Carbon-13 Chemical Shifts of 1-Substituted Norbornanes

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^{13}C chemical shifts for 12 monosubstituted 1-norbornanes are reported and the substituent effects compared with those of 1-substituted adamantanes and bicyclo[2.2.2]octanes. Except for an anisotropy effect exhibited by phenyl, β- and γ-substituent effects correlate reasonably well in the three systems and appear to operate principally via a through-bond effect. Surprisingly, α-substituent effects are apparently sensitive to the degree of strain at C-1 and do not correlate well in the three systems. The δ-substituent effects at C-4 of the 1-norbornyl system correlate with those of the 1-bicyclo[2.2.2]octyl system, but not those of the 1-adamantyl system, apparently because of either a strong 1,4 field effect or an α,γ-hyperconjugative effect in the former systems.

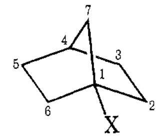
Conformationally rigid bicyclic and tricyclic systems have been quite useful in the study of substituent effects in ^{13}C spectroscopy. Because of the well-defined molecular frameworks, it has been possible, at least qualitatively, to partition some of the factors contributing to substituent effects in such systems (geometric, inductive, field, and steric effects[2]), and to assess their relative importance. Investigations have been conducted on norbornane,[3-6] bicyclo[2.2.2]octane,[5,7] adamantane,[8,9] nortricyclene,[10] and tricyclene systems.[11] However, except for studies involving bridgehead-substituted derivatives of these systems, uncertainties exist with regard to some of the chemical shift assignments, which were based on the premise that steric crowding results in upfield shifts, an assumption which is now open to question.[12] Assignments are more straightforward in bridgehead-substituted systems. Although 1-substituted adamantanes,[8,9] bicyclo[2.2.2]octanes,[7] and tricyclenes[11] have been studied extensively, their norbornyl analogues have not received attention except for the 1-methyl derivative.[3,4] It is of particular interest to examine chemical shifts in the 1-norbornyl system, which is substantially more strained than the adamantyl and bicyclo[2.2.2]octyl systems.

In the norbornyl system the carbon atoms γ to a C-1 substituent (i.e., C-3, -4, and -5) are essentially antiperiplanar with respect to the substituted carbon and have no nonbonded interactions with the substituent. This can be seen in Figure 1, which depicts Newman projections of the γ carbons with respect to the 1,7 and 1,2 carbon–carbon bonds. C-4 is conformationally locked in a true antiperiplanar arrangement with the substituent while C-3 and -5 are in a "skewed" antiperiplanar arrangement with the angle between C-3 or -5 and the substituent being somewhat less than 180°. Moreover, the absence of long-range nonbonded interactions leaves the substituted norbornane nucleus sterically unperturbed compared to that of the unsubstituted norbornane.[15] Hence, 1-substituted norbornanes, as with 1-substituted bicyclo[2.2.2]octanes and adamantanes, are excellent systems in which to isolate and study ^{13}C through-bond and field effects.

Results

Assignments were made on the basis of relative signal intensities and verified by the proton-induced splitting in the off-resonance decoupled spectra of norbornanes **2**, **4**, and **9**. The most intense peaks were assigned to the doubly degenerate carbons C-2,6 and C-3,5. The remaining three signals in order of decreasing intensity (presumably due to increased relaxation time) were assigned to C-7, -4, and -1, which bear two, one, and no hydrogen substituents, respectively.

The off-resonance decoupled spectra of 1-chloro- (**2**) and 1-iodonorbornane (**4**) and 1-norbornanecarboxylic acid (**9**) confirmed these assignments through the following observed multiplicities: C-1, singlet; C-2,6, multiplet;[16] C-3,5, multiplet;[16] C-4, doublet; and C-7, triplet. C-2,6 and -3,5 were differentiated on the basis of relative substituent shifts compared to 1-chlorobicyclo[2.2.2]octane, whose signals have been unequivocally assigned.[7]



1, X = H
2, X = Cl
3, X = Br
4, X = I
5, X = OH
6, X = OCH_3
7, X = OC_2H_5
8, X = CH_3
9, X = CO_2H
10, X = CO_2CH_3
11, X = C_6H_5
12, X = o-$C_6H_4CH_3$
13, X = $NHCOCH_3$

The ^{13}C chemical shifts for 1-substituted norbornanes and the corresponding substituent effects are listed in Tables I and II, respectively. No large shift discrepancies were noted compared to known substituent effects of bicyclic compounds. The ^{13}C chemical shifts of 1-methylnorbornane have been reported previously.[3,4] Our absolute chemical shifts for the methyl derivative are consistently 0.4 ppm upfield of those of Roberts,[3] and our substituent effects are in complete agreement with his. However, our results are at

Table I. ^{13}C Chemical Shifts of 1-Substituted Norbornanes[a]

X	C-1	C-2,6	C-3,5	C-4	C-7	C-1′	C-2′
H	36.4	29.8	29.8	36.4	38.4		
Cl	69.9	38.4	30.9	34.8	46.8		
Br[b]	62.2	40.0	31.6	34.8	48.2		
I	37.7	43.0	32.1	34.6	50.8		
OH	82.8	35.4	30.3	34.8	43.9		
OCH_3[b]	87.7	31.0	29.9	33.9	40.0	52.7	
OC_2H_5[b]	87.1	31.7	30.0	33.8	40.7	60.3	16.1
CH_3[b]	43.7	36.7	31.2	37.8	45.2	20.9	
CO_2H	52.1	32.9	30.0	37.8	42.3	183.5	
CO_2CH_3	52.2	33.1	30.0	35.6	42.3	176.6	51.4
C_6H_5[c]	51.3	37.2	30.9	37.3	42.8		
o-$C_6H_4CH_3$[b,d]	52.7	34.6	31.0	35.7	43.9		
$NHCOCH_3$[b]	62.6	33.7	29.9	35.3	41.7	169.8	24.0

[a] Shifts reported in parts per million with respect to internal tetramethylsilane, determined to ±0.05 ppm. [b] Samples run in 5-mm (o.d.) sample tubes. [c] For 1-phenylnorbornane the following additional assignments are tentatively made: C-1′, 146.3; C-2′,6′, 126.2; C-3′,5′, 127.8; and C-4′, 125.4. [d] For 1-o-tolynorbornane the following additional assignments are tentatively made: C-methyl, 22.7; C-1′, 147.0; C-2′, 135.6; C-3′, 128.5; C-4′, 125.3; C-5′, 124.8; and C-6′, 126.1.

Table II. ^{13}C **Substituent Effects of 1-Substituted Norbornanes**[a]

X	C-1	C-2,6	C-3,5	C-4	C-7
H	0.0	0.0	0.0	0.0	0.0
Cl	33.5	8.6	1.1	−1.6	8.4
Br	25.8	10.2	1.8	−1.6	9.8
I	1.3	13.2	2.3	−1.8	12.4
OH	46.4	5.6	0.5	−1.6	5.5
OCH_3	51.3	1.2	0.1	−2.5	1.6
OC_2H_5	50.7	1.9	0.2	−2.6	2.3
CH_3	7.3	6.9	1.4	1.4	6.8
CO_2H	15.7	3.1	0.2	1.4	3.9
CO_2CH_3	15.8	3.3	0.2	−0.8	3.9
C_6H_5	14.9	7.4	1.1	0.9	4.4
o-$C_6H_4CH_3$	16.3	4.8	1.2	−0.7	5.5
$NHCOCH_3$	26.2	3.9	0.1	−1.1	3.3

[a] Values refer to differences between the observed chemical shifts of a given compound and that of the unsubstituted hydrocarbon, norbornane. Positive shifts are to lower field (higher frequency) whereas negative shifts are to higher field (lower frequency).

Table III. ^{13}C **Chemical Shifts and Substituent Effects of 1-Methoxyadamantane (14)**[a]

	C-1	C-2,8,9	C-3,5,7	C-4,6,10
$\delta_C(H)$[b]	28.5	37.9	28.5	37.9
$\delta_C(OCH_3)$[c]	71.2	41.1	30.6	36.6
$\Delta\delta_C$	42.7	3.2	2.1	−1.3

[a] Shifts reported in parts per million with respect to internal tetramethylsilane, determined to ±0.05 ppm. [b] Chemical shifts for adamantane. [c] Chemical shifts for 1-methoxyadamantane; C-methyl 47.7.

variance with those of Lippmaa and Pehk,[4] with the relative shifts varying by 0.4–1.2 ppm. These differences may be due to solvent and/or concentration effects.

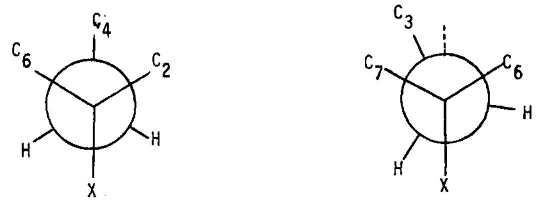
To permit more complete comparison with the 1-adamantyl system, 1-methoxyadamantane (14) was also prepared. Analysis of the ^{13}C spectrum as described previously[8,9] afforded the substituent effects given in Table III.

Discussion

The chemical substituent effects summarized in Table II exhibit a wide range of shieldings. In agreement with other reported bridgehead substituted systems, the magnitude of the effect on a given carbon is directly related to the distance it is from the substituent; i.e., α effects > β effects > γ effects > δ effects.[17] This is the expected order for a through-bond effect being transmitted through the bonding network.

As can be seen from Figure 2, the α shieldings at C-1 for the 1-adamantyl and 1-bicyclo[2.2.2]octyl systems correlate reasonably well with each other but do not correlate with those of the 1-norbornanes. This lack of correlation is apparently attributable to the large degree of strain at C-1 of norbornanes. Interestingly, the 1-norbornyl substituent effects correlate more closely with those of the 1-bicyclo[2.2.2]octyl system than those of the 1-adamantyl derivatives, as expected from the relative degrees of strain at C-1 in the three systems. It should also be mentioned that the α-substituent effect of the 1-norbornyl system compares quite favorably to the 4-substituted tricyclenes,[11] a system which is closely analogous to norbornanes at the substituted position.

By contrast the β shieldings at C-2,6 of the 1-norbornyl system correlate reasonably well with those of the 1-adamantanes and 1-bicyclo[2.2.2]octanes (Figure 3). Moreover, as can be seen from Table II, the β shieldings at C-7 correlate well with those at C-2,6; no significant effect is exhibited by the increased strain at C-7, in contrast to the marked effect noted at the α position. The one substituent for which there is no correlation between C-2,6 and C-7 is phenyl, which probably exerts an anisotropy effect at C-2,6.



1,7 Axis (Anti-periplanar)

1,2 Axis (Skewed anti-periplanar)

Figure 1. Newman projections along 1,7 and 1,2 axes of 1-substituted norbornyl system.

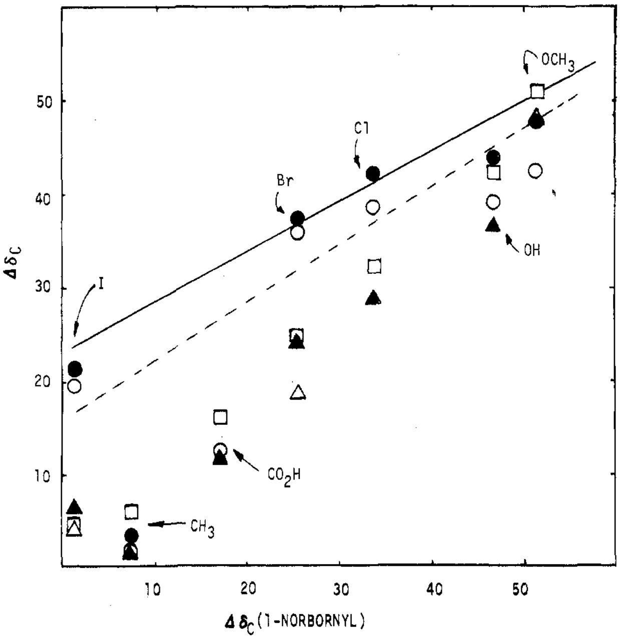


Figure 2. Plot of α-substituent effects of 1-norbornyl system vs. those of 1-bicyclo[2.2.2]octanes (●),[5,7,11] 1-adamantanes (○),[8] 2-adamantanes (▲),[8] 7-norbornanes (△),[5] and cyclohexanes (□).[23]

The interesting longer range substituent effects are seen at C-3,5 and -4. These positions are simultaneously γ and δ to the substituent, depending upon which bridge is considered. The γ arrangements are either antiperiplanar for C-4 or skewed antiperiplanar for C-3,5 (Figure 1), while the δ orientations are gauche-anti for C-3,5 and eclipsed-anti for C-4. The shieldings at C-3,5 correlate reasonably well with γ antiperiplanar shieldings of both of the other bridgehead substituted systems (Figure 4) but they do not correlate as closely as do the β shieldings at C-2,6 and C-7, presumably because the γ arrangements are not truly antiperiplanar.

The observed shieldings at C-4 of the 1-norbornyl systems show no correlation with either the γ or δ substituent effects reported for 1-adamantanes and bicyclo[2.2.2]octanes. However, a reasonable correlation of the C-4 shieldings with the δ effects for the 1-bicyclo[2.2.2]octyl system (Figure 5) is obtained if the C-4 shieldings of norbornane are adjusted by subtracting the γ and δ inductive effects (using the approximation that these are similar at C-3,5 and C-4). On the other hand, when these adjusted C-4 shieldings are plotted against either the γ or δ shielding effects of the 1-adamantyl system, no correlation is found.

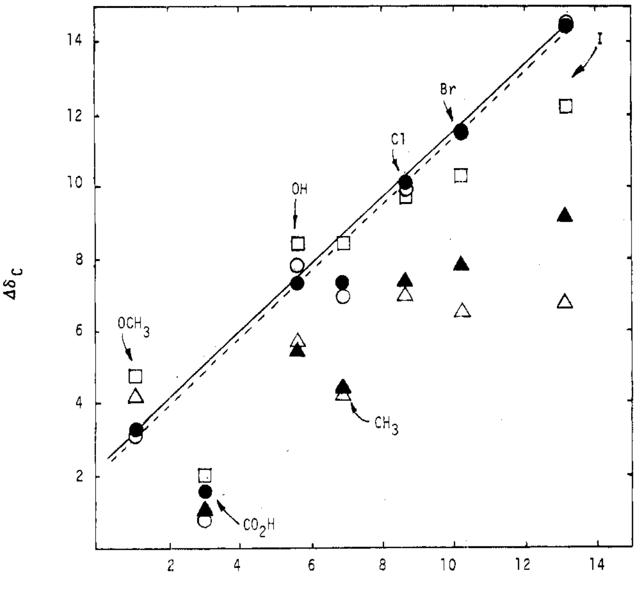


Figure 3. Plot of β-substituent effects at C-2,6 of 1-norbornyl system vs. those for systems given in Figure 2.

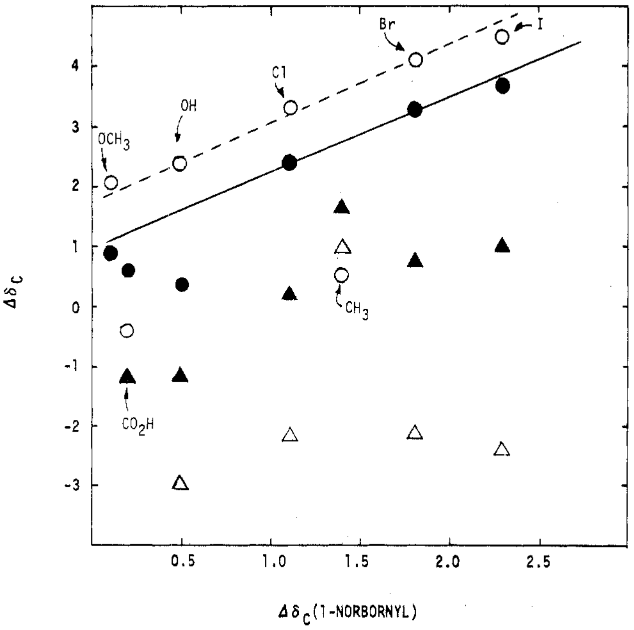


Figure 4. Plot of γ-substituent effects at C-3,5 of 1-norbornyl system vs. those for systems given in Figure 2.

It is obvious that another mechanism in addition to the through-bond effect is influencing the shift at C-4 of both the 1-norbornyl and 1-bicyclo[2.2.2]octyl systems, which have similar C-1–C-4 orientations. Whether this is an electrostatic field effect,[19,20] a through-space α,γ-hyperconjugative effect as proposed by Roberts,[3] or possibly an α,γ-hyperconjugative type interaction as proposed by Eliel et al.,[21] remains unclear. However, field effects are well known in these two systems[22] and probably play at least a contributing role.

As can be seen in Figures 2–5, there was no simple correlation of α-, β-, or γ-substituent effects in 1-norbornyl systems with those previously reported for the 2-adamantyl,[8] 7-norbornyl,[5] or cyclohexyl systems.[23] The one exception to this is the α-substituent effects in cyclohexanes, which correlate surprisingly well with those observed for 1-norbornanes. The origin of this correlation is far from obvious and may be fortuitous. Finally, it is noted that the substituent effects in 1-methyladamantane and 1-adamantanecarboxylic acid consistently fail to correlate with the effects observed for other substituents having n electrons on the central atom.

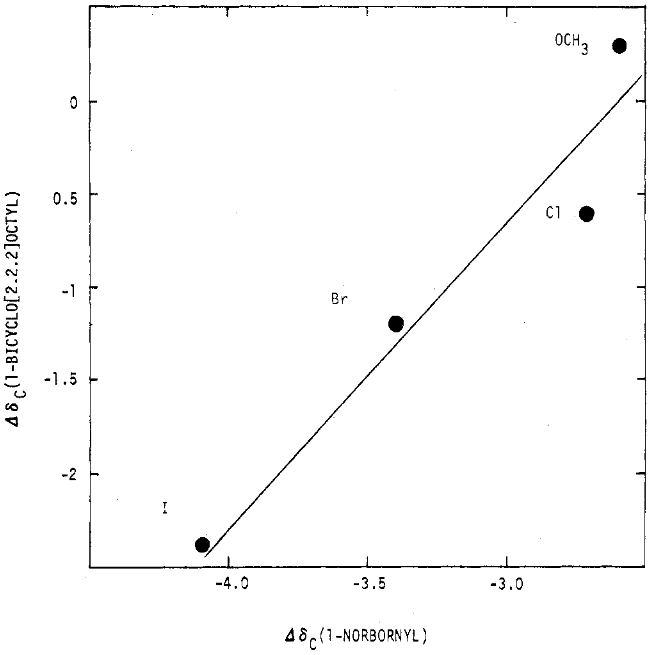


Figure 5. Plot of adjusted substituent effects at C-4 of 1-norbornyl system vs. δ-substituent effects for 1-bicyclo[2.2.2]octanes.

In summary, α-, β-, and γ-substituent effects in the 1-norbornyl system appear to arise principally from through-bond effects. α shieldings are sensitive to strain at C-α but β shieldings are not sensitive to strain at C-β. γ substituent effects at C-3,5 are apparently somewhat influenced by the fact that they do not bear a true antiperiplanar orientation with the substituent at C-1. δ substituent effects at C-4 are not purely inductive; a 1,4 field effect or α,γ-hyperconjugative effect is also involved.

Experimental Section

Measurements. All ^{13}C NMR spectra were obtained at natural ^{13}C abundance with a Varian XL-100 spectrometer operating at 25.2 MHz and employing a VFT-100-SC Fourier transform system with a VDM G20/L computer and interactive disk. FT spectra were obtained using a data length of 16 K and a pulse angle generally <90°. An internal field–frequency lock on deuterium was employed for all pulsed spectra, and pseudorandom proton noise decoupling was used to remove all ^{13}C–H couplings. Unless otherwise indicated, all samples were run in 10-mm o.d. sample tubes and were generally 2–3 M in deuteriochloroform using 3% (v/v) tetramethylsilane as internal reference. Off-resonance decoupled spectra were obtained by setting the proton resonance frequency 500 Hz upfield from Me_4Si.

Materials. All compounds studied, except norbornane, were prepared by standard procedures and their purities in all cases exceeded 98% as determined by gas chromatographic analysis. **Norbornane** (1) was purchased commercially from Aldrich Chemical Co. and used without further purification.

1-Chloronorbornane (2) was prepared according to the procedure of Bixler and Niemann[24] by treatment of 2,2-dichloronorbornane with phosphorus trichloride and pentachloride to afford in 61% yield a clear liquid, bp 70° (53 mm), which solidified to a clear waxy solid on standing at room temperature: ν_{max} (CCl_4) 2974, 2932, 2881, 1451, 1310, 1298, 1037, 992, 947, 905, and 838 cm^{-1}; ^{1}H NMR (CCl_4) δ 2.18 (br s, 1, CH-4) [lit.[24] bp 70–71 °C (54 mm)].

1-Bromonorbornane (3) was prepared by a modification of the Cristol–Firth Hunsdiecker reaction[25] by treatment of 1-norbornanecarboxylic acid[24,26] with red mercuric oxide and bromine in bromotrichloromethane to afford in 44% yield a clear liquid: bp 62–64 °C (23 mm); ν_{max} (neat) 2968, 2926, 2877, 1451, 1309, 1296, 1253, 1227, 978, 947, 897, 832, and 761 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.90 (m) [lit.[27] bp 56° (18 mm)].

1-Iodonorbornane (4) was prepared according to the procedure of Lansbury et al.[28] by treatment of 1-chloronorbornane with lithium metal and iodine to afford in 44% yield a colorless liquid, bp 80–82 °C (12 mm), which solidified when placed into a freezer: ν_{max} (CCl$_4$) 2960, 2875, 1451, 1309, 1295, 1253, 1228, 972, 932, 892, and 838 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 1.88 (br s, 9) and 1.37 (br m, 2) [lit.[28] bp 75° (10 mm)].

1-Norbornanol (5) was prepared by the general photochemical procedure of Kropp et al.[29,30] Irradiation of 1-iodonorbornane in aqueous solvents afforded approximately 60% of the alcohol as a colorless, waxy solid: mp 151–153 °C (sealed capillary); ν_{max} (CCl$_4$) 3617, 3330, 2961, 2922, 2874, 1451, 1315, 1210, 1135, 1089, and 919 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 3.50 (s, 1, OH), and 2.05 (br s, 1, CH-4) [lit.[31] mp 152–154 °C (sealed capillary)].

1-Methoxynorbornane (6) was also prepared by the same photochemical procedure.[29,30] Irradiation of iodide 4 in absolute methanol yielded approximately 90% of the methyl ether as a colorless liquid: ν_{max} (CCl$_4$) 2959, 2875, 2838, 1450, 1362, 1318, 1219, 1190, 1139, 1092, and 1035 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 3.20 (s, 3, OCH$_3$), and 2.06 (br s, 1, CH-4); *m/e* 126.1044 (calcd for $C_8H_{14}O$, 126.1045) and 97 (100).

1-Ethoxynorbornane (7) was prepared by the similar irradiation[29,30] of iodide 4 in anhydrous ether or absolute ethanol to give the desired ether in approximately 60–70% yield as a colorless liquid: ν_{max} (CCl$_4$) 2950, 2935, 2873, 1450, 1317, 1262, 1222, 1170, 1139, 1100, 1046, 937, and 895 cm^{-1}; ^{1}H NMR δ 3.44 (q, J = 7.5 Hz, 2, CH$_2$CH$_3$), 2.05 (br s, 1, CH-4), and 1.13 (t, J = 7.5 Hz, 3, CH$_2$CH$_3$); *m/e* 140.1201 (calcd for $C_9H_{16}O$, 140.1199), 111 (73), 83 (100), and 55 (28) [lit.[32] ν_{max} (CCl$_4$) 1140 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 4.38 (q, J = 7 Hz, 2), 2.0 (s, 1), and 1.1 (t, J = 7 Hz, 3)].

1-Methylnorbornane (8) was prepared by the catalytic hydrogenation of 1-methylnorbornene in methanol[33] to produce the hydrocarbon 8 as a colorless liquid: ν_{max} (CCl$_4$) 2999, 2869, 1450, 1376, 1330, 1304, and 1212 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.33 (br s, 1, CH-4) and 1.14 (s, 3, OCH$_3$).

1-Norbornanecarboxylic acid (9) was prepared by basic hydrolysis of the methyl ester 10[34] to afford the acid in 91% yield as an odoriferous, white solid: mp 109–110°; ν_{max} (CCl$_4$) 3390–2450, 1699, 1425, 1309, 1254, 1226, 940, 814, and 726 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.9 (s, 1, CO$_2$H) and 2.39 (br s, 1, CH-4) (lit.[24] mp 113.8–115.5°).

1-Norbornanecarboxylic acid methyl ester (10) was prepared by treatment of 2-*exo*-bromonorbornane-2-*endo*-carboxylic acid methyl ester[26,34] with zinc and acetic acid to afford the ester in 81% yield: bp 66–67 °C (9 mm); ν_{max} (neat) 2958, 2927, 2875, 1730, 1435, 1336, 1242, 1219, 1109, 1073, and 759 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 3.63 (s, 3, OCH$_3$) and 2.31 (br, 1, CH-4) [lit.[34] bp 52–53 °C (1.8 mm)].

1-Phenylnorbornane (11) was prepared as a clear liquid in greater than 85% yield by the general irradiation procedure of 4 in benzene:[29,30] ν_{max} (CCl$_4$) 3087, 3068, 3011, 2949, 2921, 2871, 1605, 1495, 1450, 1335, 1077, 1036, and 700 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 7.15 (m, 5, aromatic H), and 2.32 (br s, 1, CH-4) [lit.[35] ^{1}H NMR δ 7.15 (5) and 2.32 (1)].

1-*o*-Tolynorbornane (12) was prepared and separated from its isomers in approximately 50% overall yield as a clear oil by the irradiation of 4 in toluene:[29,30] ν_{max} (neat) 3097, 3055, 2949, 2869, 1597, 1481, 1446, 1371, 1319, 1229, 1238, 1112, 1050, and 708 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.31 (m, 1, aromatic H), 7.24 (d, J = 3.5 Hz, 3, aromatic H), 2.51 (s, 3, *o*-CH$_3$), and 2.34 (br s, 1, CH-4); *m/e* 186.1405 (calcd for $C_{14}H_{18}$, 186.1408), 186 (38), and 147 (100).

***N*-(1-Norbornyl)acetamide (13)** was isolated in approximately 45% yield as a colorless, crystalline solid, mp 161–162 °C (sealed capillary), from the irradiation of 4 in aqueous acetonitrile:[29,30] ν_{max} (CHCl$_3$) 3448, 3340, 2960, 2939, 2878, 1666, 1508, 1370, 1340, 1310, and 749 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.98 (br m, 1, NH), and 1.95 (s, 4, CH$_3$ and CH-4); *m/e* 153.1158 (calcd for $C_9H_{15}NO$, 153.1154), 124 (73), and 82 (100).

1-Methoxyadamantane (14) was prepared in approximately 90% yield as a clear liquid by treatment of 1-iodoadamantane[36] with an excess amount of silver perchlorate in methanol solution at room temperature: bp 60–61 °C (1.2 mm); ν_{max} (CCl$_4$) 2908, 2856, 2828, 1447, 1351, 1306, 1199, 1176, 1111, 1087, 1048, 890, and 724 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.33 (s, 3, OCH$_3$) and 2.20 (s, 3, bridgehead H) [lit.[37] bp 66–68 °C (3 mm); ν_{max} (CCl$_4$) 2907, 2849, 1445, 1350, 1302, 1111, 1086, 1050, and 890.5 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.22 (s, 3, OCH$_3$)].

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Registry No.—**2**, 765-67-3; **3**, 13474-70-9; **4**, 930-80-3; **5**, 51566-98-4; **6**, 57901-28-7; **7**, 33357-81-2; **8**, 10052-18-3; **9**, 18720-30-4; **10**, 2287-57-2; **11**, 24892-79-3; **12**, 57901-29-8; **13**, 57901-30-1; **14**, 6221-74-5.

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