their proper data are also shown in Table I.

A General Procedure for Reductive Carbon–Sulfur Bond Cleavage of 2. A mixture of **2a** ($R^1 = (CH_2)_3CO_2Me$, $R^2 = n\text{-}C_5H_{11}$, 102 mg, 0.249 mmol) and 98% H_2SO_4 (120 mg) in MeOH (20 mL) was placed in a cathode cell which was divided by a fritted glass and fitted with a carbon electrode, a gas lead pipe, a thermometer, and a magnetic stirring bar. Electrolysis was carried out at a constant current of 20 mA (7–22 V), 8 F/mol of electricity, at room temperature. After removal of 13 mg (31%) of BTSSBT by filtration, the filtrate was concentrated and the residue was taken up in AcOEt. The extract was washed with aqueous 1 N NaOH and brine, dried (Na_2SO_4), and concentrated. The crude product was chromatographed (SiO_2, 20:1 benzene/AcOEt) to give 53 mg (87%) of **3a**. The alkaline solution was acidified with aqueous 10% HCl and taken up in AcOEt. The extract was washed with brine, dried (Na_2SO_4), and concentrated to give 22 mg (53%) of BTSH.

The electrolysis results and physical properties of a series of the compounds **3** are shown in Table I.

2-(2-Pentynyl)-2-(phenylthio)cyclopentanone (4b). To a cooled solution of NaH (50% in oil, 60 mg, 1.25 mmol) in DMF (1.5 mL) was added 2-(phenylthio)cyclopentanone[8] (200 mg, 1.04 mmol) and 2-pentynyl bromide (0.13 mL, 1.25 mmol). After being stirred for 30 min at 10 °C, the mixture was worked up in the usual manner to give 127 mg (47%) of **4b** after chromatography (SiO_2, 20:10:1 benzene/hexane/AcOEt): bp 93–97 °C (0.09 torr); IR (neat) 3060 (HC=), 1735 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.10 (t, J = 7 Hz, 3), 1.69–2.94 (m, 8), 2.35 (t, J = 2 Hz, 2), 6.95–7.60 (m, 5). Anal. Calcd for $C_{16}H_{18}OS$: C, 74.38; H, 7.02. Found: C, 74.39; H, 7.04.

2-(2-Pentynyl)cyclopentanone (5). A solution of **4a**[9] (224 mg, 0.711 mmol) and Et_4NOTs (200 mg) in MeOH (20 mL) as a catholyte was electrolyzed at a current of 25 mA with a Pt electrode. After passage of 7 F/mol of electricity, the usual workup gave **5** (79 mg, 74%) [bp 149–155 °C (32 torr) (lit.[10] 101 °C (9 torr))] and BTSH (101 mg, 85%).

Registry No. 1 ($R^1 = (CH_2)_3CO_2Me$), 70203-07-5; 1 ($R^1 = n\text{-}C_6H_{13}$), 70203-06-4; 1 ($R^1 = (CH_2)_3CO$-morpholino), 70203-09-7; **2a**, 72844-40-7; **2b**, 72844-41-8; **2c**, 72844-42-9; **2d**, 72844-43-0; **2e**, 72844-44-1; **2f**, 72844-45-2; **2g**, 70905-82-7; **2h**, 72844-46-3; **2i**, 72844-47-4; **3a**, 72844-48-5; **3b**, 72844-49-6; **3c**, 72844-50-9; **3d**, 72844-51-0; **3e**, 72844-52-1; **3f**, 72844-53-2; **3g**, 72844-54-3; **3h**, 72844-55-4; **3i**, 72844-56-5; **4a**, 68898-27-1; **4b**, 72844-57-6; **5**, 57026-62-7; *n*-pentyl bromide, 110-53-2; 1-bromo-3-methyl-2-butene, 870-63-3; 2-pentynyl bromide, 16400-32-1; 1-bromo-2-propene, 106-95-6; 2-(phenylthio)cyclopentanone, 52190-40-6; $(BTS)_2$, 120-78-5; BTSH, 149-30-4.

Supplementary Material Available: IR and ^1H NMR spectral data and elemental analyses of compounds **2** and **3** (2 pages). Ordering information is given on any current masthead page.

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[8] 2-(Phenylthio)cyclopentanone was prepared in the manner described by D. Seebach and M. Teschner, *Chem. Ber.*, **109**, 1601 (1976).

[9] S. Torii, H. Tanaka, T. Kudai, and S. Watanabe, *Chem. Lett.*, 147, (1979).

[10] E. Demole and M. Winter, *Helv. Chim. Acta*, **45**, 1256 (1962).

Shielding by Methyl Groups in the ^1H NMR Spectra of Bicyclo[2.1.1]hexanes

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In the course of recent photochemical investigations[1] we have prepared a number of bicyclo[2.1.1]hexanes, most of which bear an ester or other negative group at C(5) and one or more methyl groups at C(1) and/or C(6). All of these compounds have low-field protons at one or both bridgeheads [C(1) and C(4)] and also at C(5). From examination of their ^1H nuclear magnetic resonance (NMR) spectra, along with comparisons with data already in the literature,[2] we have found effects of the methyl substituents on the chemical shifts of these low-field signals that are worthy of note.

The data are collected in Table I.[3] Because of the shielding effects discussed below, spectral assignments are based on observed integrals, spin–spin coupling, and internal consistency of the data and not on chemical shifts. In reaching these assignments, we have made use of the patterns of spin coupling previously reported by others:[2] $J_{AB} \approx 6\text{–}9$ Hz, $J_{BC} \approx 3$ Hz, $J_{AA'} \approx 7\text{–}8$ Hz, J_{AC} and $J_{BB'} \approx 0$, $J_{CC'} \approx 7$ Hz. In addition we have noted two novel long-range couplings of H_B, J_{BE} ($\equiv J_{B'D}$) $\approx$ 0–5 Hz and J_{BD} ($\equiv J_{B'E}$) $\approx$ 0–1.5 Hz. These small couplings can be seen particularly well in **13**. Spin–spin coupling constants reported for **13** were obtained by simulation[3b] and comparison with the actual 600-MHz spectrum.

We consider first shielding by bridgehead substitution. Replacement of H_C by methyl causes a small upfield shift in the remaining bridgehead hydrogen $H_{C'}$, a sizeable upfield shift in the exo proton $H_{B'}$, and apparently a much smaller change in the endo proton $H_{A'}$. The magnitude of this differential shielding of the exo proton can be great enough to cause inversion of the usual relative positions of $H_{A'}$ and $H_{B'}$ in a pair of epimers (see **5** and **6**), but this inversion does not necessarily occur (see **11** and **12**). This point is worth noting, since it has been known for some time that with hydrogen at the bridgehead in a pair of C(5)-substituted epimeric bicyclo[2.1.1]hexanes the exo proton H_B is downfield from the corresponding endo proton H_A.[2] It will be seen that in bridgehead-substituted compounds this simple rule cannot be used to assign the stereochemistry at C(5). We reported a similar finding in bicyclo[3.2.1]octanes some time ago.[4] The effects of bridgehead substitution in these two series may be contrasted with the behavior of norbornanones, where an exo proton appears reliably downfield from the corresponding endo proton, regardless of whether the adjacent bridgehead bears hydrogen or methyl.[5]

We have also noted a surprising effect of geminal methyl groups at C(6). This substitution causes the expected small shielding of the bridgehead hydrogen H_C but also leads to substantial deshielding of $H_{B'}$. Similar deshielding of a proton subject to severe steric compression by a neighboring group has been observed previously in other rigid polycyclic compounds.[6,7] In the present examples $H_{B'}$ is deshielded by 0.15–0.2 ppm by addition of two methyls at C(6), as can be seen by comparing **4** with **1** and **7** with **5**.

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[1] Wolff, S.; Barany, F.; Agosta, W. C. *J. Am. Chem. Soc.*, in press.

[2] Meinwald, J.; Lewis, A. *J. Am. Chem. Soc.* **1961**, *83*, 2769. Wiberg, K. B.; Lowry, B. R.; Nist, B. J. *Ibid.* **1962**, *84*, 1594. Gibson, T. W.; Erman, W. F. *J. Org. Chem.* **1972**, *37*, 1148. We use the proton subscripts employed by Wiberg.

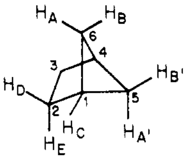
[3] (a) Data for compounds 1 and 8 are at 60 MHz and are taken from ref 2. Those for 2 and 3 are at 100 MHz as reported by: Scheffer, J. R.; Wostradowski, R. A. *J. Org. Chem.* **1972**, *37*, 4317. All other data except for those for ketone 13 are from ref 1. Those for 5 and 6 were measured at 220 MHz and those for 4, 7, and 9–12 at 60 MHz. Data for 13 are at 600 MHz and were obtained by Dr. D. H. Live of this laboratory on a spectrometer at Carnegie-Mellon University. (b) Bothner-By, A. A.; Castellano, S. M. "Computer Programs for Chemistry"; De Tar, D. F., Ed.; W. A Benjamin: New York, 1968. "Intrcal"; Nicolet Instrument Corp.: Madison, WI, 1973.

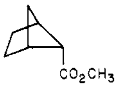
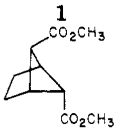
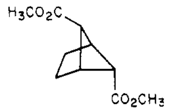
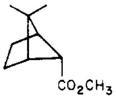
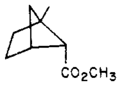
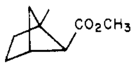
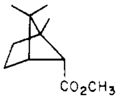
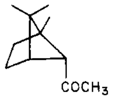
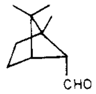
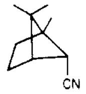
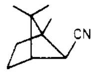
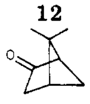
[4] Agosta, W. C.; Wolff, S. *J. Org. Chem.* **1975**, *40*, 1665.

[5] Musher, J. I. *Mol. Phys.* **1963**, *6*, 93. Kumler, W. D.; Schoolery, J. N.; Brutcher, F. V., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 2533. Flautt, T. J.; Erman, W. F. *Ibid.* **1963**, *85*, 3212. Tori, K.; Hamashima, Y.; Takamizawa, A. *Chem. Pharm. Bull.* **1964**, *12*, 924. Demarco, P. V.; Dodrell, D.; Wenkert, E. *Chem. Commun.* **1969**, 1418.

0022-3263/80/1945-1332$01.00/0

Table I. NMR Spectra of Bicyclo[2.1.1]hexanes



compd	chemical shifts (δ) and coupling constants (Hz)					
	H_A	H_B	$H_{A'}$	$H_{B'}$	H_C	CH_3 (s)
 1	0.78 (d, $J_{AB} = 6.3$)	1.38 (m)		2.74 (m)	2.70 (dd, $J_{BC} = J_{B'C} = 2.9$)	
 2	2.04 (s)			3.25 (s)	2.98 (d, 2 H, $J_{B'C} = 3$)	
 3		2.24 (t, $J_{BC} = 2.5$)		2.24 (t, $J_{B'C} = 2.5$)	2.89 (t, 2 H)	
 4				2.96 (m)	2.28 (dd, 2 H, $J_{B'C} = 3$, $J_2 \approx 0.5$)	1.28, 0.82
 5	0.94 (d, $J_{AB} = 6.3$)	1.17 (dddd, $J_{AB} = 6.3$, $J_{BC} = 2.8$, $J_{BE} = 2.8$, $J_{BE'} = 2.8$)		2.07 (m)	2.59 (m)	1.28
 6	1.06 (dd, $J_{AB} = 7$, $J_{AA'} = 7$)	2.23 (m)	2.11 (d, $J_{AA'} = 7$)		2.61 (m)	1.19
 7				2.22 (dd, $J_{B'C} = 2.5$, $J_{B'D} \approx 0.5$)	2.57 (m)	1.10, 1.04, 0.73
 8	0.75 (d, $J_{AB} = 6.6$)	1.37 (m)		2.32 (m)	2.70 (dd, $J_{BC} = 3.8$, $J_{B'C} = 3.8$)	1.88
 9				2.25 (dd, $J_{B'C} = 3$, $J_{B'D} \approx 0.5$)	2.52 (m)	2.07, 1.08 (2), 0.72
 10				2.33 (m)	2.50 (m)	1.10 (2), 0.72
 11				2.32 (dd, $J_{B'C} = 2$, $J_{B'D} \approx 0.5$)	2.65 (m)	1.15, 1.10, 0.83
 12			2.05 (s)		2.45 (br s)	1.52, 1.15, 0.75
 13[a]			1.39 (d, $J_{A'B'} = 8.0$)	2.56 (m, $J_{A'B'} = 8.0$, $J_{B'C} = 3.5$, $J_{B'C'} = 2.6$, $J_{B'D} = 5.2$, $J_{B'E} = 1.3$)	2.41 (dddd, $J_{B'C} = 3.5$, $J_{CC'} = 6.9$, $J_{CD} = 1.5$, $J_{CE} = 1.4$)	1.40, 0.94

[a] $H_{C'}$: 2.47 (dd, $J_{B'C'} = 2.6$, $J_{CC'} = 6.9$). H_D: 2.21 (ddd, $J_{B'D} = 5.2$, $J_{CD} = 1.5$, $J_{DE} = 15.8$). H_E: 2.00 (ddd, $J_{B'E} = 1.3$, $J_{CE} = 1.4$, $J_{DE} = 15.8$).

It is often difficult to ascribe proton chemical shifts to specific structural features of a molecule. If the deshielding of $H_{B'}$ is indeed due to steric compression, one would expect to see an upfield shift in the ^{13}C NMR signal for the methyl group involved. With this in mind we have measured the ^{13}C spectrum of ketone **13** and assigned the methyl signals with the aid of off-resonance decoupling. The positions of the methyl groups ($\delta_{\mathrm{Me_4Si}}$ 21.0 and 22.1) are comparable to those of similarly situated groups in norbornanes.[8] This result is consistent with a moderate steric effect for each methyl group, but the near identity of the chemical shifts of these two signals fails to provide evidence for an unusually severe steric interaction of one methyl group with the one-carbon bridge. It is then not certain that the deshielding of $H_{B'}$ is simply the consequence of steric compression.

Before obtaining and comparing all these data, we found some of our early spectra puzzling and some assignments of sterochemistry uncertain. These ambiguities were removed, however, on examination of the entire set of results. We believe that these observations make a useful addition to those spectral correlations already available and that they should facilitate future stereochemical assignments in related bicyclo[2.1.1]hexanes.

Experimental Section

The spectra of 4-7 and 9-13 were recorded for dilute CCl_4 solutions of samples purified by vapor-phase chromatography and with a Varian Model HR-220 (220 MHz, Fourier transform mode), a Varian Model T-60, or the 600-MHz spectrometer at Carnegie-Mellon University.[3,9]

Registry No. 1, 20441-29-6; 2, 32426-60-1; 3, 32426-61-2; 4, 72867-93-7; 5, 72867-94-8; 6, 72904-13-3; 7, 72867-95-9; 8, 72867-96-0; 9, 72867-97-1; 10, 6040-45-5; 11, 72867-98-2; 12, 72904-14-4; 13, 72904-15-5.

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[6] Haywood-Farmer, J.; Malkus, H.; Battiste, M. *J. Am. Chem. Soc.* **1972**, *94*, 2209 and references cited therein.

[7] Our cursory comparison of reported chemical shift data for exo protons in various norbornanes and bornanes has revealed no consistent pattern in the effect of similar methyl substitution in the bicyclo[2.2.1]heptane system.

[8] Grutzner, J. B.; Jautelat, M.; Dence, J. B.; Smith, R. A.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 7107.

[9] This research was supported by grants from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Dr. D. H. Live and Mr. W. M. Wittbold, Jr., for expert assistance.

4-(Dichloromethyl)-4-methyl-2,5-cyclohexadien-1-one Phenylhydrazone. Reaction with Bases and Conversion to 5-Methyl-2-phenyl-2*H*-indazole

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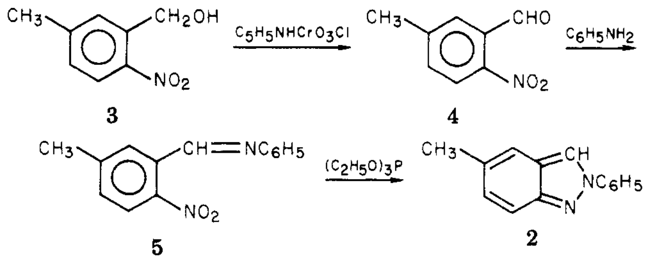
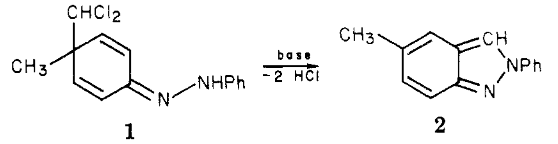
Received July 6, 1979

Scheme I



Schiff bases derived from 4-(dichloromethyl)-4-methyl-2,5-cyclohexadien-1-one undergo a reaction with primary amines in which the dichloromethyl group is cleaved from the molecule, and the remaining moiety is converted to a secondary amine.[1] The azine undergoes loss of both dichloromethyl groups and is converted to *p,p'*-azotoluene when heated with diglyme.[2] Similar loss of the dichloromethyl group occurs when the parent ketone itself is heated with secondary amines, a tertiary amine being the chief product.[3] The dienone also reacts with alkalies to give tars from which a very small yield of 5-methylsalicylaldehyde has been isolated.[4] We now report an unusual reaction of 4-(dichloromethyl)-4-methyl-2,5-cyclohexadien-1-one phenylhydrazone (**1**) with certain bases in which the dichloromethyl group is not cleaved but is rearranged. The net reaction involves the loss of two molecules of hydrochloric acid and the formation of 5-methyl-2-phenyl-2*H*-indazole (**2**). The product mixture is complex and tarry, and the conversion of **1** to **2** is moderate at best, exceeding 30% only in the most favorable case, i.e., with hydroxide ion under phase-transfer-catalysis conditions. Yields of 10% can be isolated by crystallization.



The indazole **2**, previously undescribed, was identified by its spectral properties and elemental analysis. Of particular use in the structure determination was the marked downfield shift of the proton at position 3, a characteristic noted in the NMR spectra of other 2*H*-indazoles.[5] An independent synthesis starting from 5-methyl-2-nitrobenzyl alcohol (**3**, Scheme I) confirmed the assigned structure.

The influence of various bases and conditions on the conversion of **1** to **2** was studied by using an analytical method for **2** based on isolation of the neutral (to 5% hydrochloric acid) reaction products by extraction, separation of the components by thin-layer chromatography, and estimation of the quantity of **2** present by fluorescence densitometry directly on the TLC plate with a Kontes K-495000 densitometer.[6,7] This procedure, while not highly refined, was accurate enough for the estimation of product yields.

Hydroxide ion, a strong base, is effective in converting **1** to the indazole **2** particularly under the conditions for phase-transfer catalysis where a relatively low temperature and short reaction time gave the maximum conversion obtained. Weaker bases, e.g., the primary amines aniline and phenethylamine and the secondary amine 2-(benzylamino)ethanol, are also effective in converting **1** to **2** at temperatures of 185-200 °C. On the other hand, the reaction was not promoted by tertiary amines (Bu_3N or

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[1] T. G. Miller, *J. Org. Chem.*, 31, 3178 (1966).

[2] J. R. Merchant, *Curr. Sci.*, 43, 719 (1974).

[3] N. Nagarajan and A. Venkateswarlu, *Tetrahedron Lett.*, 293 (1967).

[4] J. Leitich, *J. Org. Chem.*, 27, 1081 (1962).

[5] J. Elguero, A. Frachier, and R. Jacquier, *Bull. Soc. Chim. Fr.*, 2075 (1966).

[6] Kontes Glass Co., Vineland, NJ 08360.

[7] For a general discussion of TLC densitometry, see J. C. Touchstone and J. Sherma, Eds., "Densitometry in Thin Layer Chromatography, Practice and Applications", Wiley, New York, 1979.

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