Tetrahedron. Vol. 26, pp. 5057 to 5062. Pergamon Press 1970. Printed in Great Britain

HETEROCYCLIC ORGANOBORON COMPOUNDS—XIII

DIRECT CHLORINATION OF BIS-(1,3-DIKETONATO)-BORONIUM SALTS

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(*Received in the UK* 21 *May* 1970; *Accepted for publication* 4 *June* 1970)

Abstract—Bis(1,3-Diketonato)boronium hexachloroantimonates, (I,X = $SbCl_6^-$), of acetylacetone and benzoylacetone were chlorinated by chlorine gas in chloroform solution or suspension to obtain the boronium hexachloroantimonates of the corresponding 2-chloro-1,3-diketones.

WE HAVE previously reported the synthesis of the bis-(1,3-diketonato)-boronium cation (I), by a number of different pathways.[1,2] These cations are isoelectronic with the corresponding neutral beryllium chelates (II), which together with several other metals undergo electrophilic substitution of the 2-H atom by careful treatment with mild reactants.[3–7] It was shown[3] that e.g. the bromination of bis(acetylacetonato)-beryllium by N-bromosuccinimide is a true substitution reaction of the chelate and not a multi-stage process, namely, dissociation of the chelate, bromination of the β-diketone or of its anion, and final re-combination of the metal and the 2-bromo-1,3-diketone. Bromination by free bromine in dry dichloromethane of the bis(2,4-pentanedionato)beryllium[8] or tris(2,4-pentanedionato)aluminium[9] also proceeds without decomposition, to give the corresponding 3-chloro-chelates, whereas the copper complex[10] of 2,4-pentanedione or 3-bromo-2,4-pentanedione is decomposed by bromine under the same conditions to give copper bromides and 3-bromo-2,4-pentanedione or 3,3-dibromo-2,4-pentanedione, respectively. The bromination of some tris(3-phenyl-2,4-pentanedionato)chelates, which proceeds at the 2- and 4-Me groups is also accompanied by decomposition of the complexes;[11] however, it was clearly demonstrated that this decomposition follows the bromination.

Here we investigate the effect of the overall positive charge on the boronium chelate[12] on its reactivity to electrophilic substitution.

DISCUSSION

As the activation energy of the electrophilic attack of a positive fragment of the boron(III) cation is much higher than that of the neutral chelate no nitration of I (Y = H) by concentrated nitric acid in acetic acid occurs. No chlorination by N-chlorosuccinimide or bromination by N-bromosuccinimide takes place; the unchanged boronium salt is recovered in all cases. On introduction of [$B(acac)_2]SbCl_6$[(Ia), X = $SbCl_6^-$ Y = H] to a suspension of $Cu(NO_3)_2$, $3H_2O$ in acetic anhydride, brown

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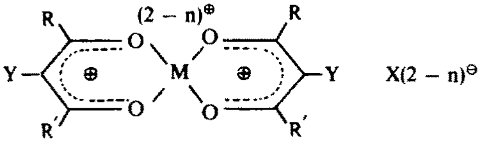
nitrogen oxides were evolved immediately, but only green inorganic solids could be recovered from the reaction mixture.

Chlorination by dry chlorine gas of $[B(acac)_2]SbCl_6$ and $[B(bzac)_2]SbCl_6$ (Ib, $X = SbCl_6^-, Y = H$) are the only successful substitution reactions. The rate of chlorine uptake decreases rapidly in the order Ia > Ib > Ic.



I: M = B, n = 1; a: R, R′ = Me; X = $SbCl_6^-, ClO_4^-$;
II: M = Be, n = 2; b: R = Me; R′ = Ph; Y = H, Cl
c: R, R′ = Ph.

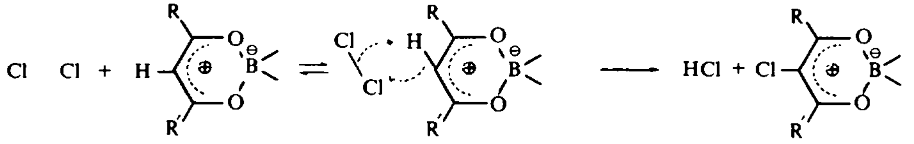
There may be two reasons for this; (i) A decrease in solubility of the boronium chelates ($X = SbCl_6^-, Y = H$) in the above series, and (ii) an increase in steric hindrance between the substituent groups R,R′ and Y in the same series; models showed that in the planar *cis*-enol configuration of the dibenzoylmethane no chlorination could take place without rotation of the R,R′ = Ph groups out of the plane of the chelated β-diketone molecule.

Analyses and spectra confirmed the postulated structures I, II of the bis(2-chloro-1,3-diketonato)beryllium(II) and boron(III) chelates. Chlorine substitution causes a characteristic bathochromic shift of the UV absorption maxima of the chelated enol form of the β-diketone: the changes are: $\Delta\lambda = 272–295 = -23$ nm for the free ligand (ref 13); $294–316 = -22$ nm (ref 1) for the beryllium chelate, and $296–327 = -31$ nm for the boron (III) chelate when the ligand is changed from β-diketone to the 3-chloro-β-diketone.

In the IR spectra the highest wavelength C—H stretching band [3110 cm^{-1} in $Be(acac)_2$ 3140 cm^{-1} in Ia, b and c ($X = SbCl_6, Y = H$) see ref 1)], attributed to the Y = H proton, is no longer present in the spectra of the Y = Cl chelates. The bands at 650–680 cm^{-1} and 490–520 cm^{-1} are tentatively assigned to the C—Cl stretching vibrations in the chloro-chelates (see Table 3).

The ^1H NMR spectra of β-diketone chelates are characteristic and are strongly dependent on the electric asymmetry of the complex. The chemical shifts of the methyl and methine protons for polar[12, 14–16] and charged[12, 16, 17] complexes suffer linear shifts from the values for neutral chelates due to the intramolecular electric fields. Similar effects are also observed in the C^{13} proton coupling constants[15, 16] and ^{13}C chemical shifts.[18] The effect of chlorine substitution in neutral, polar metal chelates of 1,3-diketones has also been related to the change in electric field within the molecule caused by the chlorine substituent.[19] Chlorine substituted in the chelates studied here leads to the disappearance of the Y = H signal and causes a characteristic downfield shift of the R,R′ = Me signal throughout: $\Delta\tau = -0{\cdot}2$ ppm for the boronium chelates and $\Delta\tau = -0{\cdot}32$ ppm for beryllium acetylacetonate (Table 4). The difference in the downfield shift produced by the Cl atom is presumably due to a similar electric field effect due to the positive charge on the B atom. The NMR spectra of these chelates will be discussed in detail elsewhere.[20] ^{11}B NMR spectra of the boronium chelates (I, Y = H, Cl) exhibit a single peak at about $-4{\cdot}0$ ppm downfield from that of boron trifluoride etherate. ^{35}Cl NQR spectra of compounds I and II which are also in accordance with the proposed structures are discussed elsewhere.[21]

No investigations of the mechanism of chlorination of the bis(β-diketonato) boronium chelates were undertaken but it seems probable that the substitution proceeds directly without dissociation and subsequent recombination of the chelate; the syntheses of the 3-chloro-acetylacetone chelates from the free diketone are always accompanied by side reactions which lead to black oily residues, whereas on direct chlorination the solutions remain clear and almost colourless; analytically pure chloro-chelate precipitates on concentration. The mode of reaction of the chlorine as a neutral molecule rather than as a formally positive reactant (see equation) may explain why only chlorination by gaseous chlorine has as yet proved successful.



A somewhat similar mechanism was proposed for the direct bromination of the neutral acetylacetone chelates.[22] However we must suppose that the $SbCl_6^-$ anion assists the chlorination process; bis(1,3-diketonato) boronium hexachloroantimonates are chlorinated smoothly in a specific position, whereas the corresponding perchlorates (Ia, b, c; X = ClO_4^-; Y = H) undergo decomposition when treated with chlorine gas. A marked difference in electron-accepting behaviour between arylpyryllium hexachloroantimonates and perchlorates was reported recently.[23]

TABLE 1. BERYLLIUM AND BORONIUM CHELATES OF THE 2-CHLORO-1,3-DIKETONES

M	R	R'	Y	X	m.p. °C	C Found	C Calc	H Found	H Calc	Cl Found	Cl Calc
Be	Me	Me	Cl	—	177	43·89	43·50	4·61	4·38	25·3	25·68
B	Me	Me	Cl	$SbCl_6$	138	18·53	19·61	1·94	1·98	46·3	46·32
B[a]	Me	Me	Cl	ClO_4	200	31·13	31·82	3·23	3·21	18·5	18·80[b]
B	Me	Ph	Cl	$SbCl_6$	155	32·38	32·61	2·84	2·19	38·5	38·51

[a] Boron content determined from the combustion residue taken as B_2O_3: Found 3·14, Calc 2·86%.
[b] Chlorine from ClO_4^- not included in this figure.

TABLE 2. UV ABSORPTION SPECTRA OF THE BERYLLIUM AND BORONIUM CHELATES OF THE 2-CHLORO-1,3-DIKETONES

M	R	R'	Y	X	UV-maxima; $\lambda_{max}/\varepsilon$		
H	Me	Me	Cl	—	—		295/17,000
Be	Me	Me	Cl	—	259sh/2,500		316/24,400
B	Me	Me	Cl	$SbCl_6$	276/11,300		327/20,700
B	Me	Me	Cl	ClO_4	277sh		328
B	Me	Ph	Cl	$SbCl_6$	278sh	296	372

Solvent: 1,2-dichloroethane.

TABLE 3. IR SPECTRA (cm.$^{-1}$) OF 3-CHLOROACETYLACETONE, BIS-(CHLOROACETYL-ACETONATO)-BERYLLIUM AND OF BIS-(1,3-DIKETONATO)-BORONIUM SALTS IN KBr DISKS

[a] In CCl_4 solution

ClacacH[a]	Be(Clacac)$_2$	[B(Clacac)$_2$] $SbCl_6$	[B(Clacac)$_2$] ClO_4	[B(Clbzac)$_2$] $SbCl_6$	Assignments
—	—	—	—	3070w	νCH (Ph)
3012 vw	3010 w	3015 w	3012 w	3012 w	—
—	2965 vw	—	2960 mw	—	—
—	2922 w	2910 m	2925 mw	2920 vw	νCH (Me)
1720 mw	—	—	—	—	νC=O (keto form)
—	—	—	—	1600 m	νC=C (Ph)
—	—	—	—	1555 ms	νC=C (Ph)
1610 s	1575 vs	1540–	1550–	1520–	νC=O and νC=C
—	1480 vs	1490 vs	1490 vs	1470 vs	(chelate ring)
—	1440 vs	—	—	—	—
1405 m	1380 vvs	1390 ms	1390 ms	1390 s	δ as CH (Me)
1378 m	1350 vs	1330 vs	1330 vs	1340 s	δ s CH (Me)
1270 ms	1320 s	—	—	1302 s	—
—	1205 w	—	—	1190 m	—
—	1150 vw–1110 vw	1160–1090 vs	—	1160 s	—
—	—	—	1128 vs	—	νCl—O (ClO_4)
—	1070 vs	1040 m	1040 ms	1080 vs	—
1040 m	1030 s	1020 m	1020 ms	1040 s	δr (Me)
—	—	980 mw	982 m	980 s	ν as ^{10}B—O (BO_4)
940 mw	—	950 ms	950 ms	950 ms	ν as ^{11}B—O (BO_4)
920 m	933 ms	920 w	920 m	920 ms	νC—CH_3 + νC=O
—	—	895 m	895 ms	975 ms	ν as ^{11}B—O (BO_4)
—	855 vs	—	—	—	νBe—O (BeO_4)
—	—	—	—	855 ms	—
—	—	—	—	792 ms	δCH (Ph)
—	—	—	—	782 ms	δCH (Ph)
—	760 m	740 w	740 w	—	—
—	—	—	—	722 s	δCH (Ph)
—	—	—	—	718 s	δCH (Ph)
665 w	665 ms	652 w	650 w	680 ms	ν as (C—Cl)
—	648 mw	—	—	632 m	—
—	—	590 mw	585 mw	610 m	δ as B—O (BO_4)
—	—	550 w	550 w	530 mw	—
520 mw	510 mw	490 mw	490 mw	502 w	ν s (C—Cl)
—	455 m	—	—	402 w	—

EXPERIMENTAL

Chlorination of [B(acac)$_2$]$SbCl_6$ (Ia, Y = H, X = $SbCl_6^-$). [B(acac)$_2$]$SbCl_6$ (15 g, 30 mmol) was dissolved in dry chloroform (200 ml) and chlorine gas was bubbled through the soln at 0° for 1 hr. Evaporation of the solvent *in vacuo* gave an almost quantitative yield of [B(Clacac)$_2$]$SbCl_6$ (Ia, Y = Cl, X = $SbCl_6^-$), m.p. 133–139°.

Chlorination of [B(bzac)$_2$]$SbCl_6$ (Ia, Y = H, X = $SbCl_6^-$). [B(bzac)$_2$]$SbCl_6$ (15 g, 20 mmol) was suspended in dry chloroform (200 ml) and chlorine was bubbled through the soln at 0° during 5 hr when the Cl content of the ppt reached the value calculated for [B(Clbzac)$_2$]$SbCl_6$ (Ib, Y = Cl, X = $SbCl_6^-$). The yield was almost quantitative, m.p. 145–155°.

Chlorination of [B(dbm)$_2$]$SbCl_6$ (Ic, Y = H, X = $SbCl_6^-$) [B(dbm)$_2$]$SbCl_6$ (16 g, 20 mmol) was suspended in dry chloroform (200 ml) and Cl_2 was bubbled through the cooled mixture. The Cl content increased very

TABLE 4. ^{1}H NMR CHEMICAL SHIFTS OF THE BIS-(1,3-DIKETONATO)-BERYLLIUM AND -BORONIUM CHELATES (τ values)

		Compound			Chemical shift		Solvent
M	R	R′	Y	X	Me (R,R′)	H (Y)	
H	Me	Me	H	—	8·0	4·6	CCl_4[a]
H	Me	Me	Cl	—	7·8	—	CCl_4[a]
Be	Me	Me	H	—	7·98	4·37	$CDCl_3$[b]
Be	Me	Me	Cl	—	7·67	—	$CDCl_3$
B	Me	Me	H	ClO_4	7·40	3·24	$CDCl_3$[b]
B	Me	Me	Cl	ClO_4	7·20	—	$CDCl_3$
B	Me	Me	H	$SbCl_6$	7·42	3·36	$CDCl_3$
B	Me	Me	Cl	$SbCl_6$	7·22	—	$CDCl_3$
B	Me	Ph	H	$SbCl_6$	7·42	2·68	CH_3CN
B	Me	Ph	Cl	$SbCl_6$	7·22	—	CH_3CN

[a] Enol tautomer, see D. C. Nonhebal, *Tetrahedron* **24**, 1869 (1968).

[b] Ref 12.

slowly and was far below the theoretical value even after 12 hr; the UV spectrum showed that chlorination occurred to some extent.

Attempts to chlorinate the corresponding 1,3-diketonatoboronium perchlorates (Ia, b, c, Y = H, X = ClO_4^-) were unsuccessful; only intractable oils were obtained.

Syntheses from 3-chloro-2,4-pentanedione

(i) 3-Chloro-2,4-pentanedione[18] (2 ml, 2·3 g, 20 mmol) were dissolved in dry dichloromethane (20 ml); the soln was cooled to $-20°$ and the required volume of BCl_3 was slowly condensed into the soln. The soln of $[B(Clacac)_2)]Cl$ (Ia, Y = Cl, X = Cl^-) was used directly in metathetical reactions as follows:

(ii) Antimony pentachloride (1·3 ml, 3 g, 10 mmol) in dichloromethane (3 ml) was introduced with vigorous stirring into a cooled soln of $[B(Clacac)_2]Cl$ (10 mmol). The mixture was set aside overnight, evaporated to dryness, pressed on a porous plate, and recrystallized several times from dichloromethane until colourless crystals of $[B(Clacac)_2]SbCl_6$ (Ia, Y = Cl, X = $SbCl_6^-$), m.p. 137–138° were obtained.

(iii) Anhydrous perchloric acid (1 g, 10 mmol) in dichloromethane (5 ml) was added to a stirred soln of $[B(Clacac)_2]Cl$ (10 mmol). The soln was set aside overnight and was then evaporated *in vacuo* to yield a black oil, containing crystals of the product. This was washed with chloroform and the crystals (m.p. 200°) were recrystallized from dichloroethane.

(iv) *Alternative preparation of* $[B(Clacac)_2]SbCl_6$. A soln of $SbCl_5$ (2·6 ml, 6 g, 20 mmol) with a drop of conc HCl in glacial AcOH (5 ml) was added to a stirred soln of 3-chloroacetylacetone (4 ml, 5 g, 40 mmol) and tri-n-butyl borate (6 ml, 4·4 g, 20 mmol) in glacial AcOH (10 ml). After 2 hr the soln was evaporated *in vacuo* and the residue was recrystallized several times from dichloromethane to yield $[B(Clacac)_2]SbCl_6$, m.p. 134–138°.

(v) *Synthesis of* $Be(Clacac)_2$ (IIa, Y = Cl). A soln of anhyd beryllium chloride (2 g; 25 mmol) in EtOAc (40 ml) was added to 3-chloroacetylacetone (6 ml, 7 g, 50 mmol) in EtOAc (10 ml). The mixture was heated under reflux until the evolution of HCl ceased (ca 3 hr) and then concentrated to dryness. The black residue was extracted in a Soxhlet extractor with light petroleum (b.p. 70–80°). The soln in light petroleum was cooled to yield yellow crystals of $Be(Clacac)_2$ (2·2 g, 30%), m.p. 177°.

Analyses and spectra. Analytical figures are summarized in Table 1. C and H were determined by standard combustion, Cl by argentometric titration of samples decomposed in boiling 2N KOH soln. 3-Chloroacetylacetone gave a correct figure for Cl by this procedure. UV spectra were taken by an Optica Milano-CF4 spectrophotometer, IR spectra were recorded with a Carl Zeiss Jena UR-10 spectrophotometer. NMR spectra were recorded on a Perkin–Elmer R 10 instrument at 60·004 MHz for protons and 19·2519 MHz for boron-11.

Acknowledgements—Thanks are expressed to Mrs. M. Paraschiv and Mrs. E. Romaş for recording UV and IR spectra and to Mrs. M. Roman for elementary analyses.

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