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1,3-DIKETO COMPOUNDS OF THE NON-METALLIC ELEMENTS

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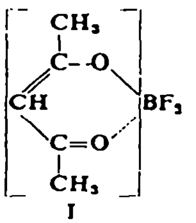
CONTENTS

A. INTRODUCTION

The last several years has seen renewed interest in the coordination compounds formed by the treatment of 1,3-diketones with the metalloids and non-metals. This is mainly due to the interest in the structure and reactivity of these materials. This review summarizes the recent work reported on this class of compounds. The elements covered include the metalloids[1] B, Si, Ge, Sb, Te and the non-metals P, S and Se. The main portion of the review is concerned with work published since 1956; however, when of historical interest reference is made to previous work for the sake of continuity. The scope of the review in regards to the non-metallic reagent used to prepare the subject compounds has been limited to the halide or organosubstituted halide; the dicarbonyl derivative has been limited to the 1,3-diketones. β-Ketoesters and tropolone[2] derivatives have been excluded.

B. BORON DERIVATIVES

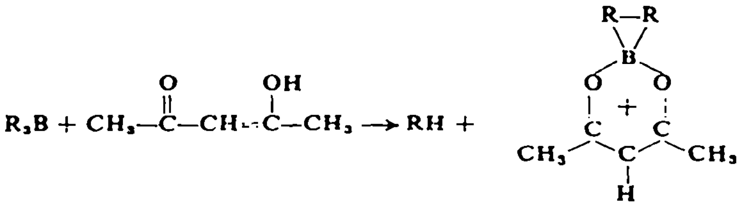
The first reported coordination compound formed between a 1,3-diketone and a boron halide was that prepared by Dilthey in 1903[3]. These compounds were a series of bis(acetylacetone) boronium salts, such as $[(C_5H_7O_2)_2B]AuCl_4$ or $[(C_5H_7O_2)_2B]_2PtCl_6$, formed by initial treatment of boron trichloride with acetylacetone. Later work[4] illustrated that boron trifluoride when passed into a benzene solution of acetylacetone gave boron acetylacetone difluoride (I).



I

Benzoylacetone and dibenzoylmethane gave similar results. In contrast to the coordination compounds derived from boron trichloride, the latter materials are non-ionic in nature. Sagredos[5] has recently prepared a series of these complexes by treatment of a ketone with a carboxylic acid anhydride in the presence of boron trifluoride.

A general synthesis of cyclic dialkylboronium acetylacetonates was reported in 1954[6]. Trialkyl boranes were used as the boron source. Other 1,3-dicarbonyl compounds gave similar results. Unsubstituted dialkyl-boronium acetylacetonates exhibit vinylic hydrogen at τ 4.6 to 4.8 and two equivalent methyl groups at τ 8.00, relative to tetramethylsilane. On this basis the cyclic structure (II) was assigned to these derivatives. The infrared and ultraviolet spectra were also reported for these materials[6]. Treatment of these boronium compounds with aqueous base at reflux temperature followed by acidification afforded the corresponding dialkylboronic anhydrides in high yields. The compounds were also reported to have been brominated, but the bromo product was unstable. However, a monobromo derivative was apparently formed which contained no vinylic hydrogen and had two equivalent methyl groups in the ^1H NMR spectra. Koster and Rotermund have recently extended the reaction of the trialkylboranes with acetylacetone to prepare a unique series of acetylacetonates[7]. The boron chelate derivatives prepared to date are summarized in Table 1.



II

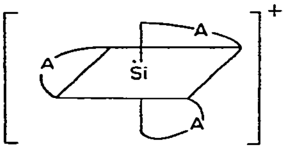
TABLE 1

BORON COORDINATION COMPOUNDS

Formula.	*Physical properties*		n_D^{20}	*Ref.*
	m.p. (°C)	*b.p. (°C)*		
$(CH_3COCHCOCH_3)_2B \cdot AuCl_4$	135			3
$(CH_3COCHCOCH_3)_2B \cdot FeCl_4$	137			3
$[(CH_3COCHCOCH_3)_2B]_2PtCl_6$	>300			3
$(CH_3COCHCOCH_3)_2BI$				3
$(CH_3COCHCOCH_3)_2BI_3$				3
$(CH_3COCHCOCH_3)_2BZnCl_3$	206			3
$(CH_3COCHCOCH_3)_2BSnCl_4$	200–212			3
$(C_6H_5COCHCOCH_3)_2B \cdot FeCl_4$	180–182			3
$(C_6H_5COCHCOCH_3)_2B \cdot ZnCl_3$	223–225			3
$(C_6H_5COCHCOCH_3)_2BI$	210			3
$(C_6H_5COCHCOCH_3)_2BI_3$				3
$[(C_6H_5COCHCOCH_3)_2B]_2SnCl_6$				3
$(CH_3COCHCOCH_3)BF_2$	43			4
$(C_2H_5COCHCOCH_3)BF_2$	−14	119–122 (3.0 mm)		5
$(n\text{-}C_3H_7COCHCOCH_3)BF_2$	−17	132–135 (3.5 mm)		5
$[CH_3COC(CH_3)COCH_3]BF_2$	94–95	125–128 (1.0 mm)		5
$[n\text{-}C_3H_7COC(CH_3)COCH_3]BF_2$	17–18	112–113 (0.2 mm)		5
$[n\text{-}C_2H_5COC(CH_3)COCH_3]BF_2$	−3	139.5–140.5 (2.5 mm)		5
$[C_2H_5COC(CH_3)COC_3H_7\text{-}n]BF_2$	15.5–17	133–134.5 (2.5 mm)		5
$[C_2H_5COC(C_2H_5)COC_2H_5]BF_2$	88–89			5
$(C_6H_5COCHCOCH_3)BF_2$	155			4
$(C_6H_5COCHCOCH_3)BF_2$	191			4
$(CH_3COCHCOCH_3)B(C_2H_5)_2$		91.5 (14 mm)	1.4662	7
$(CH_3COCHCOCH_3)B(n\text{-}C_3H_7)_2$		105–107 (10 mm)		6b, 7
$(CH_3COCHCOCH_3)B(n\text{-}C_4H_9)_2$		86 (0.1 mm)	1.4670	6a, b, 7
$(CH_3COCHCOCH_3)B(iso\text{-}C_4H_9)_2$		75 (0.1 mm)	1.4619	6a
$(CH_3COCHCOCH_3)B(sec\text{-}C_4H_9)_2$		71 (0.15 mm)	1.4709	6a
$(CH_3COCHCOCH_3)B(n\text{-}C_6H_{13})_2$		120 (0.1 mm)	1.4662	6a, 7
$(CH_3COCHCOCH_3)B(cyclo\text{-}C_6H_{13})_2$	65.5–66.0			6a
$(C_6H_5COCHCOC_6H_5)B(iso\text{-}C_4H_9)_2$	90			6a
$(CH_3COCHCOCH_3)B[CH_2CH(CH_3)CH_2CH(CH_3)_2](C_2H_5)$		60.5 (0.001 mm)	1.4727	7
$(CH_3COCHCOCH_3)B$-1,4-butylenedibutyl			1.4949	7
9-Borobicyclo[3.3.1]nonylacetylacetonate	118			7
$(CH_3COCHCOCH_3)B$-cyclooctylethyl		87–89 (0.001 mm)	1.5044	7
$(CH_3COCHCOCH_3)B(C_2H_5)[CH_2\text{-}CH(C_6H_5)CH_3]$		98–99 (0.001 mm)	1.5212	7
1-Boro-tetralinylacetylacetonate	92			7
3-Methylborolanylacetylacetonate		58–59 (0.2 mm)		7
3-Methyl-1-boroindanylacetylacetonate	78.5–79			7
$(CH_3COCHCOCH_3)B(CH_2C_6H_5)_2$	74			7
$(CH_3COCHCOCH_3)B(C_6H_5)_2$	115–116			7
$(CH_3COCHCOCH_3)B(C_6H_4\text{–}CH_3\text{–}p)_2$	132			7
$(CH_3COCHCOCH_3)B(1\text{–}C_{10}H_7)_2$	230 (dec.)			7
13-Boro-*cis*-tricyclo[7.3.1]tridecylacetylacetonate	65.5			7
13-Boro-*trans*-bicyclo[7.3.1]tridecylacetylacetonate	115			7

C. SILICON DERIVATIVES

Silicon acetylacetonates were first reported by Dilthey[8] who prepared a number of derivatives of the tris(2,4-pentanediono)siliconium ion, $(C_5H_7O_2)_3Si^+$, formed by treating silicon tetrachloride with acetylacetone. Salts such as $(C_5H_7O_2)_3Si^+ \cdot HCl_2^-$ and $(C_5H_7O_2)_3Si^+ \cdot FeCl_4^-$ were isolated and characterized. Dilthey proposed a novel structure, $(C_5H_7O_2)_3Si^+Cl^- \cdot HCl$, containing a positively changed siliconium ion in which the silicon is chelated by three acetylacetonate groups. This assigned structure (III) was confirmed by infrared analysis[9], partial resolution[10] and more recently by nuclear magnetic resonance data[11]. The resolution of this complex cation d,l-$Si(C_5H_7O_2)_3^+$ by treatment with sodium (−)-dibenzoyl-*d*-tartrate into its optical enantiomers strongly suggests that the silicon(IV) is hexacoordinate in this complex, and that the cation is octahedral. The possibility of seven coordination, *i.e.*, coordination of the chloride ion, was ruled out in view of the conductivity of the complex in anhydrous chloroform[10]. The rates of hydrolysis and racemization on $(C_5H_7O_2)_3Si^+HCl_2^-$ have also been reported[10]. Pearson and co-workers investigated the hydrolysis of the tris(acetylacetonato)-silicon cation and characterized the reaction as kinetically first order in chelate and first order in base[12]. The mechanism was visualized as one of the S_N2 type on an octahedral species with a seven-coordinate silicon intermediate. Other work[2] indicates that this may not be the case. Employing the dibenzoylmethane analog and following the basic hydrolysis in a medium enriched with ^{18}O, it was deduced that the initial attack was primarily on the ligand rather than the central atom. It is anticipated that future efforts in this field will be directed toward clarifying this fundamental point.



$HCl_2^{(-)}$

A = 2,4-pentanediono

(III)

Dilthey[8b,c] also prepared and characterized a series of chelates using other 1,3-diketones such as dibenzoylmethane. Several derivatives of these materials were synthesized (See Table 2).

West has shown that the use of the organosilicon halides, methyltrichlorosilane and phenyltrichlorosilane produces neutral, non-ionic chelate derivatives[9]. Use of the higher organo derivatives, dimethyldichlorosilane, trimethylchlorosilane and triethylchlorosilane, did not result in chelated derivatives. The products were shown to be the respective silyl enolates of acetylacetone[9].

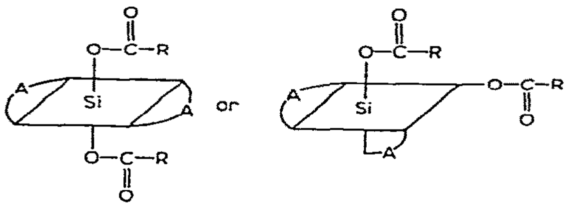
Pike and Luongo[13] have found that use of organocarboxysilanes in place of the silicon tetrachloride reagent employed by previous workers leads to the

TABLE 2

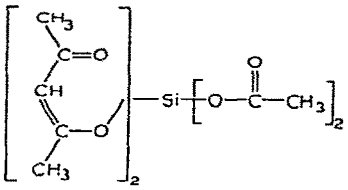
SILICON COORDINATION COMPOUNDS

Formula	*Physical properties*		*Reference*
	m.p. (°C)	*b.p. (°C)*	
$(CH_3COCHCOCH_3)_3SiCl \cdot HCl$	85–89		8, 9
$(CH_3COCHCOCH_3)_3SiFeCl_4$	186–187		8a
$(CH_3COCHCOCH_3)_3SiZnCl_3$	300		8a
$(CH_3COCHCOCH_3)_3SiAuCl_4$	162–163		8a
$[(CH_3COCHCOCH_3)_3Si]_2 \cdot PtCl_6$			8b
$(CH_3COCHCOCH_3)_3SiI$			8b
$(CH_3COCHCOCH_3)_3SiI_3$			8b
$(C_6H_5COCHCOCH_3)_3SiCl \cdot HCl$			8b
$(C_6H_5COCHCOCH_3)_3SiFeCl_4$	173, 188		8b
$(C_6H_5COCHCOCH_3)_3SiAuCl_4$	164, 185–187		8b
$(C_6H_5COCHCOCH_3)_3SiCl$			8b
$(C_6H_5COCHCOC_6H_5)_3SiCl \cdot HCl$	>300		5b, 5c
$(C_6H_5COCHCOC_6H_5)_3SiCl$	70		8c
$(C_6H_5COCHCOC_6H_5)_3SiBr \cdot HBr$			8c
$(C_6H_5COCHCOC_6H_5)_3SiBr$			8c
$(C_6H_5COCHCOC_6H_5)_3SiI$			8c
$(C_6H_5COCHCOC_6H_5)_3SiI_3$			8c
$(C_6H_5COCHCOC_6H_5)_3Si[OC_6H_2(NO_2)_3]_3$	252–253		8c
$(C_6H_5COCHCOC_6H_5)_3Si(SO_4H)$	242		8c
$(C_6H_5COCHCOC_6H_5)_3Si(NO_3)$	215		8c
$[(C_6H_5COCHCOC_6H_5)_3SiNO_3]_3AgNO_3$	180–181		8c
$(C_6H_5COCHCOC_6H_5)_3SiFeCl_4$	252–255		2
$(C_6H_5COCHCOC_6H_5)_3SiAuCl_4$	258–259		2
$(C_6H_5COCHCOC_6H_5)_3SiSbCl_6$			2
$(C_6H_5COCHCOC_6H_5)_3SiZnCl_3$			2
$[CH_3COC(CH_3)COCH_3]_3SiFeCl_4$	210		2
$[CH_3COC(CH_3)COCH_3]_3SiAuCl_4$	206		2
$[CH_3COC(CH_3)COCH_3]_3SiPtCl_6$	280		2
$[CH_3COC(CH_3)COCH_3]_3SiZnCl_3$	220		2
$[CH_3COC(C_2H_5)COCH_3]_3SiFeCl_4$	157		2
$[CH_3COC(C_2H_5)COCH_3]_3SiAuCl_4$	148		2
$[CH_3COC(C_2H_5)COCH_3]_3SiPtCl_6$	300		2
$[CH_3COC(C_2H_5)COCH_3]_3SiI_3$			2
$(CH_3COCHCOCH_3)_2Si(CH_3)Cl$			9
$(CH_3COCHCOCH_3)_2Si(C_6H_5)Cl$			9
$(CH_3COCHCOCH_3)_2Si(CH_3)_2$		125–128 (0.03 mm)	9
$(CH_3COCHCOCH_3)Si(CH_3)_3$		66–68 (4.0 mm)	9
$(CH_3COCHCOCH_3)Si(C_2H_5)_3$		96–97 (2.1 mm)	9
$(CH_3COCHCOCH_3)_2Si(OCOCH_3)_2$	180–185		13
$(CH_3COCHCOCH_3)_2Si(OCOCH_2CH_3)_2$	140–150		13
$(CH_3COCHCOCH_3)_2Si(OCOCH_2Cl)_2$	180–185		13
$(CH_3COCHCOCH_3)_2Si(OCOC_6H_5)_2$	200		13
$(C_6H_5COCHCOC_6H_5)_2Si(OCOC_6H_5)_2$	300		13
$(F_3CO\text{–}CHCO\text{–}C_4H_3S)_2Si(OCOCH_3)_2$	205		13
$(C_6H_5COCHCOC_6H_5)_2Si(OCOCH_3)_2$	230–232		13

formation of neutral, non-ionic, hexacoordinated silicon chelate derivatives. The structure of this new class of materials, (IV), was proposed based on infrared and ultraviolet data, exchange reactions of the mono- and bi-dentate ligands, and by isolation of an intermediate in the preparation of $(C_5H_7O_2)_2Si(OAc)_2$. This intermediate was proposed to be the diacetoxysilylester of the enolate of acetylacetone(V).



(IV)



(V)

The structure of bis(2,4-pentanediono)diacetatosilicon(IV) was further investigated by nuclear magnetic resonance[14]. It was reported that this chelate is predomenantly *trans* in the solid state and in very fresh solution. On standing the *trans* form isomerizes to the *cis* form until equilibrium is established, the ratio of *cis* to *trans* being of the order of 1.6:1. The silicon chelate derivatives prepared to date are summarized in Table 2.

D. GERMANIUM DERIVATIVES

Morgan and Drew[15] first reported that germanium tetrachloride reacts energetically with acetylacetone in anhydrous solvents to produce germanium bis(acetylacetone) dichloride in quantitative yield. The compounds prepared in this work are discussed in the review by Johnson[16], and are summarized in Table 3.

TABLE 3

GERMANIUM COORDINATION COMPOUNDS

Formula	*Physical properties m.p. (°C)*	*Reference*
$(CH_3COCHCOCH_3)_2GeCl_2$	240	15
$(CH_3COCHCOCH_3)_2GeBr_2$	226	15
$(C_2H_5COCHCOCH_3)_2GeCl_2$	128–129	15
$(CH_3COCHCOCH_3)_3GeCuCl_2$	147–148	15
$(CH_3COCHCOCH_3)_3GeCuBr_2$	165–166	15
$(CH_3COCHCOCH_3)_3GeCu_2Br_3$	195	15
$(CH_3COCHCOCH_3)_3GeCuBr_3$	139	15
$(CH_3COCHCOCH_3)_3Ge \cdot FeCl_4$	184	17

In the interactions between the 1,3-diketone and the germanium tetrahalides, germanium behaves in a manner similar to tin, leading to a neutral, non-ionic bis(1,3-diketonic) derivative. Silicon tetrahalides lead to the tris(1,3-ketonic) system discussed in the previous section. Morgan and Drew were able to prepare the tris(1,3-ketonic) systems of germanium by treatment of the germanium tetrahalides with the desired copper 1,3-diketone chelate[15].

In 1962 a method was reported for the preparation of tris(2,4-pentanediono)germanium(IV)iron(III) tetrachloride by direct reaction with the free 1,3-diketone[17]. Treatment of acetylacetone with germanium tetrachloride and iron(III) chloride in chloroform solution gave the desired compound. It might be noted that a recent report [R. C. Mehrotra and S. Mathur, *J. Organometal. Chem.*, 6 (1966) 11] demonstrates that alkyl- and arylgermanium oxides react smoothly with acetylacetone to give alkyl- or arylgermanium acetylacetonates. The structures of these compounds have not been established.

E. ANTIMONY DERIVATIVES

To our knowledge work in the subject area with antimony has been very limited. Rosenheim has investigated treatment of antimony pentachloride with acetylacetone[8d]. When these reagents were mixed in a 1:1 ratio in dried chloroform solution a product analyzing as $C_5H_7O_2 \cdot SbCl_5$ was isolated. Benzoylacetone behaved in a similar manner giving a material with composition $C_{10}H_9O_2 \cdot SbCl_5$. These workers further showed that if a ratio of 1 part of antimony pentachloride with 2 parts of acetylacetone were used a product having m.p. 127° was isolated with composition. $(SbCl_4) \cdot CH(COCH_3)_2$. Dilthey reported a m.p. of 137° for this material and that it was monomolecular in benzene; the molecular weight corresponded to $AcSbCl_4$. Further investigation in this area is warrented to determine the structure of these materials and to investigate the chemistry of this class of compounds.

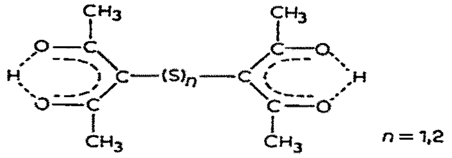
F. PHOSPHORUS DERIVATIVES

In 1966 a new chelate system containing sp^3d^2 hybridised phosphorus was reported by Brown and Bladon[16]. Treatment of an etheral solution of acetylacetone with phosphorus pentafluoride at −70° gave tetrafluoro(pentane-2,4-dionato)phosphorus(V) having m.p. 85°. The material was characterized by infrared and nuclear magnetic resonance data. The workers reported that analogous compounds were formed when benzoylacetone and dibenzoylmethane were employed, however, no data was given to characterize these materials.

G. SULFUR, SELENIUM AND TELLURIUM DERIVATIVES

These three elements are discussed in one section since from the evidence reported to date, the interaction of the respective halides with acetylacetone yields materials in which the ligands are evidently linked through bonding to carbon rather than oxygen. This conclusion is mainly based on spectroscopic information[19].

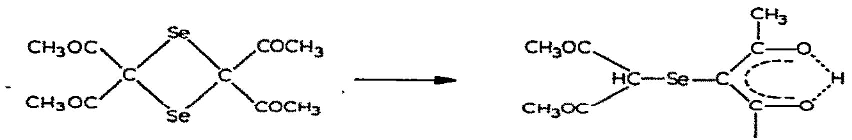
Sulfur bis(acetylacetonate) and disulfurbis(acetylacetonate) prepared from the treatment of acetylacetone with sulfur dichloride and sulfur monochloride, respectively, where shown not to have the sulfur atom linked through oxygen but through carbon. Based on the spectroscopic data[19] these compounds have been assigned structure (VI).



(VI)

The C–H out-of-plane bending absorption at 770–780 cm^{-1} characteristic of metal acetylacetonates was absent. The workers propose the hydrogen bond closure of the ligand ring in these compounds.

The treatment of selenium tetrachloride with acetylacetone has been reported to give compound (VII) which on reduction leads to compound (VIII) (see (VI) Se for S)[20,21].



(VIII) (IX)

Treatment of compound (VII) with acetylacetone gave a material (IX), which was also obtained by reaction of selenium tetrachloride with copper acetyacetonate[17]. Spectroscopic evidence indicates one ligand is in the keto state and one in the enol form.

The tellurium compounds were also shown to be formed in which the tellurium is linked through carbon and not oxygen[19].

The sulfur, selenium and tellurium derivatives are summarized in Table 4.

TABLE 4

ACETYACETONATE DERIVATIVES OF SULFUR, SELENIUM AND TELLURIUM

Formula	*Physical properties m.p. (°C)*	*Reference*
$(CH_3COCHCOCH_3)_2S$	73	19
$(CH_3COCHCOCH_3)_2S_2$	90–92	19
$(CH_3COCHCOCH_3)_2Se_2$		19, 20, 21
$(CH_3COCHCOCH_3)_2Se_2$	78	19, 20, 21
$(CH_3COCHCOCH_3)_2Se$	45	19, 20, 21
$(CH_3COCHCOCH_3)Te$		19, 20
$(CH_3COCClCOCH_3)TeCl_2$	162	19, 22
$(CH_3COCClCOCH_3)TeCl$		19, 22
$(CH_3COCHCOCH_3)_2TeCl_2$		19, 22

H. SPECTROSCOPIC DATA

The majority of the recent investigators in the subject area have found spectroscopic data an invaluable tool in elucidating the structures of the coordination compounds. In Table 5 are summarized the references wherein data of this type has been reported.

TABLE 5

SPECTROSCOPIC DATA REFERENCES

Element	*Infrared*	*Ultraviolet*	*Nuclear magnetic resonance*
Boron	6, 7	5, 6, 7	6, 7
Silicon	9, 13	13	14
Germanium	17		
Antimony			
Phosphorus	18	18	18
Sulfur, selenium, tellurium	19		19

Since renewed interest has developed in the 1,3-diketo compounds of the non-metallic elements over the last several years, it is anticipated that future work will entail complete separation of geometrical and optical species. Furthermore, this would make possible an investigation of the mechanism of displacement reactions in several of these non-metallic systems.

REFERENCES

1 E. G. Rochow, *The Metalloids*, Heath, Boston, Mass., 1966.
2 E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc.*, 87 (1965) 21.
3 W. Dilthey, *Ann.*, 344 (1906) 300.
4 G. T. Morgan and R. B. Tunstall, *J. Chem. Soc.*, (1924) 1963.

5 A. N. Sagredos, *Ann.*, 700 (1966) 29.

6a M. F. Hawthorne and M. Reintjes, *J. Am. Chem. Soc.*, 86 (1964) 5016; *J. Org. Chem.*, 30 (1965) 3851.

b B. M. Mikhailov and Yu. N. Bubnow, *Izv., Akad. Nauk USSR, Otd. Khim. Nauk*, (1960) 1883; *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, (1960) 1757; *Chem. Abstr.*, 55 (1961) 16416.

7 R. Koster and G. W. Rotermund, *Ann.*, 689 (1965) 40.

8a W. Dilthey, *Ber.*, 36 (1903) 923; b, *ibid.*, (1903) 1595; c, *ibid.*, (1903) 3207; d, See also A. Rosenheim, W. Lolwenstamm and L. Singer, *Ber.*, 36 (1903) 1833.

9 R. West, *J. Am. Chem. Soc.*, 80 (1958) 3246.

10 S. K. Dahr, V. Doron and S. Kirschner, *J. Am. Chem. Soc.*, 80 (1958) 753; *ibid.*, 81 (1959) 6372.

11 R. E. Herter, *Chem. Ind. (London)*, (1963) 1397.

12 R. G. Pearson, D. N. Edington and F. Basolo, *J. Am. Chem. Soc.*, 84 (1962) 3233.

13 R. M. Pike and R. R. Luongo, *J. Am. Chem. Soc.*, 87 (1965) 1403; *ibid.*, 88 (1966) 2972.

14 C. E. Holloway, R. R. Luongo and R. M. Pike, *J. Am. Chem. Soc.*, 88 (1966) 2060.

15 G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 125 (1924) 1261.

16 O. H. Johnson, *Chem. Rev.*, 48 (1951) 259.

17 R. Müller and L. Heinrich, *Chem. Ber.*, 95 (1962) 2276.

18 N. M. D. Brown and P. Bladon, *Chem. Commun.*, (1966) 304.

19 D. H. Dewar, J. E. Fergusson, P. R. Hentschel, C. J. Wilkins and P. P. Williams, *J. Chem. Soc.*, (1964) 688 and references therein.

20 G. T. Morgan and H. D. Drew, *J. Chem. Soc.*, 117 (1920) 1456.

21 G. T. Morgan, H. D. K. Drew and T. V. Barker, *J. Chem. Soc.*, 121 (1922) 2432.

22 G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 121 (1922) 922.