

Experimental Section

Infrared (IR) spectra were determined as films. The superscripts s, m, and w designate strong, medium, and weak absorption bands. NMR spectra were recorded in deuteriochloroform solutions on a Varian T-60 spectrometer with tetramethylsilane as internal standard. A Hewlett-Packard Model 5720 gas chromatograph equipped with 6-ft UC-W 98 10% columns was used for GC analysis. The temperature program was set from 100 to 200 °C at 10 °C/min. *Caution: Thermal instability of acetyl nitrate has been reported.^{5b} It is also recommended that nitro acetates 1 or 2 not be heated above 100 °C either neat or in solution.*

3-Methyl-4-nitro-2-buten-1-yl Acetate (1) and 3-Methyl-4-nitro-1-buten-3-yl Acetate (2). Nitric acid (90%, 100 g, 1.43 mol) was dropped into stirred and ice bath cooled acetic anhydride (735 g, 7.2 mol) at such a rate that the internal temperature was maintained at 20–25 °C.⁷ This was followed by the dropwise addition of isoprene (68 g, 1 mol), which required 1 h and continuous cooling with an ice bath in order to maintain the internal temperature at a constant 25 °C. The reaction mixture was stirred for an additional 1 h at room temperature and worked up by quenching in ice and water and extracting with methylene chloride. Solvent and excess acetic anhydride were removed in vacuo (aspirator, then high vacuum) at ≤40 °C water bath temperature⁸ to give 194.2 g of dark yellow oily residue. GC analysis indicated that besides a small amount of acetic anhydride, the crude mixture consisted essentially only of 1 and 2 in the ratio of 7:3. The *Z* isomer of 1 was estimated to be 5% of the total weight. The pure compounds *E*-1, *Z*-1, and 2 were isolated from a similar experiment via silica gel column chromatography using benzene–ethyl acetate mixtures for elution.

Nitro Ester E-1:⁹ IR 1740^s, 1635^m, 1560^s cm⁻¹; ¹H NMR (CDCl₃) δ 1.85 (broadened s, 3 H, CH₃), 2.05 (s, 3 H, OAc), 4.65 (d, *J* = 7 Hz, 2 H, OCH₂), 4.85 (s, 2 H, –CH₂NO₂), 5.78 (t, *J* = 7 Hz, 1 H, vinyl); λ_{max} (EtOH) 280 nm (ε 370); λ_{max} (0.1 N KOH) 221 nm (ε 8840), 284 (7255); MS *m/e* M⁺ not observed, 127 (8%, M⁺ – NO₂), 85 (9%, M⁺ – NO₂ – CH₃CO), 43 (100%, CH₃CO).

Nitro Ester Z-1:⁹ ¹H NMR (CDCl₃) δ 1.94 (broadened s, 3 H, CH₃), 2.05 (s, 3 H, OAc), 4.66 (d, *J* = 7 Hz, 2 H, OCH₂), 5.08 (s, 2 H, –CH₂NO₂), 5.83 (t, *J* = 7 Hz, 1 H, vinyl).

Nitro Ester 2: IR 1720^s, 1630^w, 1535^s cm⁻¹; ¹H NMR (CDCl₃) δ 1.63 (s, 3 H, CH₃), 2.05 (s, 3 H, OAc), 4.85 (s, 2 H, CH₂NO₂), 5.25–6.0 (m, 3 H, vinyl group); λ_{max} (EtOH) 280 nm (ε 250); λ_{max} (0.1 N KOH) 231 nm (ε 10 320), 285 (6720); MS *m/e* M⁺ not observed, 127 (23%, M⁺ – NO₂), 85 (95%, M⁺ – NO₂ – CH₃CO), 67 (100%, M⁺ – NO₂ – AcOH).

Allylic Rearrangement 2 → 1. Nitro ester 2 (100 mg) was dissolved in 1 mL of a solution of 230 mg of concentrated sulfuric acid in 33.7 mL of acetic acid. After 16 h at 75 °C the reaction was quenched with ice. There was obtained 91 mg of a 7:3 *E/Z* mixture of 1 as determined by GC.

Allylic Rearrangement of a Crude Mixture of 1 and 2. The crude product (194.2 g) obtained in the experiment described above was dissolved in 450 mL of acetic acid to which had been added 7.3 g of concentrated sulfuric acid. Stirring at 75 °C overnight, quenching with ice, and extractive workup yielded 162.8 g (94%) of brown oil. For the purpose of yield determination, an aliquot (1.401 g) was evaporatively distilled¹⁰ in a Kugelrohr apparatus [oven temperature 120–140 °C (0.5–0.8 mm)]. The light yellow distillate [1.158 g, 82% (based on isoprene)] was shown by GC analysis to be an 85:15 mixture of *E*1 and *Z*-1.

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Registry No.—*E*-1, 62842-04-0; *Z*-1, 62842-05-1; 2, 61447-07-2; isoprene, 78-79-5; acetyl nitrate, 591-09-3.

References and Notes

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- (a) Mechanistic studies of the HCl addition to isoprene are reported by M. D. Jordan, Jr., and F. L. Pilar, *Theor. Chim. Acta*, **10**, 325 (1968). (b) Acetyl nitrate additions to simple olefins have been studied in detail by F. G. Bordwell and F. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **82**, 3588 (1960); *J. Org. Chem.*, **27**, 3049 (1962).
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- Caution! Acetyl nitrate is reported^{5b} to be a thermally labile compound.*

- In view of the general thermal instability of aliphatic nitro compounds, we recommend that the lowest practical temperature be used.
- Assignments for the *E* and *Z* structures are based on the chemical shifts of the methyl group in relation to the allylic oxygen function: D. J. Faulkner, *Synthesis*, 175 (1971).
- It is recommended that larger amounts not be distilled since decomposition "fume-offs" have occurred in isolated instances. A safety shield is advisable.

Carbon-13 Spectral Parameters of Some Polycyclic Hydrocarbons

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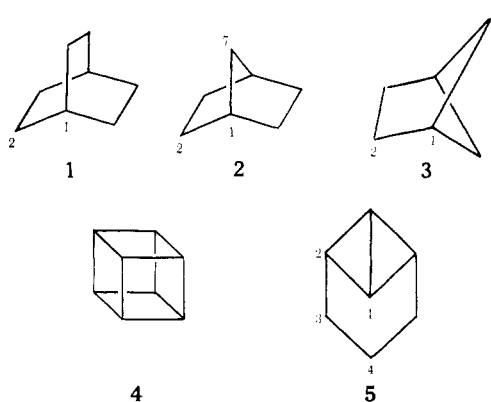
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In connection with work on polycyclic hydrocarbons substituted at the bridgehead position, in particular those derived from the molecules 1–5 below, we felt it desirable to report the ¹³C NMR spectra of the parent hydrocarbons. While chemical shifts of the carbon atoms in bicyclo[2.2.2]octane (1) and norbornane (2) have been well documented,^{1,2} and the ¹³C–H one-bond coupling constants have been reported for 2³ and tricyclo[4.1.0.0^{2,7}]heptane (5),⁴ there is a surprising lack of information on the remainder. In addition to chemical shift data, we were particularly interested in the one-bond bridgehead carbon–proton couplings. There has been considerable activity in recent years in the measurement of ¹*J*(¹³C–H), and in attempts to correlate this parameter with the s character of the carbon bonding orbital, according to the empirical relationship described by Muller and Pritchard.⁵

$$\% s = \frac{J(^{13}\text{C}-\text{H})}{5}$$

Although this suggested correlation has been criticized, there is good evidence that the empirical relationship holds for hydrocarbons, but is rather less tenuous when applied to molecules containing heteroatoms. ¹³C–H coupling constants have been suggested to correlate similarly with other phenomena that are sensitive to hybridization, and hence the electronegativity of the carbon orbital, such as the p*K*_as of the corresponding amines and carboxylic acids,⁶ as well as the acidity of the proton.⁷

The substrates 1, 2, and 4 were obtained as previously reported,⁸ and 5 was obtained by known proce-



dures.⁹ Bicyclo[2.1.1]hexane (3) was synthesized from bicyclo[2.1.1]hexan-2-one by sodium cyanoborohydride reduction of the derived *p*-toluenesulfonylhydrazone.

Table I contains the carbon-13 chemical shifts, of which the values for 1 and 2 are in excellent agreement with those recorded. For shifts previously unknown, viz., in 3, 4, and 5, assignments were made with the aid of off-resonance de-

Table I. ^{13}C Chemical Shifts of the Polycyclic Hydrocarbons 1-5

Registry no.	Compd	C ₁	C ₂	Others
280-33-1	1	24.0 ^a	26.0 ^a	
279-23-2	2	36.6 ^b	30.0 ^b	C ₇ 38.6 ^b
285-86-9	3	39.5	26.3 ^c	C ₅ 39.0 ^c
277-10-1	4	47.3	47.3	
287-13-8	5	5.6	40.0	C ₃ 20.8 C ₄ 21.3

^aFor literature values see ref 1. ^bFor literature values see ref 2. ^cShifts may be interchanged.

Table II. One-Bond ^{13}C -H Coupling Constants in the Polycyclic Hydrocarbons 1-5

Compd	$J(^{13}\text{C}_1\text{-H})$	% s character	$J(^{13}\text{C}_1\text{-H})$ others	% s character
1	134.3	26.9	C ₂ 125.7	25.1
2	140.1 ^{a,b}	28.0	C ₂ 130.3 ^b C ₇ 131.3 ^b	26.1 26.3
3	150.5	30.1	C ₂ 132.5 ^d C ₅ 135.1 ^d	26.5 27.0
4	153.8	30.8		
5	200.3 ^c	40.0	C ₂ 154.2 ^c C ₃ 126.2 ^c C ₄ 126.2 ^c	30.8 25.4 25.4

^aFor literature values see ref 3a. ^bFor literature values see ref 3b. ^cFor literature values see ref 4. ^dCoupling constants may be interchanged.

coupled spectra, and by relative intensities in the proton-decoupled spectra. Coupling constants of directly bonded ^{13}C -H are displayed in Table II. As expected there is a pronounced increase in the magnitude of the bridgehead carbon-proton coupling with increased strain at the bridgehead. Thus, the value of $J(^{13}\text{C}_1\text{-H})$ in the relatively strain-free molecule, 1, is essentially identical with that in adamantane (133.5 Hz).^{3a} On the other hand, the highly strained hydrocarbons such as cubane (4) and tricyclo[4.1.0.0^{2,7}]heptane (5) show markedly higher values. The calculated fractional s characters of the C-H bonds are also included in Table II. Clearly, in both 4 and 5, the bridgehead skeletal angles are substantially smaller than those in 1, resulting in an increase in the p character of the endocyclic hybrid orbitals of the bridgehead carbon atom with a corresponding increase in the s component of the exocyclic hybrid orbital.

Experimental Section

^{13}C NMR spectra were measured on a Bruker Scientific Inc. WH-270 Fourier transform NMR spectrometer operating at 67.89 MHz, or, in a few instances, on a WH-90 spectrometer operating at 22.625 MHz. Samples were ca. 3 M in deuteriochloroform with Me₄Si added as an internal reference. Chemical shifts are estimated to be accurate to ± 0.1 ppm, and coupling constants to ± 0.6 Hz. Bicyclo[2.2.2]octane, norbornane, and cubane were obtained from the corresponding bridgehead-substituted bromides by reaction with tributyltin hydride under ultraviolet irradiation as described.⁸ Tricyclo[4.1.0.0^{2,7}]heptane was synthesized by the improved procedure reported by Gassman and Richmond.⁹

Bicyclo[2.1.1]hexane. Bicyclo[2.1.1]hexan-2-one¹⁰ (1.0 g, 10.4 mmol) and *p*-toluenesulfonylhydrazine (2.4 g, 13.0 mmol) in ethanol (70 mL) were boiled under reflux for 20 h. The solution was cooled and the crystalline deposit was recrystallized from ethanol to give bicyclo[2.1.1]hexan-2-one *p*-toluenesulfonylhydrazone (1.9 g, 70%) as needles, mp 184-185 °C.

Anal. Calcd for C₁₃H₁₆N₂O₂S: C, 59.07; H, 6.10; N, 10.60; S, 12.13. Found: C, 59.35; H, 6.34; N, 10.57; S, 11.9.

The hydrazone (1.8 g, 6.8 mmol) was dissolved in 1:1 DMF/sulfolane (32 mL), heated to 110 °C, and then treated with three portions each containing sodium cyanoborohydride (1.7 g, 27.4 mmol) and *p*-tolu-

enesulfonic acid (0.3 g) added every 3 h as outlined by Hutchins and co-workers.¹¹ The product which distilled and was collected in a cold trap (-40 °C) was shown (VPC) to be practically pure and was identified as bicyclo[2.1.1]hexane by comparison of its physical and spectral properties (MS, IR, NMR) with those of the authentic material.

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Registry No.—Bicyclo[2.1.1]hexan-2-one, 5164-64-7; *p*-toluenesulfonylhydrazine, 1576-35-8; bicyclo[2.1.1]hexan-2-one *p*-toluenesulfonylhydrazone, 62708-51-4.

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Synthesis of

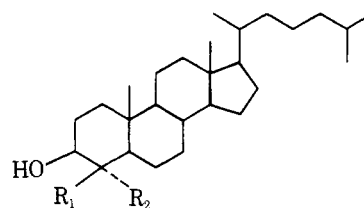
4-Spiro[cyclopropanecholestan-3 β -ol]

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Previous studies of the interaction of rat liver enzyme preparations with cholestan derivatives having various substituents at C4 have indicated that there is a high degree of substrate specificity in the biological demethylations at that position during the conversion of lanosterol to cholesterol.¹⁻³ Specifically, steroids 1-5 are converted to cholestan-3 β -ol by



- | | |
|---|--|
| 1, R ₁ , R ₂ = CH ₃ | 5, R ₁ = CH ₃ ; R ₂ = COOH |
| 2, R ₁ = H; R ₂ = CH ₃ | 6, R ₁ = CH ₂ OH; R ₂ = CH ₃ |
| 3, R ₁ = CH ₃ ; R ₂ = CH ₂ OH | 7, R ₁ = CH ₃ ; R ₂ = CH ₂ CH ₃ |
| 4, R ₁ = CH ₃ ; R ₂ = CHO | 8, R ₁ = CH ₂ CH ₃ ; R ₂ = CH ₃ |

