dinitrophenol. Hydrolysis of the triester must necessarily proceed *via* either an addition–elimination or a direct SN2(P) mechanism.[5] This would indicate (but again certainly not prove) that only in a unimolecular metaphosphate mechanism will an isotope effect be observed.

Details of these results as well as those of a diester hydrolysis and enzymatic systems will be presented later.

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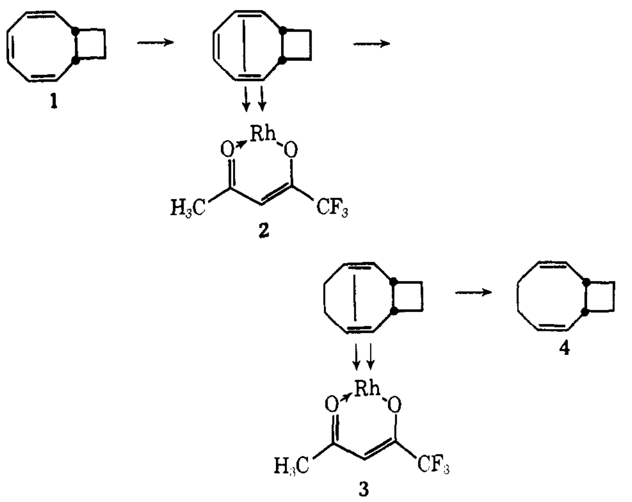
cis-Bicyclo[6.2.0]deca-2,6-diene[1]

Sir:

The visualization of a degenerate Cope rearrangement has been very fruitful, leading to the celebrated homotropilidene[2] and bullvalene[3] with fluxional structures. On the same concept was based the synthesis of *trans*-bicyclo[8.4.0]tetradeca-*trans*-2,*trans*-8-diene,[4] whose degenerate Cope rearrangement is not fast enough to give a dynamic nmr spectrum, but reveals itself by the racemization of the optically active compound.[5] In fact, the whole series of bicyclo[$(n + 4).n.0$]di-2,$(n + 4)$-enes may be expected to undergo this kind of rearrangement. We describe here the synthesis of *cis*-bicyclo[6.2.0]deca-2,6-diene (**4**), the next higher homolog of homotropilidene in this series.

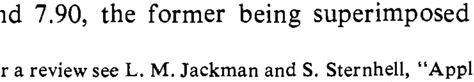
Treating *cis*-bicyclo[6.2.0]deca-2,4,6-triene (**1**)[6] with dicarbonyltrifluoroacetylacetonatorhodium(I)[7] in hexane solution yielded complex **2** (87% after sublimation at 90° (0.005 mm); mp 91°)[8] in which both outer double bonds of the starting triene are attached to the metal, due to the preferred square-planar geometry of tetracoordinated Rh(I). The complex **2** smoothly absorbed 1 mol equiv of hydrogen in hexane solution over 5% Pd/C. The resulting complex **3** (93%; mp 108°),[8] exhibiting in the vinyl region of the nmr spectrum only a singlet at τ (CCl_4) 4.25 due to the enolic proton of the trifluoroacetylacetonate ligand, was decomposed by shaking a pentane solution with 10% aqueous KCN. After filtration through alumina and evaporation of the solvent, *cis*-bicyclo[6.2.0]deca-2,6-diene (**4**) was obtained in 90% yield.



The structural assignment is based on the nmr spectrum, shown in Figure 1A [τ 4.62 (four olefinic protons), 6.65 (two bridgehead protons), 7.4–8.4 (eight methylene protons)], and on the ozonolysis followed by work-up with peracetic acid and diazomethane which gave *cis*-1,2-dicarbomethoxycyclobutane and dimethyl succinate.

The nmr spectrum of **4** does not show averaged shifts or temperature-dependent line shapes, characteristic for a rapidly reversible process. Thus, the degenerate Cope rearrangement had to be detected by isotopic labeling. 9,9,10,10-Tetradeuterio-*cis*-bicyclo[6.2.0]deca-2,4,6-triene, obtained by Staley's synthesis with tetradeuterio-1,2- dibromoethane, was selectively deuterated at the central double bond as above *via* the rhodium complex. The resulting 4,5,9,9,10,10-hexadeuterio-*cis*-bicyclo[6.2.0]deca-2,6-diene (**4-D**) shows in its nmr spectrum (Figure 1B), with H,D decoupling, three sharp signals at τ 4.66, 6.70, and 7.66 for the olefinic protons, the bridgehead protons, and the two remaining methylene protons, respectively. As indicated by their narrow peak, these latter protons are of only one type. Accordingly, the addition of D_2 was regio- as well as stereoselective and the Cope rearrangement had not occurred during the preparation, including glpc at 120°. Since the two remaining methylene protons absorb at lowest field of all the methylene protons in **4**, we assign to them the trans configuration (with respect to the attached cyclobutane ring) which, in the open conformation, locates them in the deshielding zone[9] of the flanking double bonds.

Heating to 135° for 3 hr had no effect on **4-D**; indeed, 30 min at 180° was needed to bring about a change in the spectrum of the structurally unaffected compound.



4-D **4-D′**

After heating for 3 hr at 185° in the gas phase, **4-D** gives the spectrum shown in Figure 1C, which is interpreted as arising from the equilibrium mixture of **4-D** with its Cope rearrangement product **4-D′**. The methylene protons in the cyclobutane ring of **4-D′** couple with the bridgehead protons in an A_2X_2 manner ($J_{A,X} = J_{A,X'} = 5$ Hz) giving rise to two triplets at τ 6.70 and 7.90, the former being superimposed by the

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[1] Presented at the Autumn Meeting of the Chemical Society, London, 1970.

[2] W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

[3] (a) G. Schröder, *Angew. Chem.*, **75**, 722 (1963); *Angew. Chem., Int. Ed. Engl.*, **2**, 481 (1963); *Chem. Ber.*, **97**, 3140 (1964); (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).

[4] P. S. Wharton, Y. Sumi, and R. A. Kretchmer, *J. Org. Chem.*, **30**, 234 (1965).

[5] P. S. Wharton and R. A. Kretchmer, *ibid.*, **33**, 4258 (1968).

[6] S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **92**, 7612 (1970).

[7] F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 3156 (1964).

[8] All new substances gave satisfactory analyses for C and H.

[9] For a review see L. M. Jackman and S. Sternhell, "Application of NMR Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, p 83.

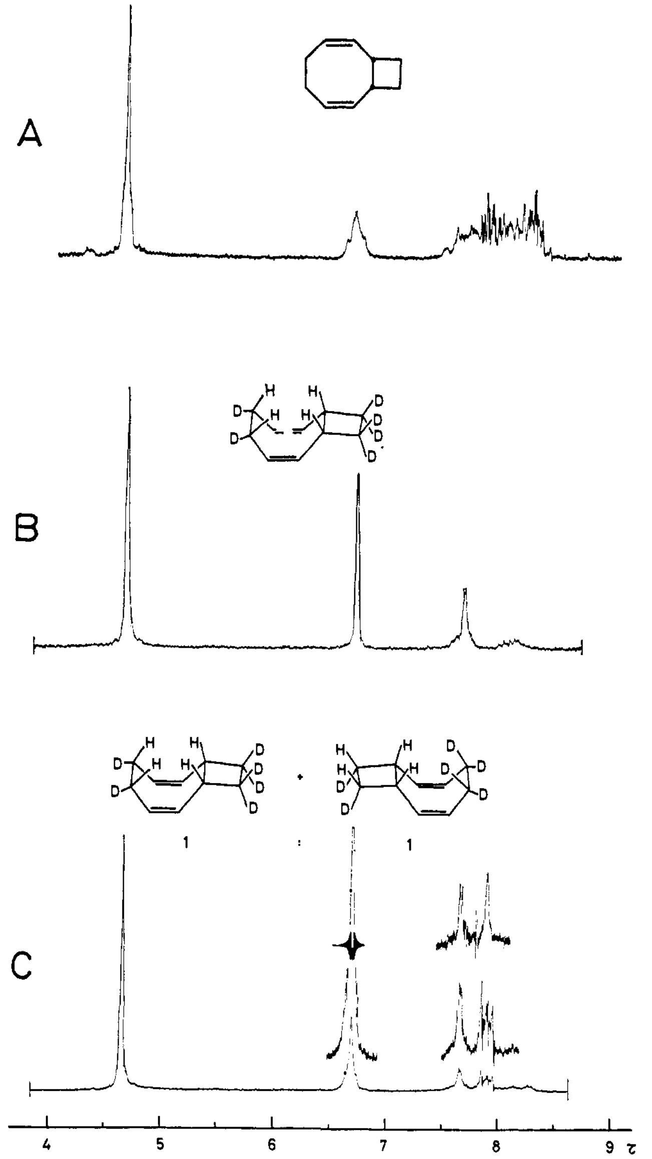
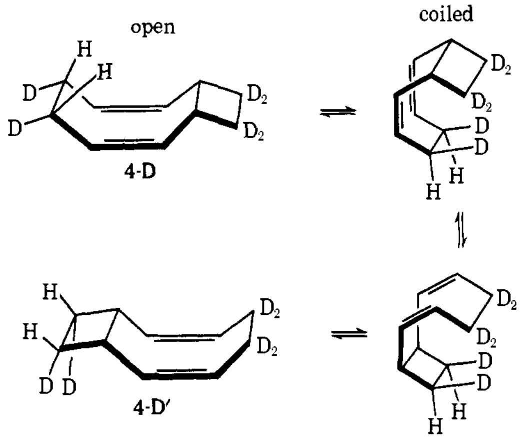


Figure 1. Proton nmr spectra of variously labeled *cis*-bicyclo[6.2.0]deca-2,6-dienes (CCl_4, 100 MHz, TMS as internal standard): A, spectrum of **4**; B, spectrum of **4-D**, H,D decoupled; C, spectrum of the equilibrium mixture of **4-D** and **4-D′**, H,D decoupled (of the inserted enlargements the upper one is with decoupled bridgehead protons).

singlet of the bridgehead protons of **4-D**. Irradiation with the frequency of the bridgehead protons causes the triplet of the cyclobutane protons to collapse to a singlet, thus confirming the assigned coupling and indicating the presence of only one kind of methylene proton in the cyclobutane ring. Their strong coupling (5 Hz) with the bridgehead protons manifests the mutual cis configuration.[10] Accordingly, the reversible Cope rearrangement proceeds stereospecifically in such a way that the methylene hydrogens trans to the cyclobutane ring in **4-D** become trans to the cyclooctadiene ring in **4-D′**; or more generally, the individual methylene hydrogens retain their geometry with respect to the attached ring.



The observed stereochemistry cannot be rationalized by the reaction occurring in the stable open conformation, for here the trans hydrogens in **4-D** are pointing inward and after ring closure between C_3 and C_6 they must appear cis to the newly formed eight-membered ring. In the coiled conformation, on the other hand, the trans-methylene hydrogens have the correct orientation to remain trans on the cyclobutane ring to be formed. Moreover, this latter conformation is ideal in all respects for the electron reorganization of the Cope rearrangement to occur with the least motion of atoms, but it suffers from a severe compression between the two pairs of cis deuterium atoms.

The stereochemistry of the reaction proves unambiguously that the coiled conformation is a prerequisite for the transition state and the higher temperature required (about 100°) than for the Cope rearrangement of *cis*-1,2-divinylcyclobutane[11] adequately reflects the high strain involved. A substantial rate enhancement should be experienced, then, by a *cis*-bicylo[6.2.0]deca-2,6-diene with direct bonding between C_4 and C_{10} and between C_5 and C_9, *i.e.*, by an analog of semibullvalene.[12,13]

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[10] *Cf.* the coupling constants between the cyclobutane protons in *endo-cis*-5,6-dimethylbicyclo[2.2.0]hex-2-ene (4 Hz) and in the exo isomer (1 Hz). The nmr spectra of both compounds were kindly provided by Professor W. R. Roth, Ruhr-Universität, Bochum.

[11] G. S. Hammond and C. D. DeBoer, *J. Amer. Chem. Soc.*, **86**, 899 (1964); R. Sundermann, Dissertation, University of Cologne, 1966.

[12] H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966).

[13] This expectation has been verified very recently by the synthesis of hypostrophane: J. S. McKennis, L. Brener, J. S. Ward, and R. Pettit, *ibid.*, **93**, 4957 (1971).

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A New Mode of Sulfur Dioxide Attachment to Halogenated Transition Metal Complexes

Sir:

The considerable interest in sulfur dioxide reactions with metal complexes[1] prompts us to report our study

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[1] (a) C. G. Hull and M. H. B. Stiddard, *J. Chem. Soc. A*, 710 (1968); (b) W. Stromeier and J. F. Gutterberger, *Chem. Ber.*, **97**, 1871 (1964); (c) R. Cramer, *J. Amer. Chem. Soc.*, **89**, 5377 (1967); (d) J. J. Levinson and S. D. Robinson, *Chem. Commun.*, 198 (1967); (e) A. Wojcicki,