*, 1121 (1963); *J. Am. Chem. Soc.*, **86**, 905 (1964); (d) G. J. Fonken and W. Moran, *Chem. Ind. (London)*, 1841 (1963); (e) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **85**, 2852 (1963); **86**, 5194 (1964); (f) E. A. LaLancette and R. E. Benson, *ibid.*, **87**, 1941 (1965); (g) T. L. Burkoth, *J. Org. Chem.*, **31**, 4259 (1966); (h) W. Grimme, *Chem. Ber.*, **100**, 113 (1967).

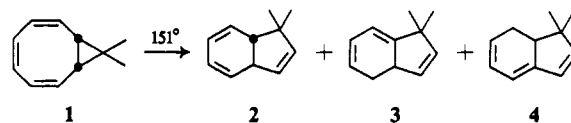
(2) (a) An 8,9-dihydroindene has been proposed as an intermediate but was not isolated: T. S. Cantrell and H. Shechter, *J. Am. Chem. Soc.*, **89**, 5868 (1967). (b) It is likely that bicyclo[6.1.0]nona-2,4,6-triene is an intermediate in the pyrolysis of *cis*-bicyclo[5.2.0]nona-2,4,8-triene to *cis*-8,9-dihydroindene: M. Jones, Jr., and S. D. Reich, *ibid.*, **89**, 3935 (1967).

(3) (a) E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 1 (1963); (b) A. G. Anastassiou, *J. Am. Chem. Soc.*, **90**, 1527 (1968); (c) J. M. Holovka, P. D. Gardner, C. B. Strow, M. L. Hill, and T. V. Van Anken, *ibid.*, **90**, 5041 (1968).

arises with this mechanism is that concerted ring opening and closing are predicted⁴ to proceed *via* a *cis,cis,cis,trans*-1,3,5,7-cyclononatetraene to give the corresponding *trans*-8,9-dihydroindene, whereas a *cis*-8,9-dihydroindene has been found to be the major product in every case in which the stereochemistry at the ring fusion has been established.^{1a-e,h} In an attempt to overcome this difficulty it has recently been suggested that an all-*cis* cyclononatetraene is formed as an intermediate in a step in which orbital symmetry is not conserved.^{3c}

In order to elucidate the steric requirements of this reaction we have synthesized 9,9-dimethylbicyclo[6.1.0]nona-2,4,6-triene (**1**). This was accomplished in 88% yield by the addition of a solution of 2,2-dichloropropane in ether to lithium cyclooctatetraene dianion in liquid ammonia at *ca.* -33°. The structure of the product follows from its typical *cis*-fused bicyclo[6.1.0]nona-2,4,6-triene uv spectrum^{1e,6} ($\lambda_{\max}^{\text{hexane}}$ 248 m μ (ϵ 3710)) and the nmr spectrum.^{7,8}

When **1** is heated at 151° (0.05 *M* in refluxing nonane) for 15.0 min the reaction mixture consists of 87% **1** and 12% **2** along with two minor components (**3** and **4**); after 60.0 min the mixture contains 53% **1**, 25% **2**, 8% **3**, 13% **4**, and a fourth unidentified product (1%). Products **2**, **3**, and **4** are isomers; the latter two were shown to arise from **2** and are themselves reasonably stable under the reaction conditions.



Isomer **2** was identified as *trans*-1,1-dimethyl-8,9-dihydroindene on the basis of its uv ($\lambda_{\max}^{\text{hexane}}$ 259.5 m μ (ϵ 3300))^{9a} and nmr (multiplet at τ 3.6-4.5 (6 H, vinyl), AB quartet at 6.88 (2 H, bridgehead, $J_{AB} = 20$ Hz),¹⁰ singlets at 8.87 and 9.06 (3 H each, methyl)) spectra and catalytic hydrogenation (3 mol equiv) to *trans*-1,1-dimethylhydrindan. Isomers **3** and **4** were assigned the structures indicated primarily on the basis of their uv ($\lambda_{\max}^{\text{hexane}}$ 265.5 (ϵ 4700) and 302 m μ (9870), respectively)⁹ and nmr spectra.¹¹ Each was catalytically hydrogenated (3 mol equiv) to give *cis*-1,1-dimethylhydrindan as the major product.

The formation of **3** and **4** from **2** can be explained by

(4) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), and references cited therein.

(5) Unsubstituted and *syn*-9-methylbicyclo[6.1.0]nona-2,4,6-triene and bicyclo[6.2.0]nona-2,4,6-triene have also been prepared by this procedure. It affords higher yields (60-90%) and is generally faster (4-5-hr stirring) and more convenient than other methods.^{1a, b, e}

(6) G. Moshuk, G. Petrowski, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 2179 (1968).

(7) The nmr spectrum displays a multiplet centered at τ 4.2 (6 H, vinyl), a singlet at 8.80 (5 H, *anti*-methyl and cyclopropyl), and a singlet at 9.04 (3 H, *syn*-methyl). Cf. the spectrum of *syn*-9-methylbicyclo[6.1.0]nona-2,4,6-triene.^{1e}

(8) All new compounds have been fully characterized and gave satisfactory elemental analyses.

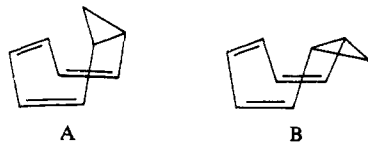
(9) (a) This value of λ_{\max} is very similar to those of *cis*-8,9-dihydroindene^{1e} and its derivatives.^{1c,e,f} (b) Cf. $\Delta^{2,4,6,22}$ -Isospirostatriene (λ_{\max} 306 m μ (ϵ 21,000)): J. Romo, H. J. Ringold, G. Rosenkranz, and C. Djerassi, *J. Org. Chem.*, **16**, 1873 (1951).

(10) *cis*-8,9-Dihydroindene has $J_{AB} = 12$ Hz for the bridgehead protons.

(11) Each isomer has five vinyl and six methyl protons; **3** has one diallylic and two allylic protons whereas **4** has three allylic protons.

1,5-hydrogen shift mechanisms.^{12,13} However, the essentially stereospecific formation of the primary product, **2**, is particularly significant in view of the fact that the stereoselectivity is *completely reversed* from that reported for the major product in all other bicyclo[6.1.0]nona-2,4,6-triene isomerizations.^{1a-e,h}

This can be explained on the basis of the two most probable conformations for bicyclo[6.1.0]nona-2,4,6-



trienes, *viz.*, A and B. We suggest that activated complexes leading to *cis*-8,9-dihydroindenes arise from conformation A,¹⁴ but that this pathway would be highly sterically strained in the case of the 9,9-dimethyl derivative **1** and therefore is not competitively formed. Thus 1,1-dimethyl-8,9-dihydroindene (**2**) is probably formed *via* conformation B, either by conrotatory opening to a *cis,cis,cis,trans*-1,3,5,7-cyclononatetraene followed by disrotatory closure, or by a direct [1,3]-antarafacial sigma-tropic migration of C₁ with retention of configuration.¹⁵ Both of these latter processes are "symmetry allowed,"¹⁶ *i.e.*, they occur *via* "aromatic"¹⁷ activated complexes. We are currently investigating additional aspects of these rearrangements.

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(12) W. R. Roth, *Chemia*, **20**, 229 (1966).

(13) We have shown that *cis*-8,9-dihydroindene is not formed from the *trans* isomer (*e.g.*, *via* two 1,5-hydrogen migrations) to a significant extent upon heating at 98° (2% v/v in heptane) for 75 min.

(14) Inspection of Dreiding models clearly shows that only a small structural reorganization is required for this process. The importance of this factor has been demonstrated by Doering in his elegant studies of the Cope rearrangement: W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(15) A 1,3 shift can occur with inversion of configuration: J. A. Berson and G. L. Nelson, *J. Am. Chem. Soc.*, **89**, 5503 (1967). This process has also been suggested by Israel, *et al.*, but an alternate mechanism involving an isocyanate intermediate is also possible: M. Israel, L. C. Jones, and E. J. Modest, *Tetrahedron Lett.*, 4811 (1968).

(16) We use this term advisedly since there is no element of symmetry in the activated complex.

(17) M. J. S. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1967).

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The Geometry of Coordinated Molecular Nitrogen. The Structure of Co(H)(N₂)(P(C₆H₅)₃)₃

Sir:

We wish to report further structural details on the molecular nitrogen complex of cobalt, Co(H)(N₂)(P(C₆H₅)₃)₃. Our original structural study¹ was carried out

(1) J. H. Enemark, B. R. Davis, J. A. McGinney, and J. A. Ibers, *Chem. Commun.*, 96 (1968).

on a limited set of 903 visually estimated X-ray intensities from a crystal, prepared in diethyl ether, of composition Co(H)(N₂)(P(C₆H₅)₃)₃ · (C₂H₅)₂O. Despite many attempts we were unsuccessful in preparing further suitable samples of this material.

However, a sample was finally grown from an *n*-butyl ether solution. The method used was a significant modification of that originally reported.² A mixture of powdered trisacetylacetonatocobalt(III) (0.375 g) and triphenylphosphine (1.5 g) was added to *n*-butyl ether (100 ml). The suspension was stirred, flushed with dry nitrogen, and cooled in an ice bath. To the cold suspension, into which a constant stream of dry nitrogen gas was passed, triethylaluminum (0.85 ml) was added drop by drop. The resultant mixture was allowed to warm to room temperature during which time a reaction took place, the color of the mixture changing from green to reddish brown. The solution was cooled and stirred in an ice-water bath under a steady nitrogen flow for 45 min. The unreacted trisacetylacetonatocobalt(III) was filtered off under a nitrogen atmosphere, and the filtrate was left to stand in a refrigerator at 0°. After 2 days a crop of thin prismatic crystals was filtered off. A Nujol mull of these crystals showed two absorption bands at 2085 and 2105 cm⁻¹, but the crystals were not suitable for X-ray analysis. A further crop of crystals was filtered off 2 days later and similarly discarded. After 2 weeks a sample was isolated from the filtrate which contained crystals suitable for X-ray analysis, and one crystal was mounted in a thin-walled glass capillary. The crystal was a parallelepiped of dimensions 0.10 × 0.15 × 0.45 mm. An infrared spectrum of the remaining sample also showed absorptions at 2085 and 2105 cm⁻¹. This sample was found to be diamagnetic by Faraday balance techniques, and the elemental composition from C, H, and N analysis was found to correspond to Co(H)(N₂)(P(C₆H₅)₃)₃ or to Co(N₂)(P(C₆H₅)₃)₃.

On the basis of Weissenberg and precession photographs we assigned the crystal to the monoclinic space group P2₁/c. The unit cell dimensions, as determined from a least-squares refinement of a number of high-angle reflections, are *a* = 37.159 (14), *b* = 11.355 (5), *c* = 21.779 (8) Å; β = 101.3(2)°, *V* = 9011 Å³ (Cu Kα₁ = 1.5406 Å). In the previous structural determination¹ the volume of the molecule was approximately 1320 Å³, and it is apparent that there are eight molecules in the present cell and hence the solution of the structure requires the huge task of locating the two independent molecules (120 non-hydrogen atoms) in the asymmetric unit.

A total of 6070 independent reflections was collected on a Picker diffractometer, in two separate runs, out to a maximum 2θ (Cu Kα) of 110°. The positions of the two cobalt and six phosphorus atoms were eventually found with difficulty by direct methods and were consistent with a sharpened, origin-removed Patterson function. The 4 nitrogen atoms and 18 phenyl rings were found from successive difference Fourier maps. An absorption correction was applied, and in the refinement the phenyl rings were treated as rigid groups. After a preliminary least-squares refinement, the cobalt and phosphorus atoms were allowed to vibrate anisotropically but the nitrogen atoms were constrained to isotropic vibration. The phenyl hydrogen atoms were then included as fixed contributions,

(2) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *ibid.*, **79** (1967).