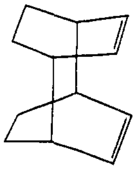
Chemistry of 9,10-Benzotricyclo[4.2.2.$2^{2,5}$]dodeca-3,7,9-triene, a Novel Polycyclic Compound

Sir:

Rigid molecules such as norbornadiene containing two isolated double bonds in spatial proximity are known to undergo chemical reactions involving participation between the two double bonds.[1-6] Another system of molecules with similar structural features is the hitherto unknown tricyclo[4.2.2.$2^{2,5}$]dodeca-3,7-diene (**1**) and its derivatives. This communication deals with the synthesis and chemistry of the first member of this system, 9,10-benzotricyclo[4.2.2.$2^{2,5}$]dodeca-3,7,9-diene (**2**). The two double bonds in **2** were found to exhibit more extensive interactions between them than those in norbornadiene, and are thus among the most strongly interacting nonconjugated π systems known.



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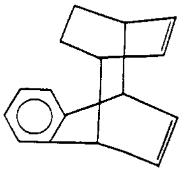
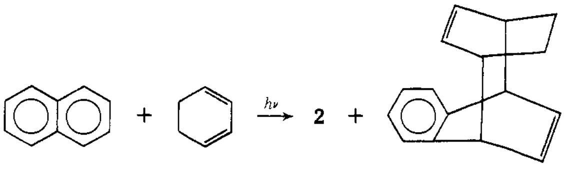


2

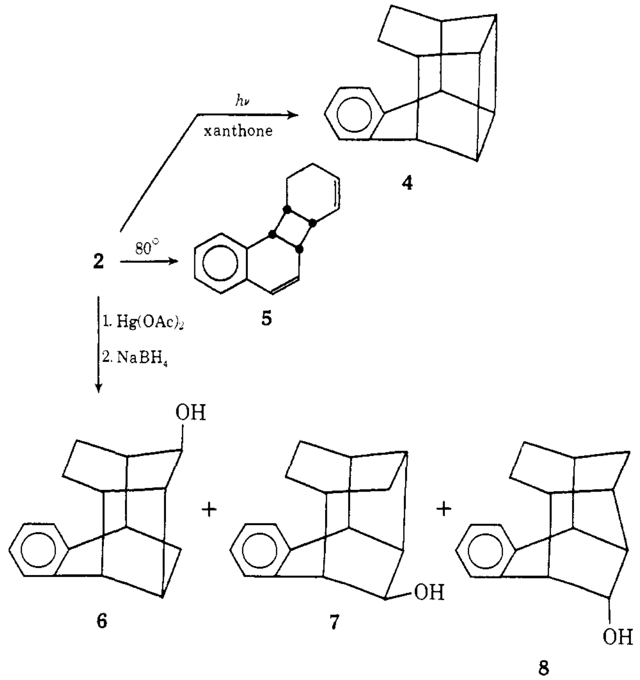
Irradiation of naphthalene (0.01 *M*) and 1,3-cyclohexadiene (1 *M*) in benzene yielded two adducts (**2** and **3**) in a 9:1 ratio (eq 1). The quantum yield of consumption of naphthalene at 313 nm is 0.23 ± 0.02. Compound **2**, which was isolated in 70% yield by extracting the reaction mixture with aqueous silver nitrate followed by crystallization,[7] exhibits: mp 62–64°; uv max (cyclohexane) 278.5 (ϵ 470) and 270 nm (ϵ 460); ir (KBr) 890, 832, 805, 772, 742, and 728 cm^{-1}; nmr (CCl_4) δ 1.32 (m, 4, CH_2), 2.95 (m, 2, C*H*), 3.52 (m, 2, ArC*H*), 5.90 (A_2B_2 sextet, 2, C*H*=C*H*),[8] 6.22 (A_2B_2 sextet, 2, C*H*=C*H*), and 6.92 ppm (s, 4, Ar*H*). Compound **3** exhibits: mp 81.5–82.0°; uv max (cyclohexane) 267 (ϵ 385) and 275 nm (ϵ 376); ir (KBr) 838, 805, 785, 755, and 728 cm^{-1}; nmr (CCl_4) δ 1.40–2.55 (m, 4, CH_2), 3.15 (m, 2, C*H*), 3.68 (m, 2, ArC*H*), 5.42 (A_2B_2 sextet, 2, C*H*=C*H*), 6.49 (A_2B_2 sextet, 2, C*H*=C*H*) and 6.90 ppm (s, 4, Ar*H*).[9] Since an exciplex may be the precursor of these products, the formation of **2** as the major product reflects the preferred configuration of this exciplex.



(1)

By examining a variety of molecular models, the π systems of the two isolated double bonds in **2** are found to be crowded against each other in a somewhat superposed position. The π systems are therefore expected to exhibit extensive participation between them in chemical reactions. The photochemical, thermal, and polar reactions of **2** substantiated this expectation. When **2** was irradiated in the presence of xanthone, it underwent a smooth cyclization to the quadracyclic cage-like **4** (Scheme I): mp 90–91°; uv max (cyclohexane) 274 nm (ϵ 288) and 266 nm (ϵ 315); ir (KBr) 755, 745 and 718 cm^{-1}; nmr (CCl_4) δ 1.21 (m, 4, CH_2), 2.72–3.50 (m, 6, C*H*), 3.95 (m, 2, ArC*H*), and 7.03 ppm (s, 4, Ar*H*). When **2** was heated above its melting point, it underwent a quantitative conversion *via* a Cope rearrangement to **5**: mp 50–52°; ir (KBr) 852, 793, 762, and 708 cm^{-1}; uv max (cyclohexane) 272 nm (ϵ 6700); nmr (CCl_4) δ 1.10–1.95 (m, 4, CH_2), 2.50 (m, 1, C*H*), 3.22–4.16 (m, 3, allylic C*H* and ArC*H*), 5.40–5.90 (m, 3, C*H*=C*H*), 6.23 (2 d, 1, *J* = 10 and 1.0 Hz, ArC*H*=CH), and 6.65–7.12 ppm (m, 4, Ar*H*).

Scheme I



Compound **2** reacted with 1 equiv of bromine to give a mixture of saturated dibromides which gave the appropriate elemental analysis but could not be separated by conventional methods. Compound **2** also reacted with only 1 equiv of mercuric acetate in acetic acid to give a mixture of crystalline oxymercurated products. The mixture was reduced with $NaBH_4$ followed by saponification to give a mixture of saturated alcohols. Three crystalline alcohols, **6** (30%, mp 134–135°), **7** (12%, mp 137–138°), and **8** (6%, mp 115–120°), were isolated by chromatography. Their structural assignments were based on their spectral properties as well as on those of the corresponding ketones obtained by oxidation with Jones reagent. The major alcoholic product **6** yielded a ketone **9** (mp 67–86°) which was shown to be a cyclopentanone by ir (ν^{CCl_4} 1755 cm^{-1}) and exhibited a normal n,π* transition in the uv ($\lambda_{\max}^{\text{cyclohexane}}$ 290 nm

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(1) S. J. Cristol and R. L. Snell, *J. Amer. Chem. Soc.*, 80, 1950 (1958).

(2) G. S. Hammond, N. J. Turro, and A. Fischer, *ibid.*, 83, 4674 (1961); G. S. Hammond, P. Wyatt, C. D. deBoer, and N. J. Turro, *ibid.*, 86, 2532 (1964).

(3) W. G. Dauben and R. L. Cargill, *Tetrahedron*, 15, 197 (1961).

(4) S. Winstein and M. Shatavsky, *Chem. Ind. (London)*, 56 (1956).

(5) K. C. Panda and S. Winstein, *Tetrahedron Lett.*, 3393 (1964).

(6) E. Vedejs and M. F. Salomon, *J. Org. Chem.*, 37, 2075 (1972).

(7) Satisfactory elemental analyses have been obtained for all new compounds reported in this communication.

(8) K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, 97, 2798 (1964); J. A. Pople, W. G. Schneider, and H. J. Bernstein, *Can. J. Chem.*, 35, 1060 (1957).

(9) Compound 3 was unreactive when a mixture of 2 and 3 was subjected to oxymercuration, and was thus separated from 2 after the oxymercuration by chromatography.

(ϵ 50)). Compound **7** yielded ketone **10** (mp 95–97°) which was shown to be a cyclohexanone by ir (ν^{CCl_4} 1735 cm^{-1}) and exhibited a red-shifted and intensified n,π^* transition indicating homoconjugation with the aromatic system [$\lambda_{max}^{cyclohexane}$ 298 (ϵ 425), 309 (ϵ 535), 320 (ϵ 470), and 332 nm (ϵ 200)].[10] Compound **8** yielded ketone **11** (mp 137–139°) which was shown to be a cyclopentanone by ir (ν^{CCl_4} 1755 cm^{-1}) and exhibited a red-shifted and intensified n,π^* transition [$\lambda_{max}^{cyclohexane}$ 290 (ϵ 505) and 300 nm (ϵ 535)].[10]

The exclusive formation of saturated products from the oxymercuration of **2** in acetic acid indicates that the participation of two π systems in **2** is even more extensive than those in norbornadiene which gives mainly unsaturated 1,2 adducts from oxymercuration under the same conditions.[5,6] Halpern and coworkers have found that **2** also displaces norbornadiene as a ligand in organometallic compounds.[11] The synthesis and chemical behavior of related compounds are being investigated.

Acknowledgment. The authors wish to thank the National Institutes of Health, Grant No. AM-11676, for the support of this work, and to express their appreciation to Professor Jack Halpern for valuable discussions.

[10] W. E. Noland, M. S. Baker, and H. I. Freeman, *J. Amer. Chem. Soc.*, 78, 2233 (1956); P. D. Bartlett and W. P. Giddings, *ibid.*, 82, 1240 (1960); R. C. Cookson and N. Lewin, *Chem. Ind.* (*London*), 985 (1956); H. Birnbaum, R. C. Cookson, and N. Lewin, *J. Chem. Soc.*, 1224 (1961).

[11] J. Halpern, unpublished results.

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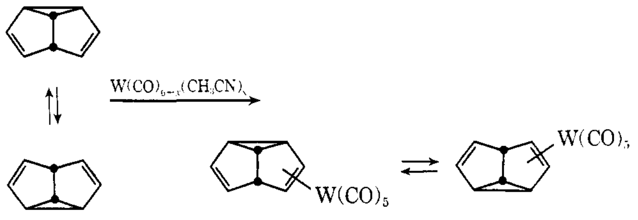
The Tungsten Pentacarbonyl Complex of Semibullvalene. Barrier Height for the Degenerate Cope Rearrangement

Sir:

The rate of the degenerate Cope rearrangement of semibullvalene (**1**) is at present immeasurably fast.[1] The activation energy has been calculated to be 3.6 kcal/mol by the MINDO/2 method.[2] An exciting goal in this area is to modify the structure of semibullvalene so as to increase or decrease the activation energy. A decrease below 3.6 kcal/mol eventually to a negative value poses an interesting philosophical problem. Theoretical calculations, on the other hand, point to modifications which could increase the activation energy. Dewar and Lo[3] using the MINDO/2 method conclude that electron-releasing substituents should destablilze the transition state for the Cope rearrangement. This conclusion agrees with the experimental finding that the activation energy for the Cope rearrangement in octamethylsemibullvalene is 6.4 kcal/mol.[4] Hoffmann and Stohrer[5] have attacked this problem from the point of view of using EHT calculations to determine the effect of substituents not only upon the transition state but also upon the stabilities ot the reactant and product in degenerate and nondegenerate Cope rearrangements of suitably substituted semibullvalene models. So far, except for the example of octamethylsemibullvalene, none of the predictions of Hoffmann and Dewar has been tested experimentally.

We have approached this problem synthetically by attempting to make a metal complex of semibullvalene in which the basic molecule is retained but the divinylcyclopropane part is perturbed by interaction with the metal.

Complexes were obtained with silver nitrate,[6] palladium,[7] and diiron nonacarbonyl.[8] These could not be used for our purpose because they were either too weakly associated, in the case of silver, no longer had the divinylcyclopropane system, in the case of palladium, or possessed a rearranged structure, in the case of iron carbonyl. Success was achieved in the form of the unusual tungsten pentacarbonyl complex **2**;[9] in fact, this is the first example of the isolation of a stable complex between tungsten pentacarbonyl and a tricyclic diene.[10]



1 **2**

Figure 1 shows the nmr spectrum at room temperature and at −34 and 62°. The relevant nmr parameters are collected in Table I.

The low-temperature spectrum defines the static structure and the high-temperature spectrum agrees with the equilibration process **2a** $\rightleftarrows$ **2b**. In this process the pairs of protons A–F, D–G, and C–E are averaged. The calculated values, $(A + F)/2$, $(D + G)/2$, and $(C + E)/2$ of 4.29, 3.03, and 3.55 ppm are in good agreement with the observed values at room temperature of 4.26, 3.03, and 3.65 ppm. Furthermore, the averaged coupling constants in the high-temperature spectrum agree with prediction. Thus, for proton B, $(J_{AB} + J_{BF})/2 = 3.1$ Hz compares well with the observed splitting of 3.9 Hz.

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[1] Rearrangement persists at −110° on the nmr time; see H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *J. Amer. Chem. Soc.*, 91, 3316 (1969).

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[5] R. Hoffmann and W.-D. Stohrer, *J. Amer. Chem. Soc.*, **93**, 6941 (1971).

[6] $C_8H_8AgNO_3$, mp 87° dec.

[7] Semibullvalene and potassium tetrachloropalladate(II) in methanol yield a methoxybicyclo[3.3.0]octadienyl π-allyl type complex: R. M. Moriarty, C.-L. Yeh, and K. C. Ramey, to be published.

[8] R. M. Moriarty, C.-L. Yeh, and K. C. Ramey, *J. Amer. Chem. Soc.*, **93**, 6709 (1971).

[9] A solution of $W(CO)_6$ was kept at reflux in 15 ml of CH_3CN for 24 hr under nitrogen. The solvent was removed *in vacuo*, a solution of 0.2 g of semibullvalene in 20 ml of hexane was added under nitrogen and the reaction was kept at reflux for 4 hr. The product was isolated by column chromatography on silica gel and 100 mg of a pale yellow-green liquid which solidified upon storage overnight at 0° was obtained. The pure complex has mp 53–54° and the yield based upon consumed semibullvalene is 38%.

Anal. Calcd for $C_8H_8W(CO)_5$: C, 36.44; H, 1.87. Found: C, 36.46; H, 1.84. The mass spectrum showed the parent peak at *m/e* 428 (30%), M − CO, *m/e* 400 (6.5%), M − 2CO, *m/e* 372 (12%), M − 3CO, *m/e* 344 (33%), M − 4CO, *m/e* 316 (83%), M − 5CO, *m/e* 288 (83%), C_8H_8, *m/e* 104 (100%), C_6H_6, *m/e* 78 (96%).

[10] For a recent spectroscopic study of $W(CO)_5$–alkene complexes, see M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 6048 (1971).