

Kinetics and Mechanism of Cleavage of Sulphur–Silicon, –Tin, –Germanium, and –Lead Bonds in Aqueous Dioxan in Some Organometallic Compounds of Bivalent Sulphur

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Rates of cleavage have been measured spectrophotometrically for some PhS–MR₃ compounds (M = Si, Ge, Sn, and Pb) in neutral and acidic aqueous dioxan. The reactivity sequences are unrelated to the electronegativity of the metals and the ease of cleavage increases in the order Si < Ge < Sn < Pb. The substituent and solvent isotope effects indicate some differences in the cleavage mechanism of these compounds. This is governed by sulphur–metal bond polarization enhanced in the heavier Sn and Pb derivatives by co-ordination between water and the metal. A dual mechanism which fits the experimental results is proposed.

We have previously reported¹ a kinetic study of the hydrolysis in aqueous dioxan of some thiosilanes and the cleavage mechanism of the sulphur–silicon bond in acidic and basic media. In order to extend this investigation on the properties and reactivity of sulphur–metal bonds to the other Group IVB elements, we have now studied spectrophotometrically the hydrolysis of the organogermanium, organotin, and organolead analogues.

RESULTS AND DISCUSSION

In aqueous dioxan trimethyl(phenylthio)-silane and -germane are very sensitive to hydrolysis, the products being benzenethiol and hexamethyl-disiloxane or -digermoxane. In contrast to the reactivity of these compounds the corresponding tin and lead derivatives are

Pseudo-first-order rate constants for neutral and acid hydrolysis with varying amounts of water are listed in Table 1. Substituent effects in the acid catalysed hydrolysis of the silicon and tin derivatives are reported in Table 2. For both systems a plot of log *k* against σ_0 (ref. 2) is linear but for phenylthiostannanes the slope ρ of 0.3 is significantly smaller than that (1.4) for phenylthiosilanes.

Solvent isotope effects have also been measured and the results are collected in Table 3. One interesting feature of these results is that, for both the compounds investigated, there is a positive solvent isotope effect which increases from 1.87 to 3.0 going from trimethyl(phenylthio)-silane to -tin.

The effects of groups bonded to the metal on the rate

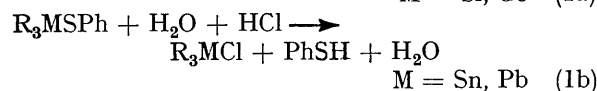
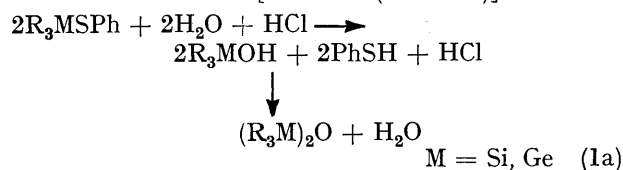
TABLE 1
First-order rate constants at 25° for the hydrolysis of Me₃MSPH in aqueous dioxan

M	Neutral medium		Acid medium ^b				λ/nm
	H ₂ O (%) ^a = 33	0.26	0.40	0.80	1.33	2.50	
$10^3 k/\text{s}^{-1}$							
Si	44,670			0.26 ^c	0.40	1.00	280
Ge	230			0.12 ^c			265
Sn	No reaction	20.9	1327	31,630			260
Pb	No reaction			79,430			272

^a ml per 100 ml solution. ^b 8.0 × 10⁻⁵M-HCl. ^c In the acid hydrolysis of the Si and Ge compounds at 0.8% water, allowance must be made for neutral hydrolysis which affects the rates by a factor not exceeding 6%.

hydrolytically stable in a neutral medium even in the presence of a large excess of water.

In an acid medium however the hydrolysis of the S–Sn and S–Pb bonds is much faster than those of the corresponding Si and Ge derivatives. The cleavage of the phenylthio-derivatives of silicon and germanium in the presence of hydrochloric acid leads to the products obtained from neutral hydrolysis, whereas trimethyltin chloride and trimethyllead chloride are obtained beside benzenethiol in the acid hydrolysis of the phenylthio-tin and -lead derivatives [reactions (1a and b)].



of hydrolysis of Si and Sn derivatives are shown in Table 4.

TABLE 2
First-order rate constants for the acid catalysed cleavage of XC₆H₄SMMe₃ in aqueous dioxan at 25 ± 0.1°

X	M = Si ^{a,c}	M = Sn ^b
	$10^3 k/\text{s}^{-1}$	k/s^{-1}
<i>p</i> -OMe	0.23	25.12
<i>p</i> -Me	0.29	25.12
H	0.62	31.64
<i>m</i> -OMe	0.87	
<i>p</i> -Cl	1.79	
<i>m</i> -Cl	3.23	39.81

^a 1.33% v/v H₂O; 13 × 10⁻⁵M-HCl. ^b 0.8% v/v H₂O; 8 × 10⁻⁵M-HCl. ^c Corrected for neutral hydrolysis.

The results for cleavage in acid medium of PhSXMe₃ (Table 1) exhibit a sequence similar to that observed in the acid catalysed hydrolysis of Ar–MR₃ bonds by

¹ R. Danieli and A. Ricci, *J.C.S. Perkin II*, 1972, 1471.

² R. W. Taft, jun., *J. Phys. Chem.*, 1960, **64**, 1805.

aqueous ethanolic perchloric acid.³ The electronegativity of the metals is unrelated to the reactivity sequence and does not correlate with the large difference in rates

TABLE 3

Isotope effect on the acid hydrolysis of Me₃MSPh

M	10 ⁵ [HCl]/ M	H ₂ O (%v/v)	10 ³ k _{H₂O} / s ⁻¹	10 ³ k _{D₂O} / s ⁻¹	k _{H₂O} / k _{D₂O}
Si	133	1.33	6.92	3.70	1.87
Sn	8.0	0.8	31,630	10,540	3.00

^a Taken from ref. 1.

TABLE 4

Relative rates (*k*_{rel}) for the cleavage of R₃MSPh by aqueous dioxan in the presence of HCl at 25 ± 0.1°

M	Me	Et	Pr ⁿ	Ph
Si ^a	85	1.2	1	
Sn ^b	14	8	1	0.04

^a 1.33 × 10⁻³M-HCl; 1.33% H₂O. ^b 8.0 × 10⁻⁵M-HCl; 0.8% H₂O.

between the S-Si and S-Sn compounds, whatever electronegativity scale is used.⁴ Trimethyl(phenylthio)-tin and -lead derivatives are cleaved by acid 10⁵ times faster than the silicon and germanium analogues and this requires considerable electron density to be transferred to the reaction centre in the transition state for the first two compounds. Therefore the main factor likely to govern the relative rates of acid cleavage of PhSMMe₃ is the ease of electron release from MMe₃.

Extensive studies⁵ on the electronic effect of MR₃ groups (M = Si, Ge, Sn, and Pb) suggest that the trend in properties of these Group IVB elements can be generally interpreted in terms of inductive electron supply and of electron withdrawal by a *p*_π → *d*_π mechanism. Recently⁶ good evidence has been found that in addition to the inductive release of electrons by an MR₃ group hyperconjugative contributions are also largely responsible for the relative reactivity of organometallic derivatives containing C-M bonds. In substrates containing sulphur-metal bonds no conclusive evidence for either *p*_π → *d*_π inductive or hyperconjugative contributions has yet been produced. However from the ¹³C n.m.r. data in Table 5 the negligible shielding at the *para*-carbon atom and the trend of chemical shifts for aliphatic and substituted carbon atoms, coupled with the S_{2p_{3/2}} ionization energies derived from e.s.c.a. measurements reported earlier⁷ suggest greater importance in the ground state of these molecules of the -M effect than of electron release. Moreover recent evidence⁸ from mass spectrometric measurements exhibits an unusual trend of ionization

³ C. Eaborn and K. C. Pande, *J. Chem. Soc.*, 1960, 1566.

⁴ A. Allred and E. G. Rochow, *J. Inorg. Nuclear Chem.*, 1958, **5**, 269.

⁵ R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1964, **2**, 154; H. Soffer and T. De Vries, *J. Amer. Chem. Soc.*, 1951, **73**, 5817; J. D. Roberts, E. A. McEhill, and R. Armstrong, *ibid.*, 1949, **71**, 2923; H. Freiser, M. V. Eagle, and J. Speier, *ibid.*, 1953, **75**, 2821; W. Adcock, S. Q. A. Rizvi, W. Kitching, and A. J. Smith, *ibid.*, 1972, **94**, 369; E. W. Abel, D. A. Armitage, and A. A. Williams, *Trans. Faraday Soc.*, 1964, **60**, 1257.

potentials (IP) with the order of electron acceptance as Si > Ge = C > Sn > Pb for PhSMMe₃ and as Si > Ge > Sn = C for (Me₃M)₂S.

This trend reflects quite clearly a *p*_π → *d*_π contribution superimposed on the S-M bond strengths for the Si and Ge derivatives. The picture is less clear for the tin and lead analogues: the presence of a *d*_π (Sn) → *p*_π (S) interaction supported by the electronic spectra of Me₃SnSC₆H₄X compounds⁹ is somewhat in contrast with

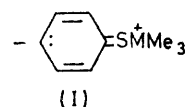
TABLE 5

Substituent ¹³C chemical shifts (p.p.m.) of PhSMMe₃ in various solvents

M	CCl ₄ ^a		CDCl ₃		Me ₂ SO		Dioxan-C ₆ D ₆	
	C-S	CH ₃	C-S	CH ₃	CH ₃	CH ₃	C-S	CH ₃
C	133.0	32.0	135.6	30.7				
Si	131.6	2.0	130.1	1.4			131.4	1.63
Ge	133.4	1.5						
Sn	134.8	-3.0	133.6	-3.8	137.1	-2.63	136.4	-4.80
Pb	138.0	10.3	133.5	8.5				

^a Taken from ref. 7.

the IP sequence from which Me₃Sn and Me₃Pb behave as weak electron donors. From this spectroscopic evidence the ground and excited state electronic properties of these compounds seem better interpreted in terms of *d*_π(M) → *p*_π(S) interactions whereas hyperconjugative contributions represented by structures such as (I) are probably less important.



To fit the spectroscopic properties to the kinetic results in acid medium (Table 1) which show for PhSMMe₃ an order of electron release Me₃Pb > Me₃Sn ≫ Me₃Ge ≫ Me₃Si, it is also important to consider the effects of the medium. Comparison of the results in Table 5 shows that whereas ¹³C chemical shifts for the silicon derivatives are insensitive to the changes in the solvent, trimethyl(phenylthio)tin exhibits a larger dependence of shift on solvent owing to interactions between solvents and the metal. In the aqueous dioxan used for the kinetic experiments the extent of the interaction between water and the metal is shown by ¹H n.m.r. spectroscopy since water molecules bound to a metal have different chemical shifts from those of the bulk solvent.¹⁰ The ¹H chemical shifts recorded in partially deuteriated dioxan are reported in Table 6: the downfield shift of the water signal on changing the metal from silicon to lead,

⁶ A. R. Bassindale, C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Organometallic Chem.*, 1969, **20**, 49; A. R. Bassindale, C. Eaborn, and D. R. M. Walton, *ibid.*, 1970, **21**, 91; W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, 1970, **92**, 7476 and references therein; M. A. Cook, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1970, **24**, 293.

⁷ S. Pignataro, L. Lunazzi, C. A. Boicelli, R. Di Marino, A. Ricci, A. Mangini, and R. Danieli, *Tetrahedron Letters*, 1972, 5341.

⁸ G. Di Stefano, A. Ricci, R. Danieli, A. Foffani, G. Innorta, and S. Torrioni, *J. Organometallic Chem.*, 1974, **65**, 205.

⁹ T. A. George, *J. Organometallic Chem.*, 1971, **31**, 233.

¹⁰ J. C. Boubel, J. J. Delpuech, M. R. Khaddar, and A. Peguy, *Chem. Comm.*, 1971, 1265 and references therein.

supports stronger co-ordination of the water to the metal in descending Group IVB.

TABLE 6

Internal ${}^1\text{H}$ n.m.r. chemical shifts at 100 MHz for the water signal in the dioxan-water-PhSMMe₃ system

M	Dioxan α^-		Δ/Hz^b	$\delta\Delta/\text{Hz}^c$
	H_2O	PhSMMe ₃		
	74.2		88.13	
C	74.2	1.4	87.75	0.38
Si	74.2	1.4	87.38	0.75
Ge	74.2	1.4	87.21	0.92
Sn	74.2	1.4	85.50	2.65
Pb	74.2	1.4	84.38	3.75

^a Partially (66.6%) deuteriated dioxan. ^b Shifts in Hz; the accuracy is ± 0.05 Hz averaged over four scans, two in the increasing and two in the decreasing mode. ^c $\delta\Delta$ is the variation of the internal shift of water due to products.

A change of the solvent from CCl_4 or CHCl_3 to the aqueous dioxan used in the kinetic study is thus likely to be important in that the strong interaction between water and the metal can increase the extent of polarization in the sulphur-metal bond leading to a large enhancement of the electron-releasing over the mesomeric effect¹¹ for the trimethyl-tin and -lead groups in line with the observed trend in reactivity (Table 1).

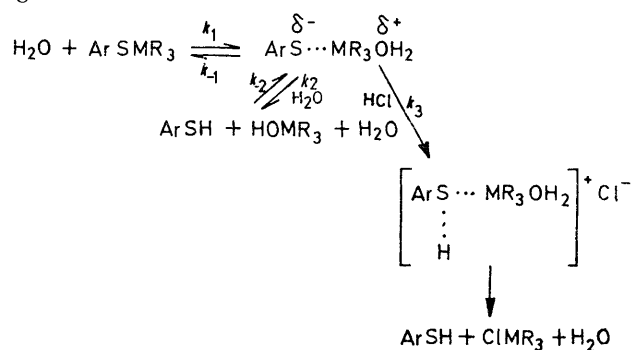
The results in Tables 1–4 suggest some differences in the cleavage mechanism of the sulphur-metal bond in descending Group IVB. Some features of these results and comments are as follows. (i) The increase of the solvent isotope effect on going from the silicon (1.87) to the tin (3.0) derivatives is large enough to be used as a criterion of mechanism¹² and suggests that in the acid catalysed hydrolysis of trimethyl(phenylthio)tin proton transfer from the oxonium ion to the organometallic compound in the transition state is much more rapid. (ii) The lower sensitivity to the effect of substituents for the tin derivatives compared with that for the silicon analogues provides some support to nucleophilic assistance by water in the hydrolysis of trimethyl(phenylthio)tin. In fact in a co-ordinative intermediate the electrons of the highly polarizable sulphur-metal bond are readily available and there is a small demand on the electrons of the ring (ρ 0.3) in marked contrast to that previously found¹ for the acid catalysed hydrolysis of trimethyl(phenylthio)silane (ρ 1.4). (iii) A plot of $\log k$ against $\log [\text{H}_2\text{O}]$ for the hydrolysis of trimethyl(phenylthio)tin in aqueous dioxan (Table 1) shows the rate is given by the expression $k[\text{PhSSnMe}_3][\text{H}_2\text{O}]^{4.5}$. The increased kinetic order in water with respect to that (1.5) of trimethyl(phenylthio)silane in the same medium (Table 1) supports greater solvation¹³ of the transition state in the hydrolysis of the tin derivative. (iv) The results in Table 4 suggest less steric hindrance for PhSSnR_3 than for the silicon analogues involving¹ a highly ordered and crowded transition state. The kinetically rapid forma-

* Electron release from R_3M ($\text{M} = \text{Sn}$ and Pb) is also likely to be supplemented to some extent by hyperconjugative electron release similar to that observed for C–M bonds.⁶ The importance of this contribution to the transition state in these cleavage reactions cannot be evaluated unambiguously and deserves more detailed study.

tion of a pentacovalent tin complex thus appears plausible.

The simplest way of fitting these experimental results is based on a dual mechanism; owing to the minor role played by co-ordination in the organosilicon and organo-germanium derivatives the previously established mechanism¹ of fast protonation of the sulphur atom followed by rate-determining attack of the nucleophile on the metal, proposed for the acid catalysed hydrolysis of phenylthiosilanes, explains in the best way the results in Table 1 for the silicon and germanium derivatives. The partial double bond character of the sulphur-metal bond revealed in these compounds by spectroscopic measurements^{8,9} can also partially account for their lower reactivity.

In the phenylthio-derivatives of tin and lead in aqueous dioxan, on the other hand, features (i)–(iv) suggest that the reactivity of the sulphur-metal bond is best interpreted by considering that the driving force is stretching of the S–M bond by nucleophilic assistance of water. Interaction between water and the metal centre will in fact favour polarization of the S–M bond giving rise to a certain amount of negative charge on the sulphur atom and thus facilitating the subsequent cleavage.*



SCHEME

The neutral and acid hydrolysis of these compounds can thus be written as in the Scheme. In a neutral medium bimolecular attack of water on the complex intermediate leading to the reaction products (k_2 in Scheme) is unimportant: the fast reverse reaction ($k_{-2} \gg k_2$) between thiol and trimethyltin hydroxide, which instantly gives the starting trimethyl(phenylthio)tin (see Experimental section) stabilizes the intermediate with respect to the final products and accounts for the stability of the tin and lead derivatives in neutral aqueous dioxan.

For the acid hydrolysis of these derivatives the simplest mechanism which best accommodates the results in Tables 1–6 involves a rate-determining attack (k_3) of a proton on the sulphur atom. This step will be largely favoured by an increase of electron release from

¹¹ A. J. Smith, W. Adcock, and W. Kitching, *J. Amer. Chem. Soc.*, 1970, **92**, 6140.

¹² C. A. Bunton and V. J. Shiner, jun., *J. Amer. Chem. Soc.*, 1961, **83**, 3207, 3214.

¹³ R. M. Prince and R. E. Timms, *Inorg. Chim. Acta*, 1967, **129**.

tin and lead toward sulphur owing to the prior co-ordination of water to the metal.

Nucleophilic attack of the halide ion on the metal to give Me_3MCl will probably occur in a fast subsequent step even if at the present time the possibility of a synchronous process cannot be ruled out.

EXPERIMENTAL

Reagent grade dioxan purified according to standard procedures,¹⁴ and conductivity water were used for the kinetic experiments.

Materials.—*t*-Butyl phenyl sulphide¹⁵ and trimethyl(phenylthio)silane¹⁶ were prepared according to literature methods. Substituted trimethyl(phenylthio)tin derivatives were synthesized by adding a suitable thiol (0.026 mol) to trimethyltin chloride (0.025 mol) dissolved in water (*ca.* 50 ml). After addition of 1*N*-sodium hydroxide (25 ml) the mixture was stirred for 2 h. The resulting oil was separated from the aqueous layer, washed with water, dried (Na_2SO_4), and distilled under high vacuum. The physical properties and yields of the products are in Table 7.

TABLE 7
Analytical data and physical properties of
 $\text{XC}_6\text{H}_4\text{SSnMe}_3$

X	B.p./°C ^a (p/mmHg)	Yield (%)	Found (%)			Required (%)		
			C	H	S	C	H	S
<i>p</i> -OMe	94—95 (0.1)	55	40.0	5.6	10.0	39.65	5.3	10.6
<i>p</i> -Me	83—84 (0.3)	60	42.0	6.0	10.9	41.85	5.6	11.15
<i>m</i> -Cl	91—92 (0.1)	53	35.5	4.4	9.9	35.15	4.25	10.4

^a Uncorrected.

Trimethyl(phenylthio)germane was synthesized by a modification of the procedure of Abel *et al.*¹⁷ To dry sodium thiolate (1.5 g, 0.0125 mol) in dry ether (*ca.* 50 ml) trimethylgermyl bromide (2.5 g, 0.0125 mol) in dry ether (20 ml) was added dropwise with vigorous stirring. The mixture was refluxed for 3 h, the solid was filtered off, and the ether removed. The residual oil was distilled under high vacuum to give the product (2.2 g, 57%) (b.p. 59—69° at 0.3 mmHg). Trimethyl(phenylthio)lead was prepared by treating sodium thiolate (1.49 g, 0.01 mol) in methanol (*ca.* 10 ml), with trimethyl-lead chloride (2.88 g, 0.01 mol)¹⁸ in methanol (10 ml). The mixture was stirred for 30 min, filtered, and the methanol removed. Careful distillation of the residual oil under high vacuum gave *trimethyl(phenylthio)lead* (1.7 g, 62%), b.p. 105—107° at 0.2 mmHg (Found: C, 29.5; H, 3.75. $\text{C}_6\text{H}_4\text{PbS}$ requires C, 29.9; H, 3.9%). Triphenyl-,¹⁹ triethyl-,²⁰ and tri-*n*-propyl-(phenylthio)tin²¹ were synthesized by literature methods.

Cleavage Reactions.—(a) *Trimethyl(phenylthio)silane.* To trimethyl(phenylthio)silane (0.5 g 0.0027 mol) in dioxan (2 ml) was added 1*N*-hydrochloric acid (2.7 ml, 0.0027 mol). After 10 min at room temperature the reaction mixture was dried (MgSO_4). Benzenethiol and hexamethyldisiloxane

were characterized by ¹H n.m.r. spectrum. G.l.c. (5% Carbowax 20 M on Chromosorb W; 5 ft × 0.12 in; 60°) of the reaction mixture afforded three peaks identified as hexamethyldisiloxane, benzenethiol, and dioxan. No evidence for the presence of trimethylsilanol was obtained.

(b) *Trimethyl(phenylthio)germane.* To trimethyl(phenylthio)germane (0.5 g, 0.0022 mol) in dioxan (2 ml) 1*N*-hydrochloric acid (2.4 ml, 0.0024 mol) was added. After drying (MgSO_4) the mixture was carefully distilled to give hexamethyldigermoxane,²² b.p. 139°.

(c) *m-Chlorophenylthiotrimethyltin.* 1*N*-Hydrochloric acid (3.2 ml, 0.0032 mol) was added to a solution of *m*-chlorophenylthiotrimethyltin (1 g, 0.0032 mol) in dioxan (2 ml). Distillation of the mixture gave initially dioxan and then trimethyltin chloride, b.p. 152°, and *m*-chlorothiophenol.

(d) *Trimethyl(phenylthio)lead.* To trimethyl(phenylthio)lead (1 g, 0.0027 mol) in dioxan (2 ml) 1*N*-hydrochloric acid (3 ml, 0.003 mol) was added. After drying (MgSO_4), the organic layer was diluted with light petroleum to afford, on cooling, trimethyl-lead chloride,¹⁸ m.p. 195°.

Rates and U.v. Measurements.—For slower runs the kinetic experiments were carried out spectrophotometrically as previously described¹ using a Perkin-Elmer 402 spectrophotometer. For very fast reactions, the rate constants were measured using a Durrum-G type stopped flow apparatus. After the rapid mixing of the dioxan-organometallic solution ($0.8\text{--}3.0 \times 10^{-4}\text{M}$) and aqueous dioxan, the reaction progress was followed by observing on the oscilloscope trace, the change of transmittance at a suitable wavelength (Tables 1 and 2). The quantitative nature of the reaction was indicated by the close superimposition upon the t_∞ spectrum by the u.v. spectra of the thiols. Pseudo-first-order rate constants, calculated as previously described,¹ were averages of three or more independent runs. The experimental error was *ca.* ±3%.

Reactions between products to give starting compounds were checked by means of u.v. spectra; reverse reactions were shown to be unimportant for the silicon and germanium derivatives under the conditions employed; however by addition of benzenethiol ($1.5 \times 10^{-4}\text{M}$) in neutral aqueous dioxan to an equimolecular amount of trimethyltin hydroxide, the resulting solution gave immediately a u.v. spectrum similar to that of the starting trimethyl(phenylthio)tin. No reverse reaction was found by mixing trimethyltin chloride and benzenethiol.

N.m.r. Measurements.—¹³C Spectra were recorded at 25.15 MHz using a JEOL PS-100 spectrometer. All ¹³C spectra were obtained for 60% (w/w) solutions of the organometallic compounds, the solvent being used as internal standard. ¹H N.m.r. spectra in partially deuteriated dioxan (66.6% isotopic purity) in the presence of 1.33% (v/v) water were obtained at 100 MHz using a JEOL PS-100 spectrometer. In these conditions hydrolysis was slow and did not interfere with the spectroscopic measurements.

[3/1597 Received, 30th July, 1973]

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²¹ R. Sasin and G. S. Sasin, *J. Org. Chem.*, 1955, **20**, 387.

²² J. E. Griffiths and M. Onyszchuk, *Canad. J. Chem.*, 1961, **39**, 339.

¹⁴ A. Weissberger, 'Technique of Organic Chemistry,' Interscience, New York, 1967, vol. 17.

¹⁵ V. N. Ipatieff, H. Pines, and B. S. Friedman, *J. Amer. Chem. Soc.*, 1938, **60**, 2731.

¹⁶ K. A. Henry and A. Allred, *Inorg. Chem.*, 1965, **4**, 671.

¹⁷ E. W. Abel, D. A. Armitage, and D. B. Brady, *J. Organometallic Chem.*, 1966, **5**, 130.