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NMR STUDIES OF THE QUINONE KETAL DIMER, OBTAINED FROM OXYDATION OF 4-ETHOXYDURENOL

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Abstract—The proton NMR spectra of 4-EDD (see Fig. 2) are strongly temperature dependent. At low temperatures ($< -60°$) there occurs a restricted rotation around the C—O bond which connects the two halves of the molecule. It is caused by steric hindrance of the ethoxy and methyl groups around the C—O bond. At temperatures above $-10°$ 4-EDD is involved in an intramolecular rearrangement reaction which interchanges the quinone and aromatic rings. For this reaction as well as for the restricted rotation the free energies of activation were determined.

Above 5° an equilibrium with durenoxy radicals formed by dissociation of 4-EDD is established by ESR measurements.

INTRODUCTION

THE CHEMICAL and physical properties of quinone ketals and quinol ethers of the type shown in Fig. 1 have been studied extensively by Müller and co-workers since 1956. From their Müller *et al.*[1a–f] and other investigations Dimroth *et al.*[2a–g] it is known that in solution these compounds can dissociate into two radicals.

An equilibrium between phenoxy radicals and the dimer molecules (cf. Fig. 1. process 2) was found in many cases.* In this connection it should be noted that many ESR data are available in literature but that very few NMR investigations have yet been published. Recently Williams and Kreilick[3] studied the temperature dependence of the NMR spectra of some quinol ethers (Fig. 1. $R_1 = t\text{-}C_4H_9$; $R_2 = H$; $R_3 =$ —$COCH_3$. —$CO\text{-}t\text{-}C_4H_9$, —$CO_2CH_3$. $CO_2C_2H_5$. $CO_2\text{-}c\text{-}C_6H_{11}$ or CN) and found that these compounds are subject both to a dissociation reaction (Fig. 1. process 2) and an intermolecular rearrangement reaction (Fig. 1, process 1). The dissociation reaction leads to an equilibrium between the dimer molecule and the radicals. while the rearrangement reaction interchanges the aromatic and quinone rings intramolecularly. Chemical evidence of such a type of rearrangement was presented by Mijs *et al.*[4] who investigated the Cu^+/amine catalysed autoxidation of some 4-aryloxyphenols into oligomers. Quinone ketals were postulated as intermediates. which. depending on the substitution pattern of the phenols. can decompose

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* For instance (cf. Fig. 1): $R_1 = t\text{-}C_4H_9$, $R_2 = H$, $R_3 = OCH_3$,[1a] SCH_3,[1c,d] $S\text{-}t\text{-}C_4H_9$,[1c] $S\text{-}C_6H_5$,[1c] $OCOCH_3$,[1b] $OCO\text{-}t\text{-}C_4H_9$,[1b] $CO_2\text{-}c\text{-}C_6H_{11}$,[1b] $CO_2C_3H_7$,[1b] $CO_2C_2H_5$,[1b] $CO_2C_2CH_3$,[1b] CN,[1f], CH_3,[2d] $CO_2C_6H_5$,[1b] $CO_2CH(C_6H_5)$,[1b] $COCH_3$,[1b, 2e] and $CO\text{-}t\text{-}C_4H_9$;[1b] $R_1 = R_3 = C_6H_5$, $R_2 = H$;[2a,b] $R_1 = R_2 = R_3 = Cl$;[1e] $R_1 = OCH_3$ and $t\text{-}C_4H_9$. $R_2 = H$, $R_3 = t\text{-}C_4H_9$;[2e] $R_1 = OCH_3$, $R_2 = H$ and $R_3 = t\text{-}C_4H_9$.[2f]

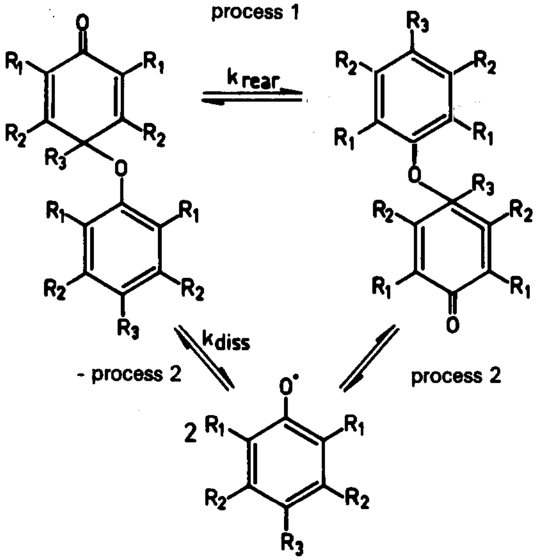

FIG. 1. The rearrangement reaction (process 1) and the dissociation reaction (process 2) of quinol ethers and quinone ketals.

either by homolytic fission or by intramolecular rearrangement. whereby two dimeric molecules giving a linear tetramer as a primary product. With respect to this interesting type of rearrangement we studied the temperature dependence of the NMR spectra of 4-ethoxydurenoxy dimer, 4-EDD, whose structural formula is given in Fig. 2.

This molecule appeared to be interesting not only for the dissociation and rearrangement reactions involved, but also because of a restricted rotation around the C—O bond connecting the two halves of the molecule, which was observed at low temperatures. A detailed description of the NMR spectra observed over a temperature range of −110° to +50°, will be given below.

Kinetic data for the restricted rotation at low temperatures and for the rearrangement reaction were derived from the line broadening in the NMR spectra.

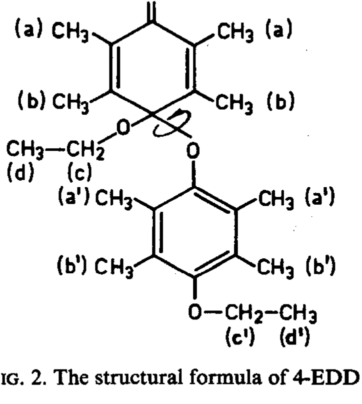

FIG. 2. The structural formula of 4-EDD.

RESULTS AND DISCUSSION

4-EDD was prepared by oxidation of 2.3.5.6-tetramethyl-4-ethoxydurenol according to Martius and Eilingsfeld.[5] As a solid it is stable but it slowly decomposes in solution at room temperature. The NMR spectra were recorded from solutions in carbon disulphide at various temperatures between −110° and +50°. They will be discussed for three temperature ranges.

(a) *The NMR spectra taken between −50° and −10°*

The spectra in this range are almost temperature independent and are simple to interpret. A representative spectrum is shown in Fig. 3c and a survey of the chemical shift data and assignments is given in Table 1. The quartets ($|J| = 7$ Hz) at $\delta = 3{\cdot}56$ and 2·86 ppm can be assigned to the CH_2(C) and CH_2(C′) protons of the aromatic and quinone ethoxy groups respectively. A double resonance experiment showed that the triplet signal at $\delta = 1{\cdot}33$ ppm is due to the CH_3 (d′) protons of the aromatic ethoxy substituent, as it changed into a singlet line on irradiation at the CH_2(c′) signal position (cf. Fig. 3c, top right). The triplet centered at $\delta = 1{\cdot}18$ ppm remains for the CH_3 (d) protons of the quinone ethoxy group. The protons of the methyl groups directly attached to the quinone ring absorb at $\delta = 1{\cdot}71$ and 1·57 ppm, the low field signal associated with the CH_3(a) groups adjacent to the carbonyl group. Both signals form a quartet (see expanded trace at top, Fig. 3c) with spacings of 0·9 Hz, owing to a long range homoallylic coupling. Further confirmation was obtained by double resonance as irradiation at either signal position changed the other signal into a narrow line of higher intensity (see Fig. 3c, top left). The signals at $\delta = 1{\cdot}92$ and 2·00 ppm remain for the aromatic methyl groups and can be safely assigned to the positions a′ and b′ for the following reason. At higher temperatures one observes a coalescence of the CH_3(a) and CH_3(a′) signals and of the CH_3(b) and CH_3(b′) signals.

Table 1. Chemical shift values* (in δ ppm) at different temperatures† for 4-EDD, dissolved in carbon disulphide

Temp.(°)	CH_3(a)	CH_3(a′)	CH_3(b)	CH_3(b′)	CH_2(c)	CH_2(c′)	CH_3(d)	CH_3(d′)
+39	1·85	1·85	1·77	1·77	3·24	3·24	1·24	1·24
+10	1·76	1·89	1·58	1·98	2·90	3·59	1·16	1·30
−26	1·71	1·92	1·57	2·00	2·86	3·56	1·18	1·33
−78	1·72	—‡	—‡	2·02	2·86	3·56	1·21	1·37
−110	1·61 1·84	1·61 2·25	1·06 2·05	2·05 2·12	2·92	3·58	1·26	1·38

* Accuracy: 0·02 ppm but 0·02–0·04 ppm for the measurements at −110°.

† Accuracy: ±1° but below −90°: ±2°.

‡ Not observable due to exchange broadening.

This is due to the rearrangement reaction (process 1) which interchanges the aromatic and quinone rings (see section c). Therefore the CH_3(a) and CH_3(a′) groups must be located at comparable positions in both rings and also the CH_3(b) and CH_3(b′) groups, which justifies the assignment of CH_3(a′) and CH_3(b′).

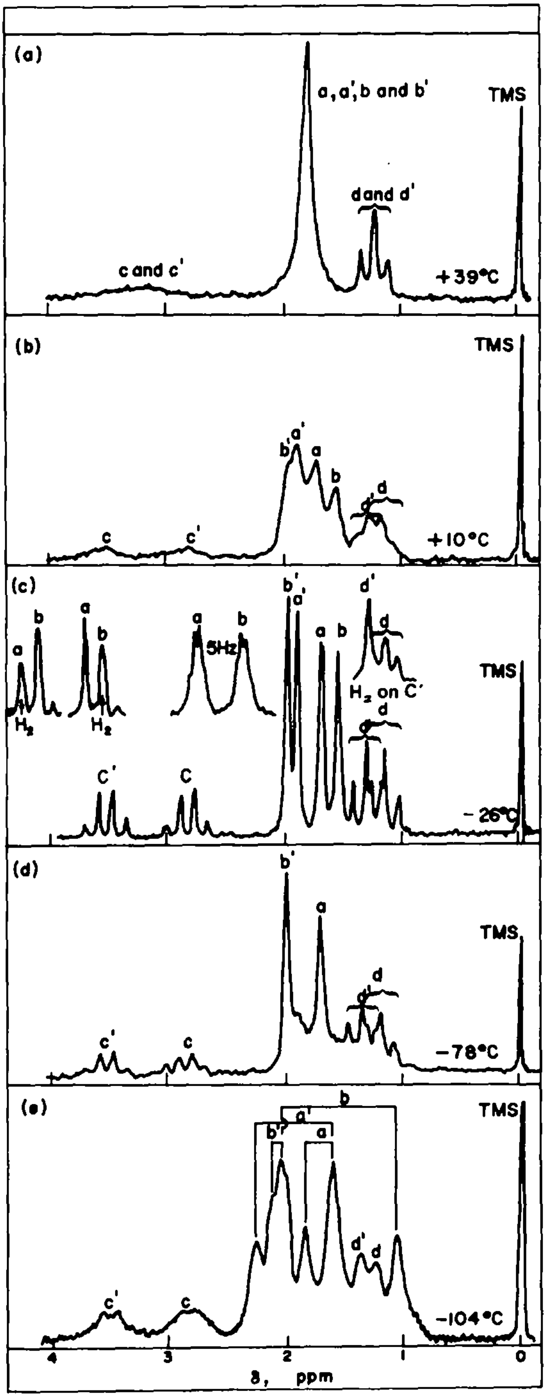

FIG. 3a–e. The NMR spectra of 4-EDD dissolved in carbon disulphide at different temperatures.

(b) *The NMR spectra taken between* $-110°$ *and* $-50°$

By gradually lowering the temperature from $-50°$ to $-110°$ there occur considerable changes in the spectra, which can be explained in terms of one exchange process operating on several signal groups. Due to a restricted rotation around the C—O bond connecting the two halves of the molecule (see Fig. 2), all eight methyl groups become magnetically inequivalent, as shown in the spectrum in Fig. 3e and in Table 1. One CH_3(a) and one CH_3(a′) signal have the same chemical shifts, which is also the case with one CH_3(b) and one CH_3(b′) signal. In Fig. 3e corresponding methyl signals have been marked. Especially the signals of the methyl groups located nearest to the C—O bond are split most strongly (0·64 ppm for CH_3(a′) and 0·99 ppm for CH_3(b) groups). In each of these pairs one methyl group absorbs at surprisingly high field, the other at low field. We suggest on the basis of diamagnetic anisotropic shielding[6] that the former methyl groups lay above their neighbouring quinone or aromatic rings. The methyl groups, responsible for the low field signals should then lie more or less in one plane with the neighbouring rings. Molecular models fully support this hypothesis. A favorable (i.e. sterically less hindered) conformation model is presented in Fig. 4.

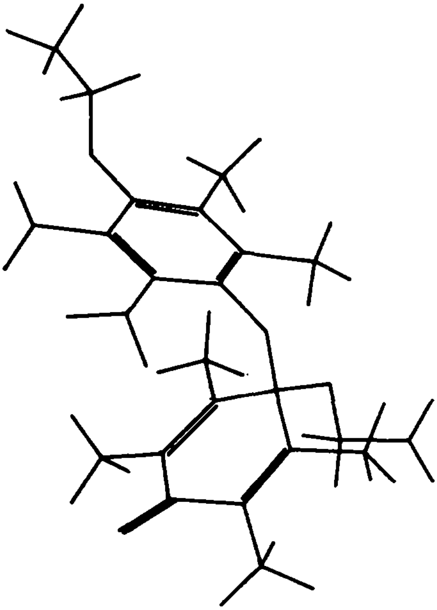

FIG. 4. A Dreiding model of 4-EDD with minimal steric hindrance of the ethoxy and methyl groups around the carbon-oxygen bond which connects the quinone and aromatic rings.

At higher temperatures the increased rotation rate first results in line broadening, then in coalescence of the broadened signals and finally in resharpening. For each of the four pairs of methyl groups the difference in chemical shifts of the initial signals determines the coalescence temperatures. Estimates of the coalescence temperatures are given in Table 2. An increased distance in the signals results in a higher coalescence temperature. Fig. 2d shows the situation at $-78°$, with broad signals for CH_3(a′) and CH_3(b) and already sharp, coalesced signals for CH_3(a) and CH_3(b′).

Table 2. Coalescence temperatures (T_C) and free energies of activation (ΔG‡ in kcal/mol) from various methyl and methylene signals of 4-EDD

Rotation exchange*				Aromatic-quinonoid exchange†			
Coalescing signals	$\Delta(\delta)$ (ppm)	T_C (°)	ΔG‡	Coalescing signals	$\Delta(\delta)$ (ppm)	T_C (°)	ΔG‡
CH_3 (a) pair	0·23	−97	8·8	CH_3(a) + CH_3(a')	0·21	+20	15·2
CH_3(a') pair	0·64	−82	9·3	CH_3(b) + CH_3(b')	0·43	+26	15·2
CH_3(b) pair	0·99	−76	9·5	CH_2(c) + CH_2(c')	0·70	+39	—
CH_3(b') pair	0·07	−103	9·0	CH_3(d) + CH_3(d')	0·15	+16	14·6

* For the rotational exchange the accuracy in coalescence temperature is estimated as ±5°. the accuracy of ΔG‡ as ±0·7 kcal/mol.

† For the aromatic quinonoidal exchange these figures are respectively ±1° and ± 0·3 kcal/mol.

‡ In kcal/mol.

From the coalescence temperatures the free energy of activation for the rotation process was calculated. The values are given in Table 2.

(c) *The NMR spectra taken between* −10° *and* +50°

A gradual increase of the temperature from −10° on gives again the sequence of broadening. coalescence to one signal and finally line sharpening. now for each of the following pairs of signals: CH_3(a) and CH_3(a'). CH_3(b) and CH_3(b'). CH_2(c) and CH_2(c') and CH_3(d) and CH_3(d'). The observed line width variations and coalescence temperatures are concentration independent. In Figs. 2a and b spectra are presented for this temperature region. In the former spectrum only one signal remains for the CH_3(a.a') and CH_3(b.b') groups. due to overlap. This characteristic behaviour for exchange between two non-equivalent diamagnetic sites can be accounted for by the above mentioned rearrangement reaction which interchanges the quinone and aromatic ring protons. viz. process 1 in Fig. 1.

Essentially similar results were obtained by Williams and Kreilick for the quinol ethers mentioned in the Introduction. They found. however. at temperatures exceeding the coalescence temperature first a decrease then an increase of the line widths. This was attributed to a dissociation reaction in which the quinolether is in equilibrium with two radicals as shown in Fig. 1. process 2. By measuring the temperature dependence of the line width and using Johnson's equation[7] which accounts for exchange broadening due to electron transfer reactions. Williams and Kreilick obtained kinetic data on the dissociation reaction. Owing to the instability of 4-EDD in solutions at temperatures >50° we were unable to observe whether 4-EDD also shows any line broadening related to the dissociation process. But ESR measurements of concentrated solutions of 4-EDD in carbon disulphide demonstrated the presence of 4-ethoxydurenoxy radicals. The signal intensity increases or decreases according to heating or cooling of the solutions and drops virtually to zero at +5°. This reversible behaviour gives evidence that the dimer dissociates and is in equilibrium with durenoxy radicals. The ESR spectrum which will be discussed later. is shown in Fig. 5.

As stated above, the NMR signals sharpen again after coalescence. At 50°* the CH_3(a.a'), CH_3(b.b') and CH_3(d.d') signals are only slightly broader (~1·5 Hz) than in the absence of exchange broadening at −20°. Probably the rate of the rearrangement reaction is not yet sufficient to give smaller line widths.[8] But it may be that between +40° and +50° the dissociation reactions begins to produce slight line broadening. In this case especially the line widths of the CH_3(a,a'), CH_3(b,b') and CH_2(c,c') signals should be affected.†

It seems, however, unlikely that the observed coalescence temperatures for the CH_3(a.a'), CH_3(b.b') and CH_3(d.d') signals, all being well below 40°, are influenced to any appreciable extent by the dissociation process. The coalescence temperatures can therefore be used to calculate the free energy of activation of the rearrangement reaction, cf. Table 2. The value for $\Delta G^{\ddagger} = 14{\cdot}9 \pm 0{\cdot}3$ kcal/mol at ~20° is significantly higher than the values of 9 and 12 kcal/mol which can be calculated by extrapolation to 20° from the kinetic data of Williams and Kreilick for two of their compounds (Fig. 1, $R_1 = t\text{-}C_4H_9$, $R_2 = H$, $R_3 = COCH_3$ or CO_2CH_3), measured in the same solvent. This difference in free energy of activation can be caused by a higher value of the activation enthalpy for 4-EDD in comparison with the two quinol ethers. These contain two *t*-butyl substituents near the C—O bond which must be broken in the rearrangement reaction. Release of steric hindrance will energetically favour the fission of this bond in the transition state of these dimers in comparison with 4-EDD. For the same reason it is understandable that 4-EDD is so little dissociated into radicals (no ESR signals measurable from 30 w/v % solutions below 5°).

The ESR spectrum of the 4-ethoxydurenoxy radical in Fig. 5 can be explained from a splitting into three (caused by the OCH_2-protons) of the 31 lines, resulting from the interaction of the unpaired electron with six ortho methyl protons

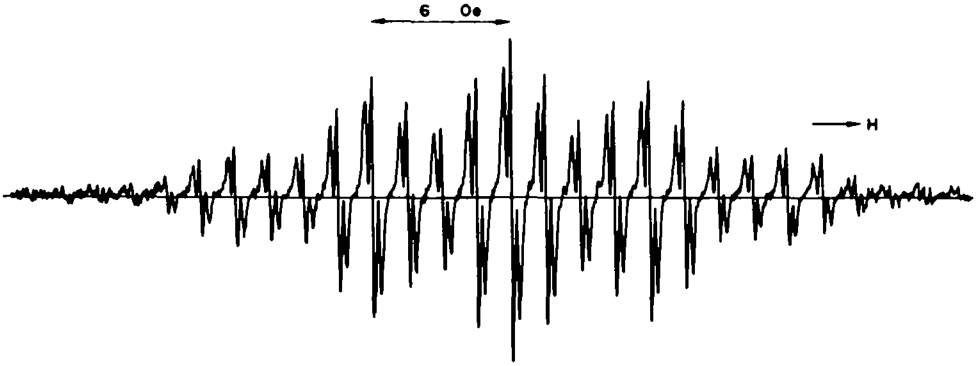

FIG. 5. The ESR spectrum of the 4-ethoxydurenoxy radical, obtained from solutions of 4-EDD in carbon disulphide.

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* The CH_2(c.c') signal is still very broad, due to its high coalescence temperature.

† According to Johnson's equation[7] which relates the NMR linewidths with the rates of exchange between paramagnetic and diamagnetic states, the linewidths of the CH_3(a.a'), CH_3(b.b') and CH_2(c.c') signals are in principle inversely proportional to the lifetime of the diamagnetic state. For these are the signals which are related to groups of protons which exhibit hyperfine splitting in the ESR spectrum. The NMR linewidth of the CH_3(d.d') signal will perhaps be less dependent on the lifetime of the diamagnetic state as the hyperfine coupling of the corresponding protons were not observable in the ESR spectrum.

($a_{o\text{-}CH_3}$ = 6·01 Oe) and six meta methyl protons ($a_{m\text{-}CH_3}$ = 1·49 Oe). The values of the hyperfine coupling constants are in good agreement with the values of 5·56 and 1·40 Oe found for the radical[9] presented in Fig. 6. From the spectrum a value of 0·32 Oe for the coupling constant of the OCH_2 group is calculated which is surprisingly low. Coupling constants of the corresponding protons in *p*-ethoxyphenoxy and other *p*-alkoxyphenoxy radicals[1d, 10] usually range from 1·4 to 2·0 Oe. The low value is probably due to a steric effect of the meta-methyl groups on the ethoxy substituent. forcing it into a position which makes overlap of the oxygen lone-pair electrons with the π-electron system more difficult. This results in a lower spin density on the oxygen atom.

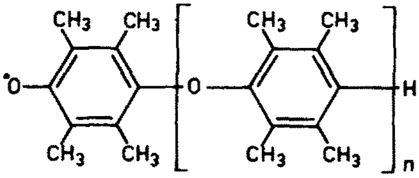

FIG. 6. The radical of polydurenol.

EXPERIMENTAL

The quinone ketal dimer of 4-ethoxydurenol. which was synthesized according to Martius and Eilingsfeld.[5] was crystallized from methanol and methanol–water between 10 and 35° (yield 20%). m.p. 82–82·5°. IR spectrum (Perkin–Elmer 221 G spectrometer, solvent carbon disulphide) showed medium to strong bands at 2972. 2915. 2870. 1470. 1246. 1108. 1082. 1055. 1038. 1025. 986 and 965 cm^{-1}. The NMR spectra were recorded from 10 (w/v) % solutions of 4-EDD in carbon disulphide with a Varian A60 spectrometer. equipped with a decoupler V6058a and a variable temperature accessory V6040 calibrated on the methanol chemical shift. Chemical shifts (in δ ppm) are given relative to TMS as an internal standard. The ESR spectra were taken on a spectrometer built at the laboratory in Delft. using a TE_{011}-transmission cavity and a magnetic field modulation of 1300 Hz. The ESR spectra were taken from 20 to 40 (w/v) % solutions of 4-EDD in carbon disulphide.

REFERENCES

[1] [a] E. Müller and K. Leij. *Chem. Ber.* **88**. 601 (1956).
[b] E. Müller. R. Mayer. B. Narr. A. Rieker and K. Scheffler. *Ann. Chem.* **645**. 36 (1961).
[c] E. Müller. H. B. Stegmann and K. Scheffler. *Ann. Chem.* **645**. 79 (1961).
[d] K. Scheffler. *Z. Elektrochem.* **65**. 439 (1961).
[e] E. Müller. A. Rieker and W. Beckert. *Z. Naturforsch.* **17**. 567 (1962).
[f] E. Müller. A. Rieker. K. Leij. R. Mayer and K. Scheffler. *Chem. Ber.* **92**. 2278 (1959).
[2] [a] K. Dimroth. F. Kalk and G. Neubauer. *Chem. Ber.* **90**. 2058 (1957).
[b] K. Dimroth. F. Kalk and K. Schlömer. *Ann. Chem.* **624**. 51 (1959).
[c] J. Petrának. J. Pilär and D. Doskočilova. *Tetrahedron Letters*. 1979 (1967).
[d] H. D. Becker. *J. Org. Chem.* **30**. 982 (1965).
[e] T. Matsuura. A. Nishinaga and H. Cahnmann. *J. Org. Chem.* **27**. 3620 (1962).
[f] C. J. R. Adderlay and F. R. Hewgill. *J. Chem. Soc.* (C). 1443 (1968).
[g] See also references cited in E. A. Altwicker. *Chem. Rev.* **67**. 475 (1967).
[3] D. J. Williams and R. Krelick, *J. Am. Chem. Soc.* **89**, 3408 (1967) and *Ibid.* **90**, 2775 (1968).
[4] W. J. Mijs, O. E. van Lohuizen, J. Bussink and L. Vollbracht, *Tetrahedron*, **23**, 2253 (1967).
[5] C. Martius and H. Eilingsfeld, *Ann. Chem.* **607**, 159 (1957).
[6] [a] J. A. Pople, W. G. Schneider and H. J. Bernstein, *High-resolution Nuclear Magnetic Resonance*, p. 180, McGraw-Hill, New York (1959).

[b] L. M. Jackman. *Application of Nuclear Resonance Spectroscopy in Organic Chemistry*. p. 112. Pergamon Press. Oxford (1962).

[7] [a] C. S. Johnson. *J. Chem. Phys.* **39**. 2111 (1963).

[b] H. M. McConnell and S. B. Berger. *J. Chem. Phys.* **27**. 230 (1957).

[8] See Ref. 6*a*. p. 221.

[9] W. G. B. Huysmans and W. A. Waters. *J. Chem. Soc.* (B). 1163 (1967).

[10] [a] T. J. Stone and W. A. Waters. *J. Chem. Soc.* 213 (1964).

[b] W. G. B. Huysmans and W. A. Waters. *J. Chem. Soc.* (B). 1047 (1966).