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THE HIGH YIELD SYNTHESIS OF $CF_3\overline{CSNSC}CF_3$; A THERMALLY STABLE, LIQUID RADICAL AND THE QUANTITATIVE REARRANGEMENT OF $CF_3\overline{CNSNS}$ TO $CF_3\overline{CNSSN}$

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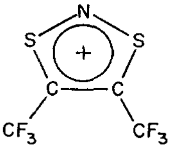
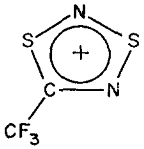
S_2NAsF_6 reacts quantitatively in a concerted, symmetry allowed, cycloaddition reaction with a number of alkynes and nitriles, e.g. with CF_3CCCF_3 and CF_3CN to give the AsF_6^- salts of (1) and (2) [J.C.S. Dalton Trans. 1985, 1405, and present work]. The CH_3, H, CO_2Me, and $Si(CH_3)_3$ analogues of (1) were reduced by an excess of $Na_2S_2O_4$, or $Ph_3Sb/N(CH_3)_4Cl$, in dilute SO_2 solution at low temperatures to give the corresponding 7 π radicals, detected by E.S.R. However these radicals decompose to give complex mixtures. In contrast (1) is reduced quantitatively in large amounts to give (3), a blue/black liquid over which is a blue gas (m.p. +12°C, v.p. = 20 torr at 25°C) that is thermally stable up to 250°C. Compound (3) has been prepared previously by the reaction of S_4N_2 and CF_3CCCF_3 in dilute solution [J.C.S. Faraday Trans. 1, 1983, 79, 925] and identified by E.S.R. (3) was characterised by i.r., elemental analysis, mass spectroscopy, E.S.R., and gas phase electron diffraction [H. Oberhammer]. Quantitative E.S.R. of the neat liquid, and a 30% w/w solution in CCl_3F showed it to be essentially monomeric. The magnetic susceptibility of the liquid was μ_{eff} = 1.52 B.M. (25°C). Thus (3) is one of a small class of stable liquid radicals which also includes various nitroxides. It is also one of a class of stable, non-sterically hindered, radicals, e.g. O_2, NO, and $(CF_3)_2NO$. We have also found that the t-butyl analogues of (4) and (5) are paramagnetic liquids, and likely many other 7 π C/N/S rings will also be strongly paramagnetic in the liquid state. (3) and (5) are diamagnetic in the solid state.

Reduction of (2) in dilute solution led quantitatively to the 7π radical (4) detected by E.S.R. The rearrangement of (4) to the known (5) [Chem. Ber., 1985, 118, 3781] was followed by E.S.R. and found to be quantitative. It was also quantitative on a preparative scale. The rearrangement of the CH_3 analogue of (4) was found by quantitative E.S.R. to be a bimolecular process and a π^*-π^* dimer involving overlap of the SOMO's of each ring (largely through the two sulphur atoms of both rings) is envisaged as an intermediate [J.C.S. Chem. Commun. 1986, 140]. The quantitative nature of the rearrangement indicates a concerted unimolecular readjustment reaction of the dimer intermediate, and the process is found to be 'Thermally symmetry forbidden' (occupied molecular orbitals of initial dimer become unoccupied molecular orbitals in product dimer), and 'Photochemically symmetry allowed'.



(1)



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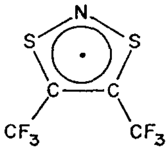
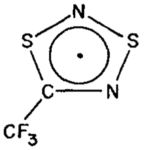
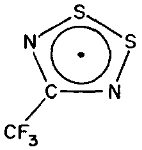


(3)



(4)



(5)