N-Phenyl-*N*-(1,1,2-trimethylprop-2-enyl)hydroxylamine and its Nitroxide

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Summary The first preparation of an alkenyl-aryl-hydroxylamine is described.

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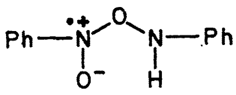
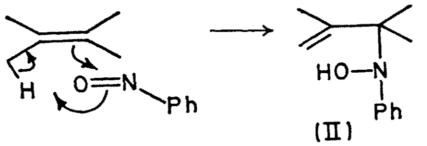
t-ALKYL-ARYLNITROXIDES have been the subject of several recent e.s.r. studies[1] and are usually prepared by oxidation of the corresponding secondary hydroxylamine. Sullivan[2] first reported the spectrum of a t-alkenyl-arylnitroxide derived from the reaction of nitrosobenzene with 2,3-dimethylbut-2-ene, but he was unable to isolate the hydroxylamine precursor. This nitroxide has a lower nitrogen splitting constant than was found for t-alkyl-aryl-nitroxides,[3] and, as pointed out by Russell,[4] has a very similar spectrum to that reported for the adduct from nitrosobenzene and phenylnitroxide (I). I now report the isolation of the intermediate t-alkenyl-arylhydroxylamine (II) formed by an 'ene' addition of nitrosobenzene to 2,3-dimethylbut-2-ene (equation 1), and the e.s.r. spectrum of the derived nitroxide. Nitrosobenzene (5×10^{-3} moles) and 2,3-dimethylbut-2-ene (5×10^{-2} moles) were dissolved in anhydrous diethyl ether (30 ml) under a nitrogen atmosphere. Examination of the reaction by t.l.c. after 16 hr. at room temperature showed no residual nitrosobenzene. The products were separated by column chromatography on grade 4 neutral alumina using mixed petroleum (b.p. 40—60°)–diethyl ether solvents. The impure hydroxylamine thus obtained was recrystallised six times at −60° from petroleum (b.p. 40—60°), to yield white crystals (320 mg), m.p. 58·2—58·4°. U.v. λ_{max} (MeOH) 249 nm, (ϵ 6840); i.r. (CCl_4), 2·77 (OH), 3·2—3·5 (CH), 5—6 (aromatic), 6·1 (double bond), 7·25 and 7·35 (split CH_3), and 11·1 μm (terminal double bond); n.m.r.: τ 8·8 (6H, C–CH_3), 8·1 (3H, =C–CH_3), 5·2 (2H, =CH_2), 4·2 (1H, N–O*H*), and 2·8 (5H, ar-*H*); radical broadening was observed if the solution was left to stand for a short time.



(I)



(II)

(1)

Nitroxide	Hyperfine splitting constant, gauss. a_n	$a_{H(p,o)}$	$a_{H(m)}$
N-Phenyl-*N*-(1,1,2-trimethylprop-2-enyl)nitroxide	11·18	2·40	0·85
N-t-Butyl-*N*-phenylnitroxide	12·40	1·91	0·85
Radical from reaction of nitrosobenzene and 2,3-dimethylbut-2-ene ..	11·14	2·41	0·85

Oxidation of the hydroxylamine by silver oxide in either benzene or ether yielded the nitroxide as a red viscous oil, u.v. λ_{max} (MeOH), 283·5, 291, 299, and 310 nm.

E.s.r. spectra were recorded on a Varian E.4 spectrometer at 20° in deoxygenated benzene as solvent. The splitting constants of this nitroxide are shown in the Table, together with those of the nitroxide prepared by oxidation of *N*-t-butyl-*N*-phenylhydroxylamine (prepared by method of Rassat *et al.*[3]) under identical conditions, and the radical product formed *in situ* from the reaction of nitrosobenzene with 2,3-dimethylbut-2-ene in deoxygenated benzene. The spectra obtained from the t-alkenyl-arylnitroxide and the radical produced in the reaction of nitrosobenzene with 2,3-dimethylbut-2-ene are identical, and agree with the reported data of Sullivan. The splitting constants of *N*-t-butyl-*N*-phenylhydroxylamine are similar to those obtained by Rassat[3] and confirm that a higher a_n value is obtained with t-alkyl-aryl- than with t-alk-2-enyl-aryl-nitroxides. The similarity of the splitting constants for alkenyl-arylnitroxides and the Russell adduct radical[4] would thus appear wholly fortuitous. This represents the first preparation of an authentic *N*-alkenyl-*N*-arylhydroxylamine.

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[3] H. Lemaine, Y. Marechal, R. Ramasseul, and A. Rassat, *Bull. Soc. chim. France*, 1965, 372 and 446.

[4] G. A. Russell, E. J. Geels, F. J. Smentowski, K.-Y. Chang, J. Reynolds, and G. Knapp, *J. Amer. Chem. Soc.*, 1967, **89**, 3821.