Investigations of Structure and Conformation. Part 13.[1] An E.s.r. Study of Restricted Rotation and Delocalization in Some Sulphur-substituted Phenoxy-radicals

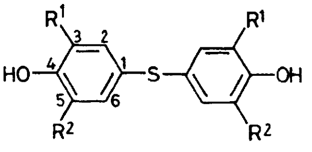
By **Bruce C. Gilbert*** and **Barbara Gill**, Department of Chemistry, University of York, Heslington, York YO1 5DD

E.s.r. spectra of some relatively stable phenoxy-radicals with *para* thioaryl substituents show line-width effects which indicate that there is restricted rotation around the C(phenoxy)–S bond. The barriers to rotation which have been measured (>50 kJ mol^{-1}) imply that in these radicals there is considerable delocalization of the unpaired electron onto sulphur.

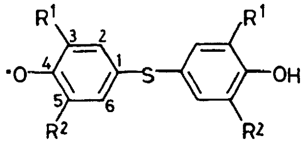
As an extension of our studies on radicals derived from sulphur-containing antioxidants,[2-4] we have employed e.s.r. spectroscopy in an investigation of some sulphur-substituted phenoxy-radicals over a range of temperature. Although many examples of phenoxy-radicals have been studied by e.s.r. (see, *e.g.*, ref. 5) few instances of sulphur-conjugated radicals have been reported (though see, *e.g.*, ref. 6). We have found that some sulphur-substituted phenoxy-radicals show anomalous line-width phenomena which are diagnostic of restricted rotation about the bond between sulphur and the phenoxy-ring; this demonstrates that there is significant delocalization of spin density onto sulphur. The results are presented here.

RESULTS AND DISCUSSION

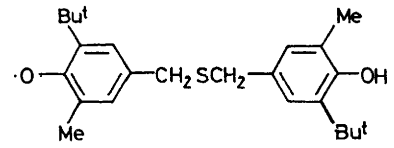
Phenoxy-radicals from Bis-(4-hydroxyphenyl) Sulphides.—Photolysis of a solution of bis-(4-hydroxy-3,5-di-t-butylphenyl) sulphide (1; $R^1 = R^2 = Bu^t$), in methylbenzene at *ca*. 250 K in the cavity of an e.s.r. spectrometer led to the detection of a strong e.s.r. spectrum with *a*(2H) 0.126 mT, *g* 2.005 5. The assignment of this spectrum to radical (2; $R^1 = R^2 = Bu^t$) was confirmed by generating the same species in other ways, for example by treating the sulphide with lead(IV) oxide in methylbenzene, a system which is known to generate phenoxy-radicals from simple phenols[7] (see also ref. 2). The same radical was detected on thermolysis of a solution of the parent sulphide in naphthalene at *ca*. 395 K, although the signal was somewhat weaker than that obtained on photolysis. For thermolysis and photolysis, the signal was enhanced when the experiments were repeated following the addition of di-t-butyl peroxide (presumably as a result of efficient hydrogen-abstraction by Bu^{t}O•), when ^{13}C splittings of 1.36 mT (1C) and 0.718 mT (2C) could also be discerned. It seems likely that these splittings are from the carbon atoms *para* and *ortho*, respectively, to the oxygen atom. The signal from (2; $R^1 = R^2 = Bu^t$) showed no significant changes with temperature, other than a slight increase in the *meta*-proton splitting.



(1)



(2)



(3)

Photolysis of bis-(4-hydroxy-2-methyl-5-t-butylbenzyl) sulphide at low temperatures gave a spectrum attributable to the phenoxy-radical (3), with splittings from the *ortho*-methyl group protons, the *meta*-protons, and the *para*-CH$_2$ group (see Table 1). A weak signal with similar splittings was detected on thermolysis (see Table 1). The lower value of a_H(CH$_2$) at the lower temperature probably reflects the increased weighting of a preferred conformation in which the (β) carbon–sulphur

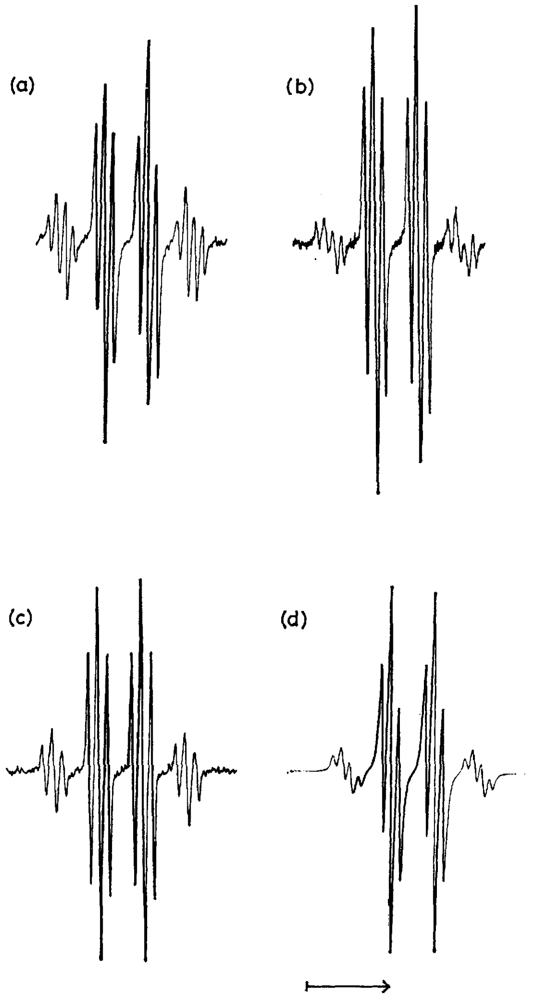
TABLE 1

E.s.r. parameters for phenoxy-radicals from bis-(4-hydroxyphenyl) sulphides and related compounds

Radical	*T*/K	Hyperfine splittings a_H/mT [c]	*g* [d]
(2; $R^1 = R^2 = Bu^t$)	250 [a]	0.126 (2,6-H)	2.0055
	395 [b]	0.138 (2,6-H)	2.0055
(3)	230 [a]	0.170 (2,6-H), 0.675 (CH$_2$), 0.655 (Me)	2.0052
	395 [b]	0.176 (2,6-H), 0.780 (CH$_2$), 0.655 (Me)	2.0052
(2; R^1 = Me, $R^2 = Bu^t$)	245 [a]	0.100 (2,6-H), 0.495 (Me)	2.0056
		0.100 (2,6-H), 0.560 (Me)	2.0056
	295 [a]	0.113 (2,6-H), 0.540 (Me)	2.0056
	417 [b]	0.132 (2,6-H), 0.554 (Me)	2.0056
(2; $R^1 = R^2$ = Me)	239 [a]	0.088 (2,6-H), 0.466 (Me), 0.553 (Me′)	2.0055
	301 [a]	0.113 (2,6-H), 0.517 (2Me)	2.0055
	393 [b]	0.138 (2,6-H), 0.529 (2Me)	2.0055
(13; $R^1 = R^2 = Bu^t$)	250 [a]	0.151 (2,6-H)	2.0052
	395 [b]	0.157 (2,6-H)	2.0052
(13; R^1 = Me, $R^2 = Bu^t$)	263 [a]	0.145 (2,6-H), 0.592 (Me)	2.0052
	300 [a]	0.151 (2,6-H), 0.604 (Me)	2.0052

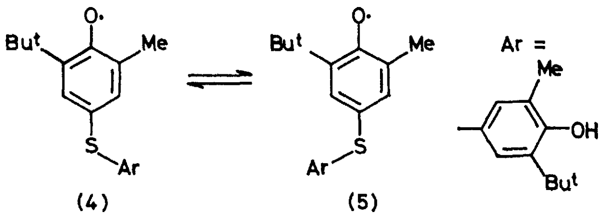
[a] Data refer to radicals generated photolytically in methylbenzene. [b] Data refer to radicals generated by thermolysis in naphthalene; see text. [c] ±0.005. [d] ±0.0001.

bond is at right angles to the ring (so that it eclipses the *p*-orbital containing the unpaired electron at the *para*-position in the ring, *cf.* $\cdot CH_2CH_2SR$ [8]): then the β-hydrogens will subtend a smaller dihedral angle (on average) and hence exhibit a smaller hyperconjugative interaction and splitting.



E.s.r. spectra of the phenoxy-radical from bis-(4-hydroxy-3-methyl-5-t-butylphenyl) sulphide (2; R^1 = Me, R^2 = Bu^t): (a), (b), and (c), experimental spectra recorded for solutions of the sulphide in methylbenzene containing di-t-butyl peroxide at 245, 268, and 295 K, respectively. (d) Spectrum for 268 K simulated using the hyperfine splittings for two separate conformers and the exchange rate given in Table 2

Generation of the phenoxy-radical (2; R^1 = Me, R^2 = Bu^t) by a variety of different methods led to spectra which were very dependent upon temperature. Thermolysis of the sulphide (1; R^1 = Me, R^2 = Bu^t) at 417 K gave a spectrum comprising a quartet of triplets (see Table 1) which can be unambiguously ascribed to this radical; virtually identical spectra were obtained by photolysis at 295 K and by oxidation with PbO_2 at room temperature. However, photolysis of the sulphide at 245 K gave a very different spectrum (see Figure); this is interpreted in terms of two overlapping quartets of triplets, with identical *g*-values, line-widths, and concentrations, but with the slightly different sets of splittings listed in Table 1. As the temperature was raised, the two signals were observed to broaden and coalesce until the simpler high-temperature spectrum was achieved (see Figure). This behaviour, which is similar to that observed [9] for the poly-2-methyl-6-t-butylphenoxy-radical, proved reproducible and reversible. We believe that at low temperatures the two forms (4) and (5) of this radical are 'frozen out' (*i.e.* that the exchange involving rotation around C(1)–S is in the slow-exchange region) and that the two forms have slightly different methyl-proton splittings. As the temperature is raised, the rate of interconversion increases, through the intermediate region, until it is in the fast-exchange ('averaged') region by *ca.* 290 K. It seems likely that these conformations are planar (at least as far as the phenoxy-ring and S–CAr are concerned) but we are unable to determine which set of splittings belong to which conformer or to draw conclusions about the conformation of the phenolic ring.



(4) (5)

Analysis of the exchange effects with the aid of spectrum simulation has been carried out, allowance being made for the slight increase in the total width of the spectrum with temperature. We interpret the increase in both *a*(2H) and *a*(Me) (average) as the result of a slight increase with temperature of the values of the hyperfine splittings of each conformer. Some of the increase $d|a(H)|/dT$ for the 2-protons, for example, could result from increased out-of-plane C–H bending; however the magnitude of the increase observed (*ca.* 0.2 μT K^{-1}) compared with that typical of the coefficients found for this type of distortion in related radicals with protons attached to sites with negative spin density (*ca.*[10] 0.02 μT K^{-1}) suggests that another mechanism is involved. It seems likely that the increases reflect slightly increased spin density in the phenoxy ring of the radical; this would follow if delocalization onto sulphur decreases at higher temperatures because of increased contributions from conformations with the S–Ar bond out of the plane containing the sulphur atom and the phenoxy-ring [*e.g. via* increased torsional oscillations in (4) and (5)].

We have assumed that the splittings in each conformer increase linearly with temperature and have estimated the *individual* methyl splittings necessary to give the observed *average* methyl splitting at all temperatures other than those where the exchange is slow; we have used these splittings in a simulation program which incorporates a simple two-jump exchange, and have hence simulated the spectra at higher temperatures (see Figure and Table 2). From the resulting values of k as a function of temperature we estimate from an Arrhenius plot of ln k vs. T^{-1} (which gave a good straight line), that the energy barrier to conformational interconversion is 72.0 ± 2.1 kJ mol^{-1}.

TABLE 2

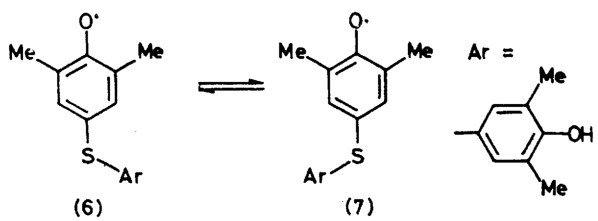
Estimated values of the hyperfine splittings and rates of exchange of the two conformers (4) and (5) of the phenoxy-radical from bis-(4-hydroxy-3-methyl-5-t-butylphenyl) sulphide [a,b]

	Hyperfine splittings/mT				
T/K	a(Me)	a(2,6-H)	a(Me′)	a(2,6-H)	k/s^{-1}
245	0.495	0.100	0.560	0.100	$\leqslant 2 \times 10^5$
258	0.499	0.103	0.563	0.103	1×10^6
268	0.502	0.106	0.565	0.106	3×10^6
276	0.504	0.108	0.566	0.108	9×10^6
283	0.506	0.109	0.568	0.109	2×10^7
295	0.510	0.113	0.570	0.113	$\geqslant 8 \times 10^7$

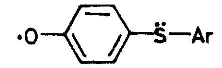
[a] Values of a(2,6-H) at 245 and 295 K as observed. Values of a(Me) for 245 K measured from the slow-exchange spectrum; other values of a(Me), a(Me′), and a(2,6-H) calculated from the observed average splittings, with allowance made for the temperature coefficients da/dT (see text). [b] Radical generated photolytically in methylbenzene in the presence of di-t-butyl peroxide.

It should also be noted that this radical, and also (2; $R^1 = R^2 = Bu^t$), proved long-lived; the signals generally decayed slowly over a period of hours after photolysis or heating was discontinued.

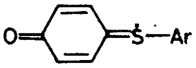
The phenoxy-radical from (1; $R^1 = R^2 =$ Me), which also proved fairly stable, showed a similar pattern of behaviour to that described for (2; $R^1 =$ Me, $R^2 = Bu^t$). The spectrum observed on both thermolysis and photolysis at room temperature showed a septet of triplets, with equivalent interaction with the two methyl groups (see Table 1). At low temperatures, however, two non-equivalent methyl-group splittings were detected, and at intermediate temperatures characteristic alternating line-width effects were observed (*cf.* the behaviour of 2,6-dimethyl-4-methoxyphenoxyl [11] and some polymeric 4-aryloxyphenoxyls [9]). Splittings again increased with temperature [compare, *e.g.*, a(2,6-H) at 239 and 301 K, or the average of the separate methyl group splittings at 239 and the averaged value observed at 310 K]. Individual methyl splittings in the intermediate and fast-exchange region were obtained as above, and the spectra were satisfactorily simulated using the data given in Table 3. Again an Arrhenius plot gave a good straight line, yielding a value for the interconversion involving rotation around C(1)–S [(6) $\rightleftharpoons$ (7)] of 54.5 ± 4.2 kJ mol^{-1}.



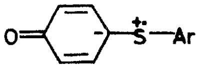
(6) (7)



(8)

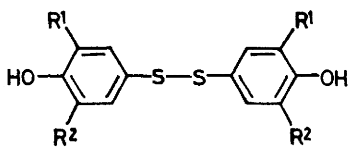


(9)

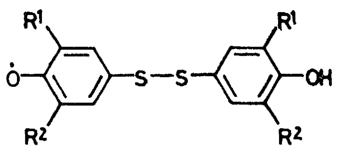


(10)

(11)



(12)



(13)

The barriers to rotation in (2; $R^1 =$ Me, $R^2 = Bu^t$) and (2; $R^1 = R^2 =$ Me) are considerably greater than estimates of the upper limits of the barriers to rotation around corresponding bonds in diphenyl sulphides [12] (< *ca.* 8 kJ mol^{-1}) and bis-(4-hydroxyphenyl) sulphide cation-radicals [13] (<16 kJ mol^{-1}) and also greater than the barrier to rotation about C–S in the radical $\cdot CH_2SBu$ (*ca.*[14] 25 kJ mol^{-1}). Barriers to rotation around C–O in many alkoxy-substituted cation-radicals appear to be *ca.*[15] 40 kJ mol^{-1}, though a value of 67 kJ mol^{-1} has been reported [16] for the cation-radical from 1,4-dimethoxybenzene; the barrier in 4-methoxy-2,6-dimethylphenoxyl is estimated [11] as 32.6 kJ mol^{-1} and those for poly-2,6-dimethylphenoxyl and poly-2-methyl-6-t-butylphenoxyl are 39.3 and 41.8 kJ mol^{-1}, respectively.[9] We attribute the magnitude of the barriers in radicals of the type (2) (and also, to some extent at least, their stability) to the considerable delocalization of the unpaired electron onto sulphur *via* p_π–p_π overlap, which presumably constrains the phenoxy-ring and the S–Ar bond effectively into the same plane [*cf.* canonical structures (8)—(11)]. That the value of the barrier is so much greater than for [14] $\cdot CH_2SR$ may reflect the extra importance of polar structures such as (11). Further delocalization into the aryl substituent on sulphur may occur to some extent, though the absence of detectable splittings from protons in this ring suggests that it is not significant. The fact that the barrier for (2; $R^1 =$ Me, $R^2 = Bu^t$) is somewhat greater than that for (2; $R^1 = R^2 =$ Me) may reflect an additional contribution from steric hindrance involving the bulky t-butyl groups in the transition state for the former. We expect that this type of hindered rotation also occurs for (2; $R^1 = R^2 = Bu^t$); however, as with (2; $R^1 =$ Me, $R^2 = Bu^t$) and (2; $R^1 = R^2 =$ Me), any difference between the individual *meta*-proton splittings is too small to resolve, so that these *appear* to be equivalent at all temperatures.

Radicals from Bis-(4-hydroxyphenyl) Disulphides.— Direct photolysis of a solution of (12; $R^1 = R^2 = Bu^t$) in methylbenzene over a range of temperature led to the detection of a signal (see Table 1) attributed to the corresponding phenoxy-radical (13; $R^1 = R^2 = Bu^t$). The same radical was also generated with PbO_2 and on thermolysis in naphthalene. The value of the *meta*-proton splitting is larger, and the *g*-value is lower, than the corresponding parameters for the related phenoxy-radical with a mono-sulphide bridge (2; $R^1 = R^2 = Bu^t$). The e.s.r. data indicate that there is less delocalization onto the disulphide bridge than onto the single sulphur.

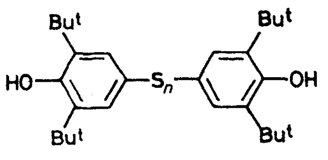
TABLE 3

Estimated values of the hyperfine splittings and rates of exchange [(6) $\rightleftharpoons$ (7)] for the phenoxy-radical from bis-(4-hydroxy-3,5-dimethylphenyl) sulphide [a,b]

	Hyperfine splittings/mT			
T/K	a(Me)	a(Me′)	a(2,6-H)	k/s^{-1}
239	0.553	0.466	0.088	$\leqslant 4 \times 10^5$
245	0.554	0.467	0.090	8×10^5
255	0.555	0.468	0.094	1.5×10^6
266	0.556	0.469	0.099	1×10^7
275	0.557	0.470	0.103	2×10^7
281	0.558	0.471	0.105	3×10^7
301	0.560	0.473	0.113	$\geqslant 8 \times 10^7$

[a] Values of a(2,6-H) at 239 and 301 K as observed; values of a(Me) and a(Me′) for 239 K measured from the slow-exchange spectrum; other values for a(Me), a(Me′), and a(2,6-H) calculated from the observed average splittings, with allowance made for the temperature coefficients, da/dT (see text). [b] Radical generated photolytically in methylbenzene.

The splittings and *g*-value for (13; $R^1 = Me$, $R^2 = Bu^t$), generated similarly, lead to the same conclusion [note, for example, the greater value for a(Me) than for (2: $R^1 = Me$, $R^2 = Bu^t$)]. Further, the phenoxy-radical from the disulphide did not show any line-width effects as the temperature was lowered [in contrast to the ' freezing-out ' of conformations (4) and (5) for the mono-sulphide radical]; even at 240 K the spectrum comprised a sharp quartet of triplets. This indicates that the barrier to rotation around C(1)–S is considerably lower for the disulphide-bridged species than for the radicals (2; $R^1 = Me$, $R^2 = Bu^t$) and (2; $R^1 = R^2 = Me$), which is again consistent with the smaller extent of delocalization into the disulphide bridge.



(14)

We also attempted to generate phenoxy-radicals from the tri- and tetra-sulphides (14; $n = 3$ or 4) using methods previously outlined. In both cases weak signals were detected with a(2H) 0.150 mT, g 2.005 2. These may be signals from the appropriate tri- and tetra-sulphide phenoxy-radicals (with no extra delocalization compared with the disulphide analogues) although we cannot rule out the possibility that they are derived from the disulphide radical itself (13; $R^1 = R^2 = Bu^t$) produced *via* the breakdown of (14).

EXPERIMENTAL

E.s.r. spectra were recorded on a Varian E-104 *X*-band spectrometer employing 100 kHz modulation. In all experiments the temperature was controlled with a Varian Variable Temperature Accessory. Details of the procedure for measuring and calibrating spectra, the photolytic apparatus, and the simulation program employed have been described previously;[17] the program was executed on a DEC KL10 computer at the University of York.

Photolysis experiments were carried out on samples which contained typically 0.1 g of substrate in 2 ml of methylbenzene which had been deoxygenated with a nitrogen purge; samples were studied in the temperature range 190—300 K. Samples for thermolysis contained *ca.* 0.05 g substrate in 0.5 g naphthalene and were heated to *ca.* 400 K. For some photolysis and thermolysis experiments, samples also contained about four drops of di-t-butyl peroxide.

Bis-(4-hydroxy-3-methyl-5-t-butylbenzyl) sulphide was kindly provided by Dr. G. Brunton, and bis-(4-hydroxy-3,5-di-t-butylphenyl) sulphide, disulphide, trisulphide, and tetrasulphide, and bis-(4-hydroxy-3-methyl-5-t-butylphenyl) sulphide were kindly provided by Dr. M. D. Sexton; these samples were used without further purification except for bis-(4-hydroxy-3,5-di-t-butylphenyl) disulphide which was recrystallised from n-heptane. Bis-(4-hydroxy-3,5-dimethylphenyl) sulphide was prepared according to the method described in ref. 2. Bis-(4-hydroxy-3-methyl-5-t-butylphenyl) disulphide was prepared[18] from the corresponding phenol *via* reaction with S_2Cl_2 and iron catalyst. Naphthalene (Fisons SLR), methylbenzene (B.D.H. AnalaR), and di-t-butyl peroxide (Koch–Light) were commercial samples; the peroxide was passed through an alumina column prior to use.

We thank Dr. M. D. Sexton and Dr. G. Brunton for gifts of chemicals and for helpful discussions. We are grateful to the S.R.C. and to ESSO Chemicals Ltd. for a C.A.S.E. award (to B. G.).

[8/1631 *Received*, 12*th September*, 1978]

REFERENCES

[1] Part 12, C. Chatgilialoglu, B. C. Gilbert, and R. O. C. Norman, preceding paper.

[2] G. Brunton, B. C. Gilbert, and R. J. Mawby, *J.C.S. Perkin II*, 1976, 1267.

[3] G. Brunton, B. C. Gilbert, and R. J. Mawby, *J.C.S. Perkin II*, 1976, 650.

[4] B. C. Gilbert, B. Gill, and M. D. Sexton, *J.C.S. Chem. Comm.*, 1978, 78.

[5] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 213.

[6] H. B. Stegmann, K. Scheffler, and E. Müller, *Annalen*, 1964, **677**, 59.

[7] C. Steelink, *J. Amer. Chem. Soc.*, 1965, **87**, 2056.

[8] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1971, **93**, 846.

[9] W. J. van den Hoek, J. F. Th. de Winter, and J. Smidt, *J. Magnetic Resonance*, 1972, **6**, 15.

[10] P. D. Sullivan and E. M. Menger, *Adv. Magnetic Resonance*, 1977, **9**, 1.

[11] W. J. van den Hoek, W. G. B. Huysmans, and M. J. C. van Gemert, *J. Magnetic Resonance*, 1970, **3**, 137.

[12] V. Galasso, G. De Alti, and A. Bigotto, *Tetrahedron*, 1971, **27**, 6151; V. A. Zubkov, T. M. Birshtein, and I. S. Milevskaya, *J. Mol. Struct.*, 1975, **27**, 139.

[13] P. D. Sullivan and L. J. Norman, *J. Magnetic Resonance*, 1976, **23**, 395.

[14] I. Biddles, A. Hudson, and J. T. Wiffen, *Tetrahedron*, 1972, **28**, 867.

[15] D. G. Ondercin, P. D. Sullivan, E. van der Drift, W. J. van den Hoek, B. Rousseau, and J. Smidt, *J. Magnetic Resonance*, 1976, **23**, 39.

[16] P. D. Sullivan, *J. Phys. Chem.*, 1970, **74**, 2563.

[17] C. Gaze and B. C. Gilbert, *J.C.S. Perkin II*, 1977, 116.

[18] 'Beilsteins Handbuch der Organischen Chemie,' 4th Auaflage, 3rd Ergänzungswerk, Band 6, Teil 6, p. 4465.