## Tricyclo[5.4.0.0^{4,11}]undeca-2,6,9-trien-8-one via a Homobullvalenyl Cation

Sir:

Ions in the $C_{11}H_{11}$ manifold can be "bicycloaromatic" or "antibicycloaromatic" depending both on the number of electrons in a particular ion and its exact topology.[1,2] Thus, limits to the extent of such through-space electronic interactions may be reflected in the solvolytic fate of an ion which has a choice of rearrangement paths.[3] We report here the solvolytic generation of a homobullvalenyl cation and its subsequent rearrangement to tricyclo[5.4.0.0^{4,11}]undeca-2,6-9-trien-8-one (1).[4] Compound 1 is of interest by virtue of its relation to the bicyclic ion 2 which has been predicted to be bicycloaromatic.[1] Indeed, the formation of 1 may be most easily rationalized by rearrangement through such an intermediate, prompting us to communicate our preliminary results at this time.
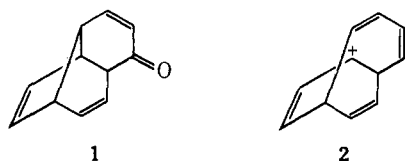

The treatment of bullvalene[5] with bromoform and potassium *tert*-butoxide[6] at 0° under argon, followed by column chromatography of the crude product, afforded dibromide 3 (mp 115–116°, 90%).[7] The struc-

ture of 3 was apparent from its *temperature-dependent* nmr spectrum[8] which clearly indicated a fluxional, bridged, homotropilidene system.[3b,9] Reaction of 3 with silver trifluoroacetate in benzene–acetic acid at 100°, followed by ether–water work-up and vacuum distillation, gave a pale amber liquid mixture which was fractionated by glpc to afford 1 (36%). The product thus isolated was a viscous, colorless, liquid, stable at room temperature for extended periods and homogeneous to glpc upon reinjection.[10]

That 1 is an α,β-unsaturated ketone in a six-membered or larger ring is apparent from the ir carbonyl absorption at 1688 cm^{-1} [11,12] and the low-field nmr absorbance at δ 6.81. Simultaneous spin decoupling of the four incompletely resolved bridgehead hydrogens ($\sim \delta$ 2.9–3.2) reveals three AB quartets in the vinyl region of the nmr spectrum indicative of three isolated and dissimilar double bonds. The magnitude of these coupling constants ($J = 11, 9, 5$ Hz) argues against three- or four-membered rings.[11]

On these grounds compounds which may reasonably be considered are the higher homologous enones of hydrocarbons 6[13] and 7[14]
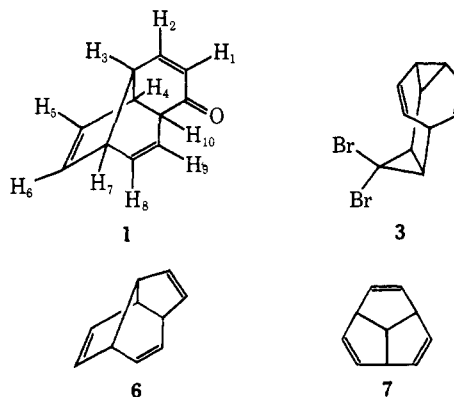

A definitive choice among these possibilities was made by complete, sequential decoupling of the nmr spectrum. Addition of Eu(fod)$_3$[15] to a solution of 1 causes complete resolution of the nmr spectrum. *One* of the vinyl resonances and *one* of the bridgehead

(1) (a) M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, 93, 6193 (1971). We are grateful to M. J. Goldstein for communicating these results to us prior to publication; (b) R. Hoffmann, XXIIIrd IUPAC, Boston, Mass., July 1971; (c) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany,; (d) M. J. Goldstein, International Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds, Sendai, Japan, 1970.

(2) M. J. Goldstein, *J. Amer. Chem. Soc.*, 89, 6357 (1967).

(3) (a) M. J. Goldstein and B. G. Odell, *ibid.*, 89, 6356 (1967); (b) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, 23, 3943 (1967); (c) J. B. Grutzner and S. Winstein, *J. Amer. Chem. Soc.*, 92, 3186 (1970); (d) J. C. Barborak and P. v. R. Schleyer, *ibid.*, 92, 3184 (1970); (e) R. E. Leone and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, 9, 860 (1970), and references therein.

(4) We have reported the synthesis of the isomeric *exo*-tricyclo-[4.3.2.0^{2,5}]undeca-3,8,10-trien-7-one (4): J. T. Groves, C. A. Bernhardt, and M. Ebner, XXIIIrd IUPAC, Boston, Mass., July 1971.

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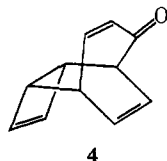
(5) (a) Bullvalene was prepared according to the method of Schröder.[5b] Cyclooctatetraene was obtained by a modification of the procedure of Reppe, *et al.*[5c] (b) G. Schröder, *Angew. Chem.*, 75, 722 (1963); (c) W. Reppe, O. Schlichting, K. Klaget, and T. Toepel, *Justus Liebigs Ann. Chem.*, 560, 1 (1948).

(6) W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, 76, 6162 (1954).

(7) Bullvalene was 98% pure by analytical glpc; the yield was based on unrecovered bullvalene at 55% conversion. An isomer of 3 is also isolated from this reaction in *ca.* 1% yield, which, on the basis of its *temperature-dependent* nmr spectrum, can only be 5. We will describe the origin and fluxional behavior of 5 in a subsequent paper.

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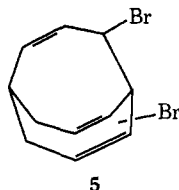
(8) 3: *m/e* (relative intensity) (45 eV) 304 (1.5), 302 (2.8), 300 (1.5), 223 (7.5), 222 (6.6), 221 (7.5), 142 (100 base), 141 (43.8); nmr δ (CDCl$_3$) 2.0 (2 H, dd, $J = 3, 4$ Hz), 2.6 (2 H, m), 3.9 (4 H, m), 5.65 (2 H, td, $J = 9, 2$ Hz). The corresponding dichloride has been reported by Schröder[9] and 3 has been prepared independently by M. J. Goldstein, R. C. Knauss, and S.-H. Dai, *J. Amer. Chem. Soc.*, 94, 680 (1972). We are grateful to M. J. Goldstein for communicating these results to us prior to publication.

(9) G. Schröder, J. F. M. Oth, and R. Merényi, *Angew. Chem., Int. Ed. Engl.*, 4, 752 (1965), and references therein.

(10) (a) Elemental analysis was within ±0.3% of expected values; (b) 1: *m/e* (relative intensity) (50 eV) 158 (100 base), 129 (77), 115 (47), 78 (40); ir (CCl$_4$) 3020, 2960, 1688, 1670, 1230 cm^{-1}; uv (cyclohexane) 216 (20,000), 265 (2000), 323 (70), 335 (150), 349 nm (170); nmr (CDCl$_3$) δ 2.92 (2 H, m), 3.06 (1 H, q, $J = 5$ Hz, resolved with Eu(fod)$_3$), 3.14 (1 H, ddd, $J = 6, 2.8, 1.2$ Hz), 5.43 (1 H, dddd, $J = 9, 5, 2, 1$ Hz), 5.67 (1 H, ddd, $J = 6, 4, 1$ Hz), 6.07 (1 H, dd, $J = 11.1$ Hz), 6.14 (1 H, ddm, $J = 9, 6.5, 1$ Hz), 6.60 (1 H, dd, $J = 3, 6$ Hz), 6.81 (1 H, ddd, $J = 11, 5, 1.2$ Hz).

(11) (a) N. Heap and G. H. Whitham, *J. Chem. Soc. B*, 164 (1966); (b) the uv λ_{max} of bicyclo[3.2.1]oct-3-en-2-one is reported to occur at 227 nm; (c) O. L. Chapman, *J. Amer. Chem. Soc.*, 85, 2014 (1963); (d) G. V. Smith and H. Kriloff, *ibid.*, 85, 2016 (1963); (e) P. Laszlo and P. v. R. Schleyer, *ibid.*, 85, 2017 (1963); (f) K. B. Wiberg and B. J. Nist. *ibid.*, 83, 1226 (1961).

(12) The ir carbonyl absorbance of 4 occurs at 1690 cm^{-1}.[4]

(13) M. Jones, Jr., *J. Amer. Chem. Soc.*, 89, 4236 (1967).

(14) R. B. Woodward, T. Fukunaga, and R. C. Kelly, *ibid.*, 86, 3162 (1964).

(15) R. E. Rondeau and R. E. Sievers, *ibid.*, 93, 1524 (1971).

resonances were observed to shift dramatically downfield, to which we assign the hydrogens flanking the carbonyl, H_1 and H_{10}, respectively. One of the three relatively unshifted bridgehead hydrogens appears as a quartet ($J = 5$ Hz) and is coupled to H_2, the hydrogen β to the carbonyl, and *both* of the remaining bridgehead hydrogens, H_4 and H_7. Only ketone **1** is consistent with these observations.[16]

The most likely mechanism for the **3 → 1** transformation appears to be silver-assisted ionization of **3**, ring opening to give the homobullvalenyl cation, **8a**, subsequent rearrangement to give **8b**, and hydrolysis to afford **9**.[16] The **9 → 1** conversion may proceed *via* 1,3-alkyl shift or through intermediate **10**, isoelectronic with
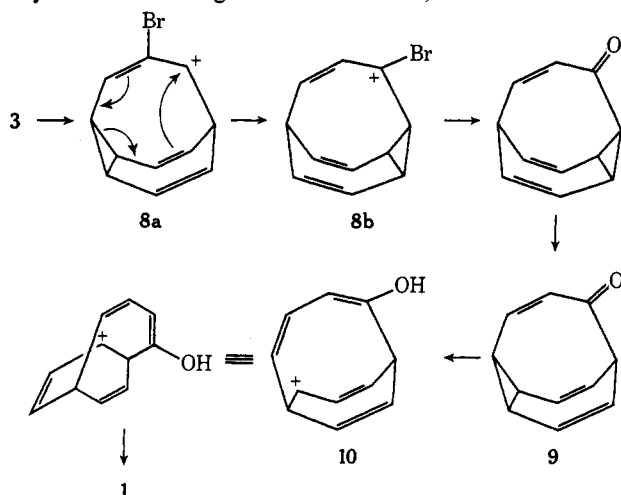
2. The relative ease with which this **3 → 1** transformation occurs may be indicative of substantial strain relief in passing from **9** to **1** or electronic stabilization of **10**. It is also possible that the orbital symmetry expectations in this rearrangement are affected by mediating silver ion.[17] We are currently studying these and other aspects of this reaction.

(16) The synthesis and interconversions of the higher homologous enones of bullvalene have recently been described; **9** is clearly inconsistent with the lack of symmetry in the nmr spectrum of **1**; see M. J. Goldstein, *et al.*, ref 8.

(17) (a) L. A. Paquette, *Accounts Chem., Res.*, **4**, 280 (1971), and references therein; (b) P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, **92**, 763 (1970).

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Separation of Nuclear Magnetic Resonance Signals of Internally Enantiotropic Protons Using a Chiral Shift Reagent. The Deuterium Isotope Effect on Geminal Proton–Proton Coupling Constants

Sir:

Recent studies[1] on a variety of chiral shift reagents have shown that such compounds are capable of induc-

(1) (a) G. M. Whitesides and D. W. Lewis, *J. Amer. Chem. Soc.*, **92**, 6979 (1970); (b) G. M. Whitesides and D. W. Lewis, *ibid.*, **93**, 5914
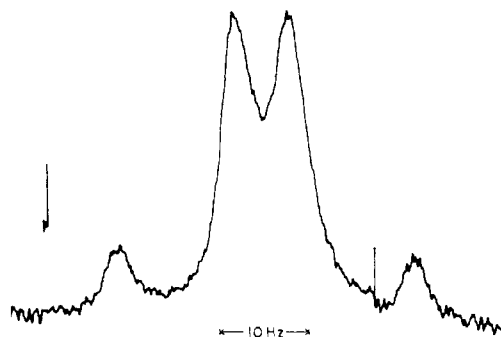
Figure 1. The methylene proton absorption of a 0.2 M solution of benzyl alcohol in CCl_4 in the presence of 0.15 mol equiv of **1**.

ing differential pseudocontact shifts[2] for corresponding protons in the R and S enantiomers of certain organic Lewis bases. Their ability to differentiate enantiotropic[3] protons at a prochiral[3] center was recognized but not observed experimentally.[1c] We wish to report that tris[3-heptafluoropropylhydroxymethylene-*d*-camphorato]praseodymium(III) (**1**) possesses the ability to induce a chemical-shift difference of up to 0.8 ppm (per molar equivalent[4] of added shift reagent) between the benzylic protons of benzyl alcohol and its derivatives. Such resolution of signals for enantiotropic protons provides an alternative to the isotopic substitution method for the determination of geminal coupling constants. In addition, the latter method will be shown to be in error due to a small isotope effect on the geminal coupling constant, and relaxation effects.

When a 0.2 M solution of benzyl alcohol in CCl_4 was treated with 0.15 mol equiv[4] of **1**, the CH_2 protons were shifted 6.63 ppm to higher field and appeared as an AB quartet having $J_{AB} = 13.0 \pm 0.2$ Hz[5] and $\Delta\nu_{AB} = 0.13$ ppm (see Figure 1). This resolution of the benzylic protons must result from their shift nonequivalence as diastereotopic protons in the complex of benzyl alcohol with **1**. The possibility exists that J_{AB} may also contain a significant contribution from this complex. We therefore determined J_{AB} at three other concentrations of **1**. As shown in Table I, J_{AB} does not vary measurably until more than 0.3 equiv of **1** has been added. We therefore conclude that $J_{AB} = 13.0 \pm 0.2$ Hz in benzyl alcohol. To confirm this value, J_{H-D} for *O*-α-dideuteriobenzyl alcohol in chloroform at 39 and at 49° was found[6] to be 1.91 $\pm$ 0.01, in fair agreement (0.6 Hz) with the direct measurement using **1**. The data for six para-substituted benzyl alcohols[7] and neopentanol are given in Table I.

(1971); (c) H. L. Goering, J. N. Eikenberry, and G. S. Koermer, *ibid.*, **93**, 5913 (1971); (d) R. R. Fraser, M. Petit, and J. K. Saunders, *Chem. Commun.*, 1450 (1971).

(2) Recent evidence indicates that lanthanide-induced shifts are produced primarily by a pseudocontact mechanism; see (a) J. K. M. Saunders and D. M. Williams, *Tetrahedron Lett.*, 2812 (1971); (b) H. Huber and C. Pascal, *Helv. Chim. Acta*, **54**, 913 (1971); for a recent compilation of references on shift reagents see W. DeW. Horrocks, Jr., J. P. Sipe III, and J. R. Luber, *J. Amer. Chem. Soc.*, **93**, 5258 (1971).

(3) M. Raban and K. Mislow, *Top. Stereochem.*, **1**, 1 (1967).

(4) Information regarding the stoichiometry of this donor–lanthanide complex in solution is not available.

(5) All geminal coupling constants discussed in this paper are assumed to be negative as has been established for other benzylic protons; see R. R. Fraser, *Can. J. Chem.*, **40**, 1483 (1962).

(6) All other protons were spin decoupled during measurement of the spectra.

(7) A plot of ^2J *vs.* Hammett σ constants for the seven benzyl alcohols gives a slope (ρ) = -1.53 ($r = 0.960$). The magnitude of ρ in compari-