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1,3,2-DIOXABORINIUM (BOROXAROPYRYLIUM) SALTS AND THEIR DECOMPOSITION TO BIS - 1,3-DIKETONATO-BORONIUM SALTS

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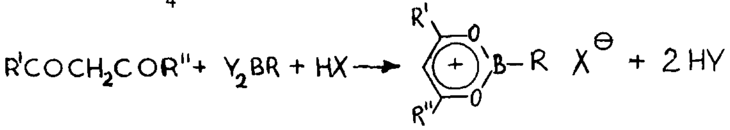
In a previous note[1] the preparation of 1,3,2-dioxaborinium salts was discussed. The present note brings further data and some corrections.

1,3-Diketones (I) react at 0° with one mole arylboronic acids (II, R = Ar, Y = OH) in dichloromethane on addition of one mole anhydrous perchloric acid (III, X = ClO_4) in dichloromethane solution[2] yielding crystalline 1,3,2-dioxaborinium (boroxaropyrylium) perchlorates (IV, X = ClO_4).



I II III IV

Thus 2,4,6-triphenyl-1,3,2-dioxaborinium perchlorate (IVb, R = R' = R" = Ph) precipitates when starting from dibenzoylmethane and phenylboronic acid. It has m.p. 104° after recrystallization from dichloromethane - acetonitrile (by adding the acetonitrile into a hot suspension of crude IVb until it dissolves and cooling rapidly).

Refluxing IVb for 2 min. with water yields an acid solution which after cooling affords dibenzoylmethane in 85 % yield, or its copper chelate with an ammoniacal solution of copper sulphate in 97 % yield. The second product of hydrolysis, phenylboronic acid, is isolated in 30 % yield from the acid aqueous solution obtained after filtration of the dibenzoylmethane by neutralization with potassium hydroxide, evaporation to dryness, acidification with acetic acid, extraction with ethanol and evaporation of the solvent. The hexachloroantimonate IVc ($X = SbCl_6$, $R = R' = R'' = Ph$) was prepared from dibenzoylmethane and phenylboronic acid in acetonitrile, on addition of an acetonitrile solution of antimony pentachloride and conc. hydrochloric acid (all four reagents in equimolar amounts).

Similarly, IVd ($R = R'' = Ph$, $R' = Me$, $X = ClO_4$) was prepared from benzoylacetone. It has m.p. 99 - 100° and is very sensitive towards heat and moisture.

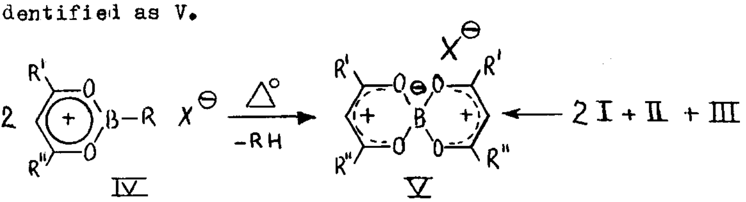
By adding at 0° an equivalent of anhydrous perchloric acid in dichloromethane into a solution of 3 g dibenzoylmethane and 2.5 g boron triacetate[3] in 40 ml dichloromethane, 3.3 g of yellow needles of IVa, ($R' = R'' = Ph$, $R = OAc$, $X = ClO_4$), m. p. 175 - 180°, were obtained. By cautious recrystallization from dichloromethane - acetonitrile the melting point is raised to 196°. The reaction was also applied to 1,3-diketones and boronic acids, with R, R' and/or R" phenyl and p-anisyl. Melting points are given in Table 1. Elementary analyses do not always give satisfactory figures owing to the formation of boron carbide.

Table 1. 1,3,2-Dioxaborinium salts

IV	R	R'	R"	X	M.p., °C
a	OAc	Ph	Ph	ClO_4	196 dec.
b	Ph	Ph	Ph	ClO_4	104 dec.
c	Ph	Ph	Ph	$SbCl_6$	148 dec.
d	Ph	Me	Ph	ClO_4	99-100
e	An	Ph	Ph	ClO_4	194
f	Ph	An	An	ClO_4	140
g	An	An	Ph	ClO_4	175
h	Ph	An	Ph	ClO_4	146

The ultraviolet absorption spectrum of IVb in dichloromethane containing 1 % anhydrous perchloric acid presents bands at 390 sh, 372, 294 sh and 271 sh mμ.

Compound IVb, R = R' = R" = Ph, X = ClO_4 resolidifies after melting with decomposition, then melts again at 300 - 320.° Thermogravimetric curves show that the decomposition is an exothermal process accompanied by a weight loss of 70 - 85 g/mole. By effecting the decomposition in vacuum, the volatile product was trapped by cooling with liquid nitrogen and identified as benzene (by dinitration)[4] : the residue melts after purification from acetonitrile at 334° (dec.) The same product was obtained, along with acetic acid (identified[4] as piperazonium diacetate) by the thermal decomposition of IVa, R = OAc, R' = R" = Ph. Decomposition of the perchlorate IVe, R = An, R' = R" = Ph obtained from dibenzoylmethane and p-anisylboronic acid afforded anisole and a residue identical with the previous one, while perchlorate IVf, R = Ph, R' = R" = An obtained from phenylboronic acid and di-p-anisoylmethane afforded benzene and a different residue. These residues are perchlorates of a different cation, identified as V.



The decomposition products of IV are therefore RH and a bis-1,3-diketonato-boronium salt (V) isoelectronic with the corresponding 1,3-diketonatoberyllium chelate. Such salts have been prepared by Dilthey[5] from 1,3-diketones and boron trichloride : symmetrical spiranic cations prepared from other bidentate ligands (tropolone[6] and biguanide[7]) are known. Indeed, the chloride Vb (R' = R" = Ph, X = Cl) prepared from dibenzoylmethane and boron trichloride in methylene dichloride, m.p. 238° (from acetonitrile) is converted by anhydrous perchloric acid in methylene dichloride into a perchlorate m.p. 332-4° identical with the residue Va from the thermal decomposition of IV, R' = R" = Ph, R = Ph, An or OAc. Thermal decomposition in vacuum of IVd, R = R" = Ph, R' = Me, $X = ClO_4$ afforded benzene and Vc, R' = Ph, R" = Me, $X = ClO_4$ m.p. 249° dec.(from acetonitrile), identical with the product prepared from benzoylacetone and boron trichloride in methylene dichloride (the hygroscopic[5] chloride X = Cl was not isolated but was converted into the perchlorate as before).

The thermal decomposition may be effected by refluxation in acetonitrile (therefore the purification of IV must be carried out cautiously and at low temperature). Salts V can be obtained directly from 1,3-diketones and arylboronic acids in presence of an excess of anhydrous perchloric acids in refluxing methylene dichloride.

When starting from boric acid or esters (R = OH or OC_4H_9), the reaction products are V, even at low temperature and in the absence of an excess of acid. Dioxaborinium salts IV, R = OH or OR are too unstable to be isolated. The reported[1] products with alleged structure IV have in fact structure V, therefore the previous note[1] must be accordingly corrected. Only when R = Ar (and apparently OAc) can 1,3,2-dioxaborinium salts IV be isolated.

Perchlorates V are not hygroscopic (excepting the compound V, R' = R" = CH_3 prepared from acetylacetone, tributylborate and anhydrous perchloric acid in dichloromethane, m.p. 176° from chloroform) ; they have high melting points and are fairly stable to hydrolysis : Va, R' = R" = Ph does not react with boiling water in neutral or acid medium. In the presence of hot alkali or of ammonia it affords after acidification dibenzoylmethane in 70 % yield along with non-hydrolyzed product. More drastic conditions lead to acid splitting of dibenzoylmethane into benzoic acid and acetophenone. The hydrolysis to dibenzoylmethane is quantitative, when effected with alcoholic potassium hydroxide at room temperature. Similarly, Ve, R' = R" = An yields di-*p*-anisoylmethane.

Melting points and absorption maxima of salts V are given in Table 2. Having no B-C bonds, they give satisfactory analytical results.

Table 2. Bis-1,3-diketonato-boronium salts.

V	R'	R"	X	M.p., °C	$\lambda_{max.}$, mμ in CH_3CN		
a	Ph	Ph	ClO_4	334 dec.	304,	379,	395
b	Ph	Ph	Cl	238	305,	378,	396
c	Ph	Me	ClO_4	247 dec.	273,	(323,	355)[a]
d	Me	Me	ClO_4	176 dec.	291		
e	An	An	ClO_4	281 dec.			

[a] Graphically resolved broad band centered on 343 mμ.

The infrared absorption spectra (in KBr pellet) of salts V are simpler than those of salts IV; for instance Va with identically-bonded phenyl groups has two medium or strong out-of-plane bending bands in the range 700 - 800cm^{-1}, while the related perchlorate IVb with two kinds of diferently bonded phenyl groups has four bands. Both IV and V present strong bands at ca. 1550, 1370 and 1250 cm^{-1}, which can be assigned to vibration modes of the dioxaborine ring.

Protodeboronation of chelates obtained from diphenylborinic esters and 1,3-diketones[8] affords a different pathway towards 1,3,2-dioxaborinium salts. Thus the compound obtained from flavognost and dibenzoylmethane[8] in dichloromethane solution yields on treatment with anhydrous perchloric acid[2] at 0° and subsequent addition of petroleum ether a perchlorate identical (m.p. and IR spectrum) with IVb.

All melting point data refer to Boetius micro hot stage.

References

1. A. T. Balaban, A. Barabas and A. Arsene, Tetrahedron Letters, 2721 (1964).
2. F. Klages and P. Hegenberg, Angew. Chem., **74**, 902 (1962).
3. H. G. Cook, I. D. Ilett, B. C. Saunders and C. F. Stacey, J. Chem. Soc., 3125 (1950).
4. L. and A. Kofler, "Thermomikromethoden", Verlag Chemie, Weinheim, 1954; E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds", Wiley, New-York, 1957.
5. W. Dilthey, Liebigs Ann., **344**, 300 (1905); cf. also N. V. Sidgwick, "The Chemical Elements and Their Compounds", Oxford Univ. Press, London, 1950, p. 408.
6. E. L. Mutterties and C. M. Wright, J. Amer. Chem. Soc., **86**, 5132 (1964); **87**, 21 (1965).
7. J. E. Milks, G. W. Kennerly, and J. H. Polevy, J. Amer. Chem. Soc., **84**, 2529 (1962).
8. J. Bally, A. Arsene, M. Băcescu-Roman and A. T. Balaban, Tetrahedron Letters, following paper.