Thiocarbonyl Compounds as Potential Scavengers of Carbon Radicals

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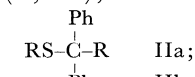
Stable free radicals, such as di-*t*-butylnitroxide,[1] garvinoxyl,[2] or DPPH,[3] are known to act as scavengers for carbon radicals. We would like to report that thiocarbonyl compounds function as powerful, *molecular-type* scavengers toward carbon radicals.

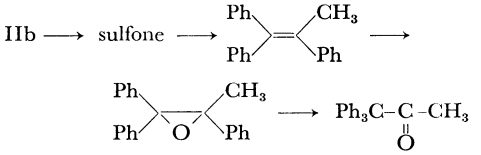
When azobisisobutyronitrile (AIBN) was decomposed in refluxing toluene containing an equimolar amount of thiobenzophenone (I), the yield of tetramethylsuccinonitrile (TMSN), a dimerization product of 1-cyano-1-methylethyl radicals, decreased from 89% (without I) to 21%. 1-Cyano-1-methylethyl radicals were efficiently captured by I, and as a result the adduct IIa was produced in 78% yield. IIa[4]: mp 168°C; IR 2200 and 2240 cm^{-1} (CN); NMR[5] 1.17 (s,6H), 1.34 (s,6H), and 7.3—7.8(m,10H); mass M^+ 334.



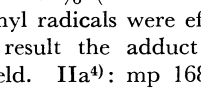
IIa; R=1-cyano-1-methylethyl

IIb; R=1-phenylethyl

Similarly, the addition of I for the decomposition of azobis(1-phenylethane) in toluene resulted in a marked decrease of the formation of 2,3-diphenylbutane:[6] 90% (without I) and 12% (with I). 1-Phenylethyl radicals were trapped by I and the addition product was obtained in 80% yield. This addition product proved to be a 1 : 1 mixture of two diastereomers of IIb, as shown by NMR: 0.86 (d,3H), 1.25(d,3H), 3.10(q,1H), 4.12(q, 1H), and ~7.1(m, 20H) for one isomer and 1.15(d,3H), 1.23(d,3H), 3.06(q,1H), 4.14(q,1H), and ~7.1 (m, 20H) for the other. The mass spectrum was also consistent with this structure, but the most convincing evidence is that oxidation of IIb with hydrogen peroxide in acetic acid produces soley methyl triphenylmethyl ketone in 98% yield. This presumably arises from oxidation of IIb to the sulfone, elimination of the sulfinic acid to form the olefin, and epoxidation, followed by rearrangement of the epoxide:



Thioacetophenone (III) also appears to be an efficient radical-capturing agent. Thus, when AIBN was decomposed in toluene with two molar equivalents of III, TMSN was formed in only 23% yield and the adduct (IVa) was produced instead of the dimer in a yield of 71%.



IVa; R=1-cyano-1-methylethyl

IVb; R=1-phenylethyl

IVa: mp 176°C; IR 2230 cm^{-1} (CN); NMR 0.97 (s,6H), 1.62(s,6H), 2.27(s,6H), and ~7.1(m,10H). Desulfurization of IVa with Ra-Ni(W-2) in ethanol gave *trans*-2,3-diphenyl-2-butene (79%). By a similar reaction of azobis(1-phenylethane) with III, adduct (IVb) was formed in 69% yield and the formation of 2,3-diphenylbutane was reduced to 27%. IVb: mp 204—205°C; NMR 1.30(d,6H), 1.45(s,6H), 3.26 (q,2H), and 6.9—7.2(m, 20H). Desulfurization of IVb with Ra-Ni(W-2) gave *trans*-2,3-diphenyl-2-butene(57%), *meso*-2,3-diphenylbutane (18%), and ethylbenzene(42%).

Hence these thioketones appear as potential radical scavengers. The capturing power is particularly strong toward a neutral carbon radical. 1-Phenylethyl radicals were trapped by I (five-fold excess)[7] and III (five-fold excess)[7] quite effectively, cutting down the yields of dimer to 6.0 and 8.2%, respectively, whereas the addition of thiophenol, in place of thioketones, to the system allowed formation of the dimer in a higher yield of 28%.[8] Apparently, these thioketones are much better scavengers than thiophenol. The use of these thioketones is further advantageous, because they possess visible absorption maxima at around 600 mμ. The extent of scavenged radical can be followed easily by measuring the disappearance of this visible absorption.

Studies on the relationship between the radical capturing power and the structure of thiocarbonyl compounds are in progress.

1) A. K. Hoffmann, A. M. Feldman, E. Gelblum and W. G. Hodgson, *J. Amer. Chem. Soc.*, **86**, 639 (1964).

2) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962).

3) C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951); G. S. Hammond, J. N. Sen and C. E. Boozer, *J. Amer. Chem. Soc.*, **77**, 3244 (1955).

4) Satisfactory elemental analyses were obtained for all new compounds reported here.

5) The NMR spectra were measured by a Varian HA-100 spectrometer. Chemical shifts are shown as δ (in ppm) from TMS in $CDCl_3$.

6) A 1 : 1 mixture of *dl* and *meso* isomers.

7) The concentrations of the thioketones and the azo compound are 1.3×10^{-2}M and 2.5×10^{-3}M, respectively.

8) F. D. Greene and M. A. Berwick, Abstracts, 156th ACS National Meeting, Atlantic City, N. J., Sep., 1968, ORGN-112.