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SOME SUBSTITUTION REACTIONS OF PENTAFLUOROBENZENESULFENYL CHLORIDE

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SUMMARY

The substitution reactions of pentafluorobenzenesulfenyl chloride, C_6F_5SCl, at carbon (aromatic compounds and active methylene groups), nitrogen, and oxygen have been studied. Physical properties of the new compounds isolated are reported together with some spectroscopic data.

INTRODUCTION

The chemistry of the sulfenyl halides has been extensively reviewed [1]. Pentafluorobenzenesulfenyl chloride is relatively new and some of its reactions have been reported [2,3]. This paper describes some of its substitution reactions, where the C_6F_5S groupis acting as an electrophile, $C_6F_5S^+$-Cl^-. The reactions can be divided into various categories,

a) Substitution at carbon, both in compounds containing active methylene groups and in aromatic compounds.
b) Substitution at nitrogen.
c) Substitution at oxygen.

These reactions show that it is not as good an electrophile as its fluorinated aliphatic analog trifluoromethanesulfenyl chloride, CF_3SCl.

RESULTS AND DISCUSSION

Reactions with compounds containing an active methylene group

Sulfenyl chlorides react readily with α-methylene groups of aliphatic or cycloaliphatic ketones and suitable carboxamides or lactams [1]. Repeated attack may occur, e.g. in the reaction of acetone with ethanesulfenyl chloride complete substitution occured after heating at 30° for five hours [4]. Pentafluorobenzenesulfenyl chloride reacted

$$6EtSCl + MeCOMe \longrightarrow (EtS)_3CCOC(SEt)_3 + 6HCl$$

readily with acetone, methyl ethyl ketone, acetophenone, and acetylacetone to give the monosubstituted products. The reaction with aldehydes was relatively slow, and the reaction with iso-butyraldehyde had to be heated. Multiple substitution was only observed with malonic acid, where a mixture of mono- and di-substituted products was isolated. No attempt

$$C_6F_5SCl + (HO_2C)_2CH_2 \longrightarrow (HO_2C)_2CHSC_6F_5 + (HO_2C)_2C(SC_6F_5)_2$$

was made to prepare compounds with multiple substitution by increasing the relative amount of the sulfenyl chloride.

Sulfenyl chlorides generally react with the sodium salts of nitroalkanes forming the 1-nitroalkyl thioether [1]; such a reaction occurred with C_6F_5SCl and the sodium salt of nitroethane. No reaction was observed

$$Na^{+-}CHMeNO_2 + C_6F_5SCl \longrightarrow C_6F_5S(Me)CHNO_2 + NaCl$$

with the sodium salt of nitromethane, but this may be due to its tendency to undergo self condensation reactions [5]. No substitution products were isolated from the reaction of pure nitromethane and the sulfenyl chloride.

Reactions with aromatic compounds

Sulfenyl chlorides, such as trifluoromethanesulfenyl chloride, react readily with aromatic compounds to give substitution of the aromatic hydrogen. This occurs particularly with aromatic rings highly activated by group such as NMe_2 or OH, where almost exclusively para

$$C_6H_5NMe_2 + CF_3SCl \longrightarrow \underline{p}\text{-}CF_3SC_6H_4NMe_2 + PhMe_2NHCl$$

substitution is observed [6]. Similar substitution reactions were observed with pentafluorobenzenesulfenyl chloride. Analogous reactions occurred

$$C_6F_5SCl + C_6H_5X \longrightarrow \underline{p}\text{-}C_6F_5SC_6H_4X + HCl$$

(X = NHMe, NMe_2, NEt_2, OH, OMe)

with o- and m-cresol giving substitution para to the OH group. In the reaction with aniline substitution at the nitrogen rather than the aromatic ring was observed. Substitution of both the aromatic hydrogen and the N-H bond occurred in the reaction of methylaniline. The ratio of the

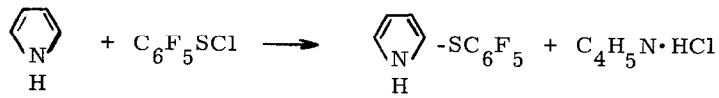
$$C_6F_5SCl + PhNHMe \longrightarrow PhNMeSC_6F_5 + \underline{p}\text{-}C_6F_5SC_6H_4NHMe + PhNMeH_2Cl$$

products $PhNMeSC_6F_5$ and $\underline{p}\text{-}C_6F_5SC_6H_4NHMe$ was approximately 2:1. It has previously been reported that diphenylamine reacted with pentafluorobenzenesulfenyl chloride to give the N-substituted compound $C_6F_5SNPh_2$ [2], but in an analogous reaction of diphenylamine with pentafluorobenzeneselenyl chloride aromatic substitution was observed forming $C_6F_5SeC_6H_4NHPh$ [7].

Examination of the various spectra of the product from diphenylamine and pentafluorobenzenesulfenyl chloride showed that it was undoubtedly primarily $\underline{p}\text{-}C_6F_5SC_6H_4NHPh$. The infrared spectrum clearly showed the presence of an NH group, with an absorption at 3400 cm^{-1}. The proton NMR spectrum was not as definite. No distinct N-H could be separated from the protons of the aromatic ring, although when the 220 MHz spectrum was rerun in the presence of D_2O the proton pattern changed somewhat, presumably due to the exchange of the N-H proton with the D_2O. The aromatic proton spectrum was more complex than that of diphenylamine, but some of the peaks could be assigned to a phenyl group attached to nitrogen. The possibility of some $Ph_2NSC_6F_5$ being present together with $C_6F_5SC_6H_4NHPh$ cannot be excluded. The integrated proton NMR spectra of all the other substitution products showed clearly that substitution on the aromatic ring had occurred and that this occurred para to the OR or NRR' group.

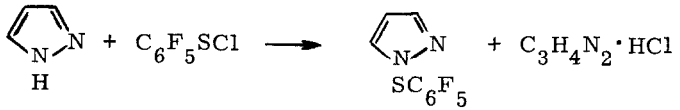
When the aromatic group was attached to an unsaturated system, such as PhC≡CH, addition to the unsaturated system was observed [8]. No substitution products were isolated from the reactions between pentafluorobenzenesulfenyl chloride and the aromatic compounds C_6H_5X (X = F, Br, Me, CH_2Ph, CHO, NCO, SMe, PMe_2, N≡NPh, COPh). Although reactions have been observed between trifluoromethanesulfenyl chloride and PhMe, PhCl, and PhBr, the reaction conditions in a "Hastelloy" lined bomb, with BF_3 as a catalyst, are somewhat more drastic than those used in the present work [6]. It must be concluded that the presence of an OR or NRR' group on the aromatic ring effectively activated the ring for substitution with pentafluorobenzenesulfenyl chloride as an electrophile. The differences in the reactivities of trifluoromethanesulfenyl chloride and pentafluorobenzenesulfenyl chloride may be due to the somewhat weaker electrophilic nature of pentafluorobenzenesulfenyl chloride when compared with trifluoromethanesulfenyl chloride [2].

Extension of this work to the heterocyclic compounds pyrrole and thiophen showed that substitution occurred in both cases at the 2-carbon atom.



The reaction with thiophen did not occur nearly as readily as that with pyrrole.

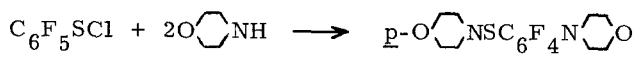
In the reaction of pyrazole with pentafluorobenzenesulfenyl chloride substitution at the nitrogen rather than the carbon was observed.



Substitution of nitrogen compounds

The reaction of pentafluorobenzenesulfenyl chloride with ammonia and aliphatic amines has been described [2, 3], and the reactions with

some aromatic amines are described in this paper. The reactions of the cyclic amines morpholine and pyrrolidine gave a product which involved substitution at the nitrogen and nucleophilic attack of the nitrogen base on the C_6F_5 group. It is likely that the pentafluorobenzenesulfenyl chloride



first attacked the N-H bond of the base and the product was subsequently attacked nucleophilically by the base, replacing an aromatic fluorine. Pentafluorobenzenesulfenyl chloride has only been reported to react with aliphatic bases to form sulfenamides [2], but nucleophilic substitution of the C_6F_5 group with nitrogen containing nucleophiles is well known [9].

Sulfenyl chlorides also react with the salts of various compounds containing an acidic N-H group [1]. The nitrogen atom in the potassium salts of phthalimide and saccharin has been substituted. The S-N bond

in these products was very labile and readily cleaved by water or hydroxylic solvents.

Substitution of hydroxy compounds

Sulfenyl chlorides react readily with hydroxy compounds such as alcohols and phenols, but the stability of the "monothioperoxides" obtained is very variable [1]. Arenesulfenic acid alkyl esters are susceptible to hydrolysis and readily react to give disulfides and thiosulfonic esters. The alkyl esters, F_3CSOR and Cl_3CSOR, have been prepared from the corresponding sulfenyl chloride and aliphatic alcohol in the presence of pyridine [10, 11].

The disulfide, $C_6F_5SSC_6F_5$, was formed when methanol and ethanol reacted with pentafluorobenzenesulfenyl chloride in the presence of pyridine. Using the sodium salts rather than the free alcohols gave unidentified products. It is conceivable that under these conditions the alkoxide ion

present attacked the C_6F_5 group replacing one or more of the fluorine atoms. When the reaction between the alcohols and the sulfenyl chloride was studied in ethylene dibromide the disulfide, $C_6F_5SSC_6F_5$, was isolated from the methanol reaction while ethyl pentafluorobenzenesulfinate, $C_6F_5S(O)OEt$, was obtained from the ethanol reaction. The latter may be formed by air oxidation of the sulfenate, C_6F_5SOEt.

Separate experiments showed that the sulfenyl chloride was hydrolysed to the disulfide in water and 15 % aqueous solutions of sodium hydroxide or carbonate. Hydrolysis of aromatic sulfenyl chlorides usually leads to the disulfide, but the thiosulfonate ester, $ArSO_2SAr$, can also be isolated [12]. No sulfonic acid was detected in the hydrolysis products of pentafluorobenzenesulfenyl chloride.

Hydrolysis of trifluoromethanesulfenyl chloride gave the unstable trifluoromethanethiol and trifluoromethanesulfinic acid. The reaction probably proceeded via the unstable sulfenic acid, CF_3SOH. The sulfinic

$$2CF_3SCl + 2H_2O \longrightarrow CF_3SH + CF_3SO_2H + 2HCl$$

acid is stable in solution and was isolated as its sodium salt [13].

Spectroscopic studies

The infrared spectra of the products were characteristic of the functional groups present. Some of the reaction products were initially partially characterized from their infrared spectra. The N-H absorption at around 3400 cm^{-1} in the product from Ph_2NH and C_6F_5SCl indicated that an N-H bond was present and that an aromatic hydrogen rather than a hydrogen bonded to nitrogen had been replaced. In analogous reactions the presence of an N-H or an O-H group was easily detected. The compound $C_6F_5S(O)OEt$ has possible >S=O and -SO-OR bands at 1095(s) and 1150(w) cm^{-1}; the literature values are within the ranges 1060-1040 and 1125-1135 cm^{-1} respectively [14].

The NMR spectra were also used to characterize the reaction products. Details of some proton spectra are tabulated in Table 1. The proton spectrum of p-$C_6F_5SC_6H_4NHPh$ at 220 MHz showed multiplets

between 6.02 and 7.64 p.p.m.. There was a change in the pattern when D_2O was added, particularly of the doublet at 7.03 p.p.m., indicating the presence of an N-H group within this range, which showed proton-deuterium exchange. Comparison of the spectra of the products from pyrrole and thiophen with that of pyrrole-2-aldehyde [15], showed that substitution had occurred at the 2-position. The presence of non separable products from the reaction of C_6F_5SCl and PhNHMe, involving substitution of the phenyl ring or the N-H group, could be detected.

The structures of the products from the reactions of morpholine and pyrrolidine with C_6F_5SCl were partially determined from their ^{19}F NMR spectra. The spectra showed clearly the presence of equivalent amounts of two different fluorine atoms, indicating the structure $\underline{p}$-XC_6F_4Y.

In compounds of the type C_6F_5X the ^{19}F NMR spectra have been used to determine the interaction between the ring and the substituent X and the equation $J_{24} = -0.453\,\delta_p + 71.98$ derived (J_{24} = $\underline{o}$-F to $\underline{p}$-F coupling constant) [16, 17]. It was found that $\underline{\pi}$-donors cause negative J_{24} values and δ_p values > 160 p.p.m., while $\underline{\pi}$ acceptors tend to cause positive J_{24} values and δ_p values < 160 p.p.m.. In compounds of the type C_6F_5SY a regular variation of J_{24} and δ_p was observed [2]. This has now been extended to observe the secondary effects of the Z group in the compounds $\underline{p}$-$C_6F_5SC_6H_4Z$, when Z = H, NHPh, OMe, OH, NMe_2, and NEt_2. The spectra have not been interpreted in detail, but a plot of J_{24} versus δ_p is virtually linear showing that all the substitutents are weak $\underline{\pi}$ electron acceptors, the magnitude increasing in the series $NEt_2 < NMe_2 < OMe < OH < NHPh < H$ [2].

TABLE 1
Proton NMR spectra of some compounds

Compound	Chemical shift (p.p.m.)			Ratios		
	ArH	Me	X	ArH	Me	X
$PhNHSC_6F_5$	6.95M	-	5.03S(NH)	5	-	1
$\underline{p}$-$C_6F_5SC_6H_4NHMe$	6.35M	2.85D	4.92S(NH)	6	3	1
$PhNMeSC_6F_5$	6.95M	3.33S	-	5	3	-
$\underline{p}$-$C_6F_5SC_6H_4NMe_2$	6.48D	2.90S	-	4	6	-
	7.37D					
$\underline{p}$-$C_6F_5SC_6H_4NEt_2$	6.45D	1.17T	3.30Q(CH_2)	4	6	4
	7.30D					
$\underline{p}$-$C_6F_5SC_6H_4OH$	6.67D	-	5.68S(OH)	4	-	1
	7.38D					
$\underline{p}$-$C_6F_5SC_6H_4OMe$	6.67D	3.70S	-	4	3	-
	7.35D					
1-C_6F_5S-3-Me-4-OH-C_6H_4	6.68D	2.20S	4.80S(OH)	3	3	1
	7.17D					
	7.23D					

S = singlet, D = doublet, T = triplet, Q = quartet

EXPERIMENTAL

Most reagents were available commercially. Pentafluorobenzenesulfenyl chloride was prepared by a literature method [2]. Microanalyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, W. Germany. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer as thin films or KBr discs. The ^{1}H NMR spectra were recorded on a Varian A 60, HA 100, or HR 220, or a Perkin-Elmer R 24 instrument, usually in CCl_4 solution with TMS as internal standard. The ^{19}F NMR spectra were recorded on a Varian A 56/60 spectrometer using CCl_4 solutions with $CFCl_3$ as an internal standard. The analytical data and physical properties of the new compounds prepared are shown

in Table 2. All the experiments were performed using 10-20 mmoles of reagents. p-$C_6F_5SC_6H_4NHPh$ was prepared as described previously [2].

Substitution with ketones

Approximately 10 mmoles of C_6F_5SCl was added dropwise to a stirred solution of ketone in 5 ml. CCl_4. C_6F_5SCl was decolorized immediately. After removal of the solvent, the residue was purified.

Substitution with Me_2CHCHO

A mixture of about 7 mmoles of C_6F_5SCl, 10 mmoles of Me_2CHCHO and 10 ml. of anhydrous ether was refluxed overnight.

Substitution with amines and derivatives

About 22 mmoles of amines or derivatives was added dropwise to a stirred solution of C_6F_5SCl in 15 ml. of anhydrous ether. The amine hydrochloride was filtered and after removing the solvent, the residue was purified.

Substitution with aromatic compounds

Approximately 10.5 mmoles of C_6F_5SCl was added dropwise to an ice cooled mixture of 10 mmoles of phenol or phenyl derivative and 10 mmoles of pyridine in 5 ml. $CHCl_3$. After completion of the reaction the $CHCl_3$ was removed and 10 ml. anhydrous ether added. The pyridinium hydrochloride was filtered off, the ether evaporated and the product isolated. No reaction occurred between Ph_2CO, Ph_2N_2, and PhNCO and C_6F_5SCl. The disulfide, $(C_6F_5S)_2$, was isolated from reactions with Ph_2CH_2, PhMe, PhF, PhBr ($AlCl_3$ catalyst). Unidentified products were obtained from the reactions with PhCHO ($AlCl_3$ catalyst, white solid, m.p. 128-9°. Found: C, 38.3; H, 0.54; S, 14.4 %), PhSMe (white solid, m.p. 206-8°. Found: C, 37.4; H, 1.3; S, 13.9 %) and $PhPMe_2$ (white

TABLE 2

Reaction Conditions, elemental analyses, and physical properties of products

Substrate	Product	M.p/°C b.p./°C/Torr	Methods †	Calculated (%)			Found (%)		
				C	H	S	C	H	S
Me_2CO	$C_9H_5F_5OS$	80-81/1	CCl_4; 1; 76	42.2	12.5	2.0	42.2	12.7	1.9
MeCOEt	$C_{10}H_7F_5OS$	79-80/0.8	CCl_4; 1; 78	44.4	11.9	2.6	44.3	12.1	2.4
PhCOMe	$C_{14}H_7F_5OS$	66-67	CCl_4; 2M; 18	52.8	10.0	2.2	52.3	10.8	2.1
$H_2C(COMe)_2$	$C_{11}H_7F_5O_2S$	53-54	CCl_4; 2M; 56	44.3	10.8	2.4	44.6	10.9	2.4
$H_2C(CO_2H)_2$	$C_9H_3F_5O_4S$	57-58	CCl_4; 2E, 3; 5	35.8	10.6	1.0	35.9	11.0	1.2
	$C_{15}H_2F_{10}O_4S_2$	109-110	CCl_4; 2Et; 3; 4	36.0	12.8	0.4	36.8	12.4	0.5
Me_2CHCHO	$C_{10}H_7F_5OS$	48-50/0.1	Et_2O; 1; 27	44.4	11.9	2.6	44.6	11.8	2.9
$O(C_2H_4)_2NH$	$C_{14}H_{16}F_4N_2O_2S$ *	102-103	Et_2O; 2Et; 5	47.7	9.1	4.6	47.9	9.1	4.4
$(CH_2)_4NH$	$C_{14}H_{16}F_4N_2S$	115-116	Et_2O; 2Et, 3; 4	52.5	10.0	5.0	52.3	9.8	5.2
C_4H_5N	$C_{10}H_4F_5NS$	70-71/0.15	Et_2O; 1; 21	45.3	12.1	1.5	45.3	12.0	1.5
C_4H_4S	$C_{10}H_3F_5S_2$	64-65/0.15	Et_2O; 1; 6	42.5	22.7	1.1	42.5	22.6	1.1
Pyrazole	$C_9H_3F_5N_2S$	119-121	$CHCl_3$; 2P, 3; 29	40.6	12.0	1.1	40.8	12.2	1.2
Phthalimide	$C_{14}H_4F_5NO_2S$	152-153	C_6H_6; 2B; -	48.7	9.3	1.2	48.6	10.0	1.7
Saccharin	$C_{13}H_4F_5NO_3S_2$	143-145	C_6H_6; 2B; 38	40.9	16.8	1.1	40.9	16.6	1.0
$EtNO_2$	$C_8H_4F_5NO_2S$	82-83/0.6	Et_2O; 1; 62	35.2	11.7	1.5	35.3	11.8	1.5
EtOH	$C_8H_5F_5O_2S$	62-63/0.6	$(BrCH_2)_2$; 1; 22	36.9	12.3	1.9	36.8	12.6	2.0
$PhNH_2$	$C_{12}H_6F_5NS$	66-67	Et_2O; 2M; 28	49.5	11.0	2.1	49.1	11.0	2.4

PhNHMe	$C_{13}H_8F_5NS$	37-39	Et_2O; 1, 2E; 4	51.1	10.5	2.6	51.4	10.9	2.6
$PhNMe_2$	$C_{14}H_{10}F_5NS$	66-67	Et_2O; 2E; 5	52.7	10.0	3.2	53.0	10.0	3.3
$PhNEt_2$	$C_{16}H_{14}F_5NS$	37-38	Et_2O; 1, 2M; 12	55.3	9.2	4.1	55.3	9.3	4.1
PhOH	$C_{12}H_5F_5OS$	94-96	$CHCl_3$; 2P; 34	49.3	11.0	1.7	49.0	11.1	1.9
PhOMe	$C_{13}H_7F_5OS$	94-95/0.15	$CHCl_3$; 1; 23	51.0	10.5	2.3	50.7	10.7	2.0
o-MeC_6H_4OH	$C_{13}H_7F_5OS$	86-87	$CHCl_3$; 2P; 11	51.0	10.5	2.3	50.8	10.6	2.6
m-MeC_6H_4OH	$C_{13}H_7F_5OS$	129-130	$CHCl_3$; 2P, 3; 16	51.0	10.5	2.3	50.6	10.6	2.5

All liquid products are colorless, all solids white

R = C_6F_5

Purification: 1 = destillation in vacuo, 2 = recrystallization; (B = C_6H_6, E = EtOH, M = MeOH, P = pentane); 3 = vacuum sublimation

* M.W. - Calc., 352.4; Found, 359 (ebullioscopic C_6H_6)

† Methods: Reaction solvent: Method of purification: Yield (%).

solid, m.p. 116-7°. Found: C, 62.6; H, 7.3 %. This may be $PhPOMe_2$, m.p. 100° [18]. Calc.: C, 62.3; H, 7.2 %).

Substitution with imides

The imides were converted to their potassium salts [19]. Approximately 10 mmoles of C_6F_5SCl in 5 ml. anhydrous C_6H_6 was added dropwise to a suspension of 10 mmoles of the potassium imide in 30 ml. C_6H_6 and heated at 50-60° until the reaction was complete. The mixture was filtered hot. The filtrate was concentrated to about 10 ml. and kept at about 5° to induce crystallization.

Substitution with alcohols

A stirred mixture of 10 mmoles of C_6F_5SCl and 10 ml. of $BrCH_2CH_2Br$ was heated at 100° for about 15 min.. The mixture was cooled and 20 mmoles of EtOH added. It was stirred overnight at room temp.. Unidentified products were obtained from the reactions of C_6F_5SCl with MeONa and EtONa: in the presence of pyridine both MeOH and EtOH reacted to form the disulfide $(C_6F_5S)_2$.

Substitution with thiophene

About 0.5 ml. $SnCl_4$ was added to a solution of 7 mmoles of C_6F_5SCl and 10 mmoles of thiophene in 10 ml. anhydrous ether and refluxed for 1.5 h.. After cooling to room temp. 200 ml. of 1N HCl was added. The mixture was extracted with ether(5 x 40 ml.). After drying ($MgSO_4$) the ether was removed and the product isolated.

Substitution with aliphatic nitrocompounds

The nitroethane was converted to its sodium salt [20]. About 10 mmoles of C_6F_5SCl in 5ml. ether was added to a ice cooled suspension of $Na^{+-}CHMeNO_2$ in 30 ml. ether. 100 ml. of water was then added and

the resultant mixture extracted with ether (3 x 50 ml.). After washing and drying the ether extract, the product was isolated by removal of the ether. No product was obtained using $MeNO_2$ instead of $EtNO_2$.

Reaction with hydrolytic agents

About 20 mmoles of a 15 % aqueous solution of NaOH or Na_2CO_3 or water was added dropwise to a solution of 10 mmoles of C_6F_5SCl in ether. The aqueous layer was further extracted with ether (2 x 15 ml.). After drying the only product that could be recovered from the ether was the disulfide, $(C_6F_5S)_2$, m.p. 50-1°, lit. m.p. 50-1° [21]. The aqueous layer was acidified with dil. HCl to a pH value in the range 1.5 - 2. Saturated $BaCl_2$ solution was added to the acidified solution to try and precipitate the barium salt, but no precipitation occurred.

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REFERENCES

1 E. Kühle, The Chemistry of the Sulfenic Acids, Georg Thieme Publishers, Stuttgart, 1973.
2 R.J. Neil and M.E. Peach, J. Fluorine Chem. 1 (1972) 257.
3 P. Sartori and A. Golloch, Chem.Ber., 103 (1970) 3936; 104(1971)967.
4 H. Britzinger and H. Ellwanger, Chem.Ber., 87 (1954) 300.
5 N. Kharasch and J.L. Cameron, J.Amer.Chem. Soc., 73 (1951) 3864.
6 S. Andreades, J.F. Harris and W.A. Sheppard, J. Org. Chem., 29 (1964) 895.

7 R.T. Poole, Ph.D. Thesis, Memorial University of Newfoundland, 1973.

8 T.S. Leong and M.E. Peach, to be published.

9 J.G. Allen, J. Burdon and J.C. Tatlow, J. Chem. Soc., (1965) 6329.

10 S. Andreades, U.S. Patent 3,081,350 (1963); Chem. Abs., 59 (1963) 5024b.

11 G. Sosnovsky, J.Chem. Soc., (1956) 3139.

12 E. Vinkler, F. Klinvényi, J. Lázár and I. Kozakiewicz, Acta Chim. Acad. Sci. Hung., 60 (1969) 167.

13 R.N. Haszeldine and J.M. Kidd, J. Chem. Soc., (1955) 2901.

14 L.J. Bellamy, The Infrared Spectra of Complex Molecules, Methuen and Co. Ltd., 2 Edn., London, 1960.

15 N.S. Bhacca, L.F. Johnson and J.N. Shoolery, NMR Spectra Catalog, Vol. 1, Instrument Division, Varian Associates, California, 1962, Spectrum No. 98.

16 M.G. Hogben and W.A.G. Graham, J. Amer. Chem. Soc., 91 (1969) 283.

17 M.G. Hogben, R.S. Gay, A.J. Oliver, J.A.J. Thompson and W.A. G. Graham, J. Amer. Chem. Soc., 91 (1969) 291.

18 J. Meisemheimer, J. Casper, M. Hörig, W. Lauter, L. Lichenstadt and W. Samuel, Liebigs Ann., 449 (1926) 213.

19 W. Hale and E. Britton, J. Amer. Chem. Soc., 41 (1919) 841.

20 L. F. Fisher, Experiments in Organic Chemistry, D.C. Heath and Co., New York, 2 Edn., 1935, p. 385.

21 P. Robson, M. Stacey, R. Stephens and J.C. Tatlow, J. Chem. Soc. (1960) 4754.