Displacement of a Nitro-group from 2,2-Diphenyl-1-picrylhydrazyl in its Reaction with 2,4,6-Tri-t-butylbenzenethiol

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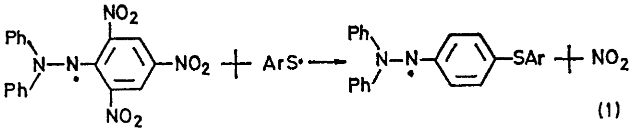
Summary The reaction of 2,2-diphenyl-1-picrylhydrazyl (DPPH) with 2,4,6-tri-t-butylbenzenethiol yields bis-(2,4,6-tri-t-butylphenyl) disulphide, 2,2-diphenyl-1-picrylhydra zine (DPPH-H), and a derivative of DPPH-H in which nitro-group has been replaced by a 2,4,6-tri-t-butylphenylthio-group.

Free radical attack on DPPH has been postulated to occur both on nitrogen at the 1-position, yielding a tetra-substituted hydrazine by combination or DPPH-H by hydrogen transfer, and on carbon at the *para*-position of a phenyl ring to yield a substituted DPPH-H.[1] In some instances the position of attack has been proved by characterization of the products[2] but in many kinetic studies the products have not been positively identified.

Solutions of DPPH (0·002M) and 2,4,6-tri-t-butylbenzenethiol (0·004M) in benzene were degassed, mixed, and allowed to react in the dark overnight. Chromatography of the mixture on alumina with benzene as eluant afforded excess of the thiol, the disulphide, DPPH-H, and a reddish orange compound (I), m.p. 157°. On oxidation (PbO_2) in benzene solution, (I) gave a stable radical whose e.s.r. spectrum was typical of a substituted hydrazyl.[3] After 10 h *in vacuo* at 25° (I) gave analytical and mass spectral data consistent with the molecular formula $C_{36}H_{42}N_4O_4S$. {Mass spectrum: m/e 626·3 (M^+), 168·078 (Ph_2N^+), 169·086 (Ph_2NH^+), and 459·215 [$H_2NC_6H_2(NO_2)_2(SC_6H_2Bu^t)]^+$}. The cracking pattern is similar to that of DPPH and DPPH-H and we conclude that (I) is a derivative of DPPH-H in which a nitro-group has been replaced by a 2,4,6-tri-t-butylphenylthio-group. Comparison of the u.v.–visible spectra of (I) and of the hydrazyl produced by oxidation (PbO_2) with those[4] for 1-(2,6-dinitrophenyl)-2,2-diphenylhydrazine and the corresponding hydrazyl and for the 1-(2,4-dinitrophenyl)-2,2-diphenyl compounds suggests that the nitro-



(1)

group has been displaced from the *para-* rather than the *ortho*-position of the picryl ring.

The rate of reaction of DPPH with 2,4,6-tri-t-butylbenzenethiol is halved when the benzenethiol is deuteriated at the SH group; thus the primary reaction involves hydrogen transfer and yields DPPH-H and the tri-t-butylphenylthio-radical. The hydrazyl related to (I) is presumably formed by the radical–radical reaction (1). The hydrazine (I) would then be produced by hydrogen abstraction from a further molecule of benzenethiol. The fate of the nitrogen dioxide has not been determined. This work supports the conclusion[1] that further studies of reaction products are desirable for many of the reactions involving DPPH.

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