Hydrogenation of Alkenes and Alkynes, Di-tert-alkyl Amines, Di-tert-alkyl Nitroxyl (Aminoxyl) Radicals, Polymerization Inhibitors

Stable di-tert-alkylnitroxyl radicals, tert-butyl-tert-pentylnitroxyl (4a), di-tert-pentylnitroxyl (4b) and tert-octyl-tert-pentylnitroxyl (4c), the homologs of di-tert-butylnitroxyl (1), were synthesized from tert-alkyl amines 7a-c via the 3-tert-alkylamino-3-methyl-1-butynes 8a-c. Oxidation of 8a,b with hydrogen peroxide lead to relatively unstable N-tert-alkyl-N-(1,1-dimethyl-prop-2-ynyl)nitroxyl radicals 15a,b. The thermal stability, vapor pressure data, ultraviolet, visible and electron paramagnetic resonance spectra of 4a-c were recorded. The radicals were explored as potential inhibitors of unwanted alkene polymerization reactions at elevated temperatures, in comparison with the aliphatic di-tert-butyl nitroxyl (1), the alicyclic nitroxyl radicals 2,2,6,6-tetramethylpiperidin-1-oxyl (2) and 4-hydroxy-2,2,6,6-tetramethyl-piperidin-1-oxyl (3), some commercial polymerization inhibitors, such as diethyl-hydroxylamine (Pennstop, 16), ammonium salt of N-hydroxy-N-nitrosobenzenamine (Cupferron, 17), bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (Tinuvin 770, 18), and the well-known spin traps 2-methyl-2-nitrosopropane (19) and tert-butylhydroxylamine (20).