added and the mixture washed with water. Removal of the solvents yielded a mixture of products (3.03 g) which contained the *cyclohemiacetal* **28**. This mixture was dissolved in THF (40 ml) and treated with vinylmagnesium chloride in THF (13.5 ml; 2 M) at 0°. After 2 h at room temperature an aqueous ammonium chloride solution (25 ml; 10%) was added and the products were isolated with ether.

Removal of the solvents *in vacuo* and chromatography of the residue (3.37 g) on silica gel (150 g) yielded pure *11,11-phenylenedioxy-7*(R),*3*(S,R)*-dihydroxy-1-dodecene* (1.9 g) on elution with ethyl acetate/benzene mixtures (25–50%). The structure was confirmed by comparison (IR., solution) and TLC. with totally racemic material prepared previously [2]. Oxidation of this material in the presence of diethylamine by the previously described procedure [2] yielded the *Mannich* base **29** (1.1 g), exhibiting the same TLC. and IR. (solution) characteristics of totally racemic material [2]. When this product was treated with 2-methylcyclopentane-1,3-dione as in the case of the methanol adduct **9**, the mixture of dienol ethers **15** and **16** was generated. Crystallization from isopropyl alcohol (3 times after chromatography on alumina) gave chemically pure **15** (170 mg), $[\alpha]_D^{25} = -116°$ ($c = 1.0$, chloroform).

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270. Electron Spin Resonance Studies of Free Radicals Arising from α-Hydrogen Abstraction from Thioethers

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(17. VI. 72)

Résumé. On rapporte les spectres de résonance paramagnétique de radicaux libres du type $R{-}S{-}\dot{C}{-}R^1R^2$, créés par photolyse d'un mélange de *t*-butylperoxyde et d'un thioéther. Pour les thioéthers cycliques, tétrahydrothiophène et thiopyranne, les spectres indiquent une interconversion rapide du cycle qui est empêchée dans le 4 *t*-butyl-thiopyranne, permettant ainsi l'attribution des couplages aux divers protons axiaux et équatoriaux.

Introduction. – The recent publication [1] of a study of the electron spin resonance spectra of various organic free-radicals having a sulfur atom directly bonded to the radical site prompts us to report the results of our own work on this problem which has been proceeding along similar lines. The object of this study has been to investigate the way in which the sulfur atom interacts with a π-center ('conjugation'), and the effect of the sulfur substituent on the geometry of the radical center.

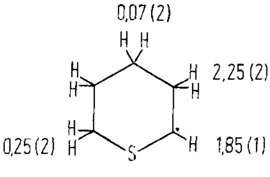
The photochemical techniques developed by *Livingstone* [2], *Kochi* [3] and *Hudson* [4] have made available for study by ESR. unstable radicals of the type $R\dot{C}HR'$ and in particular $R\dot{C}HSR'$. The starting point in the work reported here was our observation that at −60° the two methylene protons in the radical $CH_3S\dot{C}H_2$, in contrast to those of the analogous oxygen compound, were inequivalent, indicating hindered rotation of the methylene group about the carbon-sulfur bond. This greater flexibility of the oxygen-containing compound also manifested itself in the spectrum of the radical obtained by abstraction of an α-proton from tetrahydrothiophene or tetrahydrofuran [1] [5]. The latter radical shows complete time-averaged equivalence of the two β-protons whereas at the same temperature (−60°) the former radical shows slow interconversion of conformational isomers leading to alternating line-widths. It is of course possible that the difference between the two radicals in this case be as much due to the ring sizes arising from the longer C–S compared to C–O bonds rather than to any more specific electronic difference between the sulfur and oxygen atoms and their bonds to carbon.

The two pairs of results mentioned above have already bee reported by *J. Biddles, A. Hudson* & *J. T. Wiften* [1].

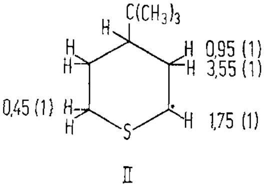
Their general results and the values of the proton hyperfine coupling constants are essentially identical with those we obtained independently and they will not therefore be separately quoted. We limit ourselves here to reporting those results which have not been published elsewhere to discussing the whole question in the light of this additional information.

Experimental. – Free-radicals were produced by UV. irradiation (*General Electric* high pressure water-cooled mercury arc, A.H.6; 1 KW focussed with a quartz lens) of a 1:2 mixture of *t*-butyl peroxide and the sulfur-containing substrate contained in 3 mm diameter quartz tubes inserted in the cavity of the ESR. x-band spectrometer (*J.E.O.L.* ME1X). The temperature of the irradiated sample could be varied from room-temperature to −170°, in general −60° proved to be appropriate. In the case of $CH_3S\dot{C}H_2$ the radical was prepared by UV. irradiation of a 1:1:1 mixture CH_3SCH_2Cl, triethylsilane and *t*-butyl peroxide [4]. Tetrahydrothiophene, thiane and chloromethyl methyl sulfide were purified commercial samples. 4-*t*-butylthiane was prepared by a published method [6].

Results. – The hyperfine coupling constants (mT) of the two radicals derived from thiane and 4-*t*-butylthiane are shown in I and II, the number in parentheses being the number of equivalent protons giving rise to the splitting in question.



I



II

Fig. 1 and 2

The assignments may be justified as follows. The spectrum of I shows marked alternating line-widths which indicate interconversion of conformational isomers and consequent equivalence of methylene protons. The value of the unique α-proton coupling is immediately available and is similar to those (1.67 and 1.75 mT) of the $CH_3S\dot{C}H_2$ radical. Similarly the large coupling of 2.25 mT can only arise from the β-protons. (In this connexion it should be noted that the spectrum clearly shows that as usual, the radical arises from abstraction of a proton adjacent to the hetero atom). Again on the basis of the results for $CH_3S\dot{C}H_2$ the splitting of 0.25 mT is assigned to the α'-protons and finally the most likely source of the very small splitting of 0.07 mT are the γ-protons.

On the basis of the results for the unsubstituted molecule the coupling of 1.75 mT is assigned to the α-proton. If the *t*-butyl substituent had no other effect on the radical than to make it rigid then the sum of the couplings of the β-protons would be the same as in the unsubstituted molecule. This is achieved with the assignment shown and as well be seen below this assignment is also in accord with the known angular dependence of β-proton couplings. Finally the α'-protons in the parent heterocycle and the assignment given in the figure implies that one of the α'-couplings is of the order of 0.05 mT which is indeed less than the line-width of the spectrum of II.

Discussion. – There is considerable indirect evidence that $RS\dot{C}R^1R^2$ radicals are almost planar and certainly more nearly planar than the analogous oxygen compounds [5]. If it is assumed that the radical center has its most stable conformation with a near-planar conformation and that there is a tendency for it to conjugate with the p-electrons of the neighbouring sulfur atom then the most likely conformation of the radical resembles the twisted chair of cyclohexene (III).

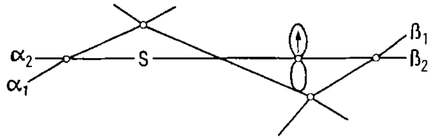


Fig. 3

In such a conformation one of the β-protons is pseudo-equatorial and lies close to the nodal plane of the unpaired electron's p-orbital and the corresponding pseudo-axial proton lies close to the plane containing the p-axis.

It is well established [7] that β-protons have coupling constants a_β given by the formula

$$a_\beta = \varrho_\alpha\,[A \cos^2\theta + B] \tag{1}$$

where ϱ_α = spin density at the α-carbon atom,
θ = dihedral angle between the planes containing respectively the p-orbital axis and the carbon-hydrogen bond.

A and B are constants with $A \approx 5.0$ mT and $0 \leqslant B \leqslant 0.5$ mT. According to this equation the pseudo-axial proton has a large coupling constant and the pseudo-equatorial proton a small coupling constant. Equation (1) yields the following relationship for the difference between the coupling constants, Δ_β, of two β-protons attached to a carbon atom having strictly tetrahedral symmetry.

$$\Delta_\beta = A\varrho_\alpha \left\{\frac{3}{4}\cos 2\theta - \frac{\sqrt{3}}{4}\sin 2\theta\right\} \tag{2}$$

The absolute value of the angular term lies in the range 0.0 to 0.75 mT. If $A = 5.0$ mT, $\Delta_\beta/A = 0.52$ and hence $0.69 \leqslant \varrho_\alpha \leqslant 1.0$.

The corresponding range of the dihedral angle is $0° \leqslant \theta \leqslant 13°$. According to equation (1) the coupling constant of a freely rotating methyl group is given by

$$a_{CH_3} = \varrho_\alpha \left\{\frac{A}{2} + B\right\} = 2.8\varrho_\alpha \text{ mT}$$

In $CH_3CH_2S\dot{C}HCH_3$ the methyl group coupling is 1.99 mT implying that $\varrho_\alpha = 0.71$. This value of ϱ_α in the cyclic molecule implies a dihedral angle corresponding to the pseudo-axial proton close to 0°.

This population is consistent with the coupling of the α-proton although it is well known that α-couplings are much more sensitive to molecular geometry than are β-couplings and are hence not reliable as quantitative indicators of spin density.

A further measure of the dihedral angle may be obtained from the ratio of the β-splittings. If $\varrho_\alpha B = 0.2$ mT then equation (1) yields the result

$$\frac{a_{\beta_1} - 0.2}{a_{\beta_2} - 0.2} = \frac{1}{4}(1 - \sqrt{3}\tan\theta)^2 \tag{3}$$

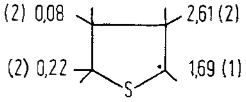
Equation (3) gives $\theta = 2°$ or 12°, the former being close to that obtained above. Both of them are consistent with the proposed cyclohexenelike structure and the assumption that the largest coupling comes from the pseudo-axial proton.

On the basis of this apparently satisfactory model for the structure we may now consider the α'-couplings. If the spin density on the sulfur atom, ϱ_S is essentially in a sulfur 3 p-orbital then the α'-couplings will be expected to have an angular dependence similar to that given by equation (1) since the mechanism of coupling will presumably be also a hyperconjugative one. The coupling of the freely rotating methyl group in $CH_3S\dot{C}H_2$ (0.31 mT) gives a measure of the quantity $\varrho_S[A'/2 + B]$ and if as before $A' \gg B'$ the large α'-coupling constant (0.45 mT) is the expected value for a pseudo-axial proton. As seen above the small coupling constant is probably of the order of 0.05 mT, again in agreement with the expected value for the pseudo-equatorial proton. Thus it would appear that the interaction of a sulfur atom with an adjacent carbon π-radical can be described as completely normal conjugation.

To complete the analysis of the coupling constants of this molecule there remains the small value of the γ-protons in the parent heterocycle and the corresponding vanishingly small coupling in the *t*-butyl derivative. The *t*-butyl group is usually considered to prefer the equatorial position and if this is the case in the present system the γ-proton occupies a pseudo-axial position. It must therefore be supposed that a coupling of an order of magnitude of 0.14 mT arises from a γ-proton in the pseudo-equatorial position and a much smaller one from the pseudo-axial γ-proton. Such marked differences in long range coupling constants are well established, both in electron spin resonance and nuclear magnetic resonance.

Turning now to the five-membered ring the coupling constants (mT) are shown in IV.

These coupling constants are essentially the same as those reported by *Biddles et al.* [1], however these authors do not mention the fact that at −60° it shows alternating line-widths leading to a virtual disappearance of the central components of the triplets arising from the two β-protons. The radical cannot therefore have a rigid planar conformation and the coupling constant quoted is thus the average coupling of the β-protons. The main point of difference between the six- and five-membered rings is the significantly larger value of the β-couplings. This however is not likely to be due to any fundamental difference in structure between the two radicals but rather to the different orientations of the methylene group with respect to the axis of the carbon 2 p-orbital containing the unpaired electron. According to equation (1) the sum of the coupling constants of the two protons of a β-methylene group is given by equation (4).



IV

Fig. 4

$$a_{\beta_1} + a_{\beta_2} = \varrho_\alpha \,[A\,(\cos^2\theta + \cos^2(\theta + 120) + 2B] \tag{4}$$

This has its maximum value of $\varrho_\alpha/2\ (3A + 4B)$ for $\theta = 30°$ and $a_{\beta_1} = a_{\beta_2}$, the situation expected for a rigid planar five-membered ring. In the six-membered ring and the open-chain molecules it was seen above that $A\varrho_\alpha = 3.6$ mT and $B\varrho_\alpha = 0.2$ mT so that for the rigid five-membered ring equation (4) predicts

$$a_{\beta_1} + a_{\beta_2} = 5.8 \text{ mT and } a_{\beta_1} = a_{\beta_2}$$

As seen above however the radical IV does not have a rigid planar conformation and the departure from $\theta = 30°$ which such non planarity implies necessarily leads to a reduction in $(a_{\beta_1} + a_{\beta_2})$ in agreement with the experimental value of $(a_{\beta_1} + a_{\beta_2}) =$ 5.22 mT.

It is at this stage unwise to attempt to extract any further information from equation (4), such as the conformation of the radical, in view of the fact that molecular strain undoubtedly affects to some extent the electron distribution between the carbon and sulfur atoms. It is nevertheless clear that the β- and α-coupling constants can be rationalised on the basis of a very simple model and the analysis which has been made here of the sulfur-containing radicals can be equally well applied to their oxygen analogues.

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