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Carbon-13 NMR Spectra of Some Methyl-Substituted Adamantanones

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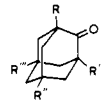
The synthesis of 1-methyl- (2), 1,5-dimethyl- (3), and 5,7-dimethyladamantanone (4) and their ^{13}C NMR spectra have been investigated. For the preparation of 3 and 4, some discrepancies existing in the literature are revealed. The carbon-13 NMR resonances of 2, 3, and 4, have been completely assigned from conventional high-resolution spectra with the use of a ^{1}H–^{13}C polarization transfer technique and lanthanide shift reagent experiments. Comparison of the chemical shift values with those of the parent adamantanone (1) and the tetramethyl derivative 5 indicates that the effects of methyl groups on the chemical shifts of adamantanone are similar in direction and magnitude to the effects observed in adamantane. The carbonyl group induces upfield shifts of the signals for carbons across the polycyclic system and for the methyl groups, especially at the adjacent bridgeheads.

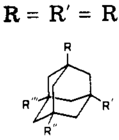
The secondary adamantyl cation is an excellent model for mechanistic studies.[1] Use of strategically placed substituents, especially alkyl groups, has enabled a number of investigators to probe fundamental questions like the existence and relative importance of solvent participation, neighboring group participation, and steric effects (acceleration or retardation) in solvolysis reactions[2] or the nature of the hydride transfer reactions in the rigid polycyclic skeleton.[3] The effects of multiple substitution, especially by alkyl groups, on reactivity and reaction mechanisms have also been investigated.[4]

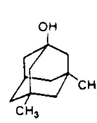
Carbon-13 NMR chemical shifts are considered a measure of the charge density distribution in the carbon skeleton of a molecule[5] and have been used in the past to make structural predictions for carbocations,[4] to assign conformations of cyclic compounds,[6] and to deduce the nature of the interaction mechanism between two sites of a molecule.[7]

We report here the results of a carbon-13 NMR study of methyl-substituted adamantanones (1–5), looking for the existence of a chemical shift–structure relationship, by comparison with the spectra of the corresponding adamantane (6) and its methylated homologues (7–10).[6,8–12]



1, R = R' = R'' = R''' = H
2, R = Me; R' = R'' = R''' = H
3, R = R'' = Me; R' = R''' = H
4, R = R' = H; R'' = R''' = Me
5, R = R' = R'' = R''' = Me





6, R = R' = R'' = R''' = H
7, R = Me; R' = R'' = R''' = H
8, R = R' = Me; R'' = R''' = H
9, R = R' = R'' = Me; R''' = H
10, R = R' = R'' = R''' = Me

11

For the substituted derivatives of lower symmetry, such as ketones 2 and 3, the carbon-13 NMR spectra are complicated enough to preclude a straightforward assignment of individual resonances by conventional techniques. This is a general problem for even moderately complicated spectra, since standard heteronuclear decoupling techniques, such as noise off-resonance decoupling (NORD),[5] result in multiple resonance patterns that overlap severely and also exhibit lower signal to noise ratios than the fully decoupled signals.

Recently, several ^{1}H–^{13}C polarization transfer pulse sequences have been reported, which overcome the drawbacks of NORD. In these methods, radio-frequency pulses are applied simultaneously at both the hydrogen and carbon resonance frequencies, separated in time by multiples of $^1/_4$ J, where J is the ^{1}H–^{13}C coupling constant. The signals for methyl, methylene, and methine carbon atoms can be made in turn to appear with positive, negative, or zero intensity, depending upon the choice of multiple of $^1/_4$ J for the time delay.[13] Non-protonated carbons, including those of deuterated solvents, are eliminated from the polarization transfer (PT) spectrum. The other carbon resonances appear as singlets, with the same chemical shift values as observed in the conventionally accumulated spectra.[13] Furthermore, other established techniques, such as the use of lanthanide shift reagents (LSR), can be combined with polarization transfer techniques. By using such a combination of PT and LSR

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experiments we were able to analyze fully the spectra of the asymmetric ketones 2 and 3.

Synthesis of the Ketones. Ketones are the normal entry point for the preparation of derivatives of polycyclic hydrocarbons functionalized at secondary positions.[1] All the methyl-substituted ketones investigated here had been prepared in connection with structural or reactivity studies.[1,2b,4] We prepared three of these compounds for our investigation: 1-methyl- (2), 1,5-dimethyl- (3), and 5,7-dimethyl-2-adamantanone (4). While obtaining pure samples of 2 is straightforward,[14] our findings about 3 and 4 were different from the literature accounts.[4,15]

Oxidation of 1,3-dimethyladamantane (8) with 96% sulfuric acid at 77 °C[4] gave a dark-colored, very complex mixture. Compounds 3, 4, 8, and 11 were identified in the product by gas-liquid chromatography on three different columns (see Experimental Section), but ketones 3 and 4 were not present in concentrations high enough for isolation in reasonable purity by any convenient technique.[16] Minor alterations in temperature, reaction time, or acid concentration did not bring about any improvement.[16] We obtained better results from the oxidation of the alcohol 11 at room temperature.[15] The reaction mixture was complex, but ketones 3 and 4 were present in concentrations sufficient for isolation.

Vacuum distillation followed by recrystallization from pentane[15] produced a recrystallized material containing 4 and 3 in about a 9:1 ratio, with some 11 also present. The mother liquor was enriched in the minor product 3,[17] but almost as much 4 was present, as well as several other products. Pure samples of 4 and 3 were obtained only when the recrystallized material and the mother liquor were chromatographed separately on silica gel (see Experimental Section).

Carbon-13 NMR Spectra. The carbon chemical shift values of adamantane (6) and the methyladamantanes (7-10), summarized in Table I,[6,8-12] are rather unexceptional. Certain regularities can be discerned: for example, a bridgehead methyl group induces downfield shifts of similar, small magnitude at C-α and C-γ (bridgeheads), a sizeable downfield shift at C-β, and an upfield shift at C-δ.[6,8-12] The latter two changes, but not the former two, are consistent with the differences observed between the spectra of cyclohexane and methylcyclohexane. The effects of methyl substitution on adamantane chemical shifts are additive.[9,18] On the other hand, the methyl carbon signal itself is first shifted downfield by a second methyl, then upfield by the third and fourth methyl groups, although the chemical shift increments due to each added methyl are small.[18]

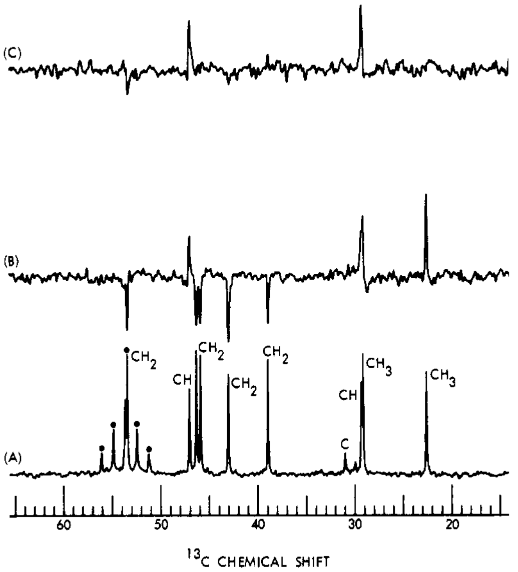

Figure 1. ^1H decoupled ^{13}C NMR spectra of ketone 3 (aliphatic region only): (A) all carbons positive; (B) CH_3 and CH positive, CH_2 negative, quaternary C zero; (C) CH positive, all others zero (·) Signals of CD_2Cl_2.

Among the ketones investigated here, the ^{13}C NMR spectra of the parent adamantanone (1) and of 1,3,5,7-tetramethyladamantanone (5) have been reported before.[6,19] These spectra and the spectra of 2-4 are presented in Table II. For the latter compounds, the assignments are based on PT experiments, as illustrated for 3 in Figure 1. We could not locate the signals for all the carbon atoms, however. Six and ten aliphatic carbon signals were observed in the ^1H decoupled spectra of 2 and 3, respectively, while six and nine signals from proton-bearing carbons remained in the spectra run with polarization transfer. Missing in the spectra were the peaks for the quaternary carbon C-1, presumably due to coincident chemical shift values. We located these peaks by lanthanide shift reagent (LSR) experiments, employing $Yb(fod)_3$. The signals superimposed in the original spectra have different lanthanide-induced shifts (LIS) and were clearly separated. The quaternary carbon signals were then identified by their disappearance from the subsequent PT spectra.[21] The LIS values reported in Table III helped also to secure the assignments for all the signals in the spectra of 2-4.

It is noteworthy that the LIS for C-1 and C-3 in each of the unsymmetrical species 2 and 3 are not equal. It has been reported that for complexes of ketones with europium reagents, the carbon-oxygen and oxygen-europium bonds are collinear.[22] Possibly, the steric interaction between the LSR and the methyl group at C-1 produces a slight deviation from collinearity, in the direction of C-3, which results in an LIS difference too small to be observed by ^1H NMR[22] but detectable by ^{13}C NMR.[23] Alternatively, our results are consistent with the two-site,[24a] or four-site,[24b] binding model for the interaction between ketones and LSR. The steric interaction with the methyl group would in this case, induce a change in the relative populations of the two (four) binding sites. The effect on the LIS

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[17] The ratio of 4 to 3 in the oxidation mixture was 5:1 to 7:1. In no experiment was the 2:1 ratio reported in ref 4 observed.

[18] Other regularities can also be discerned: the chemical shift variations at C-β and C-γ seem to depend upon whether the carbon atom examined or its neighbor are tertiary or quaternary but no such relationship is seen for C-δ. The data are not sufficient, however, to allow for a reliable generalization.

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[21] The overlapping signals for C-1 and C-4 of 3 were subsequently separated by artificially enhancing the resolution of the carbon-13 spectrum using an exponential function. The chemical shifts in Table II are based on the resolution enhancement experiment (δ 46.46 and 46.33 for C-1 and C-4, respectively).

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Table I. ^{13}C Chemical Shifts of Methyladamantanes[a]

compd	ref	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	R	R′	R″	R‴
6	8	28.5	37.8	28.5	37.8	28.5	37.8	28.5	37.8	37.8	37.8				
7	8	29.7[b] (1.2)	44.6 (6.8)	28.9 (0.4)	36.9 (−0.9)	28.9 (0.4)	36.9 (−0.9)	28.9 (0.4)	44.6 (6.8)	44.6 (6.8)	36.9 (−0.9)	31.1			
8[c]	9	30.8[d] (0.9)	52.1 (7.5)	30.8 (1.9)	44.1 (7.2)	29.5 (0.6)	36.4 (−0.5)	29.5 (0.6)	44.1 (−0.5)	44.1 (−0.5)	44.1 (7.2)	31.3 (0.2)	31.3		
9[c]	9	31.6 (0.9)	51.4 (−0.7)	31.6 (0.9)	51.4 (7.3)	31.6 (2.1)	43.4 (7.0)	30.2 (0.7)	43.4 (−0.7)	51.4 (7.3)	43.4 (−0.7)	31.0 (−0.3)	31.0 (−0.3)	31.0	
10[c]	9	32.5[e] (0.9)	50.8 (−0.6)	32.5 (0.9)	50.8 (−0.6)	32.5 (0.9)	50.8 (7.4)	32.5 (2.3)	50.8 (7.4)	50.8 (−0.6)	50.8 (7.4)	30.6 (−0.4)	30.6 (0.4)	30.6 (−0.4)	30.6

[a] Given in ppm from internal Me_4Si in $CDCl_3$ solution unless otherwise stated. The chemical shift difference from the next lower homologue is given in parentheses. [b] Reference 9 (CCl_4 solution) gives δ 29.9 for C-1. All other values are the same. [c] In CCl_4 solution. [d] Reference 10 gives δ 30.6 (C-1, -3), 51.9 (C-2), 44.0 (C-4, -8, -9, -10), 29.5 (C-3, -5), 36.2 (C-6); 31.5 (Me). [e] Reference 6 gives δ 32.1 (C-1, -3, -5, -7), 50.5 (C-2, -4, -6, -8, -9, -10), 30.3 (Me).

Table II. ^{13}C Chemical Shifts of Ketones[a]

compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	R	R′	R″	R‴
1	47.1[b] (18.6)[c]	217.9 (180.1)	47.1 (18.6)	39.4 (1.6)	27.6 (−0.9)	36.4 (−1.4)	27.6 (−0.9)	39.4 (1.6)	39.4 (1.6)	39.4 (1.6)				
2	46.8 (17.0)[c], (−0.3)[d]	218.0 (173.4), (0.1)	47.0 (18.1), (−0.1)	39.4 (2.5), (0.0)	28.4 (−0.5), (0.8)	35.8 (−1.1), (−0.6)	28.4 (−0.5), (0.8)	46.8 (2.2), (7.4)	46.8 (2.2), (7.4)	39.4 (2.5), (0.0)	22.9 (−8.2),			
3	46.5[e] (15.7)[c], (−0.3)[g]	218.2 (174.1), (0.2)	47.0 (17.5), (0.0)	46.3[f] (2.2), (6.9)	31.1 (0.3), (2.7)	43.1 (−1.0), (7.3)	29.3 (−0.2), (0.9)	45.8[f] (1.8), (−1.0)	53.4 (1.3), (6.6)	39.0 (2.6), (−0.4)	22.8 (−8.5), (−0.1)		29.2 (−2.1)	
4	46.8[e,h] (17.3)[c]	218.0 (181.6)	46.8 (17.3)	45.3 (1.2)	31.1 (0.3)	51.0 (−1.1)	31.1 (0.3)	45.3 (1.2)	45.3 (1.2)	45.3 (1.2)			29.1 (−2.2)	29.1 (−2.2)
5	45.7[i] (13.2)[c]	j	45.7 (13.2)	52.7 (1.9)	32.0 (−0.5)	49.5 (−1.3)	32.0 (−0.5)	52.7 (1.9)	52.7 (1.9)	52.7 (1.9)	22.5 (−8.1)	22.5 (−8.1)	28.7 (−1.9)	28.7 (−1.9)

[a] Given in ppm from internal Me_4Si in $CDCl_3$ solution unless otherwise stated. [b] From ref 19; ref 6 gives δ 47.0 (C-1, -3), 39.3 (C-4, -8, -9, -10), 28.5 (C-5, -7), and 36.4 (C-6). [c] Chemical shift differences from the corresponding hydrocarbon. [d] Differences from the next lower homologue, 1. [e] In CD_2Cl_2 solution. [f] Assignments might be reversed. [g] Differences from the next lower homologue, 2. [h] Reference 20 gives δ 46.0 (C-1, -3), 214.5 (C-2), 44.9 (C-4, -8, -9, -10), 31.1 (C-5, -7), 51.1 (C-6), and 29.4 (CH_3), in CCl_4 solution. [i] From ref 6. [j] Not listed.

Table III. Lanthanide Induced Shifts in Methyladamantanones[a]

compound	molar ratio[b]	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	CH_3-1	CH_3-5
2	16.4	3.38	8.72	3.64	1.75	1.30	0.98	1.30	1.82	1.82	1.75	2.40	
3	20.3	3.09	7.61	3.31	1.63[c]	1.18	0.91	1.30	1.56[c]	1.69	1.76	2.15	0.58
4	32.3	2.93	7.48	2.93	1.49	1.11	0.78	1.11	1.49	1.49	1.49		0.52

[a] Δδ is given in ppm. [b] The molar ratio is ketone/LSR. [c] These values might be reversed.

values is the same as for a deviation from collinearity in the linear binding model.

As shown in Table II, the chemical shift variations induced by the substitution of bridgehead hydrogens of 1 with methyl groups are somewhat similar to those observed for the corresponding hydrocarbons: small changes at C-α and C-γ, downfield shifts of 7 ± 0.5 ppm for C-β, and slight upfield shifts for C-δ; the chemical shift of the carbonyl carbon is unaffected. On the other hand, the replacement of a methylene group by a carbonyl in the adamantane sytem produces sizeable downfield shifts for the adjacent bridgehead carbons (C-α), of a magnitude that decreases with the increase in the number of methyl substituents. The methylene carbon atoms β to the carbonyl are consistently moved downfield ($\Delta\delta$ 1.8, SD 0.4 ppm),[25] while the γ and δ ring carbons are most often moved upfield, as are the methyl groups both β (by 8.1–8.5 ppm) and δ (by 1.9–2.1 ppm) to the carbonyl. The different response of the ring β-carbon atoms and methyl β-carbon atoms to the conversion of a methylene group to carbonyl is undoubtedly related to their stereochemical relationship to the carbonyl group in the rigid molecule.

A final note of caution must be entered about the use of the polarization transfer technique. When the signals for a hydrogen-bearing carbon and a quaternary carbon atom are not well separated, the latter signal might be missed altogether by this method, as it was seen for C-1 of 2 and 3.[21]

Experimental Section

General. Gas–liquid chromatographic analyses were performed on Perkin-Elmer 900 and Sigma-115 instruments, on three columns: (A) 5% Carbowax 20M on Gaschrom Q, 4.5 m × 3 mm o.d.; (B) 5% fluorinated silicone SP-2401 on Gaschrom Q, 3 m × 3 mm o.d.; (C) 10% methylsilicone SP-2100 on Supelcoport, 3 m × 3 mm o.d. Melting points (Fisher, model 355 digital instrument) are uncorrected. Silica gel Woelm 0.2–0.5 mm was used for column chromatography and Merck silica gel plates for TLC. The reagents procured commercially were used as purchased, unless stated otherwise.

Carbon-13 and proton NMR experiments were performed on a JEOL FX-90Q spectrometer. The PT technique was employed as described.[13] Proton and carbon pulse widths of 28 and 18 μs, respectively, were used in the pulse sequence. Typical pulse separations were 1.8 ($^1/_4$ *J*), 4.3, and 9.5 ms.

1-Methyl-2-adamantanone (2), prepared from protoadamantanone as described,[14] was first sublimed,[14b] then chromatographed on silica gel in pentane–ether (9:1),[14a] and finally recrystallized from pentane at −78 °C, giving a sample of 99.2% purity by GLC (column B, programmed from 70 to 106 °C at 3 °C/min and then to 240 °C at 24 °C/min and maintained for 30 min at 240 °C): mp 104.7–105.3 °C (lit.[14a] mp 106.5–108.5 °C); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.57 (1 H), 2.02 (6 H), 1.83 (6 H), and 0.97 (3 H).

3,5-Dimethyl-1-adamantanol (11) was obtained in 98% yield by the hydrolysis of the corresponding bromide in aqueous hydrochloric acid–dimethylformamide solution.[26] The reaction was completed in 1.5 h (TLC, 1:1 pentane–ether). The product was isolated as described,[26] except that ether was used for extraction instead of dichloromethane, mp 93–96 °C (lit.[27] mp 96.8–97.1 °C).

1,5-Dimethyl- (3) and 5,7-Dimethyl-2-adamantanone (4). The concentrations of 3, 4, and 11 could not be determined accurately on columns A, B, or C, alone. Column A (isothermal, 120 °C) separated 3 from 4 and 11, which were eluted together. Column B (the same program as for 2, above) separated 11, 3, and 4 (listed as eluted), but 3 and 4 not completely. Column C (isothermal, 150 °C) separated 11 from the mixture of 3 and 4. In each case, 8 was eluted earlier, but some impurity peaks were superimposed over the peaks for 3, 4, and 11, so in order to determine the purity of the final products, all three columns had to be used.

In preliminary experiments, the alcohol 11 (2.52 g, 14 mmol) was stirred with (a) 96% H_2SO_4 (25 mL) for 48 h; (b) 91.5% H_2SO_4 (25 mL) for 72 h, after which 96% H_2SO_4 (5 mL) was added and stirring was continued for 24 h; (c) 91.5% H_2SO_4 (25 mL) for 48 h. In each case, aliquot samples were withdrawn at 24-h intervals, quenched, and analyzed by GLC (column B). In all cases, the conversion of 11 was incomplete at the end of the experiment. Thus, the ratio (3 + 4)/11 was 14.4, 8.5, and 1.3, respectively, for the three experiments. The quantity of undesired products, of which only a few have been identified,[15] increased significantly with the acid concentration. Since unreacted 11 can be recovered and reused and purification is easier, we chose the conditions of run c for a scaled-up experiment, contacting 5.95 g (33 mmol) of 11 with 60 mL of 91.5% H_2SO_4 for 72 h at room temperature. The dark orange mixture was extracted three times with 60 mL each of pentane,[15] removing most of 8 and other hydrocarbon products (1.6 g). The acid layer was then added to 240 g of ice and extracted 6 times with 65 mL each of ether. The combined ether solution was washed with 5% sodium carbonate solution and dried ($MgSO_4$), and the solvent was evaporated to give a yellow oil (3.1 g). Distillation at 0.45 mm to a vapor temperature of 96 °C gave a white slurry of liquid and crystals. Some alcohol (11) was left in the distillation flask. The distillate was dissolved in the minimum amount of pentane and cooled in dry ice and the solvent was poured out. Evaporation of pentane gave an oil (0.19 g) containing 3, 4, some 8 and 11, and also most of the heavy impurities. The recrystallized material weighed 1.2 g. For chromatography, it was combined with recrystallized material from preliminary runs (0.56 g). A 2.6-cm i.d. column containing 250 g of silica gel packed in pentane was used. Elution with pentane removed the hydrocarbon impurities. The ketones were then eluted with a 92:8 pentane–ether mixture. The ketone 3 (86 mg) was eluted first, followed by mixtures of 3 and 4 (232 mg), almost pure 4 (containing 1% 3, 181 mg), and pure 4 (398 mg).[28] The content of ether was raised and methanol was added. The alcohol 11 was eluted with a mixture containing 25–50% ether and 10–15% methanol;[28] 0.9 g of 11 was obtained. Recalculated for 1.2 g, the combined yield of ketones was 10.4% (1% 3, 2.7% mixtures of 3 and 4, and 6.7% 4 of two levels of purity), and 10.3% starting material (11) was recovered. The material from mother liquors (0.25 g) was similarly chromatographed on 60 g of silica gel in a 1.8 cm i.d. column. The ketone 3 (45 mg) was obtained pure, followed by 10–15 mg of mixtures of 3 and 4, but 4 was then eluted together with some heavy impurities. In view of the small quantity involved, elution of 11 was not attempted.

Pure 3 is a liquid: ^{1}H NMR (CD_2Cl_2, Me_4Si) δ 2.46 (1 H), 2.13 (1 H), 1.89 (2 H), 1.70 (6 H), 1.54 (2 H), 0.90 (3 H, CH_3), and 0.88 (3 H, CH_3).[29]

Pure 4 is a solid: mp 64–5 °C (lit.[15] mp 66–7 °C; the other authors reported it as an oil[4]); ^{1}H NMR (CD_2Cl_2, Me_4Si) δ 2.40 (4 H, H-1, -3, -6), 1.51 (8 H, H-4, -8, -9, -10), and 0.91 (6 H, CH_3).

Registry No. 1, 700-58-3; 2, 26832-19-9; 3, 33794-98-8; 4, 33670-21-2; 5, 52719-86-5; 11, 707-37-9.

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[25] Contrastingly, the β-carbon atoms of both cyclohexanone and 4-methylcyclohexanone resonate upfield from the position in the corresponding hydrocarbons; see ref 10, No. 49C, 404C, 409C, and 1403C.

[26] Karim, A.; McKervey, M. A. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2475.

[27] Landa, S.; Vais, J.; Burkhard, J. *Z. Chem.*, **1967**, *7*, 233.

[28] Suprisingly, previous authors reported (ref 4) that 3 was completely separated from 4 and 11, which were eluted together and had to be subjected to repetitive column chromatography.

[29] For another preparation of this compound, see: Drivas, I.; Mison, P. *Tetrahedron Lett.* **1981**, *22*, 641.