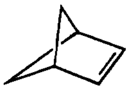
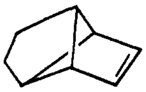
The Synthesis of Bicyclo[2.1.1]hex-2-ene[1]

Sir:

Whereas the chemistry of bicyclo[2.1.1]hexanes has been explored to a considerable extent during the last decade,[2] the corresponding parent olefin, bicyclo[2.1.1]-hex-2-ene (I), has never been described. Much to our surprise, even the Hofmann elimination sequence recently reported for the synthesis of the closely related tricyclo[3.3.0.0^{2,6}]oct-2-ene (II)[3] was unsuccessful when applied to the simpler bicyclic nucleus.[4] We now report the successful application of a newly described olefin synthesis to this problem.[5,6]


I


II


IIIA, X = O
B, X = NNHTos

The readily accessible bicyclo[2.1.1]hexan-2-one (IIIA)[7] was converted into its *p*-toluenesulfonylhydrazone (IIIB)[8] which, in a typical experiment, was treated with excess ethereal methyllithium at room temperature for 15 hr. After quenching the reaction mixture with water, most of the ether was removed by careful distillation. The residue, which contained two main hydrocarbon products, was subjected to preparative gas chromatography. The component of shorter retention time, formed in about 25% yield from IIIB, was established to be the desired I on the basis of the following evidence. (1) Its mass spectrum shows a parent peak at *m/e* 80 ($C_6H_8{\cdot}^+$) and a base peak at 79 ($C_6H_7^+$). (2) Its nmr spectrum (60 Mc, external TMS) shows olefinic absorption centered at τ 3.38 (2 H) and saturated proton absorptions centered at τ 7.66 (4 H) and 7.91 (2 H). (3) Catalytic hydrogenation in absolute ethanol over Adams catalyst resulted in the uptake of 1 equiv of hydrogen. The isolated product was indistinguishable from an authentic sample of bicyclo[2.1.1]hexane on the basis of glpc comparison on two columns, as well as by nmr and mass spectral comparisons.

Since I is the only olefin which could give rise to bicyclo[2.1.1]hexane on catalytic reduction, the success of the toluenesulfonylhydrazone–alkyllithium technique in this case is established, and it would appear that this method will be especially useful for the synthesis of highly strained olefins.[9,10]

The ultraviolet absorption spectrum of I is most unusual for a simple, disubstituted ethylene. In *n*-pentane solution maximal absorption appears at 220 mμ (ϵ ~1300), with a shoulder at 226 mμ (ϵ ~1000). In the gas phase vibrational fine structure shows maxima at 204.4, 205.2, 207.1, 207.9, 208.7, 210.8, 211.5, and 215.2 mμ. These spectral data bear a striking resemblance to those observed for II.[3] Further work with both olefins is now being undertaken.

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[1] The partial support of this research by a National Science Foundation grant and by the Chevron Research Co. is acknowledged with pleasure.

[2] For a recent review of this area, see J. Meinwald and Y. C. Meinwald, *Advan. Alicyclic Chem.*, **1**, 1 (1966).

[3] The synthesis of a tricyclic analog of I, tricyclo[3.3.0.0^{2,6}]oct-3-ene, was reported by J. Meinwald and B. E. Kaplan, *J. Am. Chem. Soc.*, **89**, 2611 (1967).

[4] Unpublished results with R. A. Chapman, and also private communication from Professor F. T. Bond.

[5] R. H. Shapiro and M. J. Heath, Abstracts of Papers of the 154th National Meeting of the American Chemcal Society, Chicago, Ill., Sept 1967, S104; R. H. Shapiro and M. J. Heath, *J. Am. Chem. Soc.*, **89**, 5734 (1967).

[6] G. Kaufman, F. Cook, H. Schechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967).

[7] F. T. Bond, H. L. Jones, and L. Scerbo, *Tetrahedron Letters*, 4685 (1965).

[8] Satisfactory elemental analytical data were obtained for this compound.

[9] Aside from unsuccessful approaches to I *via* Hofmann elimination, amine oxide pyrolysis, acetate pyrolysis, and xanthate pyrolysis of a variety of bicyclo[2.1.1]hexanes were all unrewarding in earlier studies in this laboratory.

[10] The second hydrocarbon product, of longer glpc retention time, isolated from the reaction of IIIB with methyllithium is tentatively characterized as 2-methylbicyclo[2.1.1]hexane on the basis of spectral evidence.

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Preparation and Configuration of 4,6,8-Trimethylazulenetetraruthenium Enneacarbonyl. A Complex with Azulene Coordinated to Three Metal Atoms[1]

Sir:

Recent crystallographic studies on the azulene–metal carbonyl complexes $C_{10}H_8Fe_2(CO)_5$,[2] $C_{10}H_8Mo_2(CO)_6$,[3,4] $(i\text{-}C_3H_7)(CH_3)_2C_{10}H_5Mo_2(CO)_6$,[3] $[C_{10}H_8Mo(CO)_3CH_3]_2$,[5] and $C_{10}H_8Mn_2(CO)_6$[6] have revealed a variety of azulene–metal bonding schemes. Continuing the systematization of azulene–metal carbonyl chemistry, we have investigated the reaction of 4,6,8-trimethylazulene[7] with $Ru_3(CO)_{12}$ and now report the isolation and characterization of a complex in which azulene is bonded to three atoms of a tetrahedral metal cluster.

$Ru_3(CO)_{12}$ (0.48 g) and 4,6,8-trimethylazulene (0.58 g) in ligroin (bp 90–120°, 25 ml) were heated under reflux for 96 hr. After removal of solvent under vacuum and reactants by sublimation, the resulting dry material was dissolved in 60:40 ethylene dichloride–cyclohexane and chromatographed on Florisil. Mass spectral analysis of the two products indicated them to be $Ru_6(CO)_{17}C$[8] and $(CH_3)_3C_{10}H_5Ru_4(CO)_9$ (in order of elution).

The azulene–ruthenium carbonyl species appears to crystallize in two modifications, monoclinic and triclinic.[9] Monoclinic crystals of diamagnetic, air-stable $(CH_3)_3C_{10}H_5Ru_4(CO)_9$ are obtained as small red parallelepipeds crystallizing in the spacegroup $P2_1/n$ with $a =$

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[1] Work supported by the National Science Foundation and the Advanced Research Projects Agency.

[2] M R Churchill, *Chem. Commun.*, 450 (1966); *Inorg. Chem.*, **6**, 190 (1967).

[3] M. R. Churchill and P. H Bird, *Chem. Commun.*, 746 (1967).

[4] J. S. McKechnie and I. C. Paul, *ibid.*, 747 (1967).

[5] P. H. Bird and M. R. Churchill, *ibid.*, 705 (1967); *Inorg. Chem.*, 7, 349 (1968).

[6] P. H. Bird and M. R. Churchill, *Chem. Commun.*, in press.

[7] This substituted azulene was used in order to avoid such disorder problems as are found in $C_{10}H_8Mo_2(CO)_6$[3,4] and in azulene itself.

[8] B. F. G. Johnson, R. D. Johnston, and J. Lewis, *Chem. Commun.*, 1057 (1967).

[9] Single-crystal diffraction studies on the triclinic modification are currently in progress and will be reported at a later date.