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HETEROCYCLIC ORGANOBORON COMPOUNDS—VII[1]

CHELATED BIS-(1,3-DIKETONATO)BORONIUM SALTS WITH ACETYLACETONE, BENZOYLACETONE AND DIBENZOYLMETHANE

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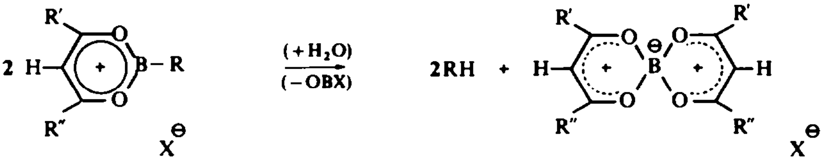
Abstract—Boronium salts (O=CR'CHCR''—O)$_2$B$^{\oplus}$ X$^{\ominus}$ (II), with the 1,3-diketone residues R', R'' as: Me, Me; Me, Ph; Ph, Ph, and the anion X as Cl, AlCl$_4$, FeCl$_4$, SbCl$_6$, ½SnCl$_6$, I, I$_3$ and ClO$_4$ have been prepared. The IR and UV spectra of boronium salts are discussed.

INTRODUCTION

Previous papers have shown[1-3] that 1,3,2-dioxaborinium salts (IC) yield bis-(1,3-diketonato)boronium salts (II) on heating.



I II

A, R' = R'' = Me; B, R' = Me, R'' = Ph; C, R' = R'' = Ph

The bis-dibenzoylmethanato-boronium perchlorate (II Cf)* thus obtained is extremely stable: it can be heated in boiling water, or at 300° in air, without decomposition. These properties are at variance with the data reported by Dilthey[4] for compounds of this class, which were obtained from 1,3-diketones and boron trichloride, and which were described as unstable and hygroscopic.

Dilthey could not prepare IIC: no definite compounds were obtained by him in the reaction of dibenzoylmethane with boron trichloride. Being isoelectronic with the well-known bis-(1,3-diketonato)beryllium chelates which strongly resist thermal and hydrolytic decompositions,[5] compounds II thus constitute an interesting problem. They were first obtained from boron trichloride and acetylacetone or ethyl acetoacetate before Dilthey's paper, but were formulated[6] as trialkoxyborane hydrochlorides, e.g. IIAa as (R'COCH = CR'O)$_3$B. 2 HCl. After Dilthey's studies,

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* The notations A–C, refer to the nature of substituents R' and R'' from the cation (A, acetylacetone; B, benzoylacetone; C, dibenzoylmethane). Small letters refer to the nature of the anion (a, chloride; b, tetrachloroferrate; c, hexachlorostannate; d, chloroantimonate; e, triiodide; f, perchlorate; g, iodide; h, chloroaluminate).

TABLE 1. BIS-(1,3-DIKETONATO)BORONIUM SALTS (II)

Comp.	Formula			M.p. °C	Elementary analysis							
	Cation		Anion		C		H		B		Cl	
	R′	R″	X		Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
IIAa	Me	Me	Cl	Not isolated pure								
IIAb			$FeCl_4$	137[a]	30·05	29·53	4·09	3·47	—	—	35·05	34·87
IIAc			$\frac{1}{2}SnCl_6$[b]	192–195[c]	31·43	32·05	3·99	3·76	—	—	28·40	28·39
IIAd	$[C_{10}H_{14}BO_4]^{\oplus}$		$SbCl_6$	133–140	22·41	22·10	2·76	2·60	—	—	39·20	39·14
IIAe			I_3[d]	138	19·91	20·36	2·46	2·39	—	—	—	—
IIAf			ClO_4	179	38·23	38·93	4·67	4·57	3·05	3·50	—	—
IIBa	Me	Ph	Cl	70–80	Not analysed							
IIBe			$FeCl_4$	177–180[e]	44·94	45·25	4·07	3·42	—	—	26·50	26·52
IIBc			$\frac{1}{2}SnCl_6$[f]	164	47·60	48·15	4·34	3·64	—	—	21·10	21·32
IIBd	$[C_{20}H_{18}BO_4]^{\oplus}$		$SbCl_6$	155–160	35·40	35·99	2·80	2·72	—	—	31·70	31·87
IIBe			I_3[g]	203 210	33·28	33·65	2·94	2·54	—	—	—	—
IIBf			ClO_4	249	54·96	55·52	4·75	4·19	2·95	2·50	—	—
IICa	Ph	Ph	Cl	240	72·63	73·12	4·56	4·49	2·29	2·19	7·80	7·20
IICb			$FeCl_4$	230–235	55·33	55·01	3·95	3·38	—	—	21·00	21·65
IICc			$\frac{1}{2}SnCl_6$[h]	253–260	57·10	57·83	3·73	3·56	—	—	17·05	17·08
IICd			$SbCl_6$	220–230	45·98	45·50	2·96	2·80	—	—	26·50	26·87
IICe			I_3[i]	263–270	—	—	2·62	2·65	—	—	—	—
IICf	$[C_{30}H_{22}BO_4]^{\oplus}$		ClO_4	335	64·36	64·71	4·25	3·98	1·95[j]	1·94	—	—
IICg			I[k]	306–308	61·22	61·67	3·88	3·80	—	—	—	—
IIh			$AlCl_4$	234–250	57·46	57·65	4·00	3·54	—	—	—	—

[a] Lit.[4] m.p. 137° dec.

[b] Found B + Sn, 18·4. Calc. 18·73%.

[c] Lit.[4] m.p. 210–212°.

[d] Found: I, 65·0. Calc. 64·56%.

[e] Lit.[4] m.p. 180–182°.

[f] Found: B + Sn, 13·0. Calc. 13·87%.

[g] Found: I, 56·0. Calc. 53·33%.

[h] Found: B + Sn, 11·0. Calc. 11·26%.

[i] Found: I, 45·5. Calc. 45·53%.

[j] Boron content determined by titration after ref. 11, found 1·98%.

[k] Found: I, 22·0. Calc. 21·72%.

compounds II were reviewed several times,[7–10] but were little investigated. As lately as 1964 their spiranic structure was considered doubtful and a covalent formula (R'COCH = CR''—O)$_2$BCl was taken into consideration.[8]

Having obtained compounds II by a different reaction (I → II), we therefore decided to reinvestigate compounds II, preparing them by several methods: four methods starting from 1,3-diketones (methods 1–4), one from 1,3,2-dioxaborinium salts (method 5), and four metathetical reactions involving the exchange of the anion X in bis-(1,3-diketonato)boronium salts (methods 5–9). Analytical data and physical constants are presented in Table 1.

DISCUSSION OF THE RESULTS

Dilthey's method for the preparation of bis-(1,3-diketonato)boronium salts[4] involved the reaction of boron trichloride etherate with 1,3-diketones. The replacement of ether by other solvents (dichloromethane, 1,2-dichloroethane) is advantageous (method 1). Other boron derivatives may be used (n-butyl borate in methods 2–4, boric acid or acetoxy borate in method 3). In the latter cases, a strong acid is necessary in order to cause dehydration and to provide a weaker nucleophilic anion than

TABLE 2. UV ABSORPTION BANDS OF 1,3-DIKETONES, BERYLLIUM BIS-(1,3-DIKETONATES) AND BIS-(1,3-DIKETONATO)BORONIUM HEXACHLOROANTIMONATES IN DICHLOROETHANE

Compound	λ_{max} mμ	ε_{max} l/mole cm	f[a]
acacH[b]	273	—	—
(acac)$_2$Be[c]	294	36,700	0·57
IIAd (acac)$_2$B$^\oplus$SbCl$_6^\ominus$	296	17,300	0·36
bzacH[d]	248	—	—
	310		
(bzac)$_2$Be	253	14,500	0·36
	329	38,500	0·815
IIBd (bzac)$_2$B$^\oplus$SbCl$_6^\ominus$	277	22,300	0·34
	348	67,000	1·03
	355 sh[e]	66,000	
dbmH[f]	252	—	—
	343		
(dbm)$_2$Be[f]	262	25,800	0·62
	362	64,000	1·02
	378 sh	40,900	
IICd (dbm)$_2$B$^\oplus$SbCl$_6^\ominus$	277	17,700	0·195
	310	28,000	0·40
	382	112,000	1·42
	400	135,000	

[a] Oscillator strengths for overlapping bands were summed up.

[b] Lit. 274 mμ in chloroform,[12] 271 mμ in isooctane,[13] 275·5 mμ in ethanol.[14]

[c] Lit. 240 and 294 mμ in hexane.[14, 15]

[d] Lit. 247 and 310 mμ in ethanol.[13]

[e] Broad maximum resolved graphically.

[f] Lit. 245–250 and 342–245 mμ in ethanol[16a] or methanol.[16b]

TABLE 3. IR ABSORPTION BANDS OF 1,3-DIKETONES, BERYLLIUM BIS-(1,3-DIKETONATES AND BIS-(1,3-DIKETONATO)BORONIUM HEXACHLOROANTIOMONATES IN KBr PELLETS

Acetylacetone			Benzoylacetone			Dibenzoylmethane			
acacH	acac$_2$Be	acac$_2$B$^\oplus$	bzacH	bzac$_2$Be	bzac$_2$B$^\oplus$	dbmH	dbm$_2$Be	dbm$_2$B$^\oplus$	Assignment
—	3110 vw	3140 vw	—	—	3140 w	—	—	3140 w	—
3004 s	3000 vw	3090 w	3060 vw	—	3050 m	—	3065 w	3078 w	ν(C—H)
2966 s	2970 vw	—	—	—	—	—	3055 w	—	—
2921 s	2930 vw	2920 w	2920 w	—	2920 vvw	—	3030 shw	—	—
—	—	—	1610 vs	1600 ms	1608 ms	1605 vs	1602 ms	1608 ms	ν(C=C)Ph
1728 m	—	—	—	—	—	1560 vs	—	—	—
1710 m	1570 vs	1570 vs	1580 s	1570 s	1558 vs	1550 vs	1555 vs	1560 vs	ν(C=O)
1620 s	1540 vs	1558 vs	1540 s	1530 vs	1525 s	1530 vs	1540 vs	1545 s	ν_{as}(C—C—C)
—	—	1548 s	1520 m	—	—	—	—	1525 s	—
—	—	—	1490 s	1498 s	1500 s	1490 vs	1490 vs	1495 vs	ν(C=C)Ph
—	—	1510 shm	—	—	—	—	1465 s	—	—
1445 s	—	—	1450–80 shms	—	1460 shw	1440 shs	1450 mw	1440 ms	—
1418 s	1450 s	1430 m	1425 ms	1460 s	1430 m	—	—	—	δ_{as}(Me)
—	1400 vs	1415 m	—	1400 vs	1390 m	—	1392 vs	1385 s	ω(O—C—C—C—O)
1355 s	—	1360 vs	1365 ms	—	1355 vs	—	—	—	ν_s(Me)
—	—	—	1310 shms	1325ms	—	1350 shm	1345 ms	1360 vs	—
1298 s	1305 m	1340 vs	1270 s	1310 m	1310 ms	1320 s	1310 m	1315 s	ν_s(C—C—C)
1244 s	1250 vw	—	—	—	1290 shw	1240 vs	1238 m	1258 s	—
—	—	—	1210 ms	1220 m	1220 mw	—	—	—	—
1168 s	1198 vw	1187 shw	1185 ms	1190 w	1190 vw	1198 ms	1182 mw	1198 m	δ(C—H) in plane
1154 s	—	1135 s	—	—	1170 vw	1170 m	1160 mw	1170 m	—
—	—	1110 vs	—	—	1115 s	—	—	1115 s	ν_{as}(^{10}B—O)
—	—	—	1110 mw	1115 m	1100 ms	1110 m	—	1100 vs	—
—	—	—	1090 m	1100 shw	—	1100 shm	1088 m	—	—
—	1050 s	—	1076 m	1075 m	1080 s	1065 m	—	1050 vs	—

1020 m	1030 shm	1032 m	1035 m	1030 m	1035 m	—	—	—	Me rocking
—	—	—	—	1018 s	—	1035 m	1032 m	—	—
—	—	1005 shmw	—	1010 ms	1005 m	1005 ms	1008 mw	1008 s	—
—	965 mw	960 m	940–1000	980 m	—	980 shm	993 vvw	989 shm	—
912 ms	940 m	920 m	(broad)	940 w	930 w	940 mw	968 ms	920 shm	—
—	—	895 mw	—	—	908 m	—	—	900 m	$\nu_{as}(^{11}B—O)$
—	—	—	865 vw	—	880 w	860 shw	865 mw	—	—
—	—	—	—	—	—	850 w	—	851 vw	—
—	830 s	—	—	820 s	—	—	—	—	$\nu_{as}(Be—O)$
—	—	815 m	810 vw	—	815 w	820 w	—	820 w	—
779 ms	790 mw	—	—	765 shm	—	795 m	798 mw	—	—
—	—	—	775 s	755 ms	789 s	765 vs	762 s	778 s	Phδ(C—H)
—	752 mw	740 vvw	—	—	720 m	—	—	736 m	—
—	—	—	700 ms	712 ms	712 m	720 ms	732 ms	720 ms	Phδ(C—H)
—	661 mw	—	680 shw	685 m	680 m	690 shm	—	—	—
639 s	—	—	—	—	—	680 s	685 ms	680 s	—
—	—	—	625 vvw	—	635 mw	620 m	615 vvw	—	—
—	—	—	—	605 vw	608 mw	610 ms	595 m	608 ms	—
—	—	—	580 w	585 mw	—	—	—	577 m	—
529 s	—	535 w	550 w	545 m	551 w	—	522 mw	—	—
—	495 w	—	—	—	—	—	—	—	ν(Be—O)
—	—	—	—	—	495 mw	495 mw	—	—	—
472 vw	—	460 w	475 vw	455 mw	—	450 w	—	465 w	—
—	422 mw	—	—	445 mw	—	—	—	—	—

$OH^{\ominus}$ or $OAc^{\ominus}$. When water is present in larger amounts, e.g. when using boric acid or 70%-perchloric acid, an excess of acid is necessary and the yields are lower.

The UV and IR absorption spectra bring further evidence as to the structure of bis-(1,3-diketonato)boronium salts. UV absorption maxima are given in Table 2, in comparison with the isoelectronic beryllium bis-(1,3-diketonates). As mentioned earlier,[17] the quantum energy absorbed by beryllium bis-acetylacetonate is practically identical with that of bis-(acetylacetonato)boronium IIA. The absorption intensity, evidenced by the molar absorptivity ε or by the oscillator strength f, is however lower in the boron chelate than in the beryllium analogue. A similar band at ca. 300 mμ appears in the spectra of various metal acetylacetonates,[12, 15, 18, 19] and is assigned to a π–π^* transition in the chelate ring.[18–20] Bands at higher wavelengths are due to transitions involving d-orbitals.[20] The absence of such bands in boron or beryllium acetylacetonates, where no d-electrons are involved is in agreement with the above assignments and substantiates the attribution of the longest-wavelength band in compounds II to a π–π^* transition in the 1,5-oxa-oxonia-pentadiene system of the ligand.[3, 21]

There can be no ring-current in these chelate rings.[22a] In transition metal chelates, interatomic distances,[22b] NMR[22c] and chemical reactivity data (lit. cited in Refs 19 and 22*a*) have not yet definitely settled the controversy about their aromaticity.

In the benzoylacetone and dibenzoylmethane chelates, the nature of the central atom exerts a pronounced influence on the absorption spectrum. Substitution of one or both Me groups by Ph groups in beryllium acetylacetonate causes a bathochromic shift of the major peak (33–35 mμ for one Ph group), and a slight hyperchromic effect (f increases with 0·2 for one Ph group). In the beryllium dibenzoylmethanate, the longest wavelength band is split and a shoulder appears on the longest wavelength branch of the band envelope. In the diketonatoboronium cation on the other hand, the major peak undergoes much higher bathochromic (52 mμ for one Me substituted by a Ph group) and hyperchromic shifts (f increases with 0·4–0·6 for one Ph group). In the boronium chelates with benzoylacetone and with dibenzoylmethane this longer-wavelength band is split.

Qualitatively, the more pronounced effect of Ph groups on the boronium than on the beryllium chelates can be accounted for as follows: the higher positive charge of the boron nucleus is assisted more effectively by the Ph groups in the boronium chelates, causing a higher delocalization and hence a lower excitation energy in these compounds.

UV absorption spectra were also recorded for boronium salts with the other anions besides hexchloroantimonate, and identical spectra were obtained, with the exception of chloroferrates and triiodides where bands due to the anion also appear. The bis-(dibenzoylmethanato)boronium iodide IICg presents in 1,2-dichloroethane a low-extinction supplementary band at 530 mμ which imparts this compound its red colour. In keeping with tropylium,[23] pyrylium[24] or pyridinium iodides,[25] we assign this band to a charge-transfer transition from a polar ground-state to a less polar excited state in which the boronium cation accepts an electron from the iodide anion.

IR absorption bands are presented in Table 3. The long discussion[26–33] concerning the assignment of the two bands of metal acetylacetonates in the 1500–1600 cm^{-1} range to C═C and C═O streching vibrations was recently solved by Musso and

Junge[34] in an unambiguous and elegant manner, by labelling copper (II)-acetylacetonate with ^{13}C and ^{18}O in various positions. The assignments of these authors are included in Table 3. Bands due to the four stretching and bending vibrations of boron–oxygen bonds have been identified by Funck[35] between 1050 and 700 cm^{-1} on the basis of a detailed analysis of reference spectra. These assignments are also included in Table 3 and they are meant to revise partly the previous assignments.[22, 36] The agreement between our data presented in Table 3 and literature data is satisfactory for acetylacetone,[27, 29, 37, 38] its beryllium[26, 28, 29, 31, 33, 35a] and boron[35b] chelates, benzoylacetone[29, 38] and dibenzoylmethane.[29, 37, 38]

The NMR spectra in liquid sulphur dioxide of $(acac)_2B^{\oplus}ClO_4^{\ominus}$ (IIAf), $(bzac)_2B^{\oplus}ClO_4^{\ominus}$ (IIBf) and $(dbm)_2B^{\oplus}ClO_4^{\ominus}$ (IICf) are consistent with the proposed formulae. Thus $(acac)_2B^{\oplus}ClO_4^{\ominus}$ presents two signals: one at τ 7·53 corresponding to 12 Me protons and another at τ 3·54 corresponding to two protons, analogously to $(acac)_2Be$ which presents the same peaks at τ 7·92 and 4·30 ppm. (lit.[12, 39] τ 8·02 and 4·53). Similarly $(bzac)_2B^{\oplus}ClO_4^{\ominus}$ shows signals at τ 7·35 (6 Me protons), at τ 2·88 (two protons) and a multiplet due to the Ph protons at τ 1·70–2·60. The same signals appear in the NMR spectrum of $bzac_2Be$ at τ 7·60, 3·39 and 1·95–2·70 ppm. Compound $dbm_2B^{\oplus}ClO_4^{\ominus}$ presents the methine peak at 2·32 τ, while dbm_2Be has this peak at 2·82 τ. A detailed study of the NMR spectra of boron chelates will be reported elsewhere.[40]

Attempts to resolve bis-(benzoylacetonato)boronium salts into enantiomers by partial hydrolysis with brucine dihydrate or by fractional crystallization of the camphorsulphonate salt have until now proved unsuccessful. Further work is in progress.

EXPERIMENTAL

I. *Starting materials*

Commercial acetylacetone (acacH) was used. Benzoylacetone (bzacH), dibenzoylmethane (dbmH) and anhyd perchloric acid in CH_2Cl_2 soln were prepared as described previously.[3]

Beryllium bis-(1,3-diketonates) were prepared for the purpose of comparing their UV and IR absorption spectra by adding the diketone into a soln of anhyd $BeCl_2$ in AcOEt, evaporating the solvent and purifying the product by recrystallization and vacuum sublimation.[41]

II. *Preparation of bis-(1,3-diketonato)boronium salts.*

Method 1: from 1,3-diketones and boron trichloride. Dilthey[4] employed abs ether as solvent, because it was convenient to use BCl_3– etherate at room temp. By employing this procedure we obtained:

IIAa $(acac_2B^{\oplus}Cl^{\ominus})$ as a white unstable ppt which darkened in the air even in the absence of moisture; it could, however, be converted into IIAf by anhyd $HClO_4$ in CH_2Cl_2.

IIBa $(bzac_2B^{\oplus}Cl^{\ominus})$ as a white ppt, m.p. 80° which did not afford correct analytical figures but was converted by $HClO_4$ in CH_2Cl_2 into IIBf.

IICa $(dbm_2B^{\oplus}Cl^{\ominus})$ as yellow crystals m.p. 240° (recrystallized from 1,2-dichloroethane) which analysed correctly and gave with $HClO_4$ in water or in CH_2Cl_2 the perchlorate IICf. These compounds could not be prepared in Dilthey's laboratory by the same procedure. Ether is not, however, a suitable solvent just because its donating ability can impair on the chelating properties of the diketone.

IIBa $(bzac_2B^{\oplus}Cl^{\ominus})$: 40 g (250 mmoles) bzacH was dissolved in 100 ml CH_2Cl_2, then the soln was cooled to −15° and the reflux condenser at −30°. With stirring, 13 g (125 mmoles) BCl_3 are added, when abundant white crystals are immediately formed. The crude product has m.p. ca. 80°; it was not purified further, but converted metathetically into other salts in the same installation.

IICa ($dbm_2B^{\oplus}Cl^{\ominus}$): 50 g (ca. 200 mmoles) dbmH was dissolved in 100 ml CH_2Cl_2 and as above 12 g (ca. 100 mmoles) BCl_3 were added with cooling. A rich orange–yellow coloured ppt was immediately formed. After 15 min' refluxing for the escape of HCl, the product was cooled, filtered off and washed with a small amount of CH_2Cl_2. By concentrating the soln, a further amount of product was obtained, leading to a quantitative yield. The crystals were dried in vacuum over NaOH and recrystallized from acetonitrile, m.p. 240°. The compound is not hygroscopic and can be stored indefinitely in the air.

Method 2: *from* 1,3-*diketones, n-butyl borate and gaseous hydrogen chloride.* IIAa ($acac_2B^{\oplus}Cl^{\ominus}$): Tri-n-butyl borate (2·8 ml, 2·2 g, 10 mmoles) and acetylacetone (acacH, 2 g, 20 mmoles) in 5 ml CH_2Cl_2 were cooled to −40°, then gaseous HCl dried over P_2O_5 was introduced into the soln. The colourless or slightly yellowish soln was worked up in the same installation.

By leaving the mixture overnight to warm up gradually to room temp and evaporating the solvent in the air, HCl was evolved and colourless crystals were obtained. They were insoluble in CH_2Cl_2 and melted starting from 250°. Since they represent probably chelate complexes of higher ketones formed by hydrolysis of IIAa and condensation reactions of acetylacetone, they were not investigated further.

IIBa ($bzac_2B^{\oplus}Cl^{\ominus}$): Into a soln of bzacH (3·3 g, 20 mmoles) and 3 ml (2·3 g, 10 mmoles) tri-n-butyl borate in 15 ml CH_2Cl_2, dry HCl was bubbled for 1 hr at 0°. The soln darkened and 30 min. after beginning the introduction of HCl deposited white crystals. The suspension was converted in the same flask into other salts of IIB. The chloride IIBa is sensitive to atmospheric moisture; the crude product has m.p. 60–80° after filtration in a dry atmosphere; for purification it was dissolved in CH_2Cl_2 and reprecipitated by bubbling HCl into the soln at 0°, m.p. 70–80°.

IICa ($dbm_2B^{\oplus}Cl^{\ominus}$): Into a soln of 18 g (80 mmoles) dbmH and 12 ml (9·2 g, 40 mmoles) tri-n-butyl borate in 50 ml 1,2-dichloroethane, dry HCl was bubbled at 0° with mechanical stirring. After 15 min yellow needles of IICa appeared. The introduction of HCl was continued for 1 hr longer, the product was filtered off, washed with dichloroethane, and dried on a porous plate, then in vacuum over NaOH. By concentrating the soln a further crop of crystals was obtained, the yield was quantitative. The crude product, m.p. 235–238° was recrystallized from acetonitrile: long, shiny yellow needles, m.p. 240°.

Method 3: *from* 1,3-*diketones, perchloric acid and a boric acid derivative.* IIAf ($acac_2B^{\oplus}ClO_4^{\ominus}$): 10 ml (10 g, 100 mmoles) acetylacetone in 30 ml CH_2Cl_2 were treated with 14·5 ml (11·5 g, 50 mmoles) tri-n-butyl borate. Into this mixture 50 mmoles of anhyd $HClO_4$ in CH_2Cl_2 (5 g, 50 mmoles of $HClO_4$) were added with stirring at 0°. After standing overnight most of the solvent was evaporated. The yellowish crystals were filtered off and washed with anhyd benzene, then recrystallized from $CHCl_3$–benzene affording the colourless perchlorate.

IIBf ($bzac_2B^{\oplus}ClO_4^{\ominus}$): 3·2 g (20 mmoles) benzoylacetone in 15 ml CH_2Cl_2 was treated with 3 ml (2·3 g, 10 mmoles) tri-n-butyl borate or 2 g (ca. 10 mmoles) acetoxy borate.[42] The resulting soln was treated under stirring with 10 mmoles anhyd $HClO_4$ in CH_2Cl_2 (1 g $HClO_4$). After several hrs' stirring the mixture was filtered off, and the soln was concentrated and filtered off again. Thus 3·5 g crude perchlorate m.p. 240–245° was isolated. It was recrystallized from acetonitrile.

In aqueous ethanol: 1·6 g (10 mmoles) bzacH and 0·31 g (5 mmoles) boric acid were dissolved in the minimum amount of EtOH, then 4·2 ml 70% $HClO_4$ (5 g $HClO_4$, 50 mmoles, 10-fold excess) were added. The soln was concentrated under reduced press, the oil was left overnight, the resulting crystals were filtered off and washed with water and a small amount of CH_2Cl_2, yield 1 g.

IICf ($dbm_2B^{\oplus}ClO_4^{\ominus}$): 4·5 g (20 mmoles) dibenzoylmethane dissolved in 15 ml CH_2Cl_2 was treated with 3 ml (2·3 g, 10 mmoles) tri-n-butyl borate, or 2 g (10 mmoles) acetoxy borate,[42] or 0·6 g (10 mmoles) boric acid. Then 10 mmoles anhyd $HClO_4$ in CH_2Cl_2 was added. The suspension of the perchlorate was stirred for several hrs and filtered off next day. By successive concentrations and filtrations, 5 g of IICf were obtained, which were recrystallized from acetonitrile.

In aqueous ethanol: 4·5 g (20 mmoles) dbmH and 0·6 g (10 mmoles) boric acid dissolved in 90 ml EtOH were treated with 12·6 ml (15 g $HClO_4$, 150 mmoles, 15-fold excess) 70% $HClO_4$. By successive concentrations in vacuum and filtrations, 3·1 g of IICf (56% conversion) were obtained along with unreacted dbmH. The same procedure afforded only 0·5 g (10% conversion) perchlorate when a 1·5-fold excess of $HClO_4$ was employed: on concentration dbmH precipitates first.

Method 4: *from* 1,3-*diketones, tri-n-butyl borate, hydrochloric acid and antimony pentachloride.* IIAd ($acac_2B^{\oplus}SbCl_6^{\ominus}$). Into a soln of acetylacetone (1 ml, 1 g, 10 mmoles) and 1·4 ml (1·1 g, 5 mmoles, tri-n-butyl borate) in 2 ml glacial AcOH, a soln of 0·6 ml (5 mmoles) $SbCl_5$ and a few drops of conc. HCl was added with cooling. The hexachloroantimonate crystallized on seeding and scratching.

The formation of n-butyl acetate which may be detected by its odour in the mother liquor seems to favor the course of the reaction. The crystals were filtered off, washed with AcOH and dried over KOH in vacuum, yield 1·2 g, m.p. 133–140°.

IIBd (bzac$_2$B$^{\oplus}$SbCl$_6^{\ominus}$) was prepared similarly from 1 g (6 mmoles) benzoylacetone, 0·8 ml (3 mmoles) tri-n-butyl borate and 0·4 ml (3 mmoles) SbCl$_5$ in 5 ml AcOH. The salt crystallized immediately, yield 1·2 g m.p. 155–160°.

IICd (dbm$_2$B$^{\oplus}$SbCl$_6^{\ominus}$) was obtained analogously from 1 g (5 mmoles) dibenzoylmethane, 0·7 ml (2·5 mmoles) tri-n-butyl borate and 0·3 ml (2·5 mmoles) SbCl$_5$ in AcOH, yield 1·2 g, m.p. 220–225° (from acetonitrile).

Method 5: *from* 1,3,2-*dioxaborinium salts*. The preparation of IICf (dbm$_2$B$^{\oplus}$ClO$_4^{\ominus}$) from I(R = R′ = R″ = Ph, X = ClO$_4$) is described in Ref. 3. The m.p. of the mixture with IICf prepared by methods 3 or 7 showed no depression.

Method 6: *from bis-*(1,3-*diketonato*)*boronium chlorides and metallic chlorides*. IIAb (acac$_2$B$^{\oplus}$FeCl$_4^{\ominus}$), IIAc (acac$_2$B$^{\oplus}\frac{1}{2}$SnCl$_6^{2\ominus}$), IIAd (acac$_2$B$^{\oplus}$SbCl$_6^{\ominus}$) from IIAa (acac$_2$B$^{\oplus}$Cl$^{\ominus}$): Into the cool (−40°) soln of IIAa prepared by method 2, a stoichiometric amount of anhyd metallic chloride dissolved in CH$_2$Cl$_2$ was added (for 10 mmoles IIAa, 1·6 g anhyd FeCl$_3$, 0·6 ml SnCl$_4$ or 1·3 ml SbCl$_5$). After stirring for several hrs at −40°, the suspension was allowed to reach room temp, the solvent was evaporated in air, the ppt was dried on a porous plate, then in vacuum over NaOH. The yield was practically quantitative. For purification, IIAb and IIAd were recrystallized from CH$_2$Cl$_2$, and IIAc from acetonitrile–dichloromethane. They are not hygroscopic.

IIBb (bzac$_2$B$^{\oplus}$FeCl$_4^{\ominus}$), IIBc (bzac$_2$B$^{\oplus}\frac{1}{2}$SnCl$_6^{2\ominus}$) and IIBd (bzac$_2$B$^{\oplus}$SbCl$_6^{\ominus}$) were prepared similarly at 0° from the suspension of IIBa prepared after method 2, in quantitative yields. For purification, IIBb and IIBc were recrystallized from acetonitrile, and IIBd from chlorobenzene.

IICb (dbm$_2$B$^{\oplus}$FeCl$_4^{\ominus}$), IICc (dbm$_2$B$^{\oplus}\frac{1}{2}$SnCl$_6^{2\ominus}$), IICd (dbm$_2$B$^{\oplus}$SbCl$_6^{\ominus}$) and IICh (dbm$_2$B$^{\oplus}$AlCl$_4^{\ominus}$) were prepared from 5 g (10 mmoles) IICa dissolved in the smallest amount of 1,2-dichloroethane and a soln of 10 mmoles metallic chloride (1·6 g FeCl$_3$, 0·6 ml SnCl$_4$, 1·3 ml SbCl$_5$ or 1·3 g AlCl$_3$) in dichloroethane. The solns were mixed with stirring for several hrs, then the solvent was evaporated under reduced press. Finally the product, obtained in quantitative yield, was dried on a porous plate, then in vacuum over NaOH. The yellowish crystals were then recrystallized from acetonitrile.

Method 7: *from bis-*(1,3-*diketonato*)*boronium chlorides and strong acids*. IIAe (acac$_2$B$^{\oplus}$I$_3^{\ominus}$) from IIAa: Into the soln of IIAa prepared after method 2, a soln of 1 ml HI 67% (1·3 g HI, 10 mmoles) and 2·5 g I$_2$ (10 mmoles) in 5 ml CH$_2$Cl$_2$ was added with stirring at −40°. After several hrs' stirring at −40°, the suspension was allowed to reach room temp, then evaporated to dryness. For removing the hydrolysis product of the chloride (the white crystals, m.p. 250°), the crystals were dissolved in CH$_2$Cl$_2$ and chromatographed on a column packed with alumina. The forerun yields after evaporation violet crystals, which were recrystallized from CH$_2$Cl$_2$.

IIBe (bzac$_2$B$^{\oplus}$I$_3^{\ominus}$) was prepared similarly from the suspension of IIBa at 0° (0·1 mmoles) and a soln of HI and I$_2$ (10 mmoles each). The yield of triodide IIBe was 5 g. It was recrystallized from acetonitrile.

IICe (dbm$_2$B$^{\oplus}$I$_3^{\ominus}$) was prepared from 5 g (10 mmoles) IICa suspended in 20 ml dichloroethane and a soln of 1 ml 67%-HI and 2·5 g I$_2$ in dichloroethane. The black crystals were agitated for 4 hrs, then filtered off, washed with dichloroethane and dried in vacuum over NaOH. The yield was quantitative. For analysis the difficulty soluble triiodide was recrystallized from acetonitrile or nitromethane.

IIAf (acac$_2$B$^{\oplus}$ClO$_4^{\ominus}$): into the soln of 10 mmoles IIAa prepared by method 2, a solution of 10 ml anhyd HClO$_4$ in CH$_2$Cl$_2$ prepared after Klages[43] (containing 1 g HClO$_4$, 10 mmoles) was added with stirring at −40°. The resulting suspension of the perchlorate was allowed to reach room temp, then the solvent was evaporated. The white–yellowish crystals were dried on a porous plate, then in vacuum over NaOH. The yield was quantitative. The purification was effected by recrystallization from CH$_2$Cl$_2$.

IIBf (bzac$_2$B$^{\oplus}$ClO$_4^{\ominus}$) was prepared from the suspension of the chloride obtained after methods 1 or 2, or from the solid chloride IIBa, and from an equimolar amount of anhyd HClO$_4$ in CH$_2$Cl$_2$ at 0°. The suspension was stirred first at room temp, then at reflux, for removing HCl. The cooled suspension was filtered off and washed with CH$_2$Cl$_2$ affording IIBf in quantitative yield and almost pure. For recrystallization, acetonitrile was employed.

IICf (dbm$_2$B$^{\oplus}$ClO$_4^{\ominus}$): 5 g (10 mmoles) of IICa in 25 ml dichloroethane were treated with 10 mmoles anhyd HClO$_4$ in CH$_2$Cl$_2$. For one moment the chloride dissolved completely, then the prismatic crystals of the perchlorate appeared. After refluxing for the evolution of HCl, the perchlorate was filtered off. The yield was quantatitive. For purification the product was recrystallized from acetonitrile. The same perchlorate was also prepared in aqueous EtOH: 0·25 g (0·5 mmoles) IICa in 2 ml abs EtOH were treated with 2 ml 70% $HClO_4$.

Method 8: preparation of bis-(1,3-diketonato)boronium iodides by reduction of triiodides. IICg ($dbm_2B^{\oplus}I^{\ominus}$): into 8·4 g (10 mmoles) IICe ($dbm_2B^{\oplus}I_3^{\ominus}$) suspended in 50 ml abs EtOH, dry SO_2 was bubbled until all the triiodide dissolved, and golden-yellowish needles were formed. On heating this suspension, or on filtration, the crystals became a brown mass. This was heated with six portions of acetonitrile, decanting the hot soln which deposited greenish-black crystals of triiodide m.p. 280–283°. The insoluble iodide remained as brick red beautiful crystals, which were washed with acetonitrile on the porous plate, yield 3 g.

Method 9: preparation of bis-(1,3-diketonato)boronium perchlorates from boronium salts with complex anions. IIBf ($bzac_2B^{\oplus}ClO_4^{\ominus}$) from IIBc ($bzac_2B^{\oplus}\frac{1}{2}SnCl_6^{2\ominus}$) or IIBe ($bzac_2B^{\oplus}I_3^{\ominus}$): 0·2 g IIBc or IIBe were heated 5 min in 2 ml 70% $HClO_4$ on the boiling water bath. After cooling, the crystals were filtered off and recrystallized from acetonitrile, m.p. and mixed m.p. 246°. Analogous treatment of IIBb ($bzac_2B^{\oplus}FeCl_4^{\ominus}$) led to complete decomposition of the boronium salt, while IIBd ($bzac_2B^{\oplus}SbCl_6^{\ominus}$) was recovered unchanged from hot 70% $HClO_4$.

IICf ($dbm_2B^{\oplus}ClO_4^{\ominus}$) from IICb ($dbm_2B^{\oplus}FeCl_4^{\ominus}$), IICc ($dbm_2B^{\oplus}\frac{1}{2}SnCl_6^{2\ominus}$), or IICg ($dbm_2B^{\oplus}I^{\ominus}$): 0·5 g boronium salt IICb or IICb was suspended in 2 ml EtOH, then 0·5 ml 70% $HClO_4$ was added and the mixture was ground in a mortar for 30 min. The resulting crystals were filtered off, washed with water, dried and recrystallized from acetonitrile, yield 0·2 g of IICf, m.p. 335°. Analogous treatment of IICg afforded IICf only on refluxing the ethanolic suspension of the sparingly soluble IICg with a large excess (10 ml) 70% $HClO_4$ until the red crystals dissolved. On the contrary, IICd ($dbm_2B^{\oplus}SbCl_6^{\ominus}$) or IICe ($dbm_2B^{\oplus}I_3^{\ominus}$) were recovered unchanged even from hot 70% $HClO_4$.

III. *Hydrolysis of* IICf ($dbm_2B^{\oplus}ClO_4^{\ominus}$)

The hydrolysis cannot be effected by boiling IICf in water or conc HCl. On boiling in KOHaq the hydrolysis was accompanied by acid splitting of dibenzoylmethane so that benzoic acid was isolated in 75% yield.

An ethanolic soln (10 ml) of 2 g KOH was left overnight with 1·8 g IICf. By dilution with distilled water and acidification with HCl, a quantitative yield (1.5 g) of dibenzoylmethane m.p. 76° was obtained (identification by mixed m.p. and eutectic mixtures).

IV. *Analytical*

Analyses and m.ps of boronium salts are included in Table 1. The errors in the C and H analyses are higher than in compounds devoid of boron. Sometimes separate combustions for C (longer heating period) and H (normal heating period) were necessary. Compound IICe ($dbm_2B^{\oplus}I_3^{\ominus}$), however, always afforded a lower figure for C. For chlorides (a) and perchlorates (f), boron could be determined from the non-volatile residue of the combustion as B_2O_3. The value thus obtained for IICf is in excellent agreement with the boron contents determined by titration.[11] Chlorine and iodine were determined by argentometric titrations, after decomposing the substance by boiling in 2N KOH.

V. *Spectra*

UV spectra were recorded with a CF-4 Optica (Milan) spectrophotometer. IR spectra were recorded with a Jena UR-10 spectrophotometer in KBr pellets.

NMR spectra were recorded in sealed vials with a JEOL-3H-60 apparatus at 25° in liquid SO_2 using TMS as internal standard.

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