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structural formulas

Figure 1: structural formulas

Abstract

Full Text

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STUDY OF THE STRUCTURE OF ORGANIC COMPOUNDS BY THE METHOD OF ELECTRON PARAMAGNETIC RESONANCE

In the present work the possibility was studied of using one of the characteristics of free radicals—their stability—for investigating the structure of organic compounds. By the stability of a radical we shall understand the half-period of the time of its disappearance ($t^t_{1/2}$) under conditions, as far as possible, of an inert medium or of a model reaction at temperature t. According to the proposed method for studying the structure of organic compounds, the compound under investigation must be converted into a radical, whose stability is then compared with the stabilities of radicals of known structure. The radicals compared must differ by one of the factors determining stability. $t^t_{1/2}$ is conveniently found with the aid of the method of electron paramagnetic resonance (e.p.r.). The possibilities of the proposed method for studying the structure of organic compounds are shown in the examples given below.

Study of the structure of "acetonanil." The structure of the product of condensation of aniline with two moles of acetone has been studied repeatedly ([1,2,3]), in particular by the methods of n.m.r., i.r., and u.v. spectroscopy. However, until recently it had not been possible to make an unambiguous choice between the two formulas proposed for "acetonanil,"2,2,4-trimethyl-1,2-dihydroquinoline (Ia) and 2,4,4-trimethyl-1,4-dihydroquinoline (Ib). Only the latest data, obtained on the basis of a study of the reaction of dicyandiamide with "acetonanil" ([2]) and an investigation of the i.r. spectra of the products of acetylation and oxidation of "acetonanil" ([1]), make it possible to consider that "acetonanil" is Ia. The results of the present work lead to the analogous conclusion, which points to the correctness of the proposed method.

(a) (b) (a) (b)
(I) (II)

structural formulas III and IV

Figure 2: structural formulas III and IV

On oxidation of "acetonanil" with peroxide compounds we obtained radical II (Fig. 1, Table 1). Depending on the structure of "acetonanil," the radical obtained may be assigned formulas IIa and IIb*. The hyperfine structure of the spectrum does not permit a choice between IIa and IIb, since the same protons may interact with the unpaired electron—

* Radicals of amine N-oxides may also be represented as having a three-electron bond (^{4}).

tones. The stability of the "acetonanil" radical is due mainly to the presence of the phenyl group and of methyl groups located in position 2. The choice between IIa and IIb and, consequently, between Ia and Ib can be made, according to the proposed method, if data are available on the stability of analogous radicals having different numbers of methyl groups in position 2. To exclude the influence of the double bond, "acetonanil" was converted into "dihydroacetonanil" (III), from which radical IV was obtained by oxidation (Fig. 2, Table 1). From tetrahydroquinoline, 2-methyltetrahydroquinoline, and 2,4-dimethyltetrahydroquinoline, the corresponding radicals V, VI, VII were obtained in an analogous manner.

Table 1

Radicals	g-factor	Number of components in the spectrum and intensity ratio* on nitrogen	Number of components in the spectrum and intensity ratio* on hydrogen	a_N, oerst.	$\tau^{20}_{1/2}$, h
V	2.0063	3,1 : 1 : 1		10.7	2.1
VI	2.0063	3,1 : 1 : 1	5,1 : 4 : 6 : 4 : 1	11.2	20
VII	2.0065	3,1 : 1 : 1	5,1 : 4 : 6 : 4 : 1	11.8	28
II	2.0065	3,1 : 1 : 1	3,1 : 2 : 1	13.6	249
IV	2.0066	3,1 : 1 : 1	4,1 : 3 : 3 : 1	13.7	250

structural formulas V, VI, VII

Figure 3: structural formulas V, VI, VII

Structural formulas VIII and IX: (a) tert-butyl tert-butoxy naphthalene; (b) di-tert-butyl-2-naphthol; and the corresponding naphthoxyl radical IX.

Figure 4: Structural formulas VIII and IX: (a) tert-butyl tert-butoxy naphthalene; (b) di-tert-butyl-2-naphthol; and the corresponding naphthoxyl radical IX.

By the EPR method the kinetics of disappearance of these radicals in benzene was studied. It was found that this reaction obeys a first-order equation. The half-periods of disappearance of the radicals are presented in Table 1. From the data of Table 1 it follows that the introduction of one methyl group into position 2 increases the stability of the radical by a factor of 10–15 (compare V, VI, VII). The stability of II and IV, if they had the structures IIb and IVb, would be close to the stability of VII. The substantial difference in the stabilities of II and IV from VII unambiguously indicates that the "acetonanil" and "dihydroacetonanil" radicals contain two methyl groups in the second position, i.e., have respectively the structures IIa and IVa. Hence it follows that "acetonanil" is 2,2,4-trimethyl-1,2-dihydroquinoline.

Study of the structure of the product of tert-butylation of 2-naphthol. In the alkylation of 2-naphthol with tert-butyl alcohol or tert-butyl chloride, Kontraktor isolated a compound insoluble in 5% NaOH solution, to which he assigned the structure 4-(?)-tert-butyl-2-butoxynaphthalene (VIIIa) (5). Later it was shown (6) that one of the tert-butyl groups is in position 6, and it was concluded

assumption (without direct proof) that the second tert-butyl group occupies position 1, i.e., that the dialkylated product is 1,6-di-tert-butyl-2-naphthol (VIIIb). By the proposed method it can be proved that the product under investigation VIII is 2-naphthol and that one tert-butyl group is in position 1. On oxidation with peroxide compounds a free radical was obtained (g-factor 2.0096). The disappearance reaction of di-tert-butyl-2-naphthoxyl obeys a first-order equation; the stability of the radical at $t = 20^\circ$ is 42 h. Comparison of the stabilities of the radicals obtained by oxidation of 6-tert-butyl-2-naphthol ($\tau_{1/2}^{-10^\circ} < 1$ sec) and 1-methyl-2-naphthol ($\tau_{1/2}^{5^\circ} < 10$ sec), and of radical IX, indicates the presence of a tert-butyl group in position 1. Thus, it may be regarded as proved that the product of alkylation of 2-naphthol with a tert-butyl group is 1,6-di-tert-butyl-2-naphthol.

(a) (VIII) (b) (IX)

Study of the structure of tritylated 2-naphthols. By tritylation of 2-naphthol with triphenylcarbinol, Hardy (7) and with triphenylchloromethane, McKenzie (8) obtained a compound with m.p. 228–230°, which, as they believed,

Fig. 1. EPR spectrum of the radical of the N-oxide of “acetonanil” .

Figure 5: Fig. 1. EPR spectrum of the radical of the N-oxide of “acetonanil” .

Structural formulas X, XI, XII: tritylated 2-naphthol isomers and the corresponding naphthoxyl radical.

Figure 6: Structural formulas X, XI, XII: tritylated 2-naphthol isomers and the corresponding naphthoxyl radical.

was 1-trityl-2-naphthol (X). X was also synthesized by the reaction of phenylmagnesium bromide with *o*-naphthofuchsone ([9]), but the product obtained had m.p. 155°. Recently it was shown that the product obtained according to ([7], [8]) undergoes condensation with 2,3-dichloro-1,4-naphthoquinone, forming a furan quinone. It was assumed that the compound with m.p. 228° is in fact 6-trityl-2-naphthol (XI) ([10]).

Fig. 1. EPR spectrum of the radical of the N-oxide of “acetonanil”

We synthesized the tritylated product by both methods. It turned out that on oxidation of the compound with m.p. 155°, obtained according to ([9]), radical XII is formed (*g*-factor 2.0093). The stability of radical XII, whose disappearance process is a first-order reaction, at $t = 20°$ is 38.5 h. The radical obtained from the compound with m.p. 228° had a stability of the order of 10 min, i.e., 90 times less. These results make it possible to conclude that the trityl-substituted 2-naphthol with m.p. 155° is X, and the tritylated 2-naphthol with m.p. 228-230° does not contain a trityl group in position 1.

(X) (XI) (XII)

Experimental Part

Tetrahydroquinoline ([11]), 2-methyl-tetrahydroquinoline ([12]), and 2,4-dimethyl-tetrahydroquinoline ([13]) were obtained respectively from quinoline, quinaldine ([14]), and 2,4-dimethylquinoline ([15]). “Acetonedianil” and its dihydro derivative were synthesized according to ([1], [3], [16]). 1-Methyl-naphthol-2, 6-tert-butyl-naphthol-2 and 1,6-di-tert-butyl-naphthol-2, 6-trityl-naphthol-2 were obtained, respectively, according to ([5], [8], [17]) from naphthol-2. 1-Trityl-naphthol-2 was synthesized according to ([9]) from *o*-naphthoquinone ([18]).

Naphthoxyl radicals were obtained by oxidizing the corresponding naphthols with lead peroxide. N-oxide radicals were obtained from the corresponding amines by oxidation with hydrogen peroxide in the presence of ammonium perwolframate or with benzoyl peroxide. The kinetics of the disappearance of radicals was studied in benzene solutions with an initial radical concentration from $2.0 \cdot 10^{16}$ to $1.0 \cdot 10^{18}$ rad/ml in vacuum.

Measurements were made on an EPA-2 spectrometer (OKBA) with double mod-

Fig. 2. EPR spectrum of the radical of the N-oxide of "dihydroacetonedianil."

Figure 7: Fig. 2. EPR spectrum of the radical of the N-oxide of "dihydroacetonedianil."

ulation of the magnetic field. Part of the measurements was carried out on an EPR-2 spectrometer with the kind assistance of A. L. Buchachenko, Ya. S. Lebedev, and G. A. Abakumov. The magnetic field was calibrated with a mixture of diphenylpicrylhydrazyl and ultramarine ([10]). The EPR signal, recorded on an EPP-09 recorder, was integrated twice and compared with a set of diphenylpicrylhydrazyl standards.

Fig. 2. EPR spectrum of the radical of the N-oxide of "dihydroacetonedianil."

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References

[1] W. Elliott, P. Yates, *J. Org. Chem.*, **26**, 1287 (1961).
[2] J. P. Brown, *Chem. and Ind.*, 1960, 233.
[3] D. Craig, *J. Am. Chem. Soc.*, **60**, 1453 (1938).
[4] J. W. Linnet, *J. Am. Chem. Soc.*, **83**, 2643 (1961).
[5] R. B. Contractor, A. T. Peters, F. M. Rowe, *J. Chem. Soc.*, 1949, 1993.
[6] Ng. Ph. Buu-Hoi, H. P. Bihan et al., *J. Org. Chem.*, **15**, 1060 (1950).
[7] D. V. N. Hardy, *J. Chem. Soc.*, 1929, 1000.
[8] C. A. MacKenzie, G. Chuchani, *J. Org. Chem.*, **20**, 336 (1955).
[9] A. Shönberg, A. Mustafa, A. Shalaby, *J. Am. Chem. Soc.*, **77**, 5756 (1955).
[10] Ng. Ph. Buu-Hoi, R. Rips, *J. Org. Chem.*, **22**, 666 (1957).
[11] H. Scita, R. Meyer, *Ber.*, **45**, 3594 (1912).
[12] W. v. Miller, V. Doebner, *Ber.*, **16**, 2465 (1883).
[13] J. Thomas, *J. Chem. Soc.*, 1912, 725.
[14] L. Gattermann, G. Wieland, *Practical Methods of Organic Chemistry*, 1948.
[15] H. Beyer, *J. Pract. Chem.*, **33**, 401 (1886).
[16] G. Reddelien, A. Thurm, *Ber.*, **65**, 1511 (1932).
[17] K. Fries, E. Hubner, *Ber.*, **39**, 442 (1906).
[18] M. Gomberg, F. W. Sullivan, *J. Am. Chem. Soc.*, **42**, 1864 (1920).
[19] D. Ingram, *Electron Paramagnetic Resonance in Free Radicals*, IL, 1961.

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