$$2RuCl_2(PPh_3)_4 \xrightarrow[-4Ph_3P]{N_2,\ THF} \underset{\mathbf{4}\ (72\%)}{(Ph_3P)_2Ru(Cl)Cl_3Ru(N_2)(PPh_3)_2}$$

$$Ru(H)(N_3Ph_2)(Ph_3P)_3{}^{8} \xrightarrow[-Ph_3P]{N_2,\ THF} \underset{\mathbf{5}\ (38\%)}{Ru(H)(N_2)(N_3Ph_2)(PPh_3)_2}$$

characterized by elemental analysis.[9] Complex **4** has $\nu_{N\equiv N}$ 2165 cm^{-1} (Nujol) and reacts with $N_2B_{10}H_8S(CH_3)_2$[9] to form the previously reported[10] $(Ph_3P)_2Ru(Cl)Cl_3Ru(PPh_3)_2N_2B_{10}H_8S(CH_3)_2$. Passage of argon through a tetrahydrofuran solution of **4** causes loss of nitrogen; however, the $[(Ph_3P)_2RuCl_2]_2$ species reported by Gilbert and Wilkinson[11] was not obtained.

The yellow complex **5** has $\nu_{N\equiv N}$ 2000 cm^{-1} (Nujol) and exhibits a hydride resonance at δ −13.58 (triplet, J_{P-H} = 21 Hz) in a benzene-d_6 solution. In sharp contrast to the behavior of $RuH_2(N_2)(Ph_3P)_3$, dinitrogen is not lost from **5** when its solutions are swept with argon or with hydrogen.

Acknowledgment. We are indebted to Mrs. C. W. Alegranti for the membranes used in this work.

(8) W. H. Knoth, *Inorg. Chem.*, **12**, 38 (1973).

(9) Complex **4**: *Anal.* Calcd for $C_{72}H_{60}Cl_4N_2P_4Ru_2$: C, 60.84; H, 4.25; Cl, 9.97; N, 1.97; P, 8.71. Found: C, 61.11; H, 4.54; Cl, 9.71; N, 1.82; P, 8.56. Complex **5**: *Anal.* Calcd for $C_{48}H_{41}N_5P_2Ru$: C, 67.75; H, 4.86; N, 8.23; P, 7.28. Found: C, 68.62; H, 4.96; N, 7.98; P, 6.94.

(10) W. H. Knoth, *J. Amer. Chem. Soc.*, **88**, 935 (1966).

(11) J. D. Gilbert and G. Wilkinson, *J. Chem. Soc. A*, 1749 (1969).

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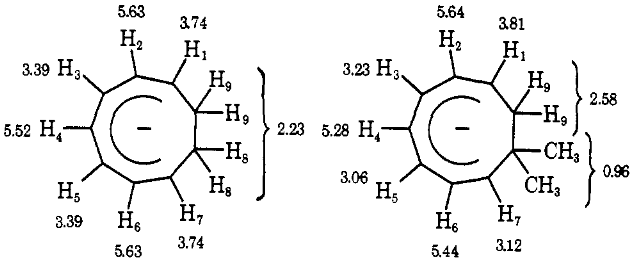
Conformational Analysis of Cyclononatrienyl Anions

Sir:

A number of nmr spectra of simple hydrocarbon anions have been reported[1] in recent years but in most cases these species have been acyclic and presumably planar. Little is known about the molecular distortions of cyclic anions (or cations) which possess substantial conformational strain. In this communication we report the first examples of cyclononatrienyl anions and also present the first analysis of the conformation of a medium ring cyclic anion.

Treatment of 1,3,6-cyclononatriene (**1**)[2] with potassium amide in liquid ammonia gave a light-red solution of anion **2** (see nmr data in Figure 1)[3] which was quenched into pentane–water to afford **1** as the sole product. This anion is also rapidly produced at 25° starting with 1,4,7-cyclononatriene.[4]

The observation of only one signal for the C_8 and C_9 protons indicates that either **2** is planar or that it is nonplanar and rapidly flipping on the nmr time scale. The relatively low value for J_{23} (7.6 Hz)[5] tends to support the latter interpretation.



$J_{12} = J_{67}$ = 10.5 Hz
$J_{23} = J_{56}$ = 7.6 Hz
$J_{34} = J_{45}$ = 11.6 Hz
$J_{19} = J_{78}$ < 6.5 Hz

2

J_{12} = 9.6 Hz J_{67} = 11.7
J_{23} = 6.2 Hz J_{56} = 8.0
J_{34} = 10.8 Hz J_{45} = 12.1
J_{19} = 8.5 Hz

3

Figure 1. Nmr spectral data for the (potassium) cyclononatrienyl (**2**) and 8,8-dimethylcyclononatrienyl (**3**) anions in potassium amide–liquid ammonia at −55° with trimethylamine ($\delta^{TMS}_{NH_3}$ 2.135) as internal standard.

Additional evidence concerning this point is provided by the preparation of the 8,8-dimethylcyclononatrienyl anion (**3**) by the addition of either 8,8- or 9,9-dimethyl-1,3,6-cyclononatriene[2] (**4** and **5**, respectively) to potassium amide in liquid ammonia. The chemical shift of the methyl protons was obtained by using ammonia-d_3[6] as the solvent. Analysis of the nmr spectrum of **3** was aided by the fact that H_3 and H_5 undergo exchange in potassium amide–ammonia-d_3 (*ca.* 1 hr at room temperature) with the result that H_4 becomes a broadened singlet and H_2 and H_6 become doublets. The fact that exchange occurs primarily at these positions is in accord with the quenching of **3** into pentane–water to afford a mixture consisting only of **4** and **5**.[7]

The remarkable observation that the values of J_{12}, J_{23}, and J_{34} in **3** are each 1–2 Hz smaller than J_{45}, J_{56}, and J_{67}, respectively, suggests that **3** is nonplanar, even though the methylene protons at C_9 and the two methyl protons are each equivalent at −55°. This point is strongly supported by the large value of J_{19} (8.5 Hz) which requires that the methylene group at C_9 be substantially twisted with respect to the adjacent π bond so that H_1 and one of the protons at C_9 are nearly *s-trans* to each other.[8]

We suggest that the above points are uniquely accommodated by **6** as the predominant conformation. The latter is perhaps best described in terms of eight carbons (C_1–C_8) located near a common plane and forming a shallow twisted tub with C_9 bent substantially above the other ring carbons. Some features of this conformation are (1) the geminate methyl groups are at C_8 rather than at the sterically more crowded C_9, (2) the substituents at C_8 are more or less staggered with respect to those at C_9 and also with H_7, in accord with the low value (<4.5 Hz) estimated for J_{78} (average) in

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(1) Reviews: (a) J. M. Brown, *Org. React. Mech.*, 127 (1969); (b) *ibid.*, 119 (1970); (c) R. C. Haddon, V. R. Haddon, and L. M. Jackman, *Fortsch. Chem. Forsch.*, **24**, 33 (1971).

(2) W. H. Okamura, T. I. Ito, and P. M. Kellett, *Chem. Commun.*, 1317 (1971). A similar reduction was discovered independently in these laboratories by T. J. Henry utilizing potassium instead of sodium.

(3) The nmr spectrum of **2** is completely different from that of the unknown species obtained by treatment of **1** with *n*-butyllithium in TMEDA–hexane; R. B. Bates, S. Brenner, and B. I. Mayall, *J. Amer. Chem. Soc.*, **94**, 4765 (1972).

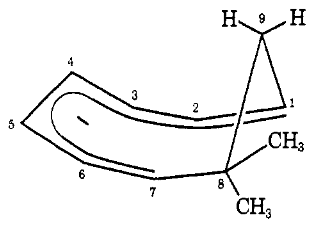
(4) Prepared by the method of P. Radlick, Ph.D. Thesis, University of California at Los Angeles, 1964.

(5) The C_2–C_3 bond is the most likely π bond to be twisted since it has the lowest HMO π bond order.

(6) I. Melczynski, *Angew. Chem.*, 74, 32 (1962). We thank Dr. John Morrison for assistance with the preparation of ammonia-d_3.

(7) A 72:28 ratio of triene B to triene A (same designation as in ref 2) was obtained. It has not been established which isomer is which; W. H. Okamura, personal communication.

(8) For an analysis of a similar coupling in 1,3,5-cycloheptatriene, see H. Günther and R. Wenzl, *Z. Naturforsch. B*, **22**, 389 (1967).



6

2,[9] (3) the π bonds between C_1 and C_4 are more twisted than those between C_4 and C_7 because they are adjacent to the "out-of-plane" C_9 rather than to the "in-plane" C_8, and (4) H_7 is located across the ring from the more twisted portion of the π system (particularly C_1) and is therefore substantially more shielded (or less deshielded) than H_1.[10] A perturbation in the counterion does not seem to have a large effect on the spectral parameters discussed above since the cesium and potassium salts of **3** have nearly identical spectra.

Interestingly, treatment of 1,2-cyclononadiene with potassium amide in liquid ammonia in an nmr tube at room temperature affords 1,5-cyclononadiene[11] with no evidence of anion formation. This presumably is due to the large strain in the latter species.[12]

In summary, the nmr spectra of anions **2** and **3** provide the most detailed information to date regarding the conformation of sterically strained anions. It is clear from this study that the need to minimize angle and torsional strain can compete effectively with the requirement for maximum overlap in the π system.[13] Furthermore, substantial delocalization of charge can occur even in a relatively highly twisted π system.

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[9] This is estimated from the value of J_{19} in 3 (8.5 Hz) and the average value of J_{19} and J_{78} in 2 (<6.5 Hz).

[10] The fact that H_7 is >0.6 ppm upfield from H_1 is probably due to an anisotropy effect rather than to the influence of excess negative charge since the effect of a twist in the C_1–C_4 portion of the ring is to increase the negative charge at C_1 relative to C_7.

[11] G. Nagendrappa and D. Devaprabhakara, *J. Organometal. Chem.*, **15**, 225 (1968). This is the most stable cyclononadiene isomer: D. Devaprabhakara, C. G. Cardenas, and P. D. Gardner, *J. Amer. Chem. Soc.*, **85**, 1553 (1963).

[12] The cyclooctadienyl anion is nonplanar but nevertheless is generated rapidly and essentially completely in potassium amide–liquid ammonia: H. Kloosterziel and J. A. A. van Drunen, *Recl. Trav. Chim. Pays-Bas*, **89**, 368 (1970).

[13] The conformation of anions 2 and 3 leads us to suggest that the *all-cis*-cyclononatetraenyl anion may be nonplanar. See (a) T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, **85**, 2852 (1963); (b) E. A. LaLancette and R. E. Benson, *ibid.*, **85**, 2853 (1963); (c) see also G. Boche, D. Martens, and W. Danzer, *Angew. Chem., Int. Ed. Engl.*, **8**, 984 (1969).

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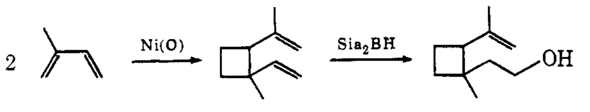
A Synthesis of (±)-Grandisol

Sir:

The limited supply of insect pheromones from natural sources places their synthesis into a strategic position with regard to procurement.[1] We wish to report a novel two-step synthesis[2] of the important monoterpene, grandisol (**2**), a key constituent of the male boll weevil pheromone (eq 1).



(1)

1 2 (grandisol)

A salient feature of the synthesis we report is based upon the remarkable discovery by Heimbach[4] that certain zero-valent nickel complexes are useful for the catalytic production of *cis*-1,2-divinylcyclobutanes from 1,3-dienes.[5]

Thus, 10.0 g (0.0364 mol) of nickel bisacetylacetonate monohydrate was dried overnight at 85° (0.5 mm) and then brought to room temperature and atmospheric pressure with rigorous exclusion of atmospheric oxygen and moisture. To this were added 30 ml of dry toluene (freshly distilled under N_2) and 25.0 g (0.23 mol) of freshly distilled 1,5-cyclooctadiene (COD). After the solid had dissolved, the solution was stirred an additional hour and cooled to $-10°$, and about 3 g of butadiene was added. This was followed by the dropwise addition (6 hr) of 26% $Al(C_2H_5)_3$ in toluene (19.7 ml, 0.038 mol) at -5 to $-10°$. After the addition was completed, the mixture was stirred an additional 4 hr, and the bright yellow crystals of $Ni(COD)_2$ were filtered in a drybox, washed with toluene, and dried *in vacuo*. Yields obtained by this method ranged from 60 to 85%.

The dimerization was carried out by addition of isoprene to a 1:1 mixture of the $Ni(COD)_2$ and tris(2-biphenylyl) phosphite.[6] Best results were obtained when isoprene was present in about a 70:1 molar ratio to nickel. The reaction vessel was sealed with a serum stopper, and the solution was magnetically stirred at room temperature until glpc monitoring indicated a maximization of product formation. The reaction was terminated by addition of 4 mol of triphenyl phosphite/mol of nickel, stirring an additional 30 min and filtering. The filtrate was distilled at 0° (100 mm) into a Dry Ice–acetone trap. After the major portion of the isoprene was removed by distillation, other fractions were collected by successively decreasing the pressure. From these crude distillates the material could be further purified.[7] Thus, the desired cyclobutane **1** was produced in 12–15% efficiency based on reacted isoprene, along with two other compounds identified as 1,5-dimethylcyclooctadiene (**3**) and the vinylcyclohexene (**4**) with the indicated uncertainty about the position of the methyl group. Above room temperature **1** undergoes a Cope rearrangement to give **3**. Surprisingly, no other cyclobutanes were produced in yields exceeding 1%.

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[1] M. Jacobson, "Insect Sex Attractants," Interscience, New York, N. Y., 1965.

[2] Previous syntheses[3] of grandisol have relied upon photochemical formation of the cyclobutane ring.

[3] J. H. Tumlinson, D. D, Hardee, R. C. Gueldner, A. C. Thompson, P. A. Hedin, and J. P. Minyard, *Science*, **166**, 1010 (1969); see also *Chem. Eng. News*, **48**, 40 (Jan 26, 1970).

[4] P. Heimbach and W. Brenner, *Angew. Chem., Int. Ed. Engl.*, **6**, 800 (1967).

[5] We thank Dr. Heimbach for making available the details of the catalyst preparation.

[6] C. L. Moyle, U. S. Patent 2,220,845 (1940).

[7] Spinning band distillation gave a fraction enriched in 1. Preparative glpc on a 15% Carbowax 20M on 80–100 Chromosorb W column operated at 65° gave pure 1. Its proton nmr spectrum shows signals at δ 1.25 (s, 3 H, methyl), 1.56 (s, 3 H, isopropenyl methyl), ~1.6–2.5 (m, 4 H, cyclopropyl), 2.27 (t, 1 H, allylic), 4.55–5.20 (m, 4 H, terminal methylene), 5.85–6.38 (m, 1 H, vinyl).