The Electron Spin Resonance of o-Substituted Benzophenone Ketyls

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Previous papers[1,2] in this series have shown that ketyls of those benzophenone derivatives which consist of non-substituted phenyl groups and ortho-substituted phenyl groups (i. e., 2-methylbenzophenone, 2, 6-dimethylbenzophenone, 2, 6-dimethyl-4-*t*-butylbenzophenone, 2, 4, 6-trimethylbenzophenone and 2-methylcyclohexyl phenyl ketone—group I) give extremely different ESR spectra from those of the ketyls of benzophenone and para-substituted benzophenone derivatives (i. e., 4-methylbenzophenone, 4, 4′-dimethylbenzophenone, 4-*t*-butylbenzophenone, 4, 4′-di-*t*-butylbenzophenone, 4-methoxybenzophenone, 4, 4′-dimethoxybenzophenone and 4-ethylbenzophenone—group II). That is, although the ketyls of group II give well-resolved spectra, the ketyls of group I give less well-resolved spectra consisting of four broad lines. We have speculated that these four broad lines might be caused by a larger accumulation of free electron spin on a non-substituted phenyl group — especially an accumulation at two ortho- and para-positions. In order to confirm this hypothesis, the ESR spectrum of the ketyl of d_5-phenyl 2-methylphenyl ketone was studied. Two other pieces of experimental evidence were also obtained in support of the authors' view.

Results and Discussion

The Ketyl of the d_5-Phenyl 2-Methylphenyl Ketone.[*2] — The ESR spectra of the ketyls of the d_5-phenyl 2-methylphenyl ketone (I) and of the phenyl 2-methylphenyl ketone (II) are shown in Fig. 1. ESR measurement was done in a dilute solution of the ketyl in tetrahydrofuran (THF). When these two spectra are compared, the difference is quite clear. II gives four broad lines with a total width of 21.7 gauss, while I gives a single line with a smaller total width of 18.5 gauss. Since the

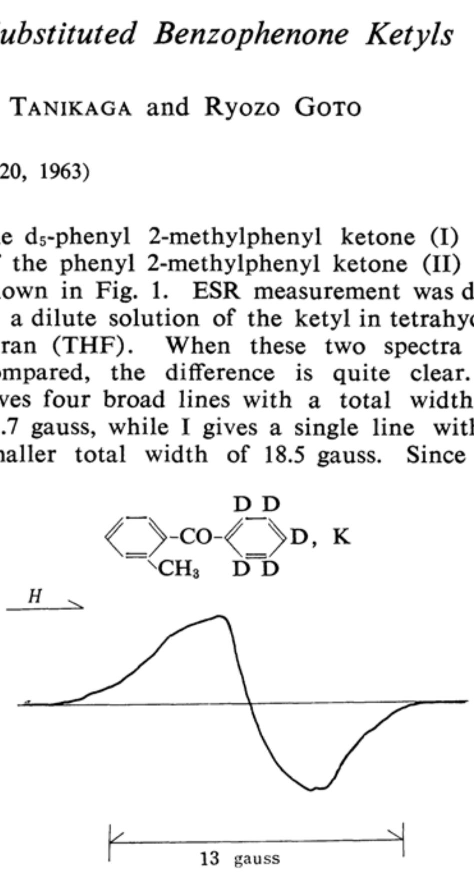

Fig. 1 (a)

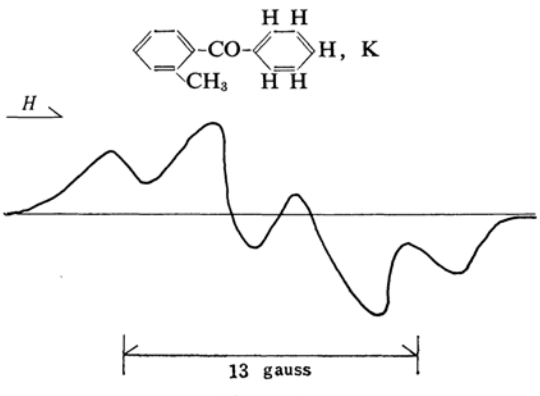

Fig. 1 (b)

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1) R. Goto, K. Maruyama, R. Tanikaga and Y. Deguchi, This Bulletin, **35**, 1746 (1962).

2) K. Maruyama, R. Tanikaga and R. Goto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 75 (1963).

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nuclear spin of deuterium is one, seven lines should be observed if the free electron spin is accumulated exclusively into two ortho- and para-positions of the non-substituted phenyl group. However, line broadening is caused by the thermal motion of the ortho methyl on the other phenyl group (time-dependent local field change), as is evident from the previous paper and from the following experimental results. The nuclear magnetic moment of deuterium is one-seventh that of protium. The results obtained above are, therefore, reasonable.

The Ketyl of the 2-Methylphenyl 4′-*t*-Butylphenyl Ketone. — The ESR spectrum of the ketyl of the 2-methylphenyl 4′-*t*-butylphenyl ketone was obtained in a dilute solution of THF (Fig. 2). The spectrum consists of three broad lines. The intensity ratio of the lines is 1 : 2 : 1. This fact also shows that the free electron spin is exclusively accumulated at two ortho-positions of the 4′-*t*-butyl-substituted phenyl group.

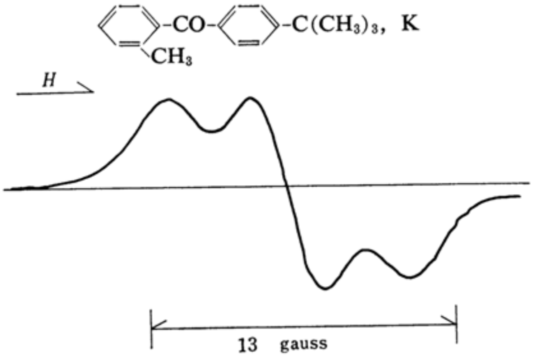


Fig. 2

The Ketyl of the 2-Methylphenyl 3′-Chlorophenyl Ketone. — The ESR spectrum of the ketyl of the 2-methylphenyl 3′-chlorophenyl ketone was observed in a dilute solution of THF (Fig. 3). The spectrum consists of four broad lines. The intensity ratio of the spectrum lines is nearly 1 : 3 : 3 : 1. This result shows that the free electron spin density of the meta positions of the non-ortho-substituted phenyl group is nearly zero or, at least, very small.

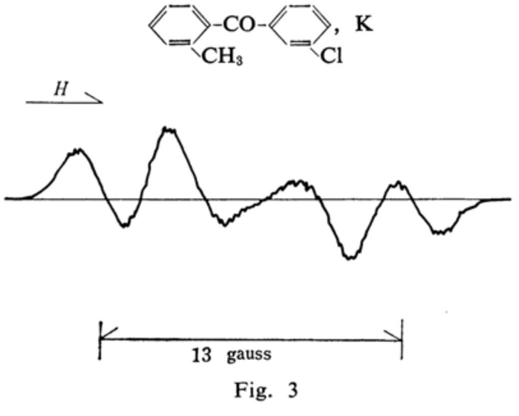
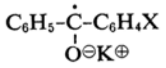


Fig. 3

Discussion

All the results so far obtained show that the free electron spin of the ketyl of the benzophenone derivative which is constructed form the non-ortho-substituted phenyl and the ortho-substituted phenyl is delocalized mainly on a non-ortho-substituted phenyl of the two phenyl groups. If we could assume that the splitting parameter for aromatic hydrocarbons (23 gauss) is also applicable to these ketyls, we could say that about fifty per cent of the free electron spin is located on the non-substituted phenyl group, since the splitting between the four broad lines is about five gauss in almost all cases. The rest of the free electron spin will reside on the $\cdot\overset{|}{\underset{|}{C}}\text{-OK}$ group. The structure of the ketyl has been the subject of extensive investigations.[3-8] Recently Hirota[9] showed the possibility of the existence of paramagnetic dimers due to the dimerization of monomer ion pairs. The simplest representation of ketyl structure, however, is III.

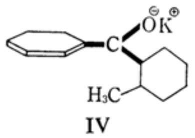


$$C_6H_5\text{-}\overset{\bullet}{\underset{\substack{|\\ O^{\ominus}K^{\oplus}}}{C}}\text{-}C_6H_4X$$

III

X=*o*-, *m*-, *p*-, CH_3, CH_3O, $C(CH_3)_3$, Cl, etc.

From the said results, the spatial arrangement of the ketyl which consists of the non-ortho-substituted phenyl group and the ortho-substituted phenyl group is to be represented by IV.



IV

That is to say, the ortho-substituted phenyl group is bent out of the plane of the three central bonds because of the steric hindrance

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[3] E. Beckmann and T. Paul, *Ann.*, **266**, 1 (1891).

[4] W. Schlenk and T. Weickel, *Ber.*, **44**, 1182 (1911).

[5] W. Schlenk and A. Thal, ibid., **46**, 2840 (1913).

[6] W. E. Bachmann, *J. Am. Chem. Soc.*, **55**, 1179 (1933).

[7] R. N. Doesher and G. W. Wheland, ibid., **56**, 2011 (1934).

[8] C. B. Wooster, ibid., **56**, 2436 (1934).

[9] N. Hirota, Thesis work in Washington University (1962).

of the ortho methyl group. Deguchi[10] reported recently that the diphenyl nitric oxide derivative, which has an ortho substituent, gave an extraordinarily broad ESR spectra although the other derivatives gave a well-resolved hyperfine structure. He was inclined to consider that most of the electron spin densities must be delocalized on nitrogen and on the ortho methyl group. However, this may be far from the truth. The same explanation as has been presented for ketyls may apply.

Experimental

The Preparation of the Ketyl and Measurement. — Ketyls were produced by the reduction of the corresponding ketones with a potassium metal. The measuring apparatus of the ESR was a usual vacuum vessel. THF was dried over K-Na alloy.

Synthesis of Material. — d_5-Phenyl 2-methylphenyl ketone was synthesized from d_6-benzene (99.5 atom%) and *o*-toluyl chloride using the usual Friedel-Crafts reaction (b. p. 131°C/2 mmHg). d_6-Benzene was synthesized by the exchange reaction between benzene and D_2SO_4 (concn. 50 mol. %). D_2SO_4 was made by mixing D_2O and anhydrous SO_3 (γ-form).

The physical constants of the other ketones are as follows:

	Boiling point
2-Methylphenyl 4'-*t*-butylphenyl ketone	160°C/2.0 mmHg
2-Methylphenyl 3'-chlorophenyl ketone	144~148°C/ 3.5 mmHg

Summary

The ESR spectra of the potassium ketyls of d_5-phenyl 2-methylphenyl ketone (I), phenyl 2-methylphenyl ketone (II), 2-methylphenyl 4'-*t*-butylphenyl ketone and 2-methylphenyl 3'-chlorophenyl ketone have been measured in a tetrahydrofuran solution.

II gave four broad lines, and I, a single line with a smaller total width. It is considered that the ortho-substituted phenyl group is bent out of the plane of the three central bonds because of the steric hindrance of the ortho methyl group, and that then the free electron spin is accumulated at a non-substituted phenyl group — especially at the ortho- and para-positions.

The findings on the other ketyls support the above hypothesis.

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[10] Y. Deguchi, This Bulletin, 35, 260 (1962).