ide. The titrated solution was evaporated to dryness and sodium acetate (8.5 mg; 56.5 %) recrystallized from ethanol-ether.

Acknowledgements. This investigation was supported by the *Swedish Natural Science Research Council*. Dr. Kirti Sheth, Tucson, Arizona, is thanked for valuable assistance in carrying out some of the feeding experiments. For interesting discussions and reference materials we are indebted to Dr. Jan Lundström of this department.

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Received December 30, 1970.

On the Existence of the 1,3,5,7-Tetramethyl-2,4,6,8-tetrathiaadamantane Dianion

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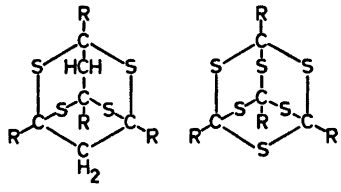
A solution of 1,3,5,7-tetramethyl-2,4,6,8-tetrathiaadamantane (I)* in tetrahydrofuran (THF) was recently reported as developing a yellow colour, when stirred with sodium-potassium alloy (Na-K).[1,2] The colour was ascribed to a dianion, formed by addition of two electrons to the otherwise unchanged I. This conclusion was based mainly on the following observations. The yellow solution gave no electron spin resonance signal, reduced quinones, and could be titrated with iodine, indicating a 4 % conversion of I into dianion after 30 min at 10°. Unlike alcohols, stronger acids caused immediate discoloration. After quenching, no organosulphur compound other than I could be detected. A multi-cycle voltammogram of I at a mercury electrode was interpreted as two reversible reduction waves.

When exposed to Na-K, tetramethylhexathiaadamantane (II) was changed to a stinking mixture of organosulphur compounds, believed to indicate extensive reductive cleavage of C—S bonds.[2] In the present note, we wish to present evidence suggesting similar cleavage in the formation of the yellow species from I. On the other hand, we were unable to reduce I electrochemically.

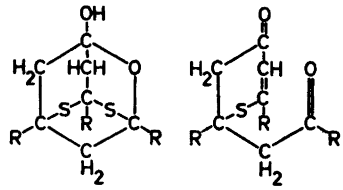


I II

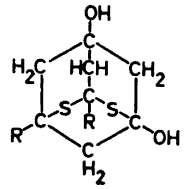
* Throughout the present paper, R = CH_3.

50 mg of dry I,[2] recrystallized from ethanol until at least 99.9 % pure by gas liquid chromatography (GLC), was stirred with an excess of Na-K at 0—10° under argon in 10 ml of THF, distilled from lithium tetrahydridoaluminate. Along with the yellow colour, a precipitate formed gradually. At suitable times, samples of the supernatant liquid were withdrawn and analyzed by GLC, showing steadily decreasing amounts of I. Preliminary quenching with methanol or formic acid did not affect the analyses. After stirring for 20 min—12 h (according to the temperature and commercial source of the THF), virtually no I remained. At this stage, the colour had disappeared but *returned* instantly on exposure to air.

Although this experiment does not reveal the structure of the yellow species, it strongly indicates ring opening. This must produce sulphide ion and/or some kind of thiolate ion and so explains the observed reductions of iodine and quinones. Considering their close structural relationship, the similar behaviour of I and II towards the extremely reactive alloy is not surprising. It may be relevant here to mention that on treatment with potassium *t*-butoxide, a by-product (III) [3,4] in the synthesis of I immediately gives rise to a yellow colour similar to that formed by I and Na-K. Neutralization of the yellow solution obtained from III yield the colourless compounds IV and V.[5] The yellow colour reappears instantly if one drop of dilute aqueous alkali is added to a methanolic solution of IV.



III IV



V

Even though moisture and peroxides were removed, some other impurity in our THF, alloy or oil adhering to it might perhaps have caused the destruction of I. For that reason, particular attention was paid to the electrochemical evidence. Nevertheless, we were unable to reproduce the voltammogram mentioned above,[2] which, incidentally, in our opinion suggests two *irreversible* waves. In fact, neither direct current polarography nor cyclic voltammetry, applied to I under greatly varied conditions revealed any sign of reduction at the mercury electrode.

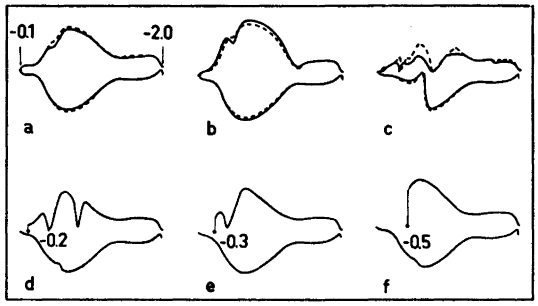


Fig. 1. Oscillographic $dE/dt-f(E)$ curves. 0.2 M ammonia buffer in 25 % ethanol. All potentials refer to SCE. Dropping mercury electrode; ——— first cycle; – – – – – – – – second cycle. a. Blank solution. b. Substance I. c. Substance III. d-f. Substance III with varying starting potential.

The oscillopolarographic technique proved to be a valuable tool in characterizing the electrochemical behaviour of this group of substances. A newly developed device[6] enabled the study of the function $dE/dt=f(E)$ separately on individual cycles as well as with a predetermined starting potential. Some applications are shown in Fig. 1. A blank solution and substance I exhibit similar oscillopolarographic patterns (Fig. 1a, b). Under the same conditions, anodic and strong cathodic indentations appear for substance III (Fig. 1c). Besides, these incisions are directly related to the starting potential (Fig. 1 d-f). This is clear evidence that the species being reduced are artefacts, formed by anodic oxidation at more positive potentials of the original substance. Analogous results were obtained with cyclic voltammetry (Fig. 2). The experiments were

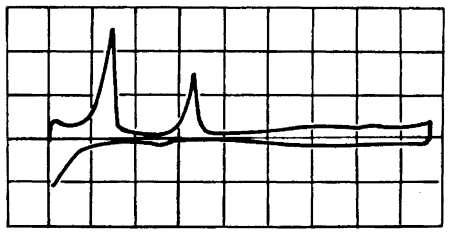


Fig. 2. Cyclic voltammogram of substance III under the same experimental conditions as in Fig. 1c. Frequency 30 cycles/s. Potential range −0.1 to −2.0 V *vs.* SCE.

repeated with some compounds related to I, *viz.* its 2,4-dioxa-6,8-dithia, oxatrithia, pentathia, and hexathia analogues (II).[3] These resembled I closely in their electrochemical behaviour, whereas substance V behaved like III.

The following conclusions can be drawn. Compound I and related substances appear as *non-reducible* in the potential range available. Strong oscillopolarographic effects emerge from III and as a result of anodic oxidation at more positive potentials. The appearance of III or analogues as impurities in I may cause the electrochemical effects previously ascribed to I.

Acknowledgements. We wish to thank Mr. Rolf Danielsson, Pharmacia AB, for valuable help with the electrochemical work, Professor Nils Hellström for all facilities placed at our disposal and Professor Arne Fredga for his interest in the present work. This was supported by a grant (to K. O.) from the *Swedish Natural Science Research Council.*

Added in proof. Professor D. L. Cohen has kindly informed us that he does not dispute our reinterpretation of his results.

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Received December 8, 1970.

ESR and ENDOR from Neutral Flavin Radicals

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Neutral flavin radicals have been investigated by electron spin resonance (ESR) and isotopic substitution.[1–3] An unambiguous determination of the various hyperfine coupling constants is not straightforward. Electron-nuclear double resonance (ENDOR) has recently proven to be of value for the determination of hyperfine couplings to methyl protons of flavin radicals in liquid and polycrystalline phase.[4] Model studies were performed with anionic and cationic radicals, and also with radical chelates. Samples of

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