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Reference Data

^{1}H and ^{13}C NMR Spectra of (*Z*)-C-Aryl *N*-*tert*-Butyl Nitrones*

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The ^{1}H and ^{13}C NMR spectra of 12 (*Z*)-*C*-aryl *N*-*tert*-butyl nitrones were measured and proton and carbon assignments made. The nitrones were synthesized by the dimethyldioxirane method.

KEY WORDS Nitrones ^{1}H NMR ^{13}C NMR Dimethyldioxirane

INTRODUCTION

As part of an ongoing program on the chemistry of dioxiranes, we have recently shown[2] that dimethyldioxirane oxidation of appropriate secondary amines leads to excellent yields of the derived nitrones. The electronic character of the nitrone group and configurational and conformational aspects have been investigated very effectively[3–6] through the use of ^{1}H and ^{13}C NMR data.

We have now synthesized several additional nitrones of the *C*-aryl *N*-*tert*-butyl series **1** described earlier.[2] The ^{1}H and ^{13}C NMR data have been measured and proton and carbon assignments made.

RESULTS AND DISCUSSION

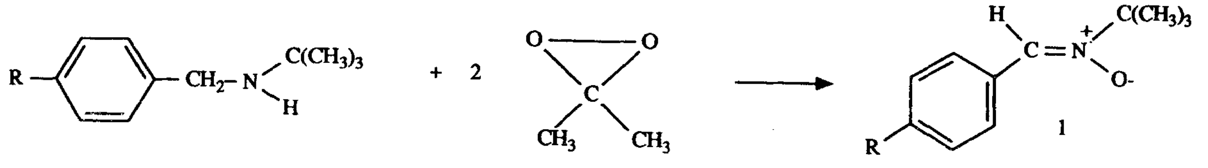
The recently described dioxirane method[2] was used to synthesize additional nitrones of structure type **1** (Scheme 1). The dioxirane method provides access to nitrones **1** cleanly and rapidly and in high yield. Exactly 2 equiv. of the dioxirane are used. Use of less than 2 equiv. will give nitrone plus hydroxylamine. On the other hand, an excess of dioxirane will lead to oxidation of the nitrone. The nitrone with a dimethylamino substituent was synthesized by an alternative method because of the reactivity of the dimethylamino group with dimethyldioxirane.

The chemical shifts of all of the protons in the nitrones **1** have been assigned and are given in Table 1. The multiplicities were assigned with the aid of the distortionless enhancement by polarization transfer (DEPT) method. The downfield shift of the *ortho* protons (H-2, 6) confirms the *Z* sterochemistry in the nitrones.[4] The fact that these protons and H-3, 5 have the same chemical shift indicates that there is free rotation about the C-α—C-1 bond. The reported chemical shifts thus represent averages for the two protons involved.

The ^{13}C chemical shifts of all of the carbons in the nitrones **1** were measured and assigned (Table 2). The quaternary carbon chemical shifts of the *tert*-butyl group in nitrones **1** gave an excellent correlation ($r = 0.96$) with Hammett[7] σ_p substituent constants. The ρ value (2.01) observed in this correlation indicates that the substituents R exert a major influence on the shift of the quaternary carbon in the *tert*-butyl group. A good correlation was also observed with $\sigma_p{}^+$ substituent constants ($\rho^+ = 1.25$). These results indicate that the nitrone group is able to transmit electronic effects through to the carbon of the *tert*-butyl group.

EXPERIMENTAL

The ^{1}H NMR spectra were obtained on a Varian XL-300 spectrometer at 300 MHz in 0.02–0.0.025 M $CDCl_3$ solutions with TMS as



Scheme 1

Table 1. ^{1}H chemical shifts of α-aryl *N*-*tert*-butyl nitrones

R	σ	H-α	H-2, 6	H-3, 5	—$C(CH_3)_3$	Other
4-NMe_2	−0.83	7.37	8.21	6.69	1.59	3.01 4-$(CH_3)_2N$—
4-OH	−0.37	7.45	8.19	6.87	1.59	9.42 4-OH
4-CH_3O	−0.27	7.47	8.29	6.93	1.60	3.85 4-CH_3O—
4-*t*-C_4H_9	−0.20	7.51	8.22	7.43	1.60	1.32 4-$(CH_3)_3$—
4-CH_3	−0.17	7.50	8.19	7.22	1.60	2.37 4-CH_3—
4-C_2H_5	−0.15	7.51	8.22	7.25	1.61	1.24 4-CH_3CH_2— (CH$_3$ italic) 2.67 4-CH_3CH_2—
4-H	0.00	7.54	8.29[a]	7.41[b]	1.62	7.36–7.46 H-4
4-F	0.06	7.53	8.34	7.10	1.61	
4-Cl	0.23	7.53	8.25	7.38	1.61	
4-Br	0.23	7.51	8.18	7.54	1.61	
4-CF_3	0.54	7.62	8.39	7.65	1.62	
4-NO_2	0.78	7.70	8.45	8.25	1.64	

[a] 8.24–8.34.
[b] 7.36–7.46.

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Table 2. ^{13}C chemical shifts of α-aryl *N*-*tert*-butyl nitrones

R	σ	C-α	$C(\mathrm{CH}_3)_3$	$\mathrm{C}(C\mathrm{H}_3)_3$	C-4	C-1	C-2	C-3	Others	
4-NME_2	−0.83	130.01	69.14	28.28	151.25	119.26	130.59	111.18	40.02	4-$(\mathrm{CH}_3)_2\mathrm{N}$—
4-OH	−0.37	129.84	69.41	27.93	158.99	122.30	130.68	115.19		
4-$\mathrm{CH}_3\mathrm{O}$	−0.27	129.41	70.01	28.25	160.73	123.98	130.66	113.66	55.27	4-$\mathrm{CH}_3\mathrm{O}$—
4-*t*-$\mathrm{C}_4\mathrm{H}_9$	−0.20	129.66	70.40	28.32	153.52	128.27	128.63	125.31	31.11	4-$(C\mathrm{H}_3)_3\mathrm{C}$—
									34.90	4-$(\mathrm{CH}_3)_3C$—
4-CH_3	−0.17	129.85	70.38	28.26	140.44	128.27	129.06	127.76	21.57	4-CH_3—
4-$\mathrm{C}_2\mathrm{H}_5$	−0.15	129.82	70.37	28.27	146.74	128.50	128.86	127.87	15.29	4-$C\mathrm{H}_3\mathrm{CH}_2$—
									28.88	4-$\mathrm{CH}_3C\mathrm{H}_2$—
4-H	0.00	129.75	70.70	28.24	130.01	130.92	128.68	128.33		
4-F	0.06	128.70	70.70	28.23	163.11	127.37	130.89	115.42		
4-Cl	0.23	128.74	71.02	28.24	135.36	129.44	129.89	128.60		
4-Br	0.23	128.81	71.11	28.24	129.83	123.73	131.43	130.04		
4-CF_3	0.54	134.09	71.60	28.25	131.00	128.48	128.61	125.25	123.8	4-CF_3—
4-NO_2	0.78	136.68	72.32	28.30	147.51	127.87	128.90	123.68		

internal reference. ^{13}C NMR spectra were obtained on the same spectrometer at 75 MHz in 0.07–0.10 M CDCl_3 solutions and are referenced to the center of the chloroform-*d* triplet at δ 77.00 which is referenced to TMS. Multiplicities were determined using DEPT and are reported as CH_3, CH_2, CH and C. The attached proton test (APT) was performed to identify CH_3, CH_2, CH and quaternary carbons.

Most of the nitrones used were prepared and characterized previously.[2] The same method was used to prepare *N*-*tert*-butyl α-(4-bromophenyl) nitrone and *N*-*tert*-butyl α-(4-ethylphenyl) nitrone.

N-*tert*-butyl α-(4-bromophenyl) nitrone

White needles, yield 98.6%, m.p. 60–62 °C (lit.[8] m.p. 60–62 °C). IR (KBr, cm^{-1}): 1578, 1564, 1549, 1476, 1454, 1409, 1391, 1363, 1355, 1308, 1244, 1195, 1188, 1126, 1102, 1070, 1006, 910, 835, 704, 667, 552, 510. Mass spectrum (EI, 70 eV): *m*/*z* 257 (M + 1, 7.5), 256 (M$^+$, 1), 57 (base peak, 100). Calculated for $\mathrm{C}_{11}\mathrm{H}_{14}\mathrm{BrNO}$: 256.13.

N-*tert*-butyl α-(4-ethylphenyl) nitrone

White microcrystalline solid, yield 98.7%, m.p. 62–63 °C (lit.[9] m.p., 62–64 °C). IR (KBr, cm^{-1}): 1608, 1576, (—C=N—), 1553, 1505, 1456, 1424, 1406, 1363, 1309, 1240, 1195, 1121, 1110, 1058, 910, 862, 662, 570, 550, 521. Mass spectrum (EI, 70 eV): *m*/*z* 206 (M + 1, 3.5), 205 (M$^+$, 24), 57 (base peak, 100). Calculated for $\mathrm{C}_{13}\mathrm{H}_{19}\mathrm{NO}$: 205.28.

N-*tert*-butyl α-(4-dimethylaminophenyl) nitrone

A mixture of *p*-dimethylaminobenzaldehyde and *tert*-butylhydroxylamine in 30 ml of benzene was refluxed for 22 h. Benzene was removed on a Rotovapor to give a pale yellow solid. This solid was purified by flash chromatography [silica gel; acetone–light petroleum (1:9, 2:8 and 4:6)]. The pure nitrone was obtained as very pale needles, m.p. 134–136 °C (lit.[10] m.p., 132–134 °C). IR (KBr, cm^{-1}): 2980, 1603, 1522, 1480, 1450, 1405, 1360, 1325, 1225, 1190, 1180, 1128, 1116, 1105, 945, 905, 840, 815. Mass spectrum (EI, 70 eV): *m*/*z* 221 (M + 1, 3.3), 220 (M$^+$, 22.8), 148 (base peak). Calculated for $\mathrm{C}_{13}\mathrm{H}_{20}\mathrm{N}_2\mathrm{O}$: 220.32.

N-*tert*-butyl α-(4-hydroxyphenyl) nitrone

A mixture of *p*-hydroxybenzaldehyde and *tert*-butylhydroxylamine in benzene was refluxed for 18 h to give a benzene-insoluble colorless crystalline solid which was homogeneous on thin-layer chromatography. This solid was recrystallized from hot acetone to give colorless needles, m.p. 256–258 °C. IR (KBr, cm^{-1}): 1610, 1578, 1510, 1455, 1398, 1370, 1315, 1298, 1260, 1240, 1195, 1170, 1095, 1040, 960, 907, 875, 830, 640, 530. Mass spectrum (EI, 70 eV): *m*/*z* 193 (M$^+$, 15.3), 57 (base peak, 100). Calculated for $\mathrm{C}_{11}\mathrm{H}_{15}\mathrm{NO}_2$: 193.23. Analysis: found, C 68.32, H. 7.77, N 7.38; calculated for $\mathrm{C}_{11}\mathrm{H}_{15}\mathrm{NO}_2$, C 68.37, H 7.82, N 7.25%.

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