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Carbon-13 Chemical Shifts in Bicyclo[3.3.0]octanes

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From a detailed analysis of the carbon-13 spectral data of 52 bicyclo[3.3.0]octanes a set of substituent effects was derived from the monosubstituted compounds. Using the shift change values (ΔS) from this basis set, it is possible to accurately predict chemical shifts for polyfunctionalized bicyclo[3.3.0]octanes. These predictions, used in conjunction with statistical tools ($|\bar{E}|$ and R values), permit regio- and stereochemical analysis of new bicyclo[3.3.0] derivatives.

As part of our general program directed at the total synthesis of natural products from bicyclo[3.3.0]octanes,[1] we had occasion to examine the ^{13}C spectra for a number of these compounds. Although the same substituent effects derived from other rigid systems[2] qualitatively applied here, it soon became apparent that we needed to develop an independent set of substituent effects if reliable structural and stereochemical assignments were to be deduced from ^{13}C spectral data. We thus undertook the accumulation and detailed analysis of the spectra of 52 mono- and polyfunctionalized bicyclo[3.3.0]octanes, and wish to report here our results, which should be of considerable utility to others working with this class of compounds.

Assignments

The influences of a variety of substituents on the chemical shifts of each carbon in the [3.3.0] framework were ascertained from analysis of the spectra of the monofunctionalized compounds listed in Table I. Besides the chemical shift assignments, we have provided the shift changes (ΔS) for each carbon vis-á-vis its counterpart in the unsubstituted hydrocarbon **1**. The assignments were based on established α, β, and γ effects,[2] and, where necessary, on stepped off-resonance decoupling (SORD) experiments, used to distinguish between methylene and methyne carbons. In ambiguous cases (usually involving differences of <2 ppm), assignments were made so as to maximize consistency within the entire collection of spectral data. We feel that this approach is justified because of the high self-consistency that is thus obtained (vide infra).

Discussion

The compounds listed in Table I, comprising the *basis set*, were used to analyze the di- and polyfunctionalized structures shown in Table II. For every Table II compound for which the necessary basis compounds were available, *predicted* chemical shifts of each nonheteroatom-substituted sp^3 carbon were calculated assuming strict additivity of ΔS values. For example, the predicted shift of 31.0 ppm (observed, 31.2) for carbon 6 in alcohol **20** was obtained by adding the requisite ΔS values from *endo*-*cis*-bicyclo[3.3.0]octan-2-ol (**2**, −4.9) and *cis*-bicyclo[3.3.0]oct-2-ene (**4**, +1.7) to 34.2 ppm (the chemical shift of C-2 in the parent hydrocarbon **1**). For each compound thus examined, we have calculated the average of the absolute values of the errors ($|\bar{E}|$) and the correlation factor R;[3] this information is compiled in Table III. For over 175 separate shift predictions, the observed errors ranged from −2.5 to +2.5 (except as noted below), and the average absolute error was 0.7 ppm (SD = 0.6).

It is instructive to consider two cases where the predictions were not as accurate. For bis-*endo*-diol **16**, $|\bar{E}|$ was 2.7 (R = 0.244). This relatively large $|\bar{E}|$ is doubtless due to intramolecular hydrogen bonding (evident in the IR spectrum), which would be expected to distort the conformation of the molecule. This contention is supported by the low $|\bar{E}|$ values for bis-*exo*-diol **22** and for bis-*endo*-diacetate **24** of 0.23 and 0.17 ppm, respectively. The second case for which poor predictions were calculated is enone **32**, showing large errors for carbons 4 and 6. Here, the electronic influence of the carbonyl is transmitted through the π system, causing an observed shift of the γ carbons that is downfield from that predicted. These two cases demonstrate that, in applying the prediction method, one cannot ignore unusual internal interactions.

Conclusions

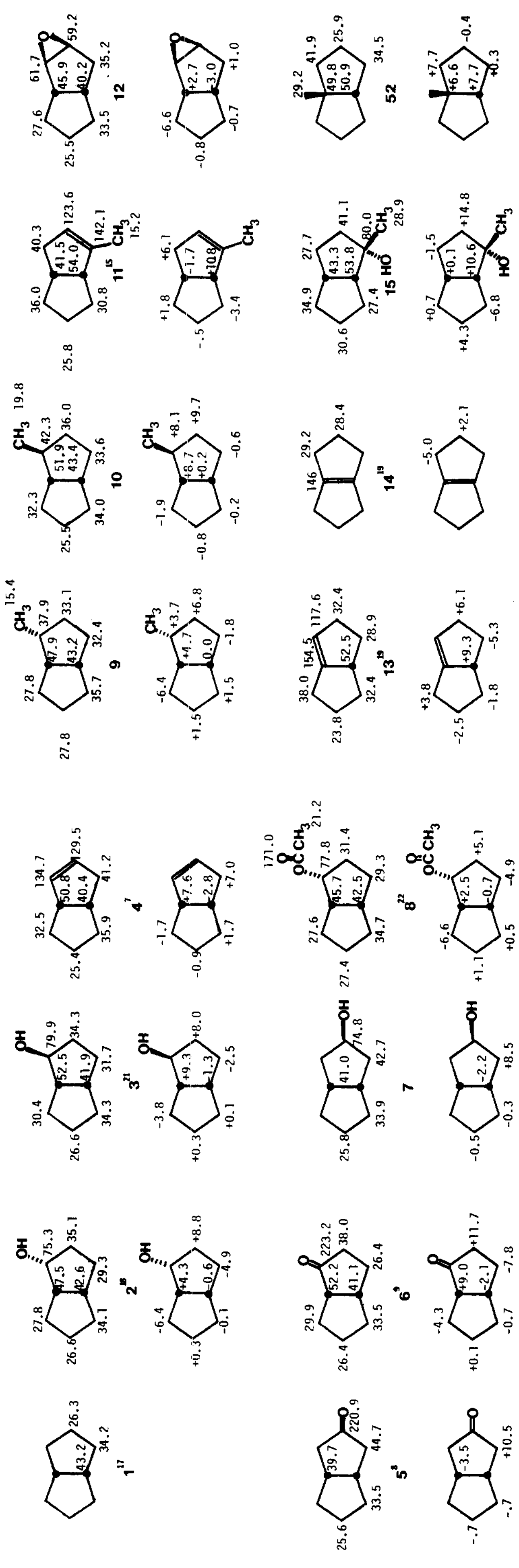
The ^{13}C NMR data presented herein provide a simple, accurate basis for the determination of regio- and stereochemical features of bicyclo[3.3.0]octanes. Given the ^{13}C spectrum of an unknown compound, one may quickly test logical structural possibilities by comparing predicted chemical shifts with observed ones. Typically, correct structures give $|\bar{E}|$ values within the standard deviation of $|\bar{E}|$ for the whole system, and incorrect structures usually give an $|\bar{E}|$ larger than the largest $|\bar{E}|$ ever observed for any single compound of known structure. This system is especially useful when the number of possible structures is low, as when only one stereochemical assignment is uncertain. In those cases, the problem is often solved by inspection. For example, an *exo*-methyl group at C-2 consistently absorbs at ca. δ 19, compared with an *endo*-methyl at ca. δ 15.

Such qualitative assessments can be placed on a quantitative, statistical footing through the use of the agreement factor R. Values of R (in Table III) were calculated using all sp^3, nonheteroatom-bearing carbons, according to the equation[4]

$$R = \left[\frac{\Sigma(|\delta_{330} - \delta_{\mathrm{obsd}}| - |\delta_{330} - \delta_{\mathrm{calcd}}|)^2}{\Sigma|\delta_{330} - \delta_{\mathrm{obsd}}|^2}\right]^{1/2} \qquad (1)$$

where δ_{calcd} is the calculated chemical shift of a carbon in the structure under consideration, δ_{obsd} is the shift for that carbon in the ^{13}C spectrum, and δ_{330} is the shift of that carbon in

Table I



parent compound 1. The application of R is illustrated for compound **38**, a key intermediate in our total synthesis of iridomyrmecin.[1] At the time of that work, although we had determined that **38** was a single isomer, we had no convenient means to assign relative configuration to the methyl-bearing carbon (other than completion of the synthesis). The R value for the *exo*-methyl configuration (the correct one) is 0.104, compared to 0.363 for the endo isomer, resulting in a ratio ($\mathcal{R} = R_{\text{endo}}/R_{\text{exo}}$) of 3.49. For a confidence level of α = 0.5%, one may calculate $R_{1,n,\alpha}$ using the equation[4]

$$R_{1,n,\alpha} = \left[\frac{1}{n}(F_{1,n,\alpha}) + 1\right]^{1/2} \qquad (2)$$

where n is the number of shifts calculated, and $F_{1,n,\alpha}$ is the requisite "percentage point" in the F distribution.[25] Thus, $R_{1,6,0.005}$ = 2.03, which is smaller than ratio $\mathcal{R}$. We may therefore exclude the endo isomer at a confidence level of >99.5%.

In conclusion, we feel that the data herein should prove quite useful for chemists working with bicyclo[3.3.0]octanes. Several related problems in the recent chemical literature, for example, could have been solved using this system.[5]

Experimental Section

Materials. Reference to procedure for the preparation of known compounds is provided by footnotes in the tables. The preparations of the remaining compounds are described below.

Procedure. Carbon-13 spectra were obtained in deuteriochloroform solutions with tetramethylsilane as internal standard using a Bruker WH90 spectrometer. Values are reported as parts per million downfield from the standard. Proton spectra were recorded on either a Varian HA-100 or a Perkin-Elmer R-12 and are reported in parts per million on the δ scale relative to tetramethylsilane as internal standard in deuteriochloroform solutions. Infrared spectra were recorded using a Perkin-Elmer 237B. All temperatures given are uncorrected.

***endo*-2-Methyl-*cis*-bicyclo[3.3.0]octane (9).** This compound was prepared by catalytic reduction of 2-methyl-*cis*-bicyclo[3.3.0]-oct-2-ene over platinum oxide in glacial acetic acid solution. The product was isolated by partitioning between pentane and aqueous bicarbonate. Removal of the solvent through a short, packed column and simple distillation afforded analytically pure material [bp 150 °C (740 mmHg)], as a single isomer by ^{13}C (>95%).

Anal. Calcd for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 87.03; H, 13.17.

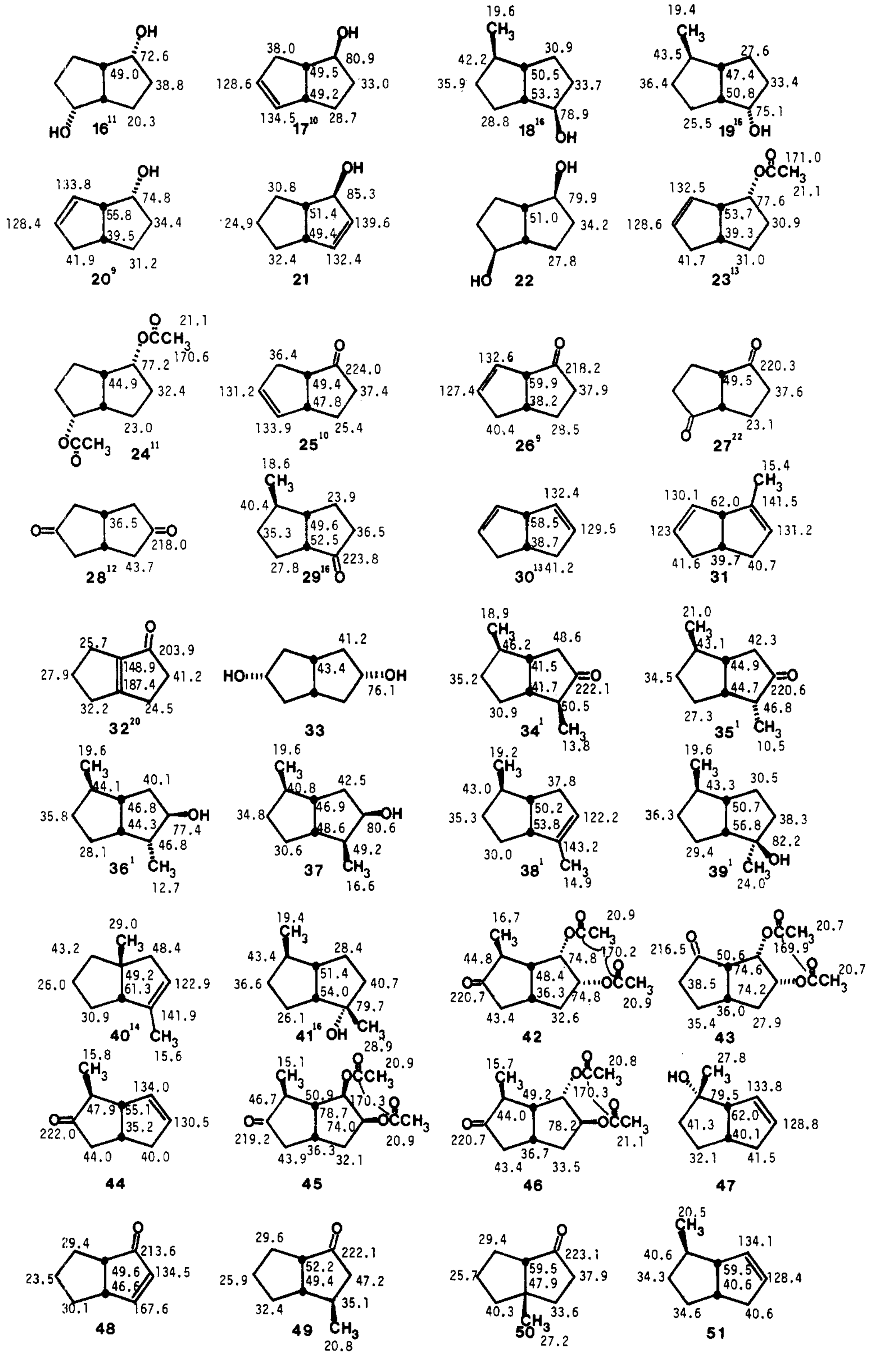
***cis*-Bicyclo[3.3.0]oct-3-ene oxide (12).** To an ice cold, stirred solution in 20 mL of dichloromethane of 1.5 g (14 mmol) of *cis*-bicyclo[3.3.0]oct-2-ene was added dropwise with stirring a solution of 3.1 g (15 mmol) of 85% *m*-chloroperbenzoic acid in 35 mL of the same solvent. The ice bath was removed and after 1 h the reaction mixture was washed with 10% aqueous sodium sulfite, 1.0 N aqueous sodium bicarbonate, and then water. The organic layer was concentrated in vacuo and the crude epoxide distilled, affording 1.5 g of material with bp 80–82 °C (29 mmHg). Analysis by VPC (5% SE-30 on Chromosorb G) indicated a mixture of three components (1:1:8). The desired, *exo*-epoxide was obtained in pure form by preparative VPC on the same column; NMR δ 3.47 (t, 1 H), 3.30 (d, 1 H), 2.2–2.8 (m, 2 H), 1.0–2.0 (m, 8 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.25; H, 9.96.

***endo*-2-Hydroxy-*exo*-2-methyl-*cis*-bicyclo[3.3.0]octane (15)** was synthesized from compound **6** by the addition of methyllithium, using normal reaction conditions.[26]

***exo*-3-Hydroxy-*cis*-bicyclo[3.3.0]oct-2-ene (21).** The following procedure was found to be superior to either allylic oxidation of alkene **4** with freshly prepared selenium dioxide, or the addition of phenylselenide anion to epoxide **11** followed by oxidative elimination. A solution of 124 mg (1.0 mmol) of epoxide **12** in 1 mL of dry ether was added to a solution of 2.5 mmol of lithium diethylamide in ether-hexane with ice cooling. The bath was removed and the reaction heated at reflux for 24 h. To the cooled reaction mixture was added sufficient 2 N hydrochloric acid to adjust the pH to ~5, the resulting mixture was extracted three times with dichloromethane, and the organic layers were combined and washed with 1 N aqueous bicarbonate solution. The crude product obtained after removal of the solvents in vacuo was purified by short-path distillation [bp 102–105

Table II



°C (25 mmHg)]. The material so obtained contained varying amounts of ketones (10–20%). Pure material was obtained via the *p*-chlorobenzoate derivative, prepared in the standard fashion, mp 33.5–35 °C (hexane).

Anal. Calcd for $C_{15}H_{15}ClO_2$: C, 68.57; H, 5.75; Cl, 13.49. Found: C, 68.51; H, 5.72; Cl, 13.23.

***exo,exo*-2,6-Dihydroxy-*cis*-bicyclo[3.3.0]octane (22)** was prepared from diol **16** by first converting **16** to the dimesylate,[23] which was then solvolyzed in water–dioxane as in ref 1. After distilling away all volatile products (aspirator vacuum), a small yield (~20%) of diol **22** was obtained.

2-Methyl-*cis*-bicyclo[3.3.0]octa-2,7-diene (31) was obtained via dehydration of compound **47** using catalytic *p*-toluenesulfonic acid in benzene at reflux, and normal workup conditions.[1]

***exo*-3-Hydroxy-*exo*-2-methyl-*exo*-6-methyl-*cis*-bicyclo[3.3.0]octane (37)** was obtained by a normal sodium borohydride reduction of compound **34**.[27]

***endo,endo*-7,8-Diacetoxy-*exo*-2-methyl-*cis*-bicyclo[3.3.0]octan-3-one (42)** was prepared from compound **44** in 70% yield using the Woodward cis-hydroxylation procedure in a manner identical with that described herein for the preparation of compound **43**. Compound **42**: NMR ($CDCl_3$) δ 1.1 (d, 3 H), 1.5–2.9 (m, 7 H), 2.05 (s, 3 H), 2.06 (s, 3 H), 5.2–5.4 (m, 2 H).

***endo,endo*-7,8-Diacetoxy-*cis*-bicyclo[3.3.0]octan-2-one (43).** To a solution of the keto olefin (1 g, 8.2 mmol) in 37 cm^3 of glacial acetic acid was added 3.08 g of dry silver acetate. To this vigorously

Table III

Compd	$\lvert\bar{E}\rvert$	R
16*	2.7	0.244
17	0.6	0.119
18	0.5	0.083
19	0.7	0.114
20	0.4	0.065
21	0.8	0.211
22	0.1	0.036
23	0.2	0.047
24	0.2	0.026
25	0.5	0.079
26	0.3	0.040
27	0.7	0.074
28	0.3	0.035
29	0.7	0.112
30	1.0	0.141
31	1.0	0.102
32*	1.9	0.254
34	0.8	0.147
35	1.3	0.219
36	1.3	0.183
37	1.1	0.174
38	0.4	0.072
39	1.0	0.122
41	0.5	0.051
44	1.6	0.185
47	0.8	0.089
48*	1.6	0.402
49	0.4	0.054
50	0.5	0.066
51	0.4	0.059

stirred heterogeneous mixture was added 2.2 g of finely powdered iodine, portionwise, over about 5 min, during which time the reaction color turned from white to cream.

After the iodine was consumed (10–15 min), 3.69 cm^3 of wet acetic acid was added (prepared by diluting 2 cm^3 of water to 50 cm^3 with glacial acetic acid), and the reaction mixture was heated at 95 °C for 3 h.

The reaction mixture was cooled, and excess sodium chloride was added; the mixture was then filtered, and the silver salts were washed with hot benzene.

The filtrate was rotary evaporated to remove the benzene, and the acetic acid was then removed under high vacuum. The residue was partitioned between methylene chloride and aqueous sodium bicarbonate. After separating the layers, the aqueous portion was twice more extracted. The combined organic portions were filtered and concentrated under vacuum to give crude alcohol acetate, which had the odor of bubble gum.

This crude material was dissolved in ~1 cm^3 of pyridine, and 1.6 cm^3 of acetic anhydride was then added, under nitrogen. After stirring at room temperature overnight, the reaction mixture was transferred to a separatory funnel with ether, and 1 N sodium bicarbonate was carefully added until the foaming stopped. The ether layer was washed with saturated copper sulfate, water, and brine. It was then dried over molecular sieves, filtered, and concentrated under vacuum to give the crude diacetate.

The crude product was purified by preparative thin-layer chromatography on silica gel, using 1:1 ethyl acetate–cyclohexane, and yielded ~785 mg of pure diacetate (40% yield); NMR (pyridine-d_5) δ 1.96 (s, 3 H), 2.02 (s, 3 H), 1.5–3.0 (m, 8 H), 5.2–5.4 (m, 1 H), 5.64 (d-d, 1 H).

***exo*-2-Methyl-*cis*-bicyclo[3.3.0]oct-7-en-3-one (44).** To a solution of 11 g of *cis*-2-methylbicyclo[3.3.0]octa-2,7-diene 2-oxide in 420 cm^3 of dry benzene, under nitrogen, was added 5.65 cm^3 of boron trifluoride etherate. After 15 min, gas chromatographic analysis showed no more starting material. The reaction mixture was filtered through a layer of sodium carbonate and activity IV alumina, then concentrated under vacuum to give the crude product, which was purified by high-pressure liquid chromatography to yield ketone **44**: NMR ($CDCl_3$) δ 1.16 (d, 3 H), 2.0–2.1 (m, 7 H), 5.8 (s, 2 H).

***exo,exo*-7,8-Diacetoxy-*exo*-2-methyl-*cis*-bicyclo[3.3.0]octan-3-one (45)** was obtained from compound **44** by cis hydroxylation using osmium tetroxide,[24] followed by acetylation using acetic anhydride in pyridine, with the usual workup: NMR ($CDCl_3$) δ 1.08 (d, 3 H), 1.7–3.2 (m, 7 H), 2.08 (s, 3 H), 2.10 (s, 3 H), 5.16 (t, 1 H), 5.20 (m, 1 H).

***exo*-7-Acetoxy-*endo*-8-acetoxy-*exo*-2-methyl-*cis*-bicyclo[3.3.0]octan-3-one (46)** was prepared in a manner identical with that described for compound **43**, expect that no wet acetic acid was added and no acetylation was performed: NMR ($CDCl_3$) δ 1.1 (d, 3 H), 1.9–2.1 (m, 7 H), 2.07 (s, 6 H), 2.3 (m, 2 H).

***endo*-2-Hydroxy-*exo*-2-methyl-*cis*-bicyclo[3.3.0]oct-7-ene (47)** was prepared from compound **26** by addition of methyllithium, using normal reaction conditions.[26]

***cis*-Bicyclo[3.3.0]oct-3-en-2-one (48).** Compound **48** was prepared by oxidation of allylic alcohol **21**, using pyridinium chlorochromate.[28]

***exo*-4-Methyl-*cis*-bicyclo[3.3.0]octan-2-one (49).** To a suspension of dry cuprous iodide (0.925 g, 5 mmol) in 7 cm^3 of dry ether, under nitrogen at 0 °C, was added 5.55 cm^3 of a 1.8 M solution of methyllithium (10 mmol) dropwise via syringe. Keto olefin **48** (0.6 g, 4.9 mmol) was then added as an ethereal solution, all at once. The cooling bath was removed, and the reaction mixture was allowed to reach room temperature, where it was stirred for 1 h. Partitioning between ether and aqueous hydrochloric acid gave, upon concentration of the organic layer, 0.428 g of the methyl ketone, pure by ^{13}C and gas chromatography: NMR ($CDCl_3$) δ 1.15 (d, 3 H), 1.4–2.9 (m, 11 H).

***exo*-2-Methyl-*cis*-bicyclo[3.3.0]octane (10).** To a flask containing 4.5 cm^3 of triethylene glycol, 0.45 cm^3 of hydrazine (95%), and 0.56 g of potassium hydroxide was added 0.43 g (3.1 mmol) of methyl ketone **49**. this mixture was slowly heated, with stirring, until the oil bath reached 180 °C. During this time, 110 mg of hydrocarbon **10** distilled out, essentially pure by ^{13}C: NMR ($CDCl_3$) δ 1.05 (d, 3 H), 1.0–2.8 (m, 13 H).

5-Methyl-*cis*-bicyclo[3.3.0]octan-2-one (50). Methyl ketone **50** was prepared from keto olefin **32** in a manner exactly analogous to the preparation of **49** from **48**, described above.

1-Methyl-*cis*-bicyclo[3.3.0]octane (52). Compound **52** was prepared by reduction of ketone **50** in a manner exactly analogous to the preparation of compound **10** from **49**, described above.

8-Methyl-*cis*-bicyclo[3.3.0]oct-2-ene (51). Compound **51** was prepared from the tosylate of alcohol **20**, following the procedure detailed in ref 29.

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Registry No.—**1**, 1755-05-1; **2**, 24454-38-4; **3**, 23359-88-8; **4**, 930-99-4; **5**, 19915-11-8; **6**, 32405-37-1; **7**, 24454-39-5; **8**, 63641-22-5; **9**, 1551-77-5; **10**, 1551-76-4; **11**, 63641-23-6; **12**, 24454-41-9; **13**, 694-73-5; **14**, 6491-93-6; **15**, 63641-24-7; **16**, 37940-19-5; **17**, 53648-79-6; **18**, 63641-25-8; **19**, 63700-71-0; **20**, 41164-15-2; **21**, 27141-89-5; **22**, 17572-86-0; **23**, 40132-71-6; **24**, 52993-36-9; **25**, 32405-38-2; **26**, 10095-78-0; **27**, 17572-87-1; **28**, 51716-63-3; **29**, 63641-26-9; **30**, 41164-14-1; **31**, 63641-27-0; **32**, 10515-92-1; **33**, 63641-28-1; **34**, 63700-72-1; **35**, 57764-39-3; **36**, 57764-38-2; **37**, 63641-29-2; **38**, 57764-37-1; **39**, 63700-73-2; **40**, 63641-30-5; **41**, 63700-74-3; **42**, 63641-31-6; **43**, 63641-32-7; **44**, 63641-33-8; **45**, 63641-34-9; **46**, 63641-35-0; **47**, 63641-36-1; **48**, 23668-30-6; **49**, 63641-37-2; **50**, 63641-38-3; **51**, 63641-39-4; **52**, 1488-79-5.

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Reactions of *exo*- and *endo*-8-Carbenatricyclo[3.2.1.0^{2,4}]octane[1]

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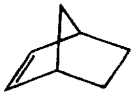
Decomposition of the tosylhydrazone of *exo*-8-tricyclo[3.2.1.0^{2,4}]octanone in bis(2-ethoxyethyl)ether/sodium methoxide produces a mixture of hydrocarbons (20%) composed of 65% of bicyclo[3.3.0]octa-1,6-diene and 35% of a mixture of two isomeric bicyclo[3.3.0]octadienes. The decomposition of the tosylhydrazone of *endo*-8-tricyclo[3.2.1.0^{2,4}]octanone (**17a**) in diglyme/sodium methoxide yields *endo-anti*- and *endo-syn*-tricyclo[3.2.1.0^{2,4}]-octan-8-yl methyl ether, *endo*-tricyclo[3.3.0.0^{4,6}]octan-2-yl methyl ether, tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane (**21**), and tricyclo[3.3.0.0^{4,6}]oct-2-ene (**22**) in an overall yield of 80%. The ratio of methyl ethers/hydrocarbons is dependent upon the concentration of methanol in the reaction medium. The decomposition of the 2-methyl derivative of tosylhydrazone **17a** (**35a**) in either diglyme/sodium methoxide or diglyme/sodium hydride generates a hydrocarbon mixture of 4-methylenetricyclo[3.3.0.0^{2,8}]octane (**36**) and 2-methyltetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane (**37**). NMR and mass spectral analyses of the hydrocarbon products of decomposition of labeled tosylhydrazones using deuterated substrates, *exo,exo*-6,7-dideuterio-**17a** (**17c**), *exo,exo*-6,7-dideuterio-**35a** (**35b**), *exo*-4-deuterio-**35a** (**47**), and 4-*exo,exo*-6,7-trideuterio-**35a** (**48**) support an intermolecular carbene to carbene rearrangement for the generation of tetracyclooctanes **21** and **37**.

If one relates the state of the art of carbene chemistry[2] to our knowledge of carbonium ion chemistry,[3] it is easy to appreciate that the development of our understanding of the mechanistic features of carbene reactions is at a relatively primitive stage. A major facet of carbonium ion chemistry which we are pursuing in carbene chemistry is the importance of homoaromatic delocalization illustrated in the carbonium ion case by the bicyclo[3.1.0]hexyl carbonium ion.[4] In a number of studies, intriguing possibilities for homoaromatic character in carbene intermediates have surfaced. Moss and co-workers[5] have described the chemistry of 7-carbenanorbornene (**1**), Fisch and Pierce[6] have generated 9-carbenabicyclo[3.3.1]non-2-ene (**2**), Klumpp and Vrielink[7] have considered 7-carbenabicyclo[4.1.0]hept-3-ene (**3**), and we have reported on the chemistry of 3-carbenabicyclo[3.1.0]hexane (**4**)[8] and *endo*-5-norbornenylcarbene (**5**).[9]



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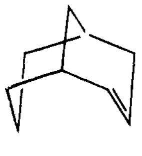

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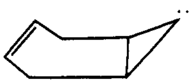

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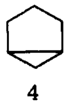

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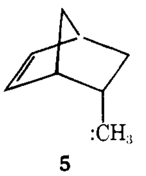

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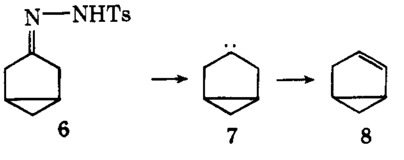
Evidence suggesting horoaromatic stabilization has been advanced for 7-carbenanorbornene (**1**), bivalent **2**, and *endo*-5-norbornenylcarbene (**5**). The simplicity of 3-carbenabicyclo[3.1.0]hexane (**4**) was appealing initially; however, the methoxide ion induced decomposition of the tosylhydrazone of 3-bicyclo[3.1.0]hexanone (**6**) generates bicyclo[3.1.0]hexene-2 (**8**) in 91% yield, most probably as a result of 1,2-hydrogen migration of 3-carbenabicyclo[3.1.0]hexane.[10] Thus, any trishomocyclopropenyl character which might actually be present in 3-carbenabicyclo[3.1.0]hexane is not revealed. If one were to bridge 3-carbenabicyclo[3.1.0]hexane across the C-2–C-4 positions with a small bridging unit, however, hydrogen migration would be prevented and transannular interactions might be revealed. For example, the incorproation of an ethano bridging unit would create the tricyclo[3.2.1.0^{2,4}]-octane ring system, which provides a very favorable geometry for interaction of remote cyclopropane with an empty p orbital at C-8 in the case of the endo arrangement. For these reasons, we chose to investigate *exo*- and *endo*-8-carbenatricyclo[3.2.1.0^{2,4}]octane (**13** and **28**).



6 7 8

Decomposition of the tosylhydrazone of *exo*-8-tricyclo[3.2.1.0^{2,4}]octanone (**9**) in bis(2-ethoxyethyl) ether (3.3 equiv of $NaOCH_3$) at 160 °C gives a 20% yield of hydrocarbons, composed of 65% of bicyclo[3.3.0]octa-1,6-diene (**10**) and