ESR and ENDOR Spectroscopy of Furan Radical Cations Obtained by Cyclisation of 1,4-Diketones in Electrophilic Media

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Identical ESR spectra are obtained when either (*Z*)-1,2-dibenzoylethylene (**1**) or (*E*)-1,2-dibenzoylethylene (**2**) react with sulphuric acid or aluminium trichloride in dichloromethane. Both spectra are identified as those of the 2,5-diphenylfuran radical cation $(\mathbf{8})^{+\bullet}$. This means that the *E*-isomer (**2**) isomerises to the *Z*-isomer (**1**). An intramolecular reaction leading to the furan ring follows. Identical behaviour has been found with the (*Z*)- and (*E*)-*p*-methyl substituted dibenzoylethylenes (**3**) and (**4**) as well as with 1,2-dibenzoylethane (**5**), 4,5-dibenzoylcyclohexene (**6**) and *o*-dibenzoylbenzene (**7**). All these 1,4-diketones give, under the above conditions, the corresponding furan radical cations. All ESR spectra have been interpreted and the assignments of the hyperfine splitting constants (hfs) are based on Hückel–McLachlan calculations except for the 4′,4″- and 3,4-positions where the assignments come directly from methyl and chlorine substitution respectively. ENDOR and TRIPLE resonance experiments with the radical cation $(\mathbf{9})^{+\bullet}$ allowed the determination of the relative signs of the hfs. A mechanism for the cyclisation is proposed.

The spectroscopic properties of cation radicals have been reviewed,[1,2] as well as the kinetics and mechanisms of their reactions.[3–5] This increasing interest in ion radical chemistry is due to evidence provided by modern experimental techniques including ESR which shows the existence of radical intermediates in various reactions where the mechanism had been believed to involve only pairwise electron transfer.[3–5]

Due to their low ionization potentials, aromatic and heteroaromatic compounds are easily oxidised to the corresponding radical cations by reaction with either concentrated sulphuric acid or with other electrophilic reagents such as aluminium trichloride in dichloromethane or in nitromethane. The radical cations derived from aliphatic compounds as esters, ketones or aldehydes are more difficult to study and these have only been referred to in the literature when obtained by γ-irradiation in a rigid $CFCl_3$ matrix.[6–12]

There is no reference to the generation of radical cations derived from non-enolizable aromatic ketones in solution which is probably due to their comparatively higher ionization potentials. In this paper we refer to the radicals observed by ESR spectroscopy in solutions obtained by the reaction of 1,4-diketones with strong electrophiles. Since the radical cations of the structurally unchanged 1,4-diketones seem to be very inaccessible, it is expected that the radicals observed have a different molecular structure than the original diketones. When interpreting the ESR spectra observed, the possibility of cyclization to a furan ring has to be considered, analogous to well known examples from heterocyclic syntheses, as well as the high stability mentioned above of radical cations derived from aromatic heterocycles.

Results and Discussion

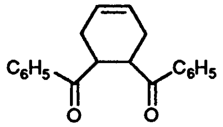
The reaction of 1,4-unsaturated diketones (1)–(4) with strong electrophilic reagents, such as concentrated sulphuric acid or aluminium trichloride in dichloromethane at 298 K, led to the formation of intensely coloured solutions with ESR spectra which did not change over several days. For diketones (1)–(4) the same spectra were obtained both from the *Z*- and *E*-isomers. The ESR spectra are well resolved and have been simulated with the values of the hyperfine splitting constants (hfs) shown in the Table. The relative signs of the hfs have been determined by studying the enhancement of ENDOR signals in general TRIPLE resonance experiments. The structures of the radicals and assignments of hfs are based on the discussion presented below.

$[\,p\text{-}R(C_6H_4)COCH=\,]_2$

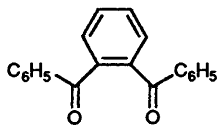
(1) – (4)

$(C_6H_5COCH_2-)_2$

(5)



(6)



(7)

- (1) R = H (*Z*)-1,2-dibenzoylethylene
- (2) R = H (*E*)-1,2-dibenzoylethylene
- (3) R = CH_3 (*Z*)-1,2-di-(*p*-toluoyl)ethylene
- (4) R = CH_3 (*E*)-1,2-di-(*p*-toluoyl)ethylene
- (5) 1,2-dibenzoylethane
- (6) 4,5-dibenzoylcyclohexene
- (7) *o*-dibenzoylbenzene

In order to interpret the spin density distribution obtained, theoretical calculations of spin densities were performed. Although many more modern methods for molecular orbital calculations are available, the spin densities obtained from the Hückel–McLachlan approximation can only occasionally be improved by the use of other methods, when one is dealing with planar, conjugated π-systems. For the identification purposes described below they are largely sufficient.

Table. Experimental and calculated hfs, in mT, for radical cations derived from compounds (1)–(12) (Q^{H}_{CH} −3.0 mT; $Q^{H}_{C-CH_3}$ 3.5 mT).

Compd.		Position					
		3,4	2′,2″	3′3″	4′,4″	5′,5″	6′,6″
(1); **(2)**; **(5)**; **(8)**	Exp.[a]	−0.236	−0.238	+0.069	−0,335	+0.073	−0.270
	Exp.[b]	−0.241	−0.242	+0.070	−0.341	+0.075	−0.275
	Calc.[c]	−0.233	−0.237	+0.075	−0.308	+0.098	−0.270
(3); **(4)**; **(9)**	Exp.[a]	−0.224	−0.224	+0.050	+0.423(6H)	+0.058	−0.278
	Calc.[d]	−0.232	−0.231	+0.064	+0.362(6H)	+0.090	−0.263
(10)	Exp.[a]	0.050	−0.235	+0.050	−0.345	+0.072	−0.270
	Calc.[e]	0.044	−0.233	+0.072	−0.308	+0.095	−0.267
(6); **(11)**	Exp.[f]	−0.320(4H)	−0.230	+0.064	−0.310	+0.072	−0.237
	Calc.[g]	+0.316(4H)	−0.240	+0.080	−0.299	+0.091	−0.256
(7); **(12)**	Exp.[a]	$a_{5.6}$ 0.073 $a_{4.7}$ 0.178	0.213	0.076	0.270	0.144	0.241
	Calc.[h]	$a_{5.6}$ 0.088 $a_{4.7}$ 0.180	−0.239	+0.088	−0.299	+0.098	−0.247

[a] Reaction with $AlCl_3$–CH_2Cl_2 at room temperature. [b] Reaction with 98% H_2SO_4 at room temperature. [c] $\gamma_{23} = \gamma_{45} = 1.1$; $\gamma_{21'} = \gamma_{51''} = \gamma_{34} = 1.05$; $\delta_2 = \delta_5 = 0.25$; $\delta_{2'} = \delta_{2''} = 0.1$; $\delta_O = 2.5$. [d] The same parameters as in (*c*) and $\delta_{4'} = \delta_{4''} = -0.1$. [e] The same parameters as in (*c*) and $\delta_{Cl} = 2.0$ and $\gamma_{3.Cl} = \gamma_{4.Cl} = 0.4$; $a_{Cl} = 0.188\ a_H$. [f] Reaction with $AlCl_3$–CH_2Cl_2 in the temperature range 180 K–220 K. [g] $\gamma_{23} = \gamma_{45} = 1.1$; $\gamma_{12} = \gamma_{15} = \gamma_{34} = 0.9$; $\delta_2 = \delta_5 = 0.2$; $\delta^{2'} = \delta_{2''} = +0.05$; $\delta_3 = \delta_4 = -0.05$; $\delta_O = 2.5$. [h] $\gamma_{12} = \gamma_{15} = 0.9$; $\gamma_{1.1'} = \gamma_{31''} = \gamma_{2'3'} = \gamma_{2''3''} = \gamma_{5'6'} = \gamma_{5''6''} = 1.05$; $\gamma_{18} = \gamma_{30} = \gamma_{1'2'} = \gamma_{1''2''} = \gamma_{3'4'} = \gamma_{3''4''} = \gamma_{4'5'} = \gamma_{4''5''} = \gamma_{1'6'} = \gamma_{1''6''} = 0.95$; $\delta_1 = \delta_3 = 0.15$; $\delta_{2'} = \delta_{2''} = +0.15$; $\delta_O = 2.5$.

We have assumed in these calculations, the following different structures for a hypothetical radical cation primarily derived from diketone (**1**) or (**2**): (*a*) a wholly planar structure, with the single correction in the Coulomb and resonance parameters of the oxygen atoms and carbonyl bonds; (*b*) a slight twist in the phenyl rings (γ_{CC} 0.9) besides the corrections referred to in the previous hypothesis; and (*c*) besides the preceeding corrections, two additional Coulomb parameters in the two *ortho*-phenyl carbon atoms nearer to the oxygen atoms (δ_C +0.05).

The Coulomb parameters for oxygen δ_O used in the calculations were varied between 2.0 and 2.5 (the value δ_O 2.5 is given by Streitwieser[13] for O^+). For the resonance parameter γ_{CO} 1.6 was taken, as usually given in the literature for carbonyl bonds in radical anions.

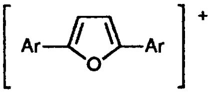
In the first two hypotheses, the calculations led to a molecular orbital (MO) pattern where the three highest occupied MOs, in the ground state, are fully degenerated. The identical energies of these three MOs render McLachlan's results meaningless (some terms in the calculations become infinite). In the third hypothesis, an electrostatic perturbation of the Coulomb integrals of only those two *o*-phenyl carbon atoms which are nearest to the oxygen was taken into account. This is equivalent to assuming a restricted rotation of the phenyl rings, in accordance with the literature for similar compounds. The introduction of these two Coulomb parameters has the advantage of changing the symmetry of the molecule, thus removing the degeneracy in the MO pattern referred to above. Nevertheless, the results of McLachlan's calculations do not agree at all with the experimental results. In particular the calculated length of the ESR spectrum is about 6.5 mT while the experimental one is only 2.44 mT.

These results suggest that the observed, probably cationic, radical may not correspond to one with the initial diketone structure, but to a species where some structural change has occurred. This hypothesis is consistent with the known experimental difficulty of oxidizing non-enolizable aromatic ketones, due to their high oxidation potentials.

In order to obtain more information about the possible structure of this radical cation, the oxidation products derived from (**1**) and (**2**) by reaction with aluminium chloride in dichloromethane, followed by work-up, were analysed by HPLC.

In the chromatograms a peak corresponding to 2,5-diphenylfuran, together with the peak of the unchanged diketone, can be seen. When a mixture of diketones (**1**) and (**2**) is used in the reaction, the relative percentage of the unchanged ketones changes. The peak corresponding to the *Z*-isomer (**1**) is smaller than the peak corresponding to the *E* isomer (**2**), which shows a much faster reaction of (**1**) than (**2**).

To sequence this observation, new spin density calculations have been performed for all five radical cations with the furan framework (**I**). The calculated spin distributions were in good

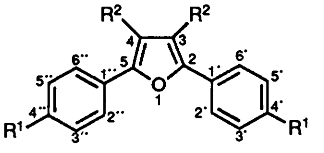


(**I**)

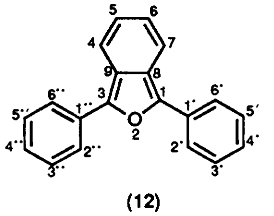
agreement with the experimentally observed ones, as shown in the Table. The structure of the radical cations referred to above, was further substantiated by cyclic voltammetry and ESR studies of several radical cations derived from 2,5-diarylfurans (**8**)–(**10**).

When 2,5-diarylfurans (**8**) or (**9**) undergo anodic oxidation in dichloromethane–trifluoroacetic acid–trifluoroacetic acid anhydride, containing $Bu_4N^+ClO_4^-$ (0.01 mol dm^{-3}) at room temperature, reversible waves are obtained with half-wave potentials $E_{\frac{1}{2}}$ 1.1 V and $E_{\frac{1}{2}}$ 0.8 V *vs.* SCE respectively, corresponding to the furan radical cations. For furan (**8**) a second irreversible wave with E_p 1.9 V (200 mV s^{-1}), probably corresponding to the oxidation of the radical cation to the dication, is observed. The irreversibility of this wave may correspond to a reaction of the dication with some nucleophile present in this medium. For furan (**9**) the corresponding second wave can be considered reversible with $E_{\frac{1}{2}}$ 1.5 V. These results show that furan (**9**) is not only more easily oxidized than (**8**), but the corresponding dication is more stable than that derived from (**8**), as expected, due to the electron releasing effect of 4′,4″-dimethyl substitution.

When diketone (**1**) is anodically oxidized under the same



(8) - (11)



(12)

(8) $R^1 = R^2 = H$ 2,5-diphenylfuran
(9) $R^1 = CH_3$; $R^2 = H$ 2,5-di-*p*-tolylfuran
(10) $R^1 = H$; $R^2 = Cl$ 3,4-dichloro-2,5-diphenylfuran
(11) $R^1 = H$; $R^2\text{–}R^2 = CH_2CH{=}CHCH_2$ 4,7-dihydro-1,3-diphenylisobenzofuran
(12) 1,3-diphenylisobenzofuran

conditions described above, a reversible wave can be observed, with the same $E_{\frac{1}{2}}$ value as (**8**), which may be due to the presence of a furan radical cation.

By oxidation of (**8**)–(**10**) either with concentrated H_2SO_4 or with $AlCl_3$ in CH_2Cl_2, stable radical cations were immediately obtained. As expected, they give rise to ESR spectra superimposable with the ones derived from the corresponding ethylenes. An identical *g*-value is also obtained for the radical cations derived from compounds (**1**), (**2**), or (**8**) (*g* 2.0040 ± 0.0001).

In order to exemplify the above statements, we include Figure 1, where the ESR spectrum of the radical cations obtained from (**1**) or (**2**) [Figure 1(*a*)] together with the ESR spectrum of $(\mathbf{8})^{+\bullet}$ [Figure 1(*b*)] and their simulation [Figure 1(*c*)] are shown.

All the hfs shown in the Table were obtained by successful simulation of the ESR spectra of the radical cations generated from the compounds (**1**)–(**4**) and (**8**)–(**10**). The Table also shows the theoretical values obtained by the Hückel–McLachlan method.

ENDOR and TRIPLE resonance experiments with the radical cation $(\mathbf{9})^{+\bullet}$ where the 4′,4″ positions are methyl-substituted allow the unambiguous assignment of the largest proton hfs to the 4′,4″ positions. The relative signs of the proton hfs were also determined by the general TRIPLE resonance spectrum of $(\mathbf{9})^{+\bullet}$. The assignments of the hfs to the 3,4 positions in the furan ring were based on the simulation of the ESR spectra of $(\mathbf{10})^{+\bullet}$ where 3,4 positions are substituted by chlorine. The assignments to the other positions were based on the hfs calculated by McLachlan's method.

The present study was extended to diketones (**5**)–(**7**), where the 1,2-double bond was substituted either by a single bond or by an aromatic bond, as well as to the furans (**11**) and (**12**). By reaction of compound (**5**) with either concentrated H_2SO_4 or $AlCl_3$–CH_2Cl_2, the radical cation $(\mathbf{8})^{+\bullet}$ is readily obtained. The reaction of (**6**) and (**11**) under the above conditions also gives rise to the same radical cation $(\mathbf{11})^{+\bullet}$ at 180 K–220 K. Above 220 K $(\mathbf{11})^{+\bullet}$ is converted by aromatization into the much more stable radical cation $(\mathbf{12})^{+\bullet}$, identical with the one obtained directly from (**12**) as well as from (**7**). The experimental and calculated hfs of $(\mathbf{11})^{+\bullet}$ and $(\mathbf{12})^{+\bullet}$, are shown in the Table [the assignment for $(\mathbf{12})^{+\bullet}$ was only based on spin density calculations].

The first noteworthy feature of our experiments lies in the observation of the same ESR spectrum, and hence the same radical cation, whether we start from (*Z*)- or (*E*)-dibenzoylethylene (**1**) or (**2**). Another interesting feature is the assignment of the radical cations thus obtained to 2,5-diphenylfuran radical cation $(\mathbf{8})^{+\bullet}$, which means that an isomerisation of the *E*-isomer to the *Z*-isomer occurred. This rearrangement may take place after the first protonation of the diketone, as discussed below. In that cation, the activation energy for the isomerisation may be lower than in the neutral molecules owing to the higher single bond character of the central ethylenic bond.

Some Considerations on the Mechanism.—Many aromatic compounds dissolve in sulphuric acid and become oxidized to their radical cations. The compounds that are not oxidized easily, as the diketones studied in the present work, are known to be protonated in this medium. The protonation of either (**5**) or (**6**) catalyses the establishment of the keto–enol equilibrium. The monoenolic form of the diketone is therefore rapidly replaced when it is removed from the equilibrium by an irreversible process. The first step may be either the acceptance of a proton or an oxidation to the enol radical cation. The first hypothesis seems the most plausible because the enolic radical cations have not been observed by us even at temperatures as low as 180 K. In these protonated enols, the cyclization is the preferred pathway since aromatic compounds can be obtained by loss of a water molecule. The further oxidation of these furans is easily accomplished in this medium, leading to the observed furan radical cations. The same reasoning applies when $AlCl_3$ is the electrophile. In this medium, instead of protonation, a complex with $AlCl_2^+$ is formed and the furan ring is obtained by elimination of $AlCl_2OH$. The cyclization of enolizable 1,4-diketones, in strong electrophilic media, is known in the literature as the Paal–Knorr synthesis of furans.[14,15]

The cyclization of 1,4-diaroylethylenes (**1**)–(**4**) or *o*-diaroylbenzenes such as (**7**), in strong electrophilic media is, however, not so easily interpreted. By the same reasoning presented for the preceeding diketones (**5**) and (**6**), we consider that the first step is the protonation (or $AlCl_2^+$ complexation) leading to a cation. In solution the cations can either lose a proton or react with a nucleophile in order to become a neutral species. Unlike the diketones (**5**) and (**6**), these diketones do not have any easily removable protons. On the other hand, the free water content and the concentration of other nucleophiles such as SO_4^{2-} and HSO_4^- ions (or Cl^- ion) are very small. Therefore, the more plausible pathway consists of an intramolecular nucleophilic addition to the γ-carbonyl group, with the formation of a cyclic cation. When the starting diketone is the *E*-isomer an isomerization must take place, since this cyclization occurs in the *Z*-configuration of the cation. The presence of an OH (or $OAlCl_2$) group bonded to an sp^3 carbon atom (and therefore out of the conjugated part of the molecule where the positive charge is delocalized) allows another protonation and a dication can be formed by loss of a water molecule [or $(AlCl_2)_2O$]. These dications are easily reduced first, to the radical cation, and later to the furans by accepting electrons from the medium. The SO_4^{2-} and HSO_4^- (or Cl^-) ions may be the reducing agents by conversion into the more oxidized forms $S_2O_8^{2-}$ or $S_2O_8H_2$ (or Cl_2).

Experimental

Materials.—The compounds (**1**)–(**12**) were synthesized and purified in this laboratory by known techniques.[16–21] 98% sulphuric acid, was used as supplied (Merck). Commercial aluminium trichloride (Merck) was sublimed under high vacuum into the sample tube. Dichloromethane (Merck) was distilled in the vacuum line from a tube where it had been kept over molecular sieves 3A (Fluka), after distillation under argon. Trifluoroacetic acid and trifluoroacetic acid anhydride (spectroscopic grade, BDH) were used without further purification.

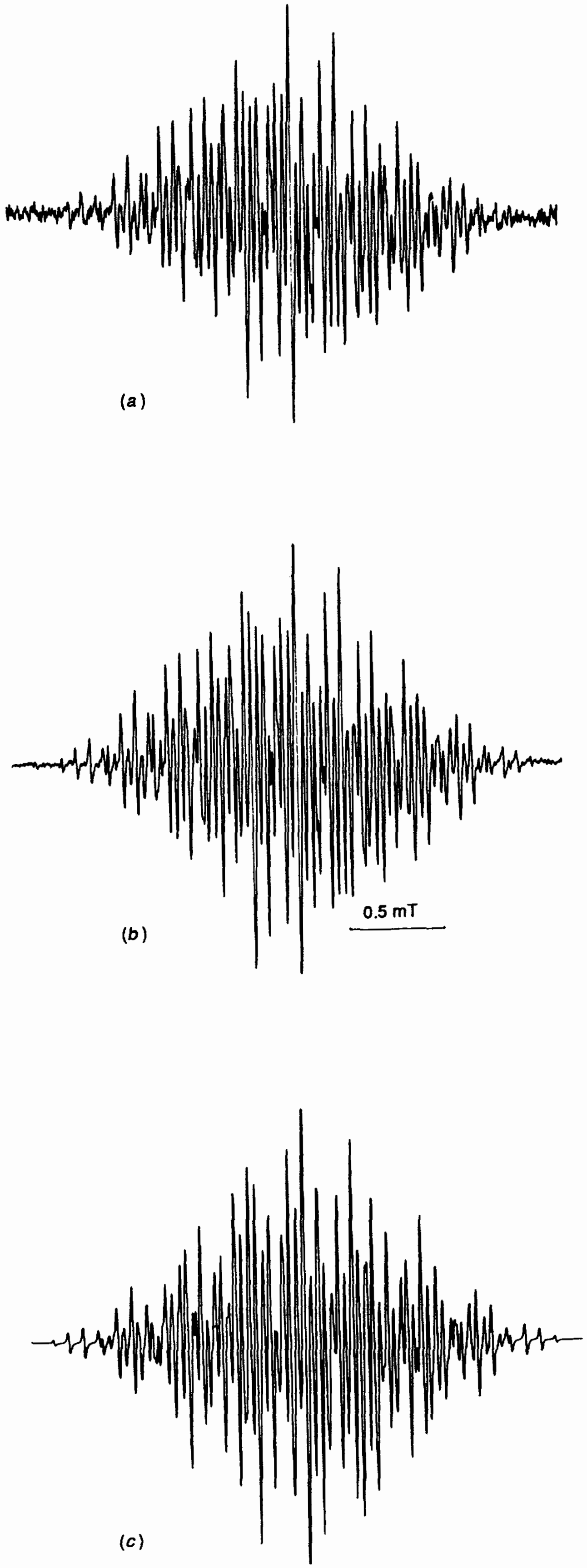
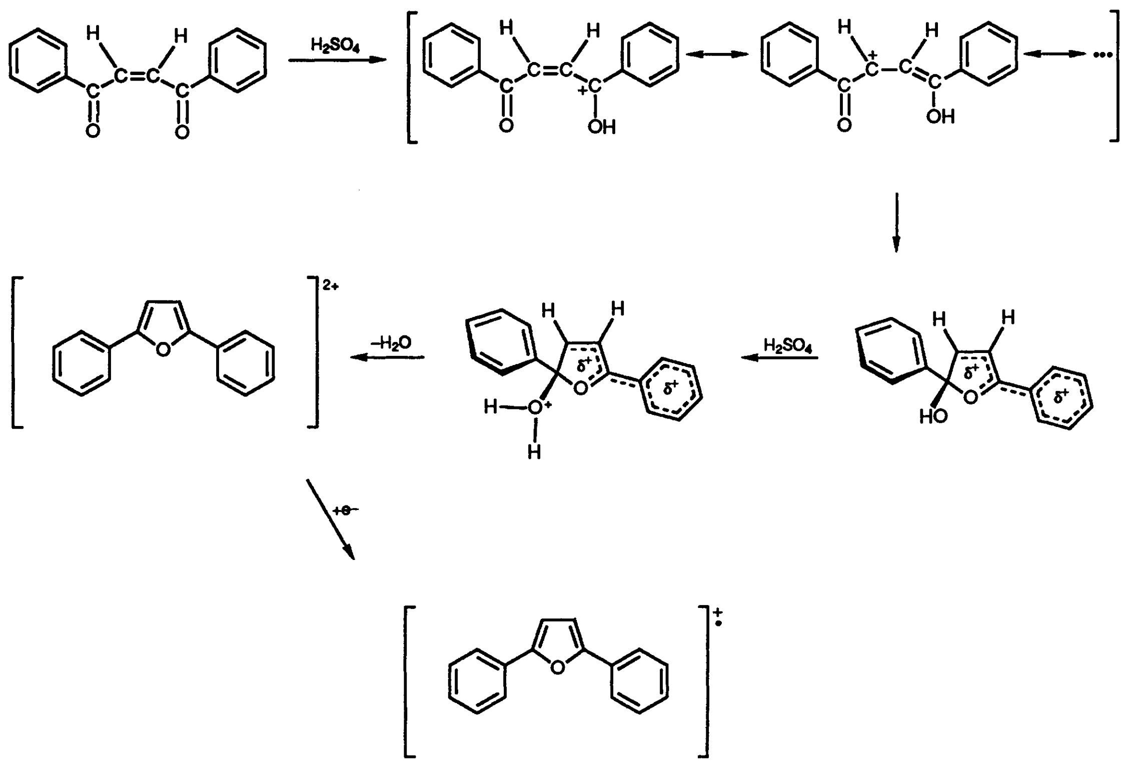


Figure 1. Experimental (*a*), (*b*) and simulated (*c*) spectra of the radical cation $(\mathbf{8})^{+\bullet}$. (*a*) Obtained from reaction of (**1**) with 98% H_2SO_4. (*b*) Obtained from reaction of (**8**) with 98% H_2SO_4. (*c*) Simulated with linewidth: 0.007 mT.



Scheme.

Tetrabutylammonium perchlorate (BDH) was dried *in vacuo* at 100 °C using P_2O_5 as a drying agent.

Procedure.—The radical cations generated by dissolving the compound in 98% sulphuric acid were introduced into a capillary tube for ESR analysis. The reactions with $AlCl_3$ in CH_2Cl_2 were carried out in a Schlenk tube containing the compound to be oxidized and, in a side arm, the $AlCl_3$. The tube was connected to a vacuum line, the $AlCl_3$ was sublimed and CH_2Cl_2 was distilled under high vacuum.

ESR spectra were recorded and simulated on an ER 200 D Bruker spectrometer, equipped with a variable temperature unit ER 400 VT. ENDOR and TRIPLE resonance spectra were run on a Bruker EN 810 spectrometer. Cyclic voltammetry was performed on a Princeton Applied Research (PAR) potentiostat–galvanostat model 173, with current follower model 176 and universal programmer model 175, at room temperature using $Bu_4N^+ClO_4^-$ (0.1 mol dm^{-3}) as the support electrolyte. The working electrode was a platinum gauze and the auxiliary electrode was a platinum wire. The values are reported in volts (±0.2) relative to SCE, measured by using a ferrocene$^{0/+}$ couple as an internal reference (with $E_{\frac{1}{2}}$ +0.55 V *vs.* SCE).

HPLC product analysis was made with a 10 μm particle size silica gel Lichrosorb Si60 column of 4 mm inner diameter and 250 mm length. Hexane with 0.5% 1,4-dioxane was used as the eluant. A UV detector was tuned to 230 nm. For determination of concentrations an internal standard was used.

The solutions of the radical cations to be analysed by HPLC were obtained as follows: the radical cations were generated by oxidation with $AlCl_3$–CH_2Cl_2, as described above, in one arm of a triple vacuum-sealed Schlenk tube, equipped with a sintered glass filter and a break-seal. The radical cation solution was filtered to the central arm and CH_2Cl_2 distilled off to the first arm which was then torched out. In the third arm a solution of either Cl_2Sn or naphthalene radical anion in THF was prepared in the vacuum line. This solution was added to the solid that remained in the central arm, through the break-seal. After some minutes of stirring, the tube was opened and the solvent evaporated, the residue obtained was then extracted with toluene and filtered.

References

1 A. J. Bard, A. Ledwith, and H. J. Shine, *Adv. Phys. Org. Chem.*, 1976, **12**, 155.
2 V. D. Parker, *Adv. Phys. Org. Chem.*, 1983, **19**, 131.
3 L. Eberson, L. Jönsson, and L.-G. Wistrand, *Tetrahedron*, 1982, **38**, 1087.
4 O. Hammerich and V. D. Parker, *Adv. Phys. Org. Chem.*, 1984, **20**, 55.
5 D. J. Cowley, *Org. React. Mech.*, 1984, 139.
6 M. C. R. Symons and P. J. Boon, *Chem. Phys. Lett.*, 1982, **89**, 516.
7 M. Iwasaki, H. Muto, K. Toriyama, and K. Nunome, *Chem. Phys. Lett.*, 1984, **105**, 586.
8 H. Muto, K. Toriyama, K. Nunome, and M. Iwasaki, *Chem. Phys. Lett.*, 1984, **105**, 592.
9 P. J. Boon, L. Harris, M. T. Olm, J. L. Wyatt, and M. C. R. Symons, *Chem. Phys. Lett.*, 1984, **106**, 408.
10 P. J. Boon and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1213.
11 D. N. R. Rao, J. Rideout, and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1221.
12 M. D. Sevilla, D. Becker, C. L. Sevilla, and S. Swarts, *J. Phys. Chem.*, 1985, **89**, 633.
13 A. Streitwieser, Jr., 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961.
14 C. Paal, *Chem. Ber.*, 1885, **18**, 367.
15 L. Knorr, *Chem. Ber.*, 1885, **18**, 299.
16 J. B. Conant and R. E. Lutz, *J. Am. Chem. Soc.*, 1923, **45**, 1303.
17 R. Adams and M. H. Gold, *J. Am. Chem. Soc.*, 1940, **62**, 56.
18 R. E. Lutz and R. J. Rowlett, *J. Am. Chem. Soc.*, 1948, **70**, 1359.
19 R. E. Lutz and F. N. Wilder, *J. Am. Chem. Soc.*, 1934, **56**, 2145.
20 P. S. Bailey and R. E. Lutz, *J. Am. Chem. Soc.*, 1948, **70**, 2412.
21 R. Adams and R. B. Wearn, *J. Am. Chem. Soc.*, 1940, **62**, 1233.

Paper 9/04821I
Received 10*th November* 1989
Accepted 22*nd February* 1990