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N-ALKENYL-N-PENTAFLUOROPHENYLHYDROXYLAMINES

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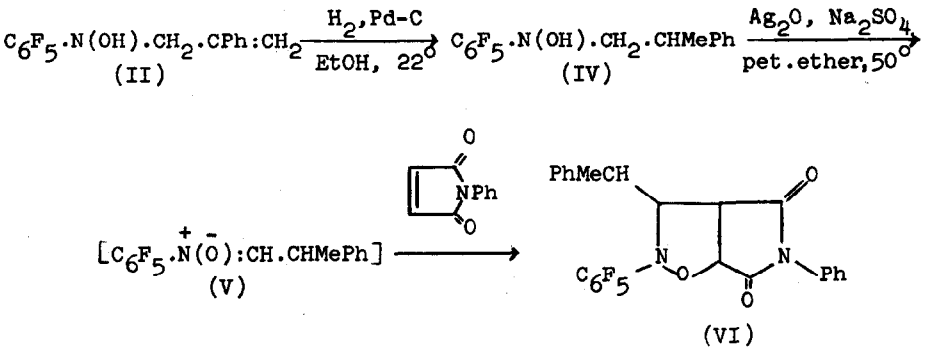
The recent description[1] of the first isolation of an N-alkenyl-N-arylhydroxylamine [$PhN(OH).CMe_2.CMe:CH_2$, obtained from nitrosobenzene and 2,3-dimethylbut-2-ene] prompts us to report that several years ago[2] we isolated the following N-alkenyl-N-pentafluorophenylhydroxylamines by conventional work-up of solutions prepared by stirring pentafluoronitrosobenzene in benzene at 10-20° with an excess of 2,3-dimethylbut-2-ene, 2-phenylpropene, and methyl methacrylate, respectively: $C_6F_5.N(OH).CMe_2.CMe:CH_2$ (I) (96% yield; white solid, m.p. 76°); $C_6F_5.N(OH).CH_2.CPh:CH_2$ (II) (82%; white solid, m.p. 90°); and $C_6F_5.N(OH).CH_2.C(CO_2Me):CH_2$ (III) [41%; fawn solid, m.p. 80° (decomp.)]. Each of these new hydroxylamines readily reduced silver oxide and possessed correct elemental compositions (C, H, and N) and consistent spectroscopic properties (i.r., u.v., ^1H and ^{19}F n.m.r., and mass). In keeping with previous work,[3] the formation of nitroxides corresponding to the hydroxylamines [e.g., $(C_6F_5)(CH_2:CMe.CMe_2)N.O.$ in the case of (I)] was detected during these pentafluoronitrosobenzene-olefin reactions by e.s.r. spectroscopy, and the following nitrogen hyperfine splitting constants were observed:

nitroxide derived from (I) 13.1, from (II) 11.0, and from (III) 11.6 gauss.

Catalytic hydrogenation of hydroxylamine (II) gave N-pentafluorophenyl-N-2-phenylpropylhydroxylamine (IV), an air-sensitive liquid that was identified spectroscopically (i.r. and n.m.r.); treatment of this saturated hydroxylamine with silver oxide gave the corresponding nitrone (V), which was trapped with N-phenylmaleimide as the isoxazolidine (VI), m.p. 154°, identified by elemental analysis (C, H, and N) and i.r. and n.m.r. spectroscopy.



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References

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