Methano-Bridged 14-π-Electron Aromatic Annulenes. 3. Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study of the 1,6-Methanofluorenyl Anion and Comparison with the Related 1,6-Methanoindenyl and Fluorenyl Anions[1a]

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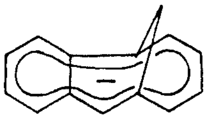
The 1,6-methanofluorenyl anion (1) has been examined by ^{13}C NMR spectroscopy and compared to similar systems: namely, the 1,6-methanoindenyl anion (2) and the florenyl anion (3). The average ^{13}C NMR chemical shift of 1 is close to the value predicted by the Spiesecke–Schneider relationship. The chemical shifts of anion 1 are discussed in relation to expected charge densities predicted by HMO theory. Also described is an improved synthesis of tricyclo[4.3.1.0^{1,6}]deca-2,4,7-triene (7) in 61–73% (45% redistilled) yields from 8-hydroxytricyclo-[4.3.1.0^{1,6}]dec-3-ene (16).

In 1978 we reported the preparation and characterization of the 1,6-methanofluorenyl anion (1) by proton NMR and UV spectroscopy.[2] At that time only selected ^{13}C NMR chemical shifts were reported in order to substantiate the assumption that this anion existed in a cycloheptatrienyl rather than a norcaradienyl form (**1a**). We now report a complete ^{13}C NMR analysis of this anion along with the experimentally determined charge densities.



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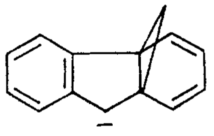

1a

Due to the inability to assign the ^{13}C NMR chemical shifts of anion 1 on the basis of proton-coupled and proton-decoupled spectra alone, recourse was made to selective proton decoupling since the complete ^{1}H NMR assignments for 1 were determined in our earlier work.[2] ^{13}C NMR assignments, therefore, were made by the use of selective proton decoupling and further confirmed by comparison with the 1,6-methanoindenyl (2),[2c] fluorenyl (3), diphenylmethyl (4),[3] and indenyl (5)[4] anions. The ^{13}C NMR chemical shifts along with the experimentally determined charge densities are given in Table I. At the time this work was performed neither the ^{13}C NMR shifts for the fluorenyl anion (3) nor those for the 1,6-methanoindenyl anion (2) were reported and therefore they were determined.[5] Since our determination, O'Brien[6] and Edlund[7] have reported variable-temperature ^{13}C NMR studies of the fluorenyl anion (3), in order to ascertain the solvation properties of various alkali metal salts of this anion, and Takahashi[8] has reported the ^{13}C NMR shifts of the 1,6-methanoindenyl anion (2).

Results and Discussion

Spectral Data. If the ^{13}C NMR chemical shift average for the 1,6-methanofluorenyl anion (1;[11] $\delta_{av} = 120.31$, $\rho_{av} = 1.077$) is compared to the value predicted by the Spiesecke–Schneider[12] relationship [calculated δ_{av} (O'Brien)[13] = 121.2, calculated δ_{av} (Olah)[14] = 117.7], we see that there

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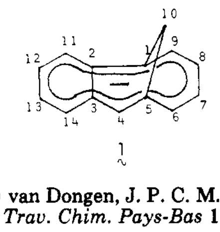
(1) (a) For part 2, see: Hunadi, R. J.; Helmkamp, G. K. *J. Org. Chem.* **1981**, *46*, 2880. (b) Hunadi, R. J. Ph.D. Thesis, University of California, Riverside, CA, 1977. (c) Present address: M&T Chemicals Inc., Furane Products Division, 5121 San Fernando Road West, Los Angeles, CA 90039.

(2) (a) Hunadi, R. J.; Helmkamp, G. K. *J. Org. Chem.* **1978**, *43*, 1586. Hunadi, R. J. *Diss. Abstr. Int. B* **1978**, *36*, 2672-B. (b) In earlier publications[2a] we have referred to 1 and 2 as 1,6-methanofluorenyl anion and 1,6-methanoindenyl anion,[2c] respectively, and the numbering was based on tricyclo[4.3.1.0^{1,6}]deca-2,4,7-triene (7). All compounds in the text are numbered in this manner to facilitate the visual comparison of data. The names, according to Chemical Abstracts convention, for 1 and 2 are 2,3-benzo-1,5-methanocyclononatetraenyl anion and 1,5-methanocyclononatetraneyl anion, respectively, and would be numbered as shown below. (c) Compound 2 was first called the 1,6-methanoindenyl anion in 1967 by: Rosen, W. Ph.D. Thesis, University of California, Riverside, CA, 1967.



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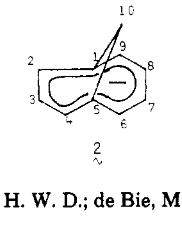

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(3) van Dongen, J. P. C. M.; van Dijkman, H. W. D.; de Bie, M. J. A. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 29.

(4) Stothers, J. B. "Carbon-13 NMR spectroscopy"; Academic Press: New York, 1972; p 269.

(5) The ^{13}C NMR shifts of C-1,6,10 of 1,6-methanofluorenyl anion (1) and 1,6-methanoindenyl anion (2) and of C-1,6,7,8 of the fluorenyl anion (3) were reported in our earlier work.[2a] We have also reported the complete ^{13}C NMR shifts of these three anions.[1b]

(6) O'Brien, D. H.; Russel, C. R.; Hart, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 633.

(7) Edlund, U. *Org. Magn. Reson.* **1979**, *12*, 661.

(8) (a) Takahaski, K.; Kagawa, T.; Takase, K. *Chem. Lett.* **1979**, 701. (b) Our assignments for C-2,3,4,5,8 of 2 differ from those reported by Takahashi.[8a] We attribute these differences to a misassignment on Takahashi's part since we have confirmed our assignments by heternuclear decoupling and integration. First, Takahashi assigns the peak at δ 125.42 to C-8 which is in contrast to our assignment of this peak to C-2 and C-4. We assign C-8 to the peak at δ 121.22, and this is further confirmed by intensity arguments since the peak at δ 125.42 corresponds to two carbons. Further confirmation of our assignment of C-2 and C-5 to the peak at 125.42 ppm and of C-3 and C-4 to the peak at 117.94 ppm comes from the comparison of the indenyl anion with the 1,6-methanoindenyl anion (2) and from Takahashi's[31] own predicted electron densities for 2. Finally, examination of the proton NMR assignments of H-2,5 and H-3,4 of the indenyl and 1,6-methanoindenyl anions show that there is a close agreement in shifts which would suggest that ^{13}C NMR assignments for C-2,5 and C-3,4 of 2 should not be reversed as suggested by Takahashi.

(9) O'Brien, D. H.; Hart, A. J.; Russel, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410.

(10) Sadtler Research Laboratories. "Sadtler Carbon-13 NMR Spectra"; Sadtler: Philadelphia, 1976; No. 338.

(11) In the calculation of the average ^{13}C NMR chemical shift, the bridge carbon is excluded.

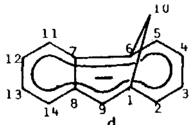
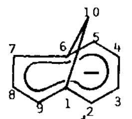
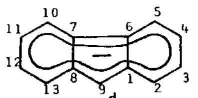
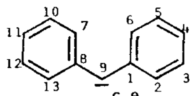
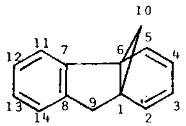
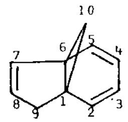
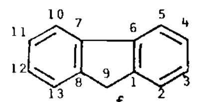
(12) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468.

(13) (a) See ref 9. (b) $\delta_{av} = 289.5 - 156.3\rho_{av}$.

(14) (a) Olah, G. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1430. (b) $\delta_{av} = 288.5 - 159.5\rho_{av}$.

0022-3263/82/1947-1940$01.25/0

Table I. ^{13}C NMR Shifts of Aromatic Anions and Their Precursors[a,b]

	 **1**[d]	 **2**[d]	 **3**[d]	 **4**[c,e]	 **6**	 **7**	 **8**[f]
C-1	119.17 (1.090)	113.73 (1.120)	136.04 (0.982)	147.3	39.57	40.07	143.1
C-2	118.84 (1.092)	125.42 (1.050)	115.50 (1.113)	117.5	126.18[g]	126.65[g]	126.6
C-3	123.35 (1.063)	117.94 (1.097)	118.61 (1.093)	128.0	119.10[h]	118.82[h]	124.9
C-4	107.86[g] (1.162)	117.94 (1.097)	107.46 (1.165)	107.3	119.66[h]	119.23[h]	126.6
C-5	130.60 (1.017)	125.42 (1.050)	118.28 (1.095)	128.0	128.23[g]	126.93[g]	119.7
C-6	101.30 (1.204)	113.73 (1.120)	121.48 (1.075)	117.5	45.57	48.07	141.6
C-7	140.64 (0.952)	114.72 (1.118)	121.48 (1.075)	117.5	140.46	135.44	141.6
C-8	142.64 (0.940)	121.22 (1.077)	136.04 (0.982)	147.3	146.89	127.78	143.1
C-9	105.12[g] (1.179)	114.72 (1.118)	82.52 (1.325)	76.8	40.65	41.49	36.7
C-10	39.83	42.07	118.28 (1.095)	128.0	26.47	28.01	119.7
C-11	121.54 (1.075)		107.46 (1.165)	107.3	121.54		126.6
C-12	110.69 (1.144)		118.61 (1.093)	128.0	126.18		124.9
C-13	119.17 (1.090)		115.50 (1.113)	117.5	126.09		126.6
C-14	123.14 (1.064)				125.64		

[a] See ref 2b. Assignments are in δ relative to Me_4Si. [b] The numbers in parentheses are experimentally determined charge densities calculated by using O'Brien's equation since this equation best predicted the $^{13}C_{av}$ chemical shifts. [c] See ref 3. [d] The spectrum was recorded in $Me_2SO\text{-}d_6$. [e] The spectrum was recorded in THF. [f] See ref 10. [g,h] Assignments can be interchanged.

Table II. Comparison of Experimentally Determined Charge Densities with Calculated Densities[a]

	2[b]	**3**[c]
C-1	1.120 (1.027)	0.982 (1.05)
C-2	1.050 (1.021)	1.113 (1.06)
C-3	1.097 (1.029)	1.093 (1.07)
C-4	1.097 (1.029)	1.165 (1.10)
C-5	1.050 (1.021)	1.095 (1.04)
C-6	1.120 (1.027)	1.075 (1.08)
C-7	1.118 (1.377)	1.075 (1.08)
C-8	1.077 (0.979)	0.982 (1.05)
C-9	1.118 (1.377)	1.325 (1.21)
C-10		1.095 (1.04)
C-11		1.165 (1.10)
C-12		1.093 (1.07)
C-13		1.113 (1.06)

[a] Calculated charge densities are given in parentheses. [b] CNDO/2; see ref 8a. [c] VESCF, see ref 7.

is good agreement between the experimentally determined and calculated average ^{13}C NMR shift. For comparison, fluorenyl anion [**3**; experimental δ_{av} = 116.71, calculated δ_{av} (O'Brien) = 121.2, calculated δ_{av} (Olah) = 117.7] and 1,6-methanoindenyl anion [**2**; experimental δ_{av} = 118.3, calculated δ_{av} (O'Brien) = 115.9, calculated δ_{av} (Olah) = 112.3] also show fairly good correlation. Although δ_{av} vs. charge density correlations have not been systematically applied to methano-bridged systems, it can be seen that these correlations can logically be extended to these cases.[15]

For both the 1,6-methanofluorenyl anion (**1**) and the fluorenyl anion (**3**), HMO theory[16] would predict that of the carbons bearing hydrogen atoms (except for C-9), C-4 and C-12 of **1** and C-4 and C-11 of **3** should have the highest electron density, and this is borne out by the chemical shifts. As compared to the fluorenyl anion (**3**), significantly less charge is localized at C-9 of **1** (the experimentally determined charge density at C-9 of **1** is 1.179 and is 1.325 for C-9 of **3**). C-1 and C-6 of **1** are found at δ 119.17 and 101.30, respectively, as compared to δ 113.73 for **2** and δ 136.04 and 121.48 for **3**. These results show, as predicted, that more electron density is found at C-6 than C-1. HMO theory also predicts that C-5 and C-10 of **3** and C-5 and C-11 of **1** should be the sites of lowest electron density (of carbons bearing hydrogens). This is not exactly the case for **3** with C-5 and C-10 at δ 118.28 (C-3 and C-12 are the sites of lowest electron density for the hydrogen-bearing carbons and are found at δ 118.61) and for the 1,6-methanofluorenyl anion (**1**) with C-5 at δ 130.60 and C-11 at δ 121.54 (although C-11 is not the carbon of lowest electron density, it is significantly electron deficient compared to the other hydrogen-bearing carbons).

As compared to their corresponding precursors, significant changes occur upon formation of the anions. The largest changes, upon formation of **1**, occur at C-1,6,9 with Δδ being 79.60, 55.73, and 64.47 ppm, respectively. Correspondingly, upon formation of **2** from **7**, the shifts for C-1,6,9 change by 73.66, 65.66, and 73.23 ppm, respectively (the changes at C-1 and C-6 are mainly due to rehybridization at these carbons). Electron densities at C-3 and C-4 of **2** and precursor **7** are very similar, showing that very little change (in electron density) occurs at these positions upon anion formation. Anion **1** is different in this respect, since electron density decreases at C-3 and increases at C-4 upon ionization. Comparison of the changes in the carbon

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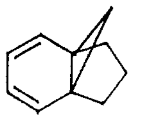
(15) This correlation is addressed in a separate paper: Hunadi, R. J., submitted for publication in *J. Am. Chem. Soc.*

(16) (a) Streitwieser, A. "Molecular Orbital Theory for Organic Chemists"; Wiley: New York; 1961. (b) Schaefer, T.; Schneider, W. G. *Can. J. Chem.* **1963**, *41*, 966.

shifts in 1 and 3 also show that almost equal delocalization of charge occurs in the ring containing C-2 through C-5 and in the ring containing C-11 through C-14 of 1.

Examination of the changes in the bridge carbon of methano-bridged anions vs. their neutral precursors reveals some interesting results. Although Günther and Vogel[17] have indicated that the bridge carbon of methano-bridged systems is not as sensitive to ring currents as the corresponding protons at this position, it can be shown that it is sensitive to the electron density of the system and the presence or lack of aromaticity. In 6, C-10 is at δ 26.47 and is at 39.83 in 1 while in 7, C-10 is at δ 28.01 and is at 42.07 in 2 which corresponds to $\Delta\delta$ = 13.36 and 14.06 ppm, respectively. It is difficult to ascertain exactly how much of the change in the bridge carbon's shift is due to rehybridization at C-1 and C-6 in the tricyclo[4.3.1.0^{1,6}]decane system since model systems with exactly the same geometry are difficult to find. To ascertain exactly how much of the Δ_{bridge} is due to just rehybridization, we would need to examine the shifts of tricyclo[4.3.1.0^{1,6}]deca-2,4-diene (9) and bicyclo[4.3.1]deca-1,3,5-triene (10). Unfortunately, 10 is just the valence tautomer of 9 and is not known in an uncomplexed state.



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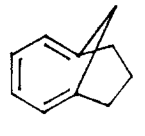

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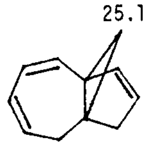

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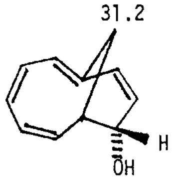

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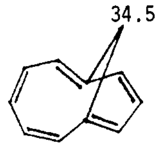

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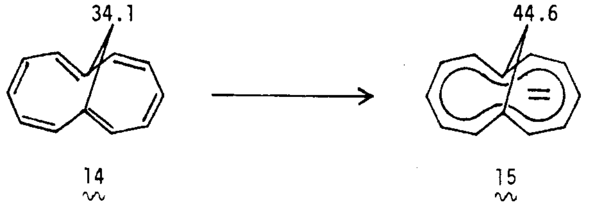
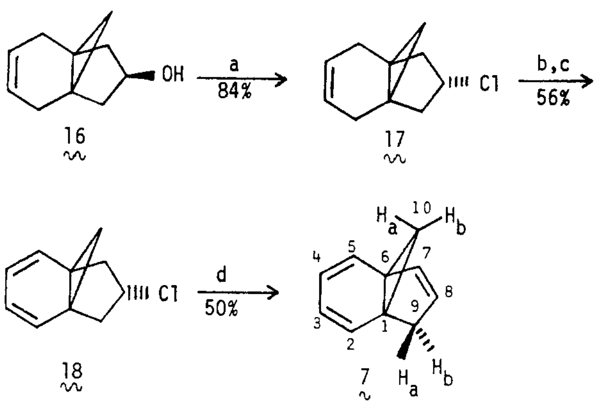
Recently the ^{13}C NMR data[18] for the tricyclo[5.3.1.0^{1,7}]undecane system (the next higher homologue of the tricyclo[4.3.1.0^{1,6}]decane system) has become available and the pertinent data is given below. When the cyclopropane ring is opened, the ^{13}C NMR shift of the bridge increases 6.1 ppm (from 25.1 in 11 to 31.2 in 12). Although a hydroxyl group is present in 12, it is anti to the bridge and should exert little influence on the shift of the bridge carbon.[19] Upon aromatization to 1,5-methano[10]annulene (13) (or 1,5-methanoazulene) another 3.3-ppm increase is observed. This would suggest that 33% of the change in the shift of the bridge carbon is due to aromatization of the system.[20] This result may or may not be totally translatable to the 1,6-methanofluorenyl and 1,6-methanoindenyl anions but would suggest that rehybridization and geometry changes are not the sole contributors to shift of the methano bridge. Oth and Vogel[20] have shown that a change of 10.5 ppm occurs at carbon 13 of 14 upon formation of the doubly charged anion 15, showing that charge density or presence of a negative charge can also influence the position of the bridge carbon. The correlation of electron density with the ^{13}C NMR shift of methano bridges will be further expounded in subsequent publications.[15]

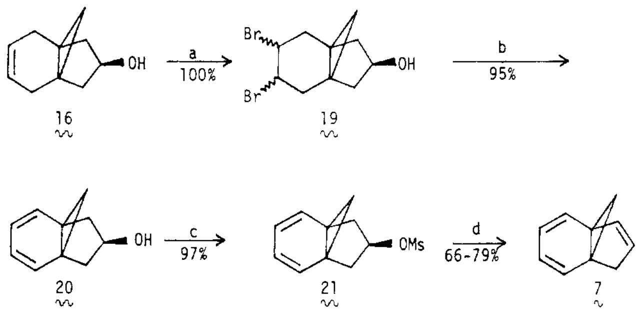


Scheme I^a



^{a} (a) $SOCl_2/N(n\text{-}Bu)_3$; (b) $Br_2/CH_2Cl_2/-78$ °C; (c) KO-*t*-Bu/*t*-BuOH; (d) 15% KOH/MeOH.

Scheme II^a



^{a} (a) $Br_2/CH_2Cl_2/-78$ °C; (b) DBN/THF/60 °C; (c) MsCl/pyridine/CH_2Cl_2/0 °C to room temperature; (d) LiBr/Li_2CO_3/DMF/125 °C.

Synthesis of Tricyclo[4.3.0^{1,6}]deca-2,4,7-triene (7). The synthesis of triene 7 has been reported independently by Radlick and Vogel in 1966, but the low overall yield of 7 from 8-hydroxytricyclo[4.3.1.0^{1,6}]dec-3-ene (16) prompted us to improve this conversion.[21,22] Radlick and Rosen were

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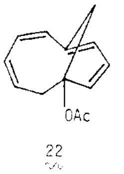
[17] (a) Günther, H.; Schmickler, H.; Königshafen, H.; Recker, L.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 243. (b) Günther, H.; Schmikler, H.; Brinker, V. H.; Nachtkamp, K.; Wassen, J.; Vogel, E. *Ibid.*, **1973**, *12*, 760. (c) Also see: Kemp-Jones, A. V.; Jones, A. J.; Sakai, M.; Beeman, C. P.; Masamune, S. *Can. J. Chem.* **1973**, *51*, 767.

[18] (a) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *J. Am. Chem. Soc.* **1981**, *103*, 5216. (b) Masamune, S.; Brooks, D. W. *Tetrahedron Lett.* **1977**, 3239.

[19] The ^{13}C NMR shift of the bridge of tetraene 22 is 31.5 ppm which is very similar to the shift of the bridge in 12. This may suggest that the arrangement of double bonds in this system does not drastically effect the shift of bridge carbon.



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[20] Oth, J. F. M.; Mullen, K.; Königshafsen, H.; Mann, M.; Sakata, Y.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 284.

[21] Radlick, P.; Rosen, W. *J. Am. Chem. Soc.* **1966**, *88*, 3461. (b) Rosen, W. Ph.D. Thesis, University of California, Riverside, CA, 1967. (c) Grimme, W.; Kaufhold, M.; Dettmeier, U.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 604.

able to obtain **7** in an overall yield of 24% from **16** as outlined in Scheme I.[21a,b,24,25]

It has been shown that 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) effect the facile dehydrobromination of vicinal dihalides under mild conditions.[26,27] When dibromide **19** was treated with DBN at 50 °C, the desired diene alcohol **20** was cleanly obtained in 95% yield (see Scheme II). In contrast to the initial findings of Rosen,[21b] it was discovered that alcohol **20** was quite stable at room temperature and could be stored at refrigerator temperatures for over 1 year without any noticable signs of decomposition.

Next, attention was directed to the conversion of alcohol **20** into the desired triene **7**. It was felt that the conversion of the alcohol function of **20** to a more labile leaving group, rather than proceeding with the direct dehydration of **20**, and elimination would allow a high-yielding conversion to **7**. Although the dehydration of **20** with $POCl_3$ does not proceed,[21b] it was felt that the mesylate **21** (see Scheme II) would be a more viable candidate for transformation to **7** due to the ease of elimination of methanesulfonate esters in these and similar systems.[1b,2a,29] The mesylate **21** was prepared in 97% yield by treatment of alcohol **20** with methanesulfonyl chloride and pyridine in methylene chloride. When mesylate **21** was exposed to lithium bromide and lithium carbonate in dimethylformamide at 125 °C, tricyclo[4.3.1.$0^{1,6}$]deca-2,4,7-triene (**7**) was isolated in yields of 66–79% (49% distilled).[30] This reaction sequence allowed the preparation of **7** in 61–73% overall yield (45% distilled) from alcohol **16** without need for purification until the last step.

Experimental Section

General Methods. 1,6-Methanofluorenyl anion (**1**), 1,6-methanoindenyl anion (**2**), fluorenyl anion (**3**), and 1,6-methanofluorene (**6**) were prepared as reported earlier.[2a,21a,b] Me_2SO-d_6 was purchased from Merck Sharpe and Dohme and used without additional purification. Sodium hydride was purchased from Alfa-Ventron. Tetrahydrofuran was redistilled from potassium benzophenone ketyl under nitrogen just prior to use; hexane and methylene chloride were redistilled; all other solvents were used as obtained from Mallinckrodt.

Spectral data were obtained on the following instruments: ^{13}C NMR spectra on a Bruker HX-90 FT multinuclear spectrometer; ^1H NMR on a Varian A-60, A-60D, or HA-100 spectrometer; ultraviolet spectra on a Carey-14 spectrometer; infrared spectra on a Perkin-Elmer Model 137 spectrometer; mass spectra on a MS-9 spectrometer. Melting points, obtained on a Thomas-Hoover capillary melting point apparatus, and boiling points are uncorrected. Analytical thin-layer chromatography was performed by using EM precoated TLC sheets (silica gel F-254, 0.25 mm on plastic support).

All reactions were conducted under an atmosphere of nitrogen.

Tricyclo[4.3.1.$0^{1,6}$]deca-2,4,7-triene (7). To a solution of 75.0 g (0.50 mol) of 8-hydroxytricyclo[4.3.1.$0^{1,6}$]dec-3-ene[21a,b] (**16**) in 1500 mL of methylene chloride at −78 °C was added 85.2 g (0.54 mol) of bromine in 100 mL of methylene chloride. When the addition was complete, the solution was allowed to warm to room temperature, and 10 g of sodium sulfite and 50 mL of methanol were added. After the mixture turned colorless, it was washed with water and brine, concentrated, and dried ($MgSO_4$) to give 155.0 g (100%) of crude dibromide **19** as a light green solid.

The crude dibromide **19** (50 g, 0.161 mol) was dissolved in 300 mL of freshly distilled THF, and DBN (45.5 g, 0.405 mol) in 100 mL of THF was slowly added via an additional funnel. The resulting solution was heated to 50 °C for 14 h, and, after cooling to room temperature, the mixture was concentrated in vacuo. The residue was taken up in CH_2Cl_2 and washed successively with water, dilute HCl solution, dilute sodium hydroxide solution, and brine. Concentration, after drying over $MgSO_4$, gave 22.5 g (95%) of diene **20** as a yellow-brown solid: mp 52–54 °C; ^1H NMR ($CDCl_3/Me_4Si$) δ 6.0 (m, 4 H, H-2,3,4,5), 4.1 (m, 2 H, H-7,8), 3.4 (br s, 1 H, OH), 2.1 (m, 3 H, H-7,9,10b), −0.3 (d, J = 4 Hz, 1 H, H-10a).

A solution of 30.3 g (0.264 mol) of methanesulfonyl chloride in 50 mL of CH_2Cl_2 was added dropwise to a 0 °C solution of 26.1 g (0.176 mol) of crude diene **20** in 100 mL of pyridine and 200 mL of CH_2Cl_2. After the addition was complete, the flask was warmed to room temperature, and stirring at this temperature was continued for 19.5 h. The reaction mixture was cooled at 0 °C, and water was added. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were washed successively with dilute sulfuric acid, sodium bicarbonate solution, and brine, dried over MgO_4, and concentrated in vacuo to give 38.6 g (97%) of **21** as a brown oil.

A mixture of 38.9 g (0.172 mol) of crude mesylate **21**, 63.0 g (0.860 mol) of LiBr, 22.4 g (0.258 mol) of Li_2CO_3, and 500 mL of DMF was heated at 125 °C for 7 h. After the mixture cooled to room temperature, the solids were removed by filtration, and water was added to the filtrate. The organics were extracted into ether and washed with water and brine. Removal of solvent in vacuo, after drying over $MgSO_4$, gave 14.8 g (66%) of triene **7** as a green liquid. Purification could be accomplished by either distillation or chromatography (silica gel, eluted with hexane) to give 10.8 g (49% from **21**, 45% from **16**) of triene **7** as a yellow liquid: bp 46–48 °C (3.0 mm) [lit.[21a] 64–65 °C (10 mm)]; ^1H NMR[31] ($CDCl_3/Me_4Si$) δ 6.15–6.40 (2 H, m, H-2,5), 5.79–5.97 (2 H, m, H-3,4), 6.03 (m, J = 6.0 Hz, H-7), 5.30 (ddd, J = 6.0, 2.2, 2.2 Hz, H-8), 2.71 (ddd, J = 17.0, 2.2, 2.2 Hz, H-9_b), 2.47 (ddd, J = 17.0, 2.2, 2.2 Hz, H-9_a), 1.47 (d, J = 3.1 Hz, H-10_b), 0.03 (d, J = 3.1

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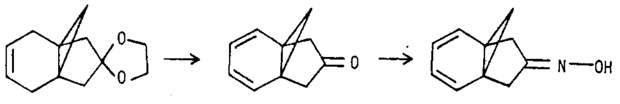
(22) Vogel, et al.[21c] obtained triene **7** in 10% overall yield from i. Recently Lipa and Helmkamp's[23] improvements in the conversion of i to iii increased the overall yield of **7** to 13% (from i).



i ii iii

(23) Lipa, W. J.; Crawford, H. T.; Radlick, P. C.; Helmkamp, G. K. *J. Org. Chem.* **1978**, *43*, 3813.

(24) Murata et al.,[26] in a footnote without any detailed experimental data, have reported an improved conversion of chloride **17** to **18** by using DBU as the base in the dehydrobromination step. Subsequent treatment of **18** with DBU/Me_2SO gave **7** in an overall yield (from **17**) of 68%. They did not indicate if this was a crude or purified yield, but this would correspond to a 57% yield of **7** from **16**.

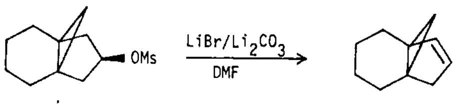
(25) Radlick and Rosen had prepared the chloride **17** since problems were encountered with the direct bromination/dehydrobromination of alcohol **16**.[21a,b] Attempted dehydrobromination of **19** (see Scheme II) with *t*-BuOK/ether, $NaOCH_3$/ether, *s*-collidine/pyridine, and pyridine/benzene (all conducted at reflux) gave recovered starting material while treatment of **19** with *t*-BuOK/Me_2SO at 60–70 °C resulted in the formation of **16**.[21b] Treatment of dibromide **19** with KOH/MeOH at reflux resulted in the recovery of a complex mixture containing approximately 20% of diene **20**.[21b]

(26) Murata, I.; Nakasuji, K.; Morita, T. *Chem. Lett.* **1974**, 743.

(27) (a) Oediger, H.; Möller, F.; Eiter, K. *Synthesis* **1972**, 591. (b) Vogel, E.; Schubart, R.; Böll, W. A. Angew. *Chem.* **1964**, *76*, 535; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 510.

(28) Diene alcohol **20** was obtained in a fairly pure state by simple workup of the crude reaction mixture and was used, as such, for subsequent reactions without additional purification.

(29) (a) Brown, L. R. Ph.D. Thesis, University of California, Riverside, CA, 1973. (b) Brown[29a] has shown that mesylate i can be easily transformed to ii by treatment with LiBr and Li_2CO_3.



i ii

(30) Treatment of **21** with KO-*t*-Bu/Me_2SO did not cleanly give triene **7**.

(31) Recently the original assignment of H-9a and H-9b of **7** by Rosen and Radlick[21a,b,32] has been shown by Takahashi et al. to be incorrect, and we have reversed the chemical shift assignments of these two protons as suggested in ref 33.

(32) Radlick, P.; Rosen, W. *J. Am. Chem. Soc.* **1967**, *89*, 5308.

(33) Takahashi, K.; Takase, K.; Kagawa, T. *J. Am. Chem. Soc.* **1981**, *103*, 1186.

Hz, H-10$_a$); UV (cyclohexane) 260 nm (ϵ 2150), 270 (2070); mass spectrum, *m/e* 130 (M$^+$).

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Dehydrobromination of Secondary and Tertiary Alkyl and Cycloalkyl Bromides with 1,8-Diazabicyclo[5.4.0]undec-7-ene. Synthetic Applications

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The alkene proportions from the dehydrohalogenation of eight secondary and six tertiary aliphatic bromides, four 1-bromo-1-alkylcycloalkanes, three dibromobutanes, and 2-hexyl chloride and iodide with the hindered amidine 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) have been determined. For secondary bromides, the ratios of the more substituted alkene (Saytzeff product) to less substituted alkene (Hofmann product) are on the order of 9:1; for tertiary bromides, the corresponding ratios are 2–3:1 for aliphatic systems and >6:1 for cycloalkyl systems. The presence of a tertiary or benzylic β-H favors the Saytzeff product. Chain branching or elongation of the tertiary aliphatic bromides has only a small effect upon the regioselectivity. Activation of the β-H with a bromine atom considerably reduces the regioselectivity. For 2-halohexanes, the proportion of Saytzeff product increases in the order chloride < bromide < iodide, while the trans/cis ratio increases in the same order from 4.9 to 9. Reduced regio- and stereoselectivities were observed when 2-hexyl *p*-toluenesulfonate was treated with DBU. The thermolysis of the same compound gave a mixture of 1-, 2-, and 3-hexene.

The formation of a carbon–carbon double bond by β elimination (eq 1) is an ever-important operation in organic

$$\mathrm{RR'CHCHXCH_3} \xrightarrow[-\mathrm{HX}]{} \underset{\text{Hofmann}}{\mathrm{RR'CHCH{=}CH_2}} + \underset{\text{Saytzeff}}{\mathrm{RR'C{=}CHCH_3}} \; (\mathrm{R} \neq \mathrm{R'}, \text{ cis/trans}) \quad (1)$$

chemistry[1] and has been the object of extensive research both for synthetic purposes and also for gaining mechanistic information aimed at obtaining an understanding of the factors which affect and determine alkene proportions.[2] Numerous conditions in which the base and solvent have been varied have been examined to determine the effects on regioselectivity (the proportions of Saytzeff and Hofmann products that are formed) and stereoselectivity (in the case of geometrical isomers that are formed).

While 1-alkenes may be formed from primary alkyl bromides and *t*-BuOK in *tert*-butyl alcohol,[3] it is clearly much more difficult to find simple conditions which provide high regioselectivity and stereoselectivity with good yields in eliminations from secondary or tertiary substrates. Thus treatment of 2-bromopentane with EtOK in refluxing ethanol afforded 74% total yield of 1- and 2-pentene, respectively, in a ratio of 1:2 and with a trans/cis ratio of the latter of 2.8;[4] the regioselectivity could be reversed, however, by using instead of ethoxide the highly hindered *t*-BuOK.[5,6] Ag$^+$-promoted eliminations of 2-bromoalkanes were found to proceed with a very high regioselectivity (Saytzeff products preferred) and with trans/cis ratios ranging from 1.1 to 2.8.[7] Ultrahigh regioselectivity favoring the Saytzeff product can be achieved when 2-alkyl bromides or sulfonate esters are treated under E2C-like conditions with a very weak (and soft) base.[6,8] From a preparative viewpoint, these reactions are associated in general with disadvantages such as tedious isolation procedures, moderate yields (in part due to competitive substitution reactions[3]), and long reaction times.[9]

It is thus clear that a method which combines regioselectivity and stereoselectivity with an easy isolation procedure and good yield is needed. Highly hindered tertiary amines are finding an increasing use in synthetic work;[10]

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