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ELECTRON SPIN RESONANCE SPECTRA OF RADICAL ANIONS DERIVED FROM CYCLOHEPTA-3,6-DIENE-1,2,5-TRIONE AND CYCLOHEPTA-4,6-DIENE-1,2,3-TRIONE

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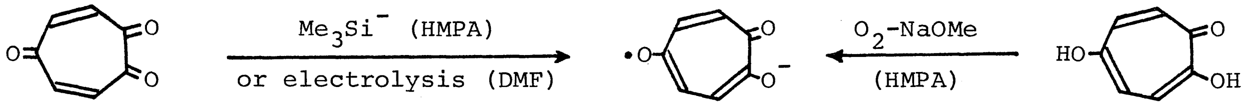
The tropolone analoques of p- and o-benzosemiquinone (p- and o-troposemiquinone) were generated from cyclohepta-3,6-diene-1,2,5-trione and cyclohepta-4,6-diene-1,2,3-trione, respectively, and characterized by e.s.r. spectroscopy.

Although trione radical anions (semitriones) are considered to be thermodynamically more stable than semidiones, facile ring contractions to semidiones may occur due to decarbonylation, and hence, there has been no report on semitriones except for five-membered rings where such ring contractions would be highly unlikely.1) We wish to report preparation and e.s.r. spectra of fairly stable seven-membered semitriones, cyclohepta-3,6-diene-1,2,5-trione radical anion (p-troposemiquinone, I) and cyclohepta-4,6-diene-1,2,3-trione radical anion (o-troposemiquinone, II).

Very recently, after our work had been completed,2) Dixon and Murphy3) have reported an e.s.r. spectrum of the short-lived (I) which was prepared by oxidation of 5-hydroxytropolone (III). Their assignments of the hyperfine coupling constants (hfcc) were made by analogy to the similar benzenoid cases, but were erroneous judging from our unequivocal data.

p-Troposemiquinone (I) was prepared by three methods: (a) reduction of cyclohepta-3,6-diene-1,2,5-trione(p-tropoquinone, IV)4) with trimethylsilylsodium in hexamethylphosphoramide (HMPA);5) (b) electrolytic reduction of (IV) in DMF with tetraethylammonium perchlorate as a supporting electrolyte; (c) autoxidation of (III) at room temperature in the presence of sodium methoxide in HMPA. The spectrum obtained by the method (a) at -10° was identical to that by (c), although the former was overlapped with weak signals of p-benzosemiquinone, the decarbonylation product of (I). The method (b) gave a similar spectrum with slightly different hfcc values due to a solvent effect. The e.s.r. spectrum of (I) in HMPA is composed of a triplet (0.199 mT) of triplets (0.120 mT) as shown in Figure 1a.



(IV) (I) (III)

Dixon and Murphy obtained a spectrum of (I) composed of a triplet (0.20 mT) of triplets (0.12 mT), these hfcc being assigned to be a_3^H and a_4^H, respectively.3) For an unequivocal assignment of hfcc, 3,7-dideuterio-5-hydroxytropolone (V)6) was oxidized to the corresponding radical anion (VI) by the method (c).

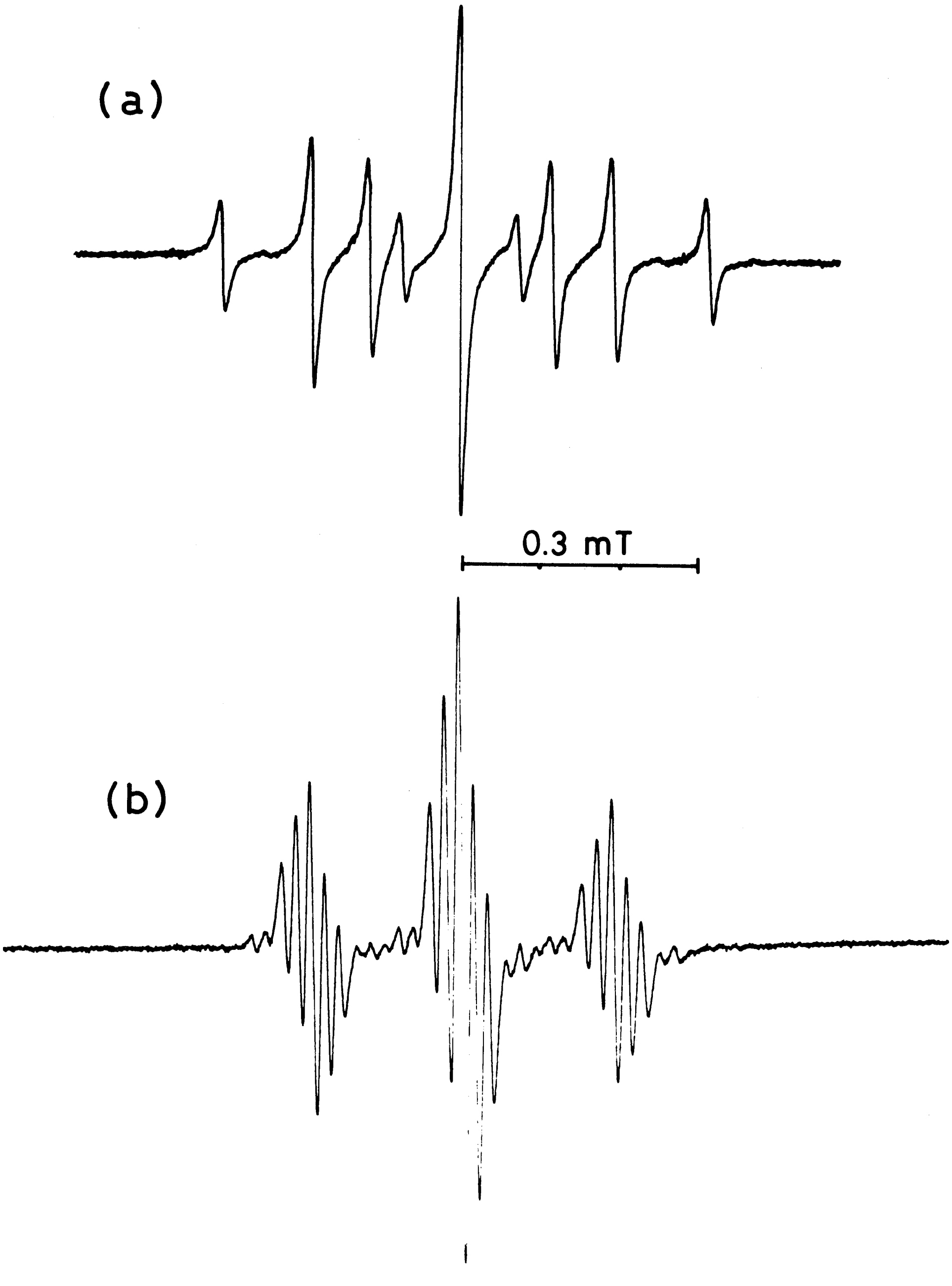


Figure 1. E.s.r. spectra of (a) p-troposemiquinone and (b) 3,7-dideuterio-p-troposemiquinone.

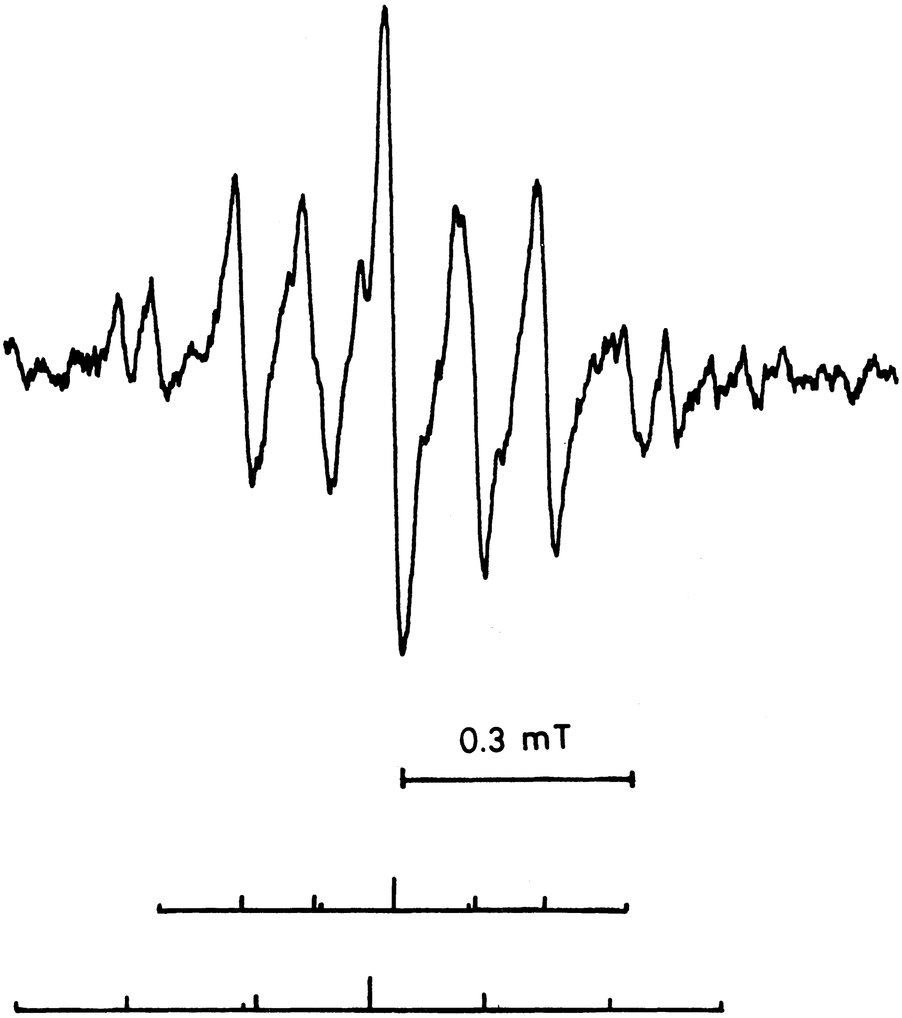
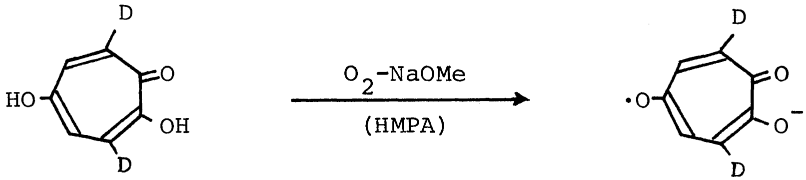


Figure 2. E.s.r. spectrum of the mixture of *o*-troposemiquinone and *o*-benzosemiquinone. Upper and lower stick spectra indicate *o*-troposemiquinone and *o*-benzosemiquinone, respectively.

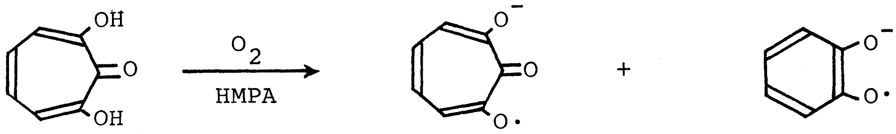


(V) (VI)

The e.s.r. spectrum of (VI) is clearly composed of a triplet (0.196 mT) of quintets (0.018 mT), as shown in Figure 1b. Therefore, the splitting constant of the larger triplet of (I) should be assigned to a_4^H. The quintet seen in (VI) is a splitting due to two equivalent deuterium atoms (a_3^D). The experimental a_3^D agrees excellently with the theoretical value.$^{7)}$

$$a_3^D \text{ (calculated)} = a_3^H \cdot (g_D/g_H) = 0.120 \cdot (0.857/5.585) = 0.018 \text{ (mT)}$$

Since cyclohepta-4,6-diene-1,2,3-trione(o-tropoquinone) has not been isolated,$^{8)}$ oxidation of 3-hydroxytropolone (VII) to (II) by the method (c) was examined in an attempt to the preparation of (II). It appears that decomposition of (II) is much easier than (I) which makes the e.s.r. spectrum of (II) overlapped with that of o-benzosemiquinone (VIII, a_3^H=0.154 mT and a_4^H=0.347 mT) as seen in Figure 2. Nevertheless, two hfcc values, 0.109 mT and 0.205 mT, can be obtained for (II) and are assigned to a_4^H and a_5^H, respectively, by comparison with the authentic spectrum of o-benzosemiquinone produced by the method (c).$^{9)}$ The assignments were further comfirmed by the McLachlan molecular orbital calculations.$^{10)}$



(VII) (II) (VIII)

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