Table I. Physical Properties of 9-Alkylbicyclo[3.3.1]nonan-9-ols Produced *via* Carbonylation of B-alkyl-9-borabicyclo[3.3.1]nonanes

9-Alkyl	Mp or bp (mm), °C	$n^{20}D$	Anal, % C, calcd	H, calcd	C, found	H, found	Yield,[a] %	*p*-Nitrobenzoate mp, °C (pentane)
Ethyl	62.8–63.2		78.51	11.78	78.80	11.99	90.3	126.5–127.5
1-Pentyl	106 (0.15)	1.4967	79.93	12.46	79.79	12.70	85.5	93.5–94.0
Isobutyl	94 (1.0)	1.4982	79.53	12.32	79.37	12.47	86.5	103.8–104.0
3-Methyl-2-butyl	95 (0.5)	1.5011	79.93	12.46	80.23	12.59	31.0[b]	137 dec
2,3-Dimethyl-1-butyl	105 (0.3)	1.4988	80.29	12.58	80.23	12.70	85.0	130 dec
Cyclohexyl	108.0–108.2		81.02	11.79	81.23	11.84	96.8	180 dec
Cyclopentyl	77.7–78.1		80.71	11.61	80.62	11.67	46.4[c]	180 dec

[a] Yields are of isolated crude alcohol of about 95% purity. [b] Two other products were formed in about equal yields: *cis*-5-hydroxycyclooctyl 3-methyl-2-butyl ketone and a second tertiary alcohol, presumably the 3-methyl-1-butyl isomer formed by a rearrangement of the organoborane. [c] A second product formed in about equal yield was (*cis*-5-hydroxycyclooctyl)cyclopentylcarbinol.

phenylhydrazone mp 190.0–190.2° (lit.[6] mp 155–158.5°, 2,4-DNP mp 191.8–192.3°).

We attempted to achieve the synthesis of bicyclo[3.3.1]nonan-9-one directly by carrying out the carbonylation of appropriate B-alkyl derivatives in the presence of water.[3b] However, the products indicated that the B-alkyl group migrates in preference to the bridging boron–carbon bonds. Thus, after carbonylating at 100°, the B-*n*-pentyl derivative yielded 32% *cis*-1,5-cyclooctanediol (from uncarbonylated organoborane), 34% 9-*n*-pentylbicyclo[3.3.1]nonan-9-ol, and 34% of a third component identified as *cis*-5-hydroxycyclooctyl *n*-pentyl ketone. The isobutyl derivative gave similar results. The thexyl[3d,f] derivative failed to carbonylate prior to rearrangement of the thexyl group to the 2,3-dimethyl-1-butyl grouping.[8] Consequently, the best available route to the 9-ketone proceeds through the tertiary alcohol, as utilized in the degradation sequence.

In many of the new reactions utilizing organoboranes for synthetic purposes,[3h,9] only one of the three groups on boron are utilized. The observation that the B-alkyl group in B-alkyl-9-BBN undergoes preferential migration during the carbonylation reaction suggests the possibility of utilizing these derivatives to overcome this difficulty.[10]

We previously demonstrated that hydroboration–carbonylation–oxidation serves as a new, convenient route to monocyclic[3d] and unbridged polycyclic[3i,11] structures. The present study establishes that this procedure also provides a remarkably simple route to a bridged polycyclic, the bicyclo[3.3.1]nonane structure. We are presently examining the cyclic hydroboration of cycloheptadiene, cyclohexadiene, and cyclopentadiene followed by carbonylation of the intermediates in an attempt to establish the scope and possible limitations of this new synthesis of bridged polycyclics.[12]

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(8) The B-thexyl-9-borabicyclo[3.3.1]nonane molecule is evidently severely sterically hindered. Its oxidation by alkaline hydrogen peroxide is unusually difficult.

(9) J. J. Tufarillo, L. T. C. Lee, and P. Wojkowski, *J. Am. Chem. Soc.*, **89**, 6804 (1967); A. Suzuki, A. Arase, H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogić, and M. E. Rathke, *ibid.*, **89**, 5708 (1967); H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1967); H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, **90**, 818, 1911 (1968).

(10) Indeed, we have achieved considerable success in this endeavor (research in progress with E. F. Knights, M. W. Rathke, and M. M. Rogić). We hope to report these results shortly.

(11) H. C. Brown and E. Negishi, *Chem. Commun.*, 594 (1968).

(12) Research in progress with P. Burke.

(13) Graduate research assistant on Grant GM 10937 from the National Institutes of Health.

Evord F. Knights,[13] Herbert C. Brown
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Received August 2, 1968

Flash Vacuum Pyrolysis. IV. The Isolation and Rearrangement of 9,10-Dihydrofulvalene[1]

Sir:

Although substantial physical[2] and theoretical[3] data have been obtained on the cyclopentadienyl radical, very little is known about its simplest chemistry. Our initial investigation of this species[1a] was based on its formation by flash vacuum pyrolysis (fvp) of allyl phenyl ether, most likely through the intermediacy of the phenoxy radical which decarbonylates.[2a] We found that allylcyclopentadiene and biallyl were the predominant stable products resulting from the rapid quenching of the pyrolysate on a liquid nitrogen cooled surface. The product formed from coupling of two cyclopentadienyl radicals was not detected even though our mass spectral investigation[4] of the pyrolysis indicated the presence of the dimer in the gas phase.

Recently we have found that the same dimer is generated, along with cyclopentadienyl and nickelcyclopentadienyl radicals, when nickelocene is pyrolyzed in an oven coupled directly to the ionization chamber of

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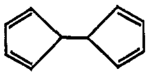
(1) (a) Part I: E. Hedaya and D. W. McNeil, *J. Am. Chem. Soc.*, **89**, 4213 (1967); (b) part II: C. L. Angell, E. Hedaya, and D. McLeod, *ibid.*, **89**, 4214 (1967); (c) part III: Paul Schissel, D. J. McAdoo, and E. Hedaya, to be published.

(2) (a) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960); (b) R. F. Pottie and F. P. Lossing, *ibid.*, **85**, 269 (1963); (c) S. Ohnishi and S. Nitta, *J. Chem. Phys.*, **39**, 2848 (1963); (d) P. Zandstra, *ibid.*, **40**, 612 (1964); (e) R. Fessenden and S. Ogawa, *J. Am. Chem. Soc.*, **86**, 3591 (1964); (f) G. R. Liebling and H. M. McConnell, *J. Chem. Phys.*, **42**, 3931 (1965); (g) G. Porter and B. Ward, *Proc. Roy. Soc.*, **A303**, 139 (1968); G. Porter and B. Ward, *Proc. Chem. Soc.*, 288 (1964).

(3) (a) N. Bouman, *J. Chem. Phys.*, **35**, 1661 (1961); (b) H. C. Longuet-Higgins and K. L. McEwen, *ibid.*, **26**, 719 (1957); (c) F. A. Cotton and G. Wilkinson, *J. Am. Chem. Soc.*, **74**, 5764 (1952); (d) A. Streitwieser, Jr., *ibid.*, **82**, 4123 (1960); (e) L. C. Snyder, *J. Phys. Chem.*, **66**, 2299 (1962).

(4) P. Schissel, D. J. McAdoo, and E. Hedaya, unpublished results.

a mass spectrometer. The data obtained (Figure 1)[5] suggested an excellent approach using fvp techniques to the isolation and characterization of the interesting, highly unsaturated hydrocarbon, 9,10-dihydrofulvalene (**1**), and/or its isomers (*e.g.*, **2**, **3**, or **4**). Although **1** was implicated as an intermediate in the fulvalene synthesis of Doering and Matzner,[6] it has never been isolated and fully characterized.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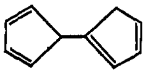
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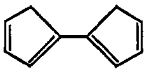
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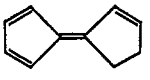
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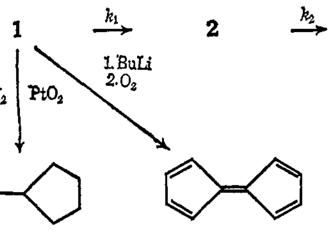
About 1.0 g of sublimed nickelocene was pyrolyzed in the apparatus previously described[1a] at about 0.08 torr and 950°. The pyrolysate was rapidly quenched on the surface of a large, liquid nitrogen dewar closely coupled to the tubular oven (radical gun). At the completion of the pyrolysis, the volatile products were distilled into a small vacuum manifold and fractionated. The most volatile fraction was cyclopentadiene, while the least volatile material consisted of small amounts of nickelocene and naphthalene. The middle fraction was a colorless unstable liquid at 0° which was subsequently identified as 9,10-dihydrofulvalene (**1**): *m/e* 130; nmr ($CDCl_3$, $-10°$) δ 6.5 (m, 4), 3.1 (s, 1); uv max (heptane, 0°) 240 mμ (ϵ $\sim$7.5 × 10^3). About 15% yields of **1** were generally obtained on the basis of quantitative nmr measurements. Chemical evidence for the structural assignment consisted of the reduction of **1** over PtO_2 to dicyclopentanyl ($\geq$50%) (whose ir spectrum was superimposable with that of authentic material) and its dehydrogenation *via* air oxidation of the dianion to fulvalene:[6] uv max (n-C_6H_{14}) 314, 301, 289, 278, 266 mμ [lit.[6b] uv max (n-C_5H_{12}) 314, 300, 289, 278, 266 mμ]. The relative intensities of our uv maxima corresponded with those previously reported.[6b] Although **1** readily polymerizes on exposure to air or *in vacuo* at ambient temperatures, it could be manipulated at low temperatures using vacuum line techniques.

As expected, **1** readily undergoes rearrangement to another isomer in dilute solution at room temperature, as does 5-methylcyclopentadiene.[7] The product was assigned the 1,5-dihydrofulvalene structure (**3**): *m/e* 130; nmr ($CDCl_3$), δ 6.5 (m, 2), 6.4 (m, 1), 3.0 (m, 2); uv max (heptane) 336 mμ (ϵ 1.4 × 10^4) [lit.[6b] uv max (pentane) 336 mμ]. The first-order rate constants ($t_{1/2}$ (30.0°) 52.3 min) were obtained in heptane for this rearrangement and were found to be independent of the intial concentration of **1**. The activation parameters were $\Delta H^{\ddagger}$ = 18.6 kcal/mol and $\Delta S^{\ddagger}$ = -16 eu.



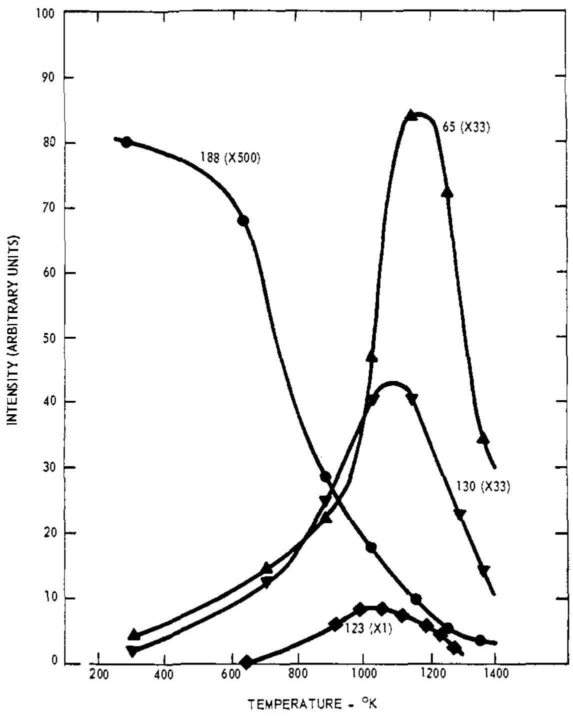
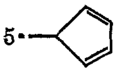
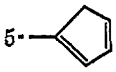


Figure 1. Nickelocene pyrolysis: ●, $Ni(C_5H_5)_2$; ▲, C_5H_5; ▼, $C_{10}H_{10}$; ◆, NiC_5H_5. Intensity attenuations are indicated in parentheses. Electron-bombardment spectrum obtained using 11-eV electrons.

The rearrangement is best represented as two sequential 1,2 or 1,5 hydrogen shifts where **2** is an intermediate. Since good first-order kinetics were observed without buildup of **2**, $k_1 \ll k_2$. Roth[8] has shown that the rate of rearrangement of 5-1H-pentadeuteriocyclopentadiene ($\Delta H^{\ddagger}$ = 24.3 kcal/mol) is considerably slower than that for 5-methylcyclopentadiene ($\Delta H^{\ddagger}$ = 19.6 kcal/mol).[7a] Consequently, the rate of hydrogen shift in cyclopentadienes apparently depends on the 5 substituent with the relative rates falling in the order

5-H < 5-CH_3 ≈ 5-  < 5- 

Apparently, little data have been accumulated on the effect of structure on sigmatropic hydrogen rearrangements in an analogous series. Current theory for these intramolecular conversions[9] of cyclopentadienes involves a model where the transition state consists of a cyclopentadienyl radical and a hydrogen atom in which the latter retains a memory for symmetry in the former (*i.e.*, bonding with the pentadienyl system is retained in the transition state). Obviously, this model, which has primarily been used to rationalize hydrogen migration termini, does not exclude the notion that the rate of rearrangement can depend on the stability of the cyclopentadienyl radical or the corresponding dienylic C–H bond strength. It is interest-

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(5) The ionization and/or appearance potentials were measured for the observed species, and, along with similar data for atomic nickel, lead to estimates for dissociation energies for nickelocene to cyclopentadienyl and nickelcyclopentadienyl radicals or to cyclopentadienyl radicals and nickel.[1c] These data suggest that thermal fragmentation occurs on the oven wall. Consistently, we find that a carbon-containing nickel deposit is formed during the pyrolysis.

(6) (a) W. von E. Doering in "Theoretical Organic Chemistry . . . The Kekule Symposium," Butterworth & Co. (Publishers) Ltd., London, 1959, p 45; (b) E. A. Matzner, Ph.D. Thesis, Yale University, 1958.

(7) (a) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965); (b) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *ibid.*, **19**, 1939 (1963).

(8) W. R. Roth, *Tetrahedron Letters*, 1009 (1964).

(9) (a) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); (b) A. G. Anastassiou, *Chem. Commun.*, 15 (1968).

ng that the dienylic C–H dissociation energy in cyclopentadiene is very much larger (by *ca.* 50 kcal) than the activation energy for sigmatropic rearrangement. The former (70–75 kcal)[1c,10a] has been estimated on the basis of the heat of formation of the cyclopentadienyl radical derived from mass spectroscopic studies involving the direct measurement of its ionization potential[1c,2a] and the appearance potential of the cyclopentadienyl cation from nickelocene[1c] or cyclopentadiene.[10b]

In a few cases the rearrangement of **1** took an alternate course in deuteriochloroform. A red color developed, and the nmr spectrum was different from that of **3**. The nmr, uv, and ir spectra of the red product correspond to that reported[11] for 1,2-dihydrofulvalene (**4**) which has previously been obtained by the carefully controlled acid-catalyzed dehydration of 1-dicyclopentadienol.[11] We believe that the rearrangement of **1** to **4** was similarly catalyzed by traces of acid in the solvent. Indeed, deliberate addition of small quantities of trifluoroacetic acid to a dilute cold chloroform solution of **1** did lead to detectable amounts of **4**.

(10) (a) H. S. Hull, A. F. Reid, and A. G. Turnbull, *Inorg. Chem.*, **6**, 805 (1967); (b) F. Dorman, *J. Chem. Phys.*, **43**, 3507 (1965).

(11) K. V. Scherer, *J. Am. Chem. Soc.*, **85**, 1550 (1963).

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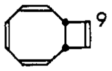
Low-Temperature Photolysis of Bicyclo[6.2.0]deca-2,4,6,9-tetraene and *trans*- and *cis*-9,10-Dihydronaphthalenes. Tetracyclo[4.4.0.$0^{2,10}$.$0^{5,7}$]deca-3,8-diene

Sir:

We have observed remarkable rearrangements of compounds **1**,[1] **2**,[1,2] and **3**.[3] Photolysis of all these compounds has provided in 65–70% yield the same, thermally unstable $(CH)_{10}$ hydrocarbon (**4**). Furthermore, we have proven that **4** is indeed tetracyclo[4.4.0.$0^{2,10}$.$0^{5,7}$]deca-3,8-diene, an intermediate frequently discussed in many important isomerizations of $(CH)_{10}$ hydrocarbons.[4] Evidence for this structural assignment is now presented herein.



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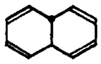

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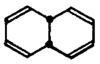

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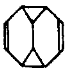

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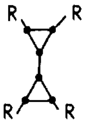
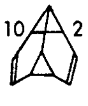


6: R = CH_2-OAc

7: R = C_6H_5

8



4'

The light source employed in the present photolysis was a doubly coiled (3.5-cm diameter) low-pressure mercury lamp surrounded by a cylindrical reflection mirror (10 cm diameter).[5] A 0.25∼0.5 M[6] solution of **1**, **2**, or **3** in tetrahydrofuran-d_8 was irradiated at −110 ± 10°, and the progress of the photolysis was followed by 100-MHz nmr spectra taken at −70° at intervals. Initial rates of disappearance of these compounds were rapid (half-lives of **1**, **2**, and **3** were approximately 30, 60, and 30 min, respectively), and in *all* cases the product distribution reached within 2.5 hr a *similar* composition (the yield of each component deviated within 5% from those given below) which was essentially unaffected by further irradiation. As shown in Figure 1 in the case of the photolysis of **3**, for instance, the photolysate consisted of **2**! (19% yield), **3**

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[1] S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Am. Chem. Soc.*, **89**, 4804 (1967). We have received many inquiries concerning the degenerate tautomerization of **1**. Because of theoretical significance of this problem, we describe briefly the observed results and answer the question whether or not this tautomerization is indeed occurring in this system. Over a range of −110 to 75° no line broadening of any nmr signals of **1** was observed. Therefore, the tautomerization, if it does proceed, must be slower than at least 10 sec^{-1} below 75° because the spectrum is interpretable only on the basis of two allylic protons (τ 6.32), two olefinic protons of the cyclobutene (τ 3.98), and six other olefinic protons. Further, if a conformational change occurs, then this process must be fast even below −110°. Since **1** isomerizes to **2** ($\Delta H^{\ddagger} = 25$ kcal/mol, $\Delta S^{\ddagger} = 0$ eu) the range of experimentally observable rate of **1** is thus limited. We prepared monodeuterated **1′** (0.86 D/molecule), and its nmr spectrum clearly showed that deuterium was introduced solely at C-9 as evidenced by a 0.57 ± 0.03 ratio of intensity of signals at τ 3.98 and 6.32. This ratio remained unchanged for 10 days at 0° and an additional 5 days at 25°, during which time **1′** isomerized slowly to monodeuterated **2′**. Therefore, we conclude that the tautomerization demands an energy barrier of at least 25 kcal. There is good reason to believe that ΔF between the two conformers of **1** would be more than 10 kcal, mainly responsible for the absence of line broadening of the nmr signals of **1**. The ratio of intensities of olefinic to aliphatic protons in the spectrum of **2′** was 3.64 ± 0.05, supporting our previous proposal for this stereospecific transformation.

[2] (a) M. Jones, Jr., and L. T. Scott, *ibid.*, **89**, 150 (1967); (b) E. E. van Tamelen and T. L. Burkoth, *ibid.*, **89**, 151 (1967). Compound **2** used in our work showed $\lambda_{max}^{methylcyclohexane}$ 276 mμ (ϵ 3850), $\lambda_{min}^{methylcyclohexane}$ 244 (1720), which differs vastly from that (λ_{max}^{MeOH} 231 mμ (no molar extinction coefficient)) reported by the latter group.[2b] The Dreiding model reveals that the diene system of **2** is nearly coplanar without any significant distortion of bond angles. Compound **2** was treated with a 300-fold molar excess of diimide (KCOON=NCOOK + AcOH) at room temperature repeatedly until no **2** was present in the reaction product, and then a mixture of partially hydrogenated **2** was catalytically hydrogenated with 10% Pd–C in methanol to provide *trans*-decalin in more than 90% yield. Since we found that thermolysis of **2** proceeded partly as a parallel *second*-order reaction [to provide naphthalene, 1,2-dihydronaphthalene, hydrogen, and a hydronaphthalene (minor) (S. Masamune, unpublished)], it was nearly impossible to prepare a substantial amount of neat **2** by ordinary workup techniques including preparative glpc. We prepared a solution of **1** in deuterated methylcyclohexane (known concentration) and converted it to **2** (quantitative, *first* order). Nmr spectra showed no impurities.

One of the referees requested us to record an nmr spectrum of our sample employed throughout our work, and it is shown in Figure 3. In view of thermal behavior of **2** (*vide supra*), very likely some of the room-temperature (2 min) photoproducts of their *trans*-9,10-dihydronaphthalene[2b] are thermal products of **2** (*e.g.*, naphthalene and 1,2-dihydronaphthalene) and were present in their starting material, because we could not detect these compounds in our photolysis of **2** under similar conditions.

[3] Prepared according to the procedure reported by W. von E. Doering, *et al.*, *Tetrahedron*, **23**, 3943 (1967). We thank Mr. K. Hojo for the preparation.

[4] First proposed by G. Schröder, *Chem. Ber.*, **97**, 3140 (1964), and appeared in ref 2a; W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, **88**, 2078 (1966); W. von E. Doering and J. W. Rosenthal, *Tetrahedron Letters*, 349 (1967); G. Schröder and J. F. M. Oth, *Angew. Chem. Intern. Ed. Engl.*, **6**, 414 (1967); G. Schröder, "Cyclooctatetraen," Verlag Chemie, GmbH, Weinheim, 1965; S. Masamune, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Am. Chem. Soc.*, **90**, 2727 (1968).

[5] The lamp was constructed by Mr. C. Shott of this department and connected with a Jefferson Luminus Tube Outdoor Type transformer (Catalog 721–561, primary 115 V, secondary 5000 V). The total stretched length of the lamp is 1.8 m. A diagram of this photoapparatus is available upon request.

[6] The concentration must be kept in the range specified in order to obtain the reproducible distribution of the photoproducts.