Interpretation of the EPR Spectrum of the Anion Radical of *trans*-1-Phenyl-1-propene*

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The radical presented in this paper is the anion radical of *trans*-1-phenyl-1-propene. It is formed by chemical reduction of the parent compound with sodium metal employing the usual high vacuum technique [1] (vacuum 10^{-4} mm Hg) in 1,2-dimethoxyethane solution. The EPR spectrum was run on a Varian E 3 model spectrometer, and care was taken to avoid saturation effects.

trans-1-Phenyl-1-propene was a commercial product from Fluka AG., chromatographically pure, distilled and dried over Molecular Sieve 4 A before use. The infrared spectrum run at room temperature between KBr disks and in the gas phase at 80 and 137°C on a Perkin Elmer 237 model spectrometer showed a very strong band at 963 cm^{-1}, which is typical of a *trans*-ethylenic group and caused by CH wagging vibrations. The band in the $730-650$ cm^{-1} region is probably due to ring bend vibrations and not to *cis*-ethylenic CC stretch, and the compound shows no *cis*-ethylenic absorption in the $1429-1397$ cm^{-1} region. The CC stretch absorption in the $1678-1668$ cm^{-1} region was very weak at 1665 cm^{-1}, giving further evidence for the *trans*-ethylenic configura-tion. The following bands in the $4000-650$ cm^{-1} region were recorded at room temperature between KBr disks (the figures in italics denote strong absorption); 3087, 3065, *3050*, 2965, 2940, 2920, 2857, 2737 (CH stretch in CH$_3$, ethylenic double bond and aromatic ring) 1950, 1875, 1800, 1770 (combination and overtone bands typical of monosubstituted benzene rings, spectrum run with the sample thicker than normal) 1668 (*trans*-ethylenic C=C stretch) *1601*, 1582, *1499*, *1445* (benzene ring stretching) 1332, 1305, 1280, (very weak unassigned bands, sample run thicker than normal) 1210, 1169, 1157, 1070, 1030 (very weak in plane hydrogen rocking typical of monosubstituted benzene rings, sample run thicker than normal) *963* (*trans*-ethylenic CH wagging) *735* (five adjacent H wagging vibrations) *690* cm^{-1} (ring bend vibrations). The assignments are made according to Colthup *et al.*[2]

Polarography of the compound in non-aqueous solvents indicates the molecule to have degenerate orbitals, only one wave at $E_{1/2} = -2.60$ V *vs.* SCE could be detected in dimethylsulphoxide, sulpholane, dimethylformamide, and acetonitrile solutions with tetrabutylammonium iodide as an electrolyte. Addition of water to the solutions did not affect the reduction potential. Accordingly, attempts to generate the radical electrolytically were not successful. The solution showed a yellow colour upon electrolysis, probably due to the formation of the dianion radical of the parent compound. These experiments are going to be continued.

Considerable difficulty was encountered in obtaining a mono-radical in detectable amounts from *trans*-1-phenyl-1-propene. Upon standing five days out of direct contact with the distilled sodium, the fairly concentrated (12 mg substrate, about 4 ml solvent) solution exhibited a pale yellow colour, the yellow solution giving the EPR signal recorded.

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* A preliminary communication on this subject was given by F.S. at the meeting of *Finska Kemistsamfundet*, 3rd of March 1969.
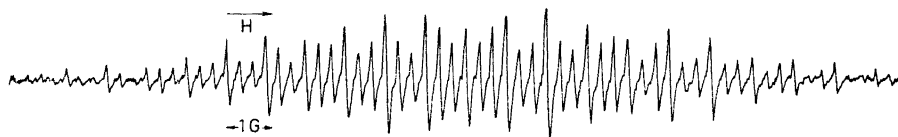

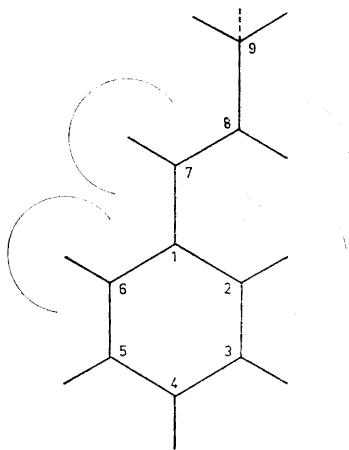*Fig. 1.* The EPR spectrum of the anion radical of *trans*-1-phenyl-1-propene.

Fig. 2. The Dreiding structural model of *trans*-1-phenyl-1-propene with van der Waals radii on the hydrogen atoms on carbon atoms 2, 6, 7, and 8.

asymmetry of the molecule. By this we mean that the five ring protons are non-equivalent, as are the two ethylenic protons, presumably because of steric hindrance. This is indicative of the hindered rotation about the 1,7-bond. The Dreiding structural model with van der Waals radii, Fig. 2, gives evidence for this assumption. Accordingly, only the three methyl protons in the side chain are equivalent.

Furthermore, comparison of the EPR spectra of the anion radicals of aceto-phenone and benzaldehyde fully assigned by Steinberger and Fraenkel [3] led us to the conclusion that the greatest spin density is localized to the methyl protons in the side chain, that the spin density at carbon atom 8 is greater than at 7, due to the interaction of the electron clouds of the hydrogen atoms on carbon atoms 2 and 8, that the density at 2 is greater than at 6 for the same reason, that the spin densities at 3 and 5 are small and the spin density at 4 is of the same magnitude as at 9 and considerably greater than other spin density values in the molecule. This means that one should get a $4 \times 2^7 = 512$ line EPR spectrum. The occurrence of eight splitting constants giving even splitting of the spectrum also explains the low intensity of the bands at the center of the spectrum.

The even spacing of the 69 lines in the experimental EPR spectrum with a constant distance of 0.29 G from each other,
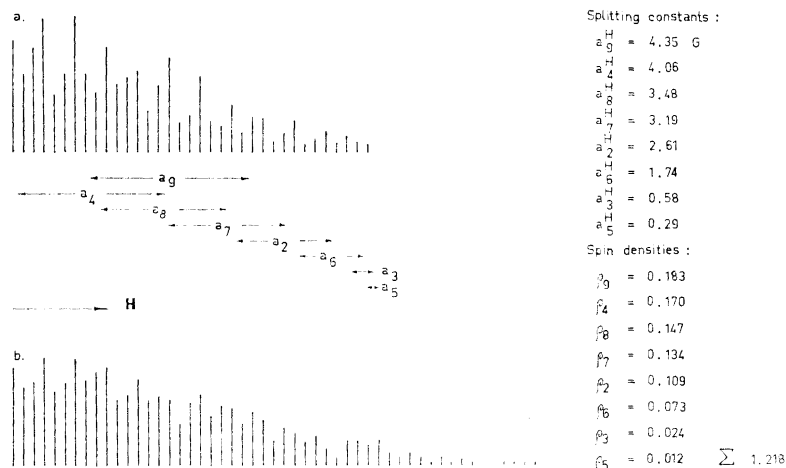
Attempts were also made to generate the radical by chemical reduction with lithium and potassium, but they were not successful, possibly for the same reason as above.

For the interpretation of the well-resolved 69-line EPR spectrum, Fig. 1, we took into consideration the interesting

Splitting constants :

a_9^H = 4.35 G
a_4^H = 4.06
a_8^H = 3.48
a_7^H = 3.19
a_2^H = 2.61
a_6^H = 1.74
a_3^H = 0.58
a_5^H = 0.29

Spin densities :

ρ_9 = 0.183
ρ_4 = 0.170
ρ_8 = 0.147
ρ_7 = 0.134
ρ_2 = 0.109
ρ_6 = 0.073
ρ_3 = 0.024
ρ_5 = 0.012 Σ 1.218

Fig. 3. "Stick" spectra of a) half of the experimental spectrum and b) half of the calculated spectrum of *trans*-1-phenyl-1-propene as well as the splitting constants and the spin densities.

led us to the conclusion that every coupling constant must be a multiple of this value. This also means that many of the lines will overlap each other.

The interpretations were checked by calculation of the theoretical spectrum. Fig. 3 shows the "stick" spectra of a) half of the experimental and b) half of the calculated spectrum. The coupling constants and the spin density values are listed in the same figure. According to Bowers [4] the odd electron of the anion radical of a monosubstituted benzene nucleus would, if the substituent were electron with-drawing, prefer the symmetric energy level. The average coupling constant of the ortho- and meta-protons is in this case one third of the coupling constant of the para-proton; this result agrees well with the theoretical model of Bowers. The spin density values are calculated using the value -23.8 for Q. The sum of the experimental spin densities is 1.218, consequently there may be regions in the molecule were the spin density is negative.[5] Agreement between the calculated and experimental spectra is good, and one must conclude that the anion radical of trans-1-phenyl-1-propene is the responsible species.

We have carried out a variety of calculations using the HMO method. The difficult question in these calculations is how to treat the perturbing methyl group in the side chain. Use of the inductive model [6] and the heteroatom model [7] did not give satisfactory results. This is in fact not surprising since the HMO method does not take the configuration interaction into consideration. Combining the theory with our experimental results will, as we hope, give parameters which may be useful in other molecules of the same class. The work is continued in this field.

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The Formation of 3,3'-Thenil in the Reaction Between 3-Thienyl-lithium and Dimethyl Oxalate at −70°

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A romatic 1,2-diketones are usually prepared in high yield through condensation of aromatic aldehydes in the presence of cyanide ion and subsequent oxidation of the resulting benzoin.[1,2] However, the condensation of heterocyclic aldehydes is often an exception. Thus 2-thiophene aldehyde is condensed to 2,2'-thenoin in 30 % yield [3,4] and similar results are observed with the 3-thiophene aldehyde.[5] Since the aldehydes are not always easily accessible the overall yields in preparing the thenils are rather poor.[6] We now report a new way to the thenils.

3-Thienyllithium, prepared from ethyllithium and 3-bromothiophene,[7] cooled to −70°, was dropwise added to an equivalent amount of dimethyl oxalate in ether at −70°. After work-up the NMR spectrum of the crude reaction residue

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