Electron Spin Resonance Detection of the Intermediate Radicals occurring in Homolytic Aromatic Substitutions of Furan and Thiophen

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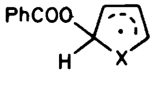
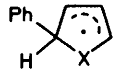
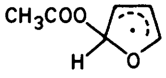
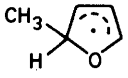
A number of radicals generated by photolysis add to furan and thiophen giving radicals involved in homolytic aromatic substitution: the corresponding e.s.r. spectra were observed. Photolysis of $(PhCOO)_2$ in furan or thiophen gives the spectra of both (A) and (B). On the other hand photolysis of $(MeCOO)_2$ in furan gave the spectrum of (C) at −110° but that of (D) at higher temperature (⩾ −10°). The interpretation of the a_H hyperfine splitting constants suggests that the structure of these radicals is not planar. They seem rather to prefer envelope-like conformations with the substituents either in pseudoaxial or in pseudoequatorial positions or in equilibrium between the two, depending on the substituent.


(A)

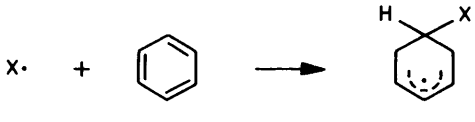

(B)

(X = O,S)


(C)


(D)

THE initial steps in homolytic aromatic substitution involve addition of a radical X· to the aromatic ring to give a cyclohexadienyl intermediate radical. Analogous intermediates occur when the aromatic molecule is a heterocyclic derivative.[1-6] The existence of these intermediates was inferred from analysis of the products: direct e.s.r. detection, on the other hand, was more difficult. This is particularly true in the case of organic media, even though many homolytic aromatic substitutions are carried out in organic solvents. The first e.s.r. observation of such an intermediate was obtained in aqueous solution where the OH· radical adds to benzene yielding the e.s.r. spectrum of the corresponding cyclohexadienyl derivative.[7,8]



Recently spectra due to addition of OH· to furan [9,10] and thiophen [11] in water were detected. Examples of e.s.r. detection of radicals adding to aromatic substrates in organic solvents were also reported. Ingold *et al.* observed [12] such spectra using, as substrates, benzenes hindered by the presence of a number of t-butyl substituents. Subsequently a variety of radicals were shown to add to the hindered 1,3,5-tris(trimethylsiloxy)benzene yielding the corresponding e.s.r. spectra.[13] Addition of Ph_3Si· to benzonitrile and other cyano-substituted thiophen derivatives also gives radicals detectable by e.s.r.[14] Finally Griller *et al.* succeeded in observing [15] the e.s.r. spectra of cyclohexadienyl radicals due to addition of a number of radicals [R_3Si·, Ph·, $(EtO)_2\text{-}\dot{P}O$] to benzene itself.

In the e.s.r. studies so far reported, attempts of obtaining spectra due to addition of thiyl radicals to aromatic substrates failed. Nonetheless radical intermediates resulting from addition of RS· or ArS· to aromatic systems have been proposed in order to explain the reaction products of thiols or disulphides with anthracene,[16] halogenobenzenes,[17] thiophen,[18] and furan.[19] Thiophen and furan also undergo radical reactions involving addition intermediates with a variety of radicals, as substantiated by the identification of products of homolytic aromatic substitution.[20-31] In the present work we report direct e.s.r. identification of intermediate radicals involved in the homolytic aromatic substitution of furan and thiophen. They were produced by addition of methylthiyl (CH_3S·) and other radicals (Et_3Si·, C_6H_5·, Bu^{t}O·, PhCOO·, CH_3·, CH_3COO·) to thiophen and furan in non-aqueous solutions. The e.s.r. parameters also give an indication of the structure and conformation of these elusive intermediates.

RESULTS AND DISCUSSION

Radicals X· which added to furan and thiophen were generated according to reactions (I)—(VI). Radicals (1)—(11) had an e.s.r. spectra which could be detected. The corresponding a_H values and g factors are reported in Table 1.

It has to be pointed out that reaction of Bu^{t}OOBu^t with furan gives the radical (2) whereas the same reaction with thiophen gives a number of radicals of different persistence: none of them, however, corresponds to the addition of Bu^{t}O•. This can be due to the occurrence of reactions of thiophen with radicals other than Bu^{t}O•, that are known [32-34] to be generated by side-reactions of Bu^{t}OOBu^t itself.

It is also interesting to outline the behaviour of both furan and thiophen in the presence of $(PhCOO)_2$. Whereas Griller *et al.*[15] observed only the e.s.r. spectrum arising from the addition of the phenyl radical to benzene, Davies and Roberts [13] reported only the spectrum corresponding to addition of PhCOO• to a trisubstituted benzene derivative. We have simultaneously observed the spectra of radicals (10) and (11) in the case of thiophen and of the corresponding radicals (4) and (5) in the case of furan. In both cases, however, the radical due to addition of PhCOO• gave more intense signals. Unambiguous identification of these radicals could be achieved since radicals (5) and (11) were also obtained without the simultaneous presence of (4) and (10), by generating the phenyl radical *via* reaction (IV). The spectra of (4) and (10) could then be identified by subtraction.[35]

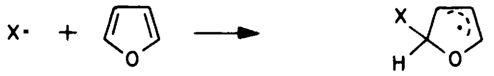
$$\begin{array}{llll}
\text{MeSSMe} & \xrightarrow{h\nu} & 2\,\text{MeS}\cdot & (\text{I}) \\
\text{Bu}^t\text{OOBu}^t & \xrightarrow{h\nu} & 2\,\text{Bu}^t\text{O}\cdot & (\text{II}) \\
\text{Bu}^t\text{O}\cdot + \text{Et}_3\text{SiH} & \longrightarrow & \text{Bu}^t\text{OH} + \text{Et}_3\dot{\text{S}}\text{i} & (\text{III}) \\
\text{Bu}^t\text{O}\cdot + \text{Ph}_3\text{As} & \longrightarrow & \text{Bu}^t\text{OAsPh}_2 + \text{Ph}\cdot & (\text{IV}) \\
(\text{PhCOO})_2 & \xrightarrow{h\nu} & 2\,\text{PhCOO}\cdot & (\text{V}) \\
\text{PhCOO}\cdot & \longrightarrow & \text{CO}_2 + \text{Ph}\cdot & \\
(\text{MeCOO})_2 & \xrightarrow{h\nu} & 2\,\text{MeCOO}\cdot & (\text{VI}) \\
\text{MeCOO}\cdot & \longrightarrow & \text{CO}_2 + \dot{\text{M}}\text{e} &
\end{array}$$

TABLE 1

Hyperfine splitting constants (G) and *g* factors of radicals (1)—(11) obtained by addition of radicals X• to furan and thiophen. The spectra were obtained in cyclopropane as solvent. The values of 3- and 5-H can be interchanged

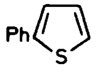
Radical	$a_{2\text{-H}}$/G	$a_{3\text{-H}}$/G	$a_{4\text{-H}}$/G	$a_{5\text{-H}}$/G	$a_{\text{H(others)}}$/G	*g* Factor ($\pm$0.0001)	Temperature (°C)
(1)	29.3	13.1	1.9_5	13.5	0.3 (Me)	2.0039	−120
(2)	22.2_5	13.7_5	1.9	14.0	0.25 (Bu^t)	2.0031	−120
(3)	42.4	12.0	2.0	12.7_5		2.0038	−100
(4)	20.0	13.5	1.9_5	14.2_5		2.0026	−100
(5)	34.1	13.4	2.0	13.4		2.0030_5	−30
(6)	20.1	13.5	1.9_5	14.2_5		2.0025_5	−110
(7)	32.9	13.2	2.0	13.2	0.55 (Me)	2.0031_5	−10
(8)	26.9	11.5_5	2.2_5	13.0_5		2.0041_5	−120
(9)	35.9	11.1	2.2_5	12.5		2.0048_5	−70
(10)	19.3	12.0	2.4	13.7_5		2.0041_5	−80
(11)	31.0	11.5	2.4	13.0		2.0042	−40

The observations of both intermediates in the case of reaction of $(PhCOO)_2$ with thiophen agrees with the results of Tiecco and Tundo in ref. 30, where the homolytic substitution products recovered after thermal decomposition of $(PhCOO)_2$ in thiophen required the existence of both (10) and (11) to explain, for instance, the presence of (12) and (13). On the other hand, in the case of the thermal reaction of $(PhCOO)_2$ in furan, product analysis showed that addition rather than substitution occurs and, furthermore, only intermediates involving PhCOO• rather than phenyl radical are required to explain the composition of the reaction mixture.[36] As often happens with radical reactions the different conditions employed can favour a reaction pathway with respect to one other.[37] A clear example of how dependent the nature of these radicals is upon the experimental conditions is provided by the photolysis of diacetyl peroxide [reaction (VI)] in the presence of furan.

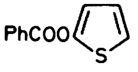


(1) X = MeS
(2) X = Bu^{t}O
(3) X = Et$_3$Si
(4) X = PhCOO
(5) X = Ph
(6) X = MeCOO
(7) X = Me

(8) X = MeS
(9) X = Et$_3$Si
(10) X = PhCOO
(11) X = Ph

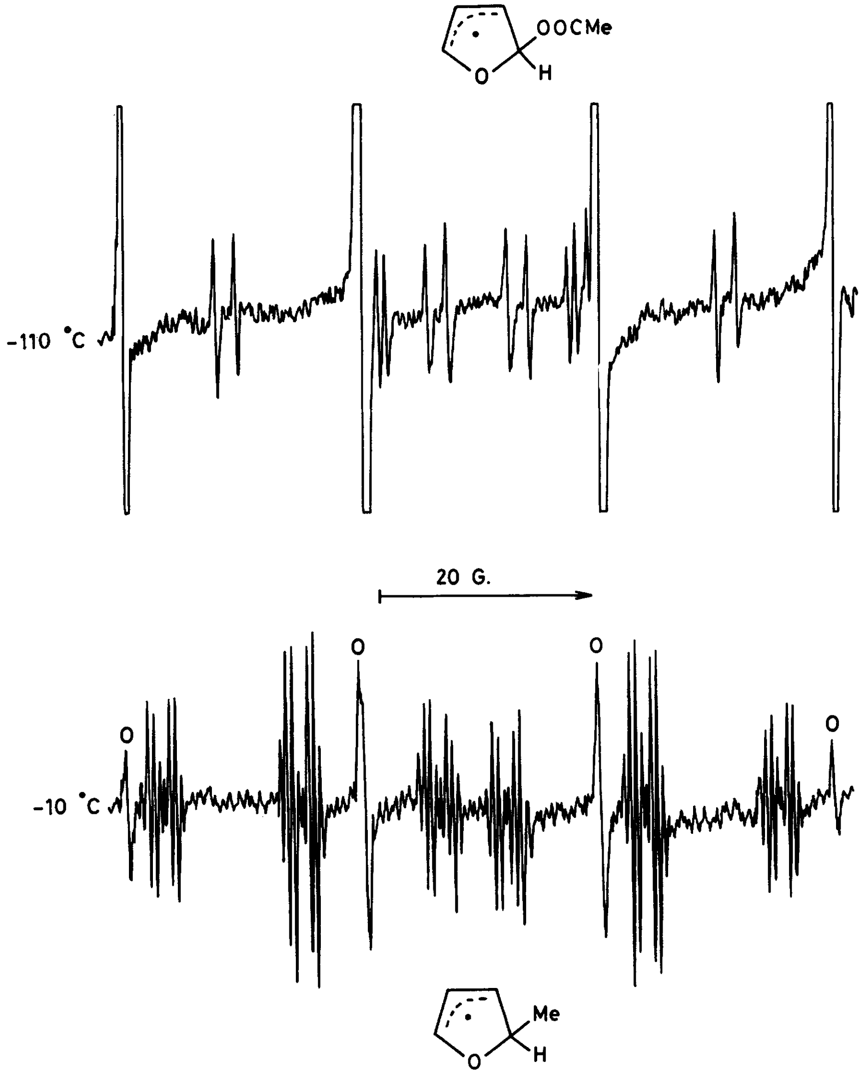


(12)



(13)

At low temperature (−110 °C), in addition to the quartet for CH_3•, also the spectrum of radical (6) due to addition of CH_3COO• to furan is observed. Clearly the activation free energy for addition to furan is lower for CH_3COO• than for CH_3•, so that radical (7) is not generated at low temperature, despite the presence of an intense signal from the CH_3• radical (Figure). At higher temperatures the spectrum of radical due to addition of CH_3• to furan (7) is observed whereas the spectrum of (6) disappears (Figure). The higher temperature makes it possible to overcome the $\Delta G^{\ddagger}$ term for the addition of CH_3· to furan so that radical (7) can be detected. The disappearance of radical (6) can be either due to a lower persistence of (6) with respect to (7) at these relatively high temperatures or to the fact that, at such temperatures, the decomposition rate of MeCOO· into CO_2 and CH_3· becomes faster than the addition rate of MeCOO· to furan.



E.s.r. spectra obtained by photolysis of $(CH_3COO)_2$ in presence of furan using cyclopropane as solvent. At −110 °C in addition to the spectrum of CH_3· (intense quartet), is visible the spectrum of the radical (6) resulting from addition of CH_3COO· to furan. At higher temperature (−10 °C) the CH_3· quartet is much weaker and the spectrum due to addition of methyl to furan is observed [radical (7)]. At intermediate temperatures one can see the three spectra simultaneously

It is well known, however, that the decomposition rate of MeCOO· in Me· and CO_2 is extremely fast and it is thus difficult to admit that the addition of MeCOO· to furan is even faster. An alternative sequence to explain the e.s.r. observation of (6) could thus involve a charge transfer from the excited peroxide to a neighbouring molecule of furan (Scheme). The same reaction with thiophen did not produce any e.s.r. signals.

In our experiments radicals due to addition to position 3 were never observed. Although the relative proportions of products due to attack to positions 2 and 3 depends [4] on the method employed to generate radical X·, all the product studies agree that reaction at position 2 is much more likely to occur.[4,20,23-25,31]

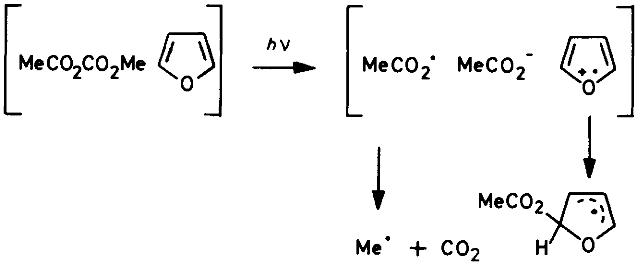
The hyperfine splitting constants also throw light on the structural and conformational properties of these radical intermediates. Inspection of Table 1 shows that, whereas the hyperfine splitting constants of the three allylic hydrogens do not change very much when X changes, those of 2-H do.

The latters are typical H_β splittings and are known to depend upon the electronic character [38] of X (*via* a reduction of the electron releasing power of the β-C–H bond) [39] and, to a much larger extent, upon the dihedral angle θ between the β-C–H bond and the p_z orbital bearing the unpaired electron.[40,41] The relationship is

(1) where ρ is the spin density on the vicinal atoms. Depending on the substituent and on the kind of radical

$$a_{H_\beta} = A + \rho B\cos^2\theta \qquad (1)$$

involved, the constants A and B were empirically found to lie in the following range:[42] $A = 2 \pm 2$ and $B = 48 \pm 5$ G. Recently values of A and B were estimated, by means of INDO calculations,[38] for some $\cdot CH_2CH_2X$ radicals ($X = H$, SMe, $SiMe_3$): in the present work we have also made the analogous calculations for X = OMe. The sets of values are collected in Table 2. Although the radicals under investigation do not necessarily have the same values of A and B of the substituted ethyl radicals mentioned, the trend reported in Table 2 is likely to hold in this series also. From these values it appears that the largest difference observable between the a_{H_β} splittings of radicals with $X = SiR_3$ and OR should not exceed 10 G, if both radicals have the same conformation (*i.e.* equal values of θ). Furthermore this difference can only occur in the particular case of $\theta = 0$ and $\rho = 1$. In our radicals ρ is certainly <1 because the spin density is distributed along the allylic system. Accordingly Δa_{H_β} between the case $X = SiR_3$ and OR, *i.e.* between (3), (4) or (9), (10), should be much smaller than 10 G, if both pairs of radicals had the same value of θ. The very large Δa_{H_β} experimentally observed (22 and 17 G for the furan and thiophen derivatives, respectively) thus requires different θ values: as a consequence these radicals cannot be planar. To account for the very large variations of a_H we must assume a nonplanar conformation and this hypothesis is supported by the observation of diastereotopic methylene hydrogens in the analogous five-membered cyclopentenyl radical (14).[43] To have diastereotopic methylene hydrogens structure (14) has to be nonplanar, with the substituent in a biased equilibrium between a pseudoaxial and a pseudoequatorial conformation.



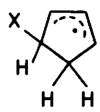
SCHEME

TABLE 2

Values of the constants (G) of the equation $a_H = A + \rho B\cos^2\theta$ as computed by INDO calculations for radicals $\dot{C}H_2CH_2X$

X	A	B
Me_3Si	2.2	54
H	1.7	50.1
SMe	1.8	47.6
OMe	2.3	43.5

To check, albeit approximately, the order of magnitude of the deviation from planarity we tried to estimate roughly the θ values required to match the hyperfine splitting constants of radical (3). The reasonable assumption can be made that the large size of Et_3Si in (3) keeps the substituent totally in the pseudoequatorial conformation.

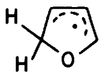


(14)

Following ref. 10 we can write the equation as (2)

$$a_{H_\beta} = A + (c_C + c_O)^2 B\cos^2\theta \qquad (2)$$

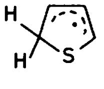
where $(c_C + c_O)^2$ represents the spin density on C-3 and on oxygen, and A and B have the appropriate values for the case $X = SiR_3$ (Table 2). The term $c_C = (\rho^{\frac{1}{2}}{}_C)$ can be estimated[10] from the McConnell equation[44] $a_H = Q\rho_C$, using the a_H value for 3-H (here 12 G) and $Q = 27$, which is typical for heterocyclic compounds.[45] To have an estimate of the term $c_C = (\rho_O)^{1/2}$ we made use of the splittings observed in radical (15), which was obtained by hydrogen abstraction, with Bu^{t}O·, from 2,3-dihydrofuran. The values are $a_{2\text{-}H} = 36.2$, $a_{3\text{-}H} = a_{5\text{-}H} = 13.2_5$, $a_{4\text{-}H} = 2.0_5$ G. In this case either the molecule is planar or, if not planar, the ratio of pseudoaxial and pseudoequatorial hydrogens is obviously 1 : 1. By solving the second-order equation we can thus extract c_O in the case of planarity (θ 30°) or for any other θ value using the appropriate A and B terms for $X = H$ (Table 2). Unless the deviation from planarity exceeds ±20° the term c_O is almost unaffected, its value being 0.26 or 0.29, respectively. As long as deviation from planarity is not too large we can thus use the same c_O value (which corresponds to a spin density on oxygen of 0.07) for all the substituted radicals obtained from furan.



(15)

In the case of (3) we obtain θ 21°, *i.e.* a conformation halfway between planar (θ 30°) and envelope (θ 15°). With the same approach we can estimate θ for the radicals (2), (4), and (6) (*i.e.* those with X = OR) where the very low a_{H_β} value is indicative of an equilibrium biased toward a single conformer. Indeed, the θ value obtained for (2) and (4) is 48 ± 1, which seems to correspond to a pseudoequatorial arrangement for H_β (or a pseudoaxial situation for OR) in an envelope conformation (θ is expected to be 45° in the envelope conformer).[41] This conclusion is also supported by a not negligible a_H value for the t-butyl hydrogens of (2), which could receive some spin density by direct overlap with the unpaired electron allowed by the quasiaxial arrangement of OBu^t. As a consequence an envelope-like conformation with θ 17 ± 5° for the pseudoaxial hydrogen (or pseudoequatorial substituent) which corresponds to $60-17=43\pm5°$ for the pseudoequatorial hydrogens (or pseudoaxial substituent) would account for the largest and smallest a_{H_β} constants observed in the present series. The intermediate a_{H_β} splittings for (1), (5), and (7), *i.e.* X = SMe, Ph, Me, would then be the consequence of different ratios of pseudoaxial and pseudoequatorial conformers present at equilibrium.

Analogous results were found for the radicals derived from thiophen where, to estimate the spin density on sulphur, we made use of the a_H values of radical (16) obtained by addition of H· to thiophen ($a_{2\text{-}H}=32$, $a_{3\text{-}H}=a_{5\text{-}H}=13$ G).[46]



(16)

The c_S values obtained (0.041) yields, when introduced into the appropriate equations, values of θ of 21 and 48° for (9) and (10), respectively, indicating a similar envelope-like conformation with X = Et_3Si pseudoequatorial and X = OOCPh pseudoaxial.

A second possibility to be considered is that all the observed radicals (and not only those with X = $SiEt_3$ and OR) adopt a preferred nonplanar conformation rather than experiencing the proposed equilibrium between the pseudoaxial and pseudoequatorial conformers. The deviation from the planarity (*i.e.* the θ value) would then be different for each substituent, varying continuously within the two extremes 21 (for X = $SiEt_3$) and 48° (for X = OR).

Obviously we do not pretend that these numerical values are accurate, we only wish to stress the fact that nonplanar structures could account for the observed trend of the experimental a_{H_β} splittings.

Finally the reason why the radicals with X = OR should prefer the more crowded axial conformation for the substituent (*i.e.* H_β equatorial) could be attributed to the so called anomeric effect. This attractive interaction between the σ-electrons of the C–O bond and the lone pair electron of oxygen (or sulphur) in the ring has been recently advanced as a reason for a number of conformational features.[47]

EXPERIMENTAL

Radicals (1)—(11) were obtained photolysing, within the cavity of the e.s.r. spectrometer, solutions of furan and thiophen in cyclopropane in presence of the appropriate reagents described in reactions (I)—(VI). The samples were prepared by connecting Suprasil quartz tubes, containing the required compounds, to a vacuum line and introducing gaseous cyclopropane by using liquid nitrogen. The samples were then sealed and introduced into the precooled cavity of the e.s.r. spectrometer.

A 500 W high pressure mercury lamp, carefuly focused on the sample, was employed.

In few cases, notably in radical (1), the heights of the highfield lines appeared to be smaller with respect to those of the corresponding lowfield lines: the effect was more noticeable at low temperature (−100 °C). An analogous effect was observed in the radicals reported in ref. **14** and attributed to the fast decay of the signal. This was not so in our case since the effect was independent of the direction of the field sweep. Although we do not have a clear explanation we suspect this might depend on a remarkable dependence of the linewidth upon the quantum number.[48]

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REFERENCES

[1] D. H. Hey and W. A. Waters, *Chem. Rev.*, 1937, **21**, 169.

[2] M. J. Perkins in ' Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1973, vol. 2, ch. 16, p. 231.

[3] M. Tiecco and A. Tundo, *Internat. J. Sulphur Chem.*, 1973, **8**, 295.

[4] D. C. Nonhebel and J. C. Walton, ' Free Radical Chemistry,' Cambridge University Press, Cambridge, 1974, ch. 11.

[5] F. Minisci and O. Porta, *Adv. Heterocycl. Chem.*, 1974, **16**, 123.

[6] F. Minisci, *Top. Curr. Chem.*, 1976, **62**, 1.

[7] W. T. Dixon and R. O. C. Norman, *Proc. Chem. Soc.*, 1963, 97; *J. Chem. Soc.*, 1964, 4857.

[8] C. R. E. Jefcoate and R. O. C. Norman, *J. Chem. Soc. B*, 1968, 48.

[9] R. H. Schuler, G. P. Laroff, and R. W. Fessenden, *J. Phys. Chem.*, 1973, **77**, 456.

[10] B. C. Gilbert, R. O. C. Norman, and P. S. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1980, 647.

[11] B. C. Gilbert, R. O. C. Norman, and P. S. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1981, 207.

[12] D. Griller, K. Dimroth, T. M. Fyles, and K. U. Ingold, *J. Am. Chem. Soc.*, 1975, **97**, 5526.

[13] P. G. Cookson, A. G. Davies, and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1976, 289.

[14] A. Alberti and G. F. Pedulli, *Gazz. Chim. Ital.*, 1979, **109**, 395.

[15] P. C. Wong, P. R. Marriot, D. Griller, D. C. Nonhebel, and M. J. Perkins, *J. Am. Chem. Soc.*, in the press.

[16] A. L. J. Beckwith and B. S. Low, *J. Chem. Soc.*, 1964, 2571; C. M. M. da Silva and W. A. Waters, *J. Chem. Soc. C*, 1968, 1880.

[17] L. Benati, C. M. Camaggi, and G. Zanardi, *J. Chem. Soc., Perkin Trans. 1*, 1972, 2817.

[18] Yu. A. Gol'dfarb, G. P. Pokhil, and L. I. Belen'ki, *Dokl. Chem. SSSR*, 1966, **167**, 385; R. M. Kellogg in ' Methods in Free Radical Chemistry,' ed. E. S. Huyser, M. Dekker, New York, 1969, vol. 2, p. 95.

[19] L. Benati, C. M. Camaggi, and G. Zanardi, *J. Org. Chem.*, 1975, **40**, 966.

[20] M. C. Ford and D. MacKay, *J. Chem. Soc.*, 1957, 4620; C. E. Griffin and K. R. Martin, *Chem. Commun.*, 1965, 154.

[21] D. C. Ayres and J. R. Smith, *J. Chem. Soc. C*, 1968, 2737.

[22] P. A. S. Smith and J. H. Bayer, *J. Am. Chem. Soc.*, 1951, **73**, 2626.

[23] C. M. Camaggi, R. Leardini, M. Tiecco, and A. Tundo, *J. Chem. Soc. B*, 1969, 1251.

[24] L. Benati, N. La Barba, M. Tiecco, and A. Tundo, *J. Chem. Soc. B*, 1969, 1253.

[25] L. Benati, F. Taddei, M. Tiecco, and A. Tundo, *J. Chem. Soc. B*, 1970, 1443.

[26] C. M. Camaggi, R. Leardini, M. Tiecco, and A. Tundo, *J. Chem. Soc. B*, 1970, 1683.

[27] L. Benati, C. M. Camaggi, M. Tiecco, and A. Tundo, *J. Heterocycl. Chem.*, 1972, **9**, 919.

[28] C. M. Camaggi, G. De Luca, and A. Tundo, *J. Chem. Soc., Perkin Trans. 2*, 1972, 412 and 1594.

[29] L. Benati, C. M. Camaggi, and G. Zanardi, *J. Chem. Soc., Perkin Trans. 2*, 1972, 2817.

[30] C. M. Camaggi, R. Leardini, A. Tundo, and M. Tiecco, *J. Chem. Soc., Perkin Trans. 2*, 1974, 271.

[31] L. Benati, C. M. Camaggi, and G. Zanardi, *J. Org. Chem.*, 1975, **40**, 966.

[32] E. R. Bell, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, 1950, **72**, 337; S. K. Wong, *ibid.*, 1979, **79**, 1235.

[33] A. J. Bloodworth, A. G. Davies, I. G. Griffin, B. Muggleton, and B. P. Roberts, *J. Am. Chem. Soc.*, 1974, **96**, 7599.

[34] M. L. Poutsma in ' Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1973, vol. 2, ch. 14, p. 134.

[35] L. Grossi, L. Lunazzi, and G. Placucci, *Tetrahedron Lett.*, 1981, **22**, 251.

[36] K. Kolb and W. A. Black, *Chem. Commun.*, 1969, 1119.

[37] L. Lunazzi, G. Placucci, and L. Grossi, *J. Chem. Soc., Chem. Commun.*, 1979, 533.

[38] L. Lunazzi, G. Placucci, L. Grossi, and M. Guerra, *J. Chem. Soc., Perkin Trans. 2*, 1982, 43.

[39] J. A. Brivati, K. D. J. Root, M. C. R. Symons, and D. J. A. Tinling, *J. Chem. Soc. A*, 1969, 1942; A. R. Lyons and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, 1972, 622.

[40] J. A. Kochi, *Adv. Free Radical Chem.*, 1975, **5**, p. 189.

[41] L. Lunazzi, G. Placucci, and L. Grossi, *J. Chem. Soc., Perkin Trans. 2*, 1980, 717.

[42] J. C. Scaiano and K. U. Ingold, *J. Phys. Chem.*, 1976, **80**, 277.

[43] T. Kawamura and J. K. Kochi, *J. Organomet. Chem.*, 1973, **47**, 79.

[44] H. M. McConnell, *J. Chem. Phys.*, 1956, **24**, 764.

[45] 1. Degani, L. Lunazzi, and G. F. Pedulli, *Mol. Phys.*, 1968, **14**, 217; L. Lunazzi, A. Mangini, G. F. Pedulli, and M. Tiecco, *Gazz. Chim. Ital.*, 1971, **101**, 10; I. Degani, L. Lunazzi, G. F. Pedulli, C. Vincenzi, and A. Mangini, *Mol. Phys.*, 1970, **18**, 613; L. Lunazzi, A. Mangini, G. Placucci, C. Vincenzi, and I. Degani, *ibid.*, 1970, **19**, 543.

[46] V. I. Trofimov, I. I. Ch. Kheidze, L. I. Belerikii, and N. Y. Buben, *Khim. Geterokskl. Akad. Nauk. Latv. SSR*, 1967, 606.

[47] C. Chatgilialoglu and K. U. Ingold, *Can. J. Chem.*, 1981, **59**, 1745; S. Wolfe, M. H. Wangbo, and D. J. Mitchell, *Carbohydr. Res.*, 1979, **69**, 1.

[48] L. Lunazzi, G. Placucci, M. Tiecco, and G. Martelli, *J. Chem. Soc., Perkin Trans. 2*, 1971, 1820.