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Carbon-13 NMR Spectra of Di-*t*-alkyl Ethers and Related Hindered Ethers

Hiromitsu Masada* and Yoshiharu Murotani

Department of Industrial Chemistry, Faculty of Engineering, Kanazawa University, Kodatsuno, Kanazawa 920

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Synopsis. The C-13 NMR spectra of hindered *t*-alkyl ethers and dineopentyl ether have been presented and the electronic and steric effects discussed. The resonances for the α-, methylene β-, and methyl β-carbons of di-*t*-alkyl ethers shifted downfield by +45, +1.2, and −0.2 ppm, respectively, relative to the corresponding alkanes.

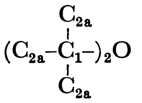
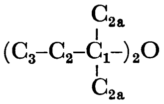
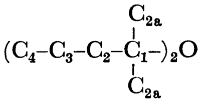
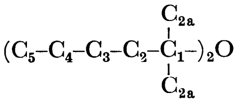
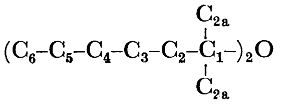
The C-13 NMR spectra of primary and secondary alkyl ethers have been investigated in detail.[1,2] However, the spectra of hindered *t*-alkyl ethers except di-*t*-butyl ether[3] have not been reported. This paper deals with the elucidation of the skeletal structures of several hindered ethers together with a spectroscopic study of their electronic and steric effects.

Results and Discussion

Table 1 shows the C-13 NMR chemical shifts of di-*t*-butyl ether (**1**), di-*t*-pentyl ether (**2**), bis(1,1-dimethylbutyl) ether (**3**), bis(1,1-dimethylpentyl) ether (**4**), and bis(1,1-dimethylhexyl) ether (**5**). The values in parentheses indicate the differences in chemical shifts between the di-*t*-alkyl ethers and the corresponding alkanes in which a methyl group has replaced the alkoxyl function. The chemical shifts of the alkanes were the values reported by Lindeman and Adams.[4] The resonance signals for the α-carbons (C-1) of di-*t*-alkyl ethers shifted downfield by 44.8—45.6 ppm relative to the alkanes. The downfield shifts are smaller than in the cases of the corresponding linear and secondary alkyl ethers containing more than eight carbons (48—50 ppm).[2] The difference in the α-effect may be due to steric hindrance of the *t*-alkyl group and variations in the electron density with branching of the alkyl chain. The resonances for the methylene β-carbons of the ethers (C-2) shifted downfield by 0.9—1.5 ppm, while those for the methyl β-carbons (C-2a) shifted upfield by 0.1—0.4 ppm, relative to the alkanes. The chemical shifts of the γ carbons (C-3) and more remote carbons (C-4, C-5, and C-6), in most cases, agreed reasonably with those of the alkanes.

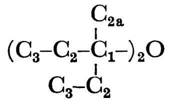
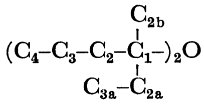
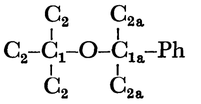
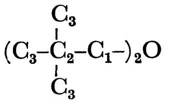
Table 2 shows the C-13 NMR chemical shifts for bis(1-ethyl-1-methylpropyl) ether (**6**), bis(1-ethyl-1-methylbutyl) ether (**7**), *t*-butyl α,α-dimethylbenzyl ether (**8**), and dineopentyl ether (**9**). The resonance shifts of more-crowded di-*t*-alkyl ethers, **6** and **7**, exhibit a similar tendency to those of **1**—**5**. The shielding of a phenyl substituent is observed in **8**. The resonance for the α-carbon attached to the phenyl group (C-1a) moved downfield by 1.2 ppm relative to that for the α-carbon (C-1) in **8**. The effect of the phenyl group was, however, hardly observed on the β-carbon (C-2a). The α-carbon resonance of the hindered primary ether, **9**, shifted by approx. 45 ppm, as much as that of the isomeric di-*t*-pentyl ether. Furthermore, the β- and γ-carbon resonances deviated by +2.1 and −1.9 ppm, respectively, from those of the corresponding alkane. The unusual deviations have been attributed to the steric effect of the neopentyl group, which is also observed to some extent in the case of neopentyl propyl

Table 1. C-13 NMR chemical shifts of di-*t*-alkyl ethers[a)]

Identification	C-1	C-2	C-2a	C-3	C-4	C-5	C-6
 $(C_{2a}-\overset{C_{2a}}{\underset{C_{2a}}{C_1}}-)_2O$ (**1**)	73.6 (+45.6)		31.7 (+0.1)				
 $(C_3-C_2-\overset{C_{2a}}{\underset{C_{2a}}{C_1}}-)_2O$ (**2**)	75.4 (+45.1)	38.0 (+1.5)	28.5 (−0.2)	8.7 (+0.2)			
 $(C_4-C_3-C_2-\overset{C_{2a}}{\underset{C_{2a}}{C_1}}-)_2O$ (**3**)	75.4 (+44.8)	48.2 (+0.9)	29.1 (−0.4)	17.6 (−0.5)	14.8 (−0.3)		
 $(C_5-C_4-C_3-C_2-\overset{C_{2a}}{\underset{C_{2a}}{C_1}}-)_2O$ (**4**)	75.4 (+45.3)	45.4 (+1.3)	29.1 (−0.1)	26.6 (−0.4)	23.5 (−0.2)	14.3 (+0.4)	
 $(C_6-C_5-C_4-C_3-C_2-\overset{C_{2a}}{\underset{C_{2a}}{C_1}}-)_2O$ (**5**)	75.4 (+45.2)	45.6 (+1.2)	29.1 (−0.1)	24.0 (−0.4)	32.7 (−0.3)	22.9 (+0.1)	14.1 (+0.3)

a) δ ppm downfield from TMS. $\Delta\delta=(\delta_C^{ROR}-\delta_C^{RCH_3})$ given in parentheses.

Table 2. C-13 NMR chemical shifts of hindered *t*-alkyl ethers and dineopentyl ether[a)]

Identification	C-1	C-1a	C-2	C-2a	C-2b	C-3	C-3a	C-4	Aromatic
 $(C_3-C_2-\overset{C_{2a}}{\underset{C_3-C_2}{C_1}}-)_2O$ (**6**)	78.0 (+45.7)		33.7 (+0.3)	25.5 (−0.1)		8.6 (+0.9)			
 $(C_4-C_3-C_2-\overset{C_{2b}}{\underset{C_{3a}-C_{2a}}{C_1}}-)_2O$ (**7**)	78.0 (+45.2)		44.1 (−0.2)	34.4 (+0.1)	26.0 (−0.5)	17.5 (+0.2)	8.8 (+0.7)	14.9 (+0.1)	
 $C_2-\overset{C_2}{\underset{C_2}{C_1}}-O-\overset{C_{2a}}{\underset{C_{2a}}{C_{1a}}}-Ph$ (**8**)	74.4	75.6	31.4	31.8					150.2, 127.7 126.1, 125.4
 $(C_3-\overset{C_3}{\underset{C_3}{C_2}}-C_1-)_2O$ (**9**)	81.9 (+45.4)		32.4 (+2.1)			26.8 (−1.9)			

a) δ ppm downfield from TMS. $\Delta\delta=(\delta_c^{ROR}-\delta_c^{RCH_3})$ given in parentheses.

ether.[2)]

Experimental

Materials and Preparation. Barium and sodium were commercial extra pure reagents (purity 99%). 2-Chloro-2-phenylpropane was derived from 2-phenylpropene.[5)] Neopentyl tosylate was prepared from neopentyl alcohol and tosyl chloride in pyridine. Organic chemicals were distilled from calcium hydride before use and the purity confirmed by GLPC. Di-*t*-alkyl ethers (**1**—**7**) were prepared from *t*-alkyl chlorides and silver carbonate by the method reported previously.[6)] The ethers, **8** and **9**, were prepared and identified by their physical constants, ^{1}H-NMR, IR, and mass spectra, as described below. Proton NMR spectra were conducted on a JEOL-PS-100 spectrometer operating at 100 MHz using TMS as an internal standard. IR spectra were conducted on a JASCO DS-301 spectrometer and mass spectra on a JEOL-JMS-01SG spectrometer. GLPC analyses were performed on a Shimadzu GC-3AH chromatograph using 3 m×3 mm columns packed with 5 % DNDP and 5 % Silicone DC 550.

t-Butyl α,α-Dimethylbenzyl Ether (8): A mixture of barium (3.30 g, 24 mg-atom) and *t*-butyl alcohol (40 cm^3) was refluxed for 8 h to give barium *t*-butoxide. The solution was cooled to 20 °C and 2-chloro-2-phenylpropane (6.18 g, 40 mmol) added. The mixture was stirred for 6 h, hydrolyzed, and extracted with pentane (30 cm^3×3). The organic layer was washed with water (50 cm^3×8), dried over sodium sulfate, and fractionated *in vacuo* to give 1.29 g (17 %) of pure *t*-butyl *α,α*-dimethylbenzyl ether: bp 97—98 °C/17 Torr; IR (neat) 1150 (C–O–C) and 768, 702 (aromatic) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.08 (9H, s, *t*-Bu), 1.56 (6H, s, *gem*-CH_3), and 7.1—7.5 (5H, m, aromatic).

Dineopentyl Ether (9): Prepared by a modification of the literature procedures.[7,8)] A mixture of sodium (0.55 g, 24 mg-atom) and neopentyl alcohol (8.82 g, 0.1 mol) was refluxed for 0.5 h, and a solution of neopentyl tosylate (4.84 g, 20 mmol) in dimethyl sulfoxide (10 cm^3) added. The mixture was stirred for 4 h at 120 °C, cooled, hydrolyzed with 1 M hydrochloric acid, and extracted with pentane (20 cm^3×3). The organic layer was washed with ethylene glycol (20 cm^3×8) and water, dried over sodium sulfate, and fractionated to give 1.96 g (62 %) of pure dineopentyl ether: bp 138 °C; IR (neat) 1126 (C–O–C) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=0.91 (18H, s, CH_3) and 3.02 (4H, s, CH_2); MS (75 eV), *m/e* (rel. intensity), 158 (M$^+$, 7), 101 (15), and 71 (100).

C-13 NMR Spectra. C-13 NMR spectra were conducted on a JEOL model PFT-100 pulse-Fourier transform NMR spectrometer at 25.15 MHz locked on deuterium using 10 mmϕ sample tubes. Data were obtained for 2 M solutions in $CDCl_3$ at 25 °C. Measurement conditions were as follows: pulse width, 12 μs (*ca.* 45°); repetition time, 4 s; spectral width, 5000 Hz; data points, 8191; delay time, 330 μs. The resonance assignments were confirmed by off-resonance decoupling experiments. Chemical shifts are expressed in δ ppm downfield from the internal TMS.

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