Electron Spin Resonance Spectra of Radicals derived from Tropolones and Benztropolones

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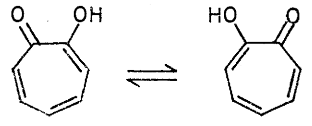
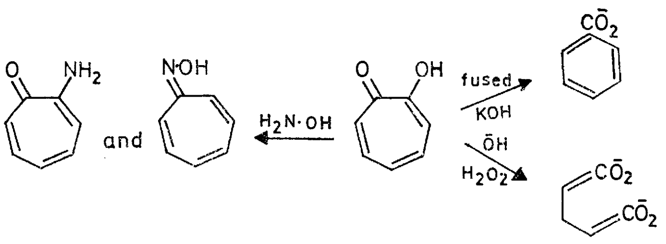
The oxidation of tropolones and benztropolones such as purpurogallin by cerium(IV) in a flow system yields radicals which can be characterised by means of e.s.r. spectroscopy. The spin distribution can be related to non-bonding orbital coefficients in model compounds. In alkaline solutions 1′,2′-dihydroxy-3,4-benztropolone and its derivatives can be autoxidised to corresponding semiquinones from which intense e.s.r. spectra can be obtained. Secondary radicals may also be formed when the 4′-position is vacant. The tropolone analogue of *p*-benzosemiquinone can be observed in hexamethylphosphoramide, but ring contraction takes place too quickly for this to be detected in aqueous solution.

THE existence of the tropolone structure was first realised [1] in 1945, and since then it has been found that derivatives of 2-hydroxycycloheptatrienone (I) occur quite widely in nature,[2] *e.g.* in the Thuja conifers, some penicillin moulds, and the autumn crocus.

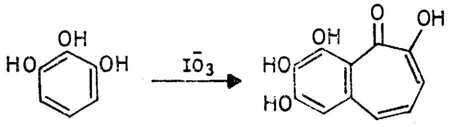

(I)

Dewar [1] rationalised the properties of tropolone and predicted that it should undergo ready electrophilic substitution and generally resemble phenol. In fact electrophilic attack is more or less confined to the 5-position and tropolones have additional possibilities of nucleophilic substitution as well as ring-opening reactions [2] (Scheme 1).



SCHEME 1

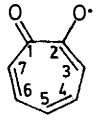
Previous work on radicals containing the tropolone skeleton has largely been confined to the di- and trihydroxybenztropolones [3,4] - the most well-known of which is purpurogallin (II) (easily formed from pyrogallol). Until recently [5] no e.s.r. spectra of directly related radicals had been reported, though radicals containing the tropone skeleton [6,7] have been observed. A spectrum ascribed to the semiquinone of purpurogallin [3] has subsequently proved to be due to that of pyrogallol (see later).



(II)

TABLE 1

E.s.r. parameters (a/mT) of radicals from Ce^{IV} oxidation of tropolones (splittings for the corresponding phenoxyl radicals in parentheses)



Substituents	a_3	a_4	a_5	a_6	a_7
	0·7 (0·66)	0·25 (0·18)	1·03 (1·02)	0·25 (0·18)	0·7 (0·66)
4-Pr^i (β-Thujaplicin) *	0·625 (0·59)	a_H 0·10 (0·08)	1·05 (1·02)	0·25 (0·18)	0·725 (0·70)
6-$CH_2{\cdot}CO_2H$,7-CO_2H	0·725	0·275	1·05	a_{CH_2} 0·113	
4,7-$(CO_2H)_2$,6-$CH_2{\cdot}CO_2H$	0·77		1·00	a_{CH_2} 0·117	
4,6,7-$(CO_2H)_3$	0·75		1·00		

* Assignments made by comparison with the corresponding phenoxyl radical, which we have studied together with its isomers.

With the phenol-like properties of tropolone in mind, we oxidised it in a flow system with cerium(IV) and were able to observe tropolone analogues of phenoxyl and some accessible derivatives, showing that the balance between production and destruction is similar for the two types of radical. The e.s.r. parameters of the tropolonyl radicals are, surprisingly, nearly the same as those of the corresponding phenoxyl radicals,[8] the main difference being a larger value of what we assume is negative spin density at the '*meta*'-position of the seven-membered ring radical. It seems that the two carbon–oxygen groups of tropolonyl behave as if they were only one, and this can be partly rationalised by

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[1] M. J. K. S. Dewar, *Nature*, 1945, **50**, 141, 479.

[2] P. L. Pauson, *Chem. Rev.*, 1955, **55**, 9.

[3] P. D. Collier, *J. Chem. Soc.* (*C*), 1966, 2255.

[4] P. D. Collier, *J. Chem. Soc.* (*C*), 1969, 612.

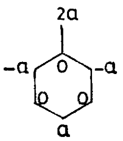
[5] W. T. Dixon, W. E. J. Foster, and D. Murphy, *Mol. Phys.*, 1974, **27**, 1709.

[6] T. Toda, E. Mori, and K. Murayama, *Bull. Chem. Soc. Japan*, 1972, **45**, 1852.

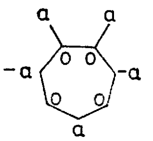
[7] G. A. Russell and G. R. Stevenson, *J. Amer. Chem. Soc.*, 1971, **93**, 2432.

[8] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 213.

comparison with simple MO models consisting of corresponding frameworks of carbon $2p_\pi$ orbitals: both in the model system for phenoxyl (i) and in that for tropolonyl (ii) the odd electron occupies a non-bonding orbital.[9]

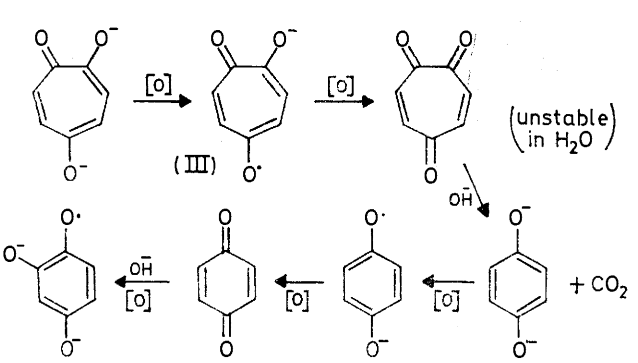


(i) Alternant model for phenoxyl (*i.e.* benzyl) with NBO coefficients (a = $1/\sqrt{7}$)

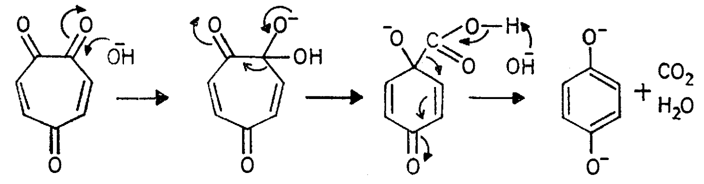


(ii) Corresponding model for tropolonyl (a = $1/\sqrt{5}$)

Analogues of p-*Semiquinones*.—Pressing the analogy between phenol and tropolone still further, we prepared 5-hydroxytropolone in the hope of obtaining a relatively stable radical, in alkaline solution, which could resemble *p*-semiquinone. In faintly alkaline solution an e.s.r. spectrum identical with that of *p*-benzosemiquinone was obtained, which in more alkaline solution was quickly replaced by the familiar spectrum of hydroxysemiquinone.[10] Evidently the seven-membered ring must have contracted. The most likely explanation for this is that since tropolone or its simple derivatives are stable at ordinary temperatures, and require drastic conditions for ring contraction, oxidation to the unstable quinone may have occurred (Scheme 2). The mechanism for the loss of CO_2 could be as shown in Scheme 3. This is similar to other mechanisms proposed for the production of six-membered rings from tropone and tropolone derivatives.[2]



SCHEME 2



SCHEME 3

The ring contraction step could result in the formation of the anion of 2,5-dihydroxybenzoic acid. However, experiments carried out with this acid under similar conditions did not lead to the above pattern of radical products, and only the spectrum of the primary radical (IV) was observed. When the solutions were made strongly alkaline some decarboxylation did occur, however. This evidence is consistent with the decarboxylation of the tropoquinone being concerted with the formation of the six-membered ring as indicated in the suggested mechanism.

The foregoing results by no means prove that the radical (III) is in fact formed, though it does seem likely that it exists for a short time. In order to detect this intermediate we resorted to an aprotic solvent,[11] hexamethylphosphoramide (HMPA), in which it seems that many free radicals are much longer-lived than in aqueous solutions.* It appears that by using the sparingly soluble sodium methoxide in conjunction with this solvent, the base concentration can be kept low enough to slow down the overall oxidation rate without preventing the first step. We obtained spectra from hydroxytropolone and hydroxythujaplicin, which correspond to tropolone analogues of the *p*-semiquinones and which decayed in the former case to give *p*-benzosemiquinone. The results are summarised in Table 2. The primary radical from 5-hydroxy-3,4-benztropolone (V) was not observed even in HMPA; only the corresponding naphthosemiquinone (VI) was obtained.

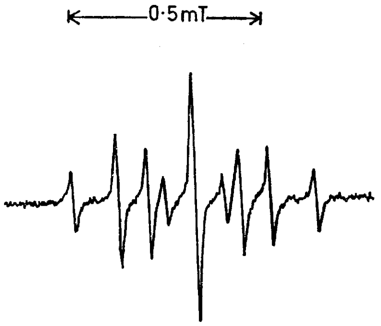


FIGURE 1 E.s.r. spectrum of the tropolone analogue of *p*-benzosemiquinone

Radicals from Di- and Tri-hydroxybenztropolones.—These hydroxylated benztropolones are formed by the interaction of *ortho*-quinones with pyrogallol or an appropriate derivative. They behave in two distinct

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* We have, for example, observed the semiquinone of 2,6-dihydroxynaphthalene [coupling constants 0·42, 0·13, and 0·07 mT (all twice)] in this solvent, whereas only degradation products could be detected in aqueous solutions.

[9] See, *e.g.* N. V. Riggs, ' Quantum Chemistry,' Macmillan, London, 1969, ch. 5, p. 160.

[10] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1972, 1130.

[11] H. Normant, *Angew. Chem. Internat. Edn.*, 1967, **6**, 1046.

TABLE 2

E.s.r. spectra from autoxidation of 5-hydroxytropolones; assignments made by comparison with the benzenoid cases (effects of the isopropyl group assumed to be similar to those of methyl)

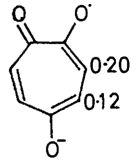
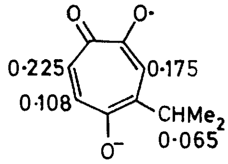
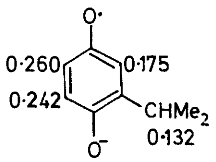
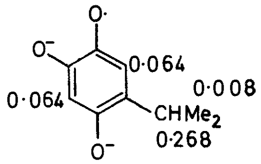
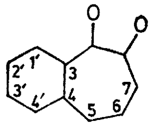
Starting material	Solvent	Radical(s)
5-Hydroxytropolone	HMPA	
	H_2O	*p*-Benzosemiquinone (0·235 × 4) Hydroxysemiquinone (0·06, 0·48, 0·135)
5-Hydroxy-4-isopropyl tropolone	HMPA	
	H_2O	 
5-Hydroxy-3,4-benztropolone	HMPA H_2O	Naphthosemiquinone (0·33, 0·025, 0·065) Naphthosemiquinone (0·33, 0·058, 0·065)

TABLE 3

E.s.r. parameters (a/mT) from 3,4-benztropolones

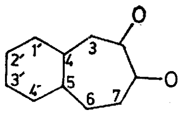


(a) Oxidation by Ce^{IV} in acid solution; corresponding naphthoxyl splittings in parentheses

(b) Autoxidation in aqueous alkaline solution

Substituents		a_7	a_6	a_5	$a_{4'}$	$a_{3'}$	$a_{2'}$	a_1
	(a)	0·85 (0·825)	0·25 (0·175)	1·05 (1·075)	0·25 (0·25)	0·10 (0·065)	0·25 (0·25)	0·0 (0·0)
1',2'-$(OH)_2$,6-CO_2H	(a)	0·75		1·00	0·065	0·065		
	(b)	0·013		0·05	0·358	0·045		
1',2'-$(OH)_2$,6-CO_2Et	(a)	0·70		1·025	0·081	0·081		
	(b)	as with 6-CO_2H						
1',2'-$(OH)_2$, 3'-Me,6-CO_2H	(a)	0·775		1·025	0·07	a_{Me} 0·07		
	(b)	0·013		0·013	0·46	a_{Me} 0·013		
1',2'-$(OH)_2$, 4'-Me,6-CO_2H	(a)	0·75		1·025	a_{Me} 0·086	0·086		
	(b)	0·03		0·085	a_{Me} 0·049	0·0		
1',2',3'-$(OH)_3$ (purpurogallin)	(a)	0·70	0·25	0·90	0·85			
	(b)	0·055	0·28	0·075	0·11			
1',2',3'-$(OH)_3$,6-CO_2H	(a)	0·75		0·925	0·85			
	(b)	0·05		0·05	0·145			

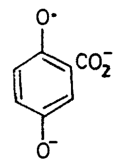
Spectrum from 4,5-benztropolone:



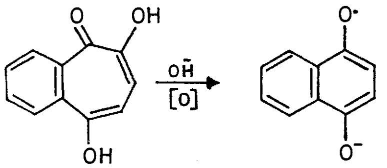
(a) a_3 1·04 (1·075), a_7 0·15 (0·145), a_6 0·0 (0·0), a_4 0·11 (0·145), $a_{3'}$ 0·56 (0·54), $a_{2'}$ 0·06 (0·12), $a_{1'}$ 0·48 (0·43).

ways, depending on the conditions, and therefore form a class of their own.

(a) *Autoxidation in alkaline solutions.* As one might expect by analogy with hydroxylated naphthoquinones, in alkaline solution semiquinones are formed in which spin densities generally differ little from those observed



(IV)



(V) (VI)

(or expected) for the corresponding naphthosemiquinones[12] (see Table 3).

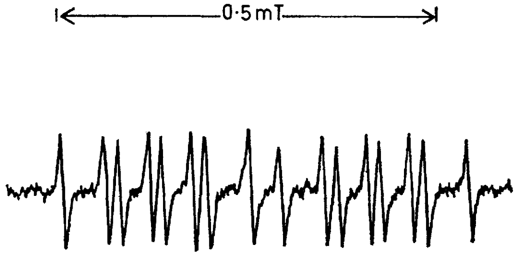
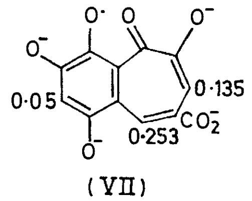


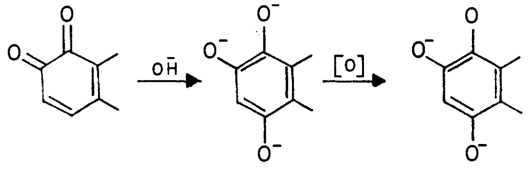
FIGURE 2 E.s.r. spectrum of purpurogallosemiquinone

The authentic e.s.r. spectrum of the semiquinone from purpurogallin is clear and long-lived and we would expect to see it if purpurogallin were a major intermediate in the autoxidation of 1′,2′-dihydroxy-3,4-benztropolone as suggested previously.[4] Secondary radicals are formed in the autoxidations of derivatives of this last compound, and in one case we obtained a pure spectrum which we ascribe tentatively to the

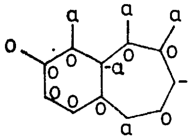


(VII)

species (VII). No secondary radicals were observed when the 4′-position was blocked by a methyl group. These results suggest that the secondary radicals are derived from the quinone in the usual way rather than by oxygenation at the 3′-position.[4]

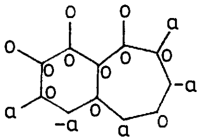


(b) *Spectra in acidic solution.* Oxidation by cerium(IV) in the flow system took place under acidic conditions, and completely different patterns of coupling constants were observed (see Table 3). The spectra can be rationalised by looking upon these radicals as being derived from the tropolone unit, which in protonated molecules seems to be the most easily oxidised part. The patterns of coupling constants can be explained as before with the help of simple hydrocarbon models: thus for 1′,2′-dihydroxy-3,4-benztropolone, the NBO coefficients are as shown in (iii), and for the purpurogallin model as shown in (iv). It appears that the presence of the 3′-oxygen atom in purpurogallin makes a different pattern of delocalisation possible.



($a = 1/\sqrt{6}$)

(iii)



($a = 1/\sqrt{5}$)

(iv)

EXPERIMENTAL

Commercial samples were purified by vacuum sublimation. 3,4-Benztropolone,[13] 4,5-benztropolone,[14] 1′,2′-dihydroxy-3,4-benztropolones,[15] 4-hydroxytropolones,[16] the tropolone carboxylic acids,[3] and purpurogallin carboxylic acid[17] were prepared by literature methods. The conditions and flow system for the cerium(IV) oxidations were as previously reported,[18] and the autoxidations were conducted in the usual way for generating semiquinones.[10]

[4/861 *Received*, 30*th April*, 1974]

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[16] W. D. Crow, R. D. Haworth, and P. R. Jeffries, *J. Chem. Soc.*, 1952, 3705.

[17] W. D. Crow and R. D. Haworth, *J. Chem. Soc.*, 1951, 1325.

[18] W. T. Dixon, W. E. J. Foster, and D. Murphy, *J.C.S. Perkin II*, 1973, 2124.