Tetramethyltetrathia-adamantane Dianion

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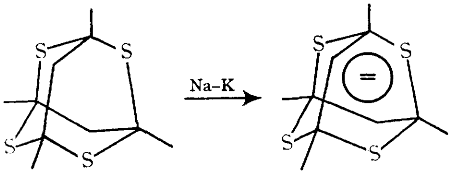
THE cage-like structure of adamantane has suggested itself to several investigators as a possible electron receptor whereby, under suitable reducing conditions, radical anions of adamantane may be produced as moderately stable species. Attempts to reduce the purely carbocyclic ring system, however, have been without success.[1]

Known radical anions and dianions have in common the fact that their progenitors possess low-lying vacant antibonding or nonbonding molecular orbitals. It was thus reasoned that cyclic multi-sulphur compounds in which sulphur atoms are suitably disposed to maximize overlap of vacant 3*d*-orbitals should constitute suitable electron acceptors so that stable reduced species might be obtained.[4]

1,3,5,7-Tetramethyl-2,4,6,8-tetrathia-adamantane (I), readily obtained by a one-step synthesis,[5] was selected for study because of the relationship to the previous work on the carbocyclic analogue. In addition, the sulphur atoms in this molecule lie on the corners of a square permitting favourable *d*-orbital overlap.

When a solution of compound (I) in tetrahydrofuran was stirred with sodium–potassium alloy under nitrogen, a bright yellow colour (λ_{max} 430 mμ) developed which faded on long standing at $-10°$ under nitrogen, or on exposure to air. Compound (I) is the only organosulphur compound which can be detected (t.l.c.) in or isolated from this solution after quenching with various reagents. Since the yellow solution gives no e.s.r. signal, the



(I) (II)

yellow colour does not arise from the formation of the expected radical anion. We concluded that reduction must proceed to the dianion (II) and the following observations were made in support of this conclusion.†

The yellow solution can be diluted with methanol or ethanol without immediately quenching the colour, although it faded at once on addition of stronger (*e.g.* formic) acids. This result is consistent with the fact that stable, neutral species cannot be derived from dianion (II) simply by protonation. In comparison the dianion of cyclo-octatetraene[3a] can react with a variety of electrophilic reagents to produce a variety of polycyclic compounds.[6] Addition of an excess of benzoquinone caused immediate formation of the deep green colour of quinhydrone. Naphthoquinone and anthraquinone were reduced by the dianion giving colourless solutions. Electrochemical reduction of compound (I) was also effected; a cyclic voltammogram at a hanging mercury drop electrode shows two waves in the reduction of (I). The solution of dianion (II) can be titrated with a standard solution of iodine in tetrahydrofuran to produce a colourless end-point. By this method a 4% conversion of (I) into (II) was observed at a concentration of 5 mg./ml. (30 min. at 10°).

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† The excess of alloy was frozen and removed from the reaction flask before these experiments were conducted.

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