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THERMAL DECOMPOSITION OF TRITIATED 2,4,6-TRIPHENYL-5-t-1,3,2-DIOXABORINIUM PERCHLORATE

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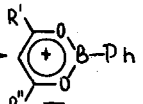
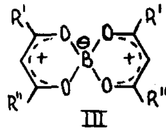
In the preceding paper[1] the following reactions were described (the compound in parentheses was not evidenced or isolated) :

$R'COCH_2COR'' + PhB(OH)_2 + HClO_4 \longrightarrow$  $ClO_4^{\ominus} + 2H_2O$ /1/

I II

2 II $+ H_2O \xrightarrow{\Delta^{\circ}}$  $ClO_4^{\ominus} + 2PhH + (OBClO_4)$ /2/

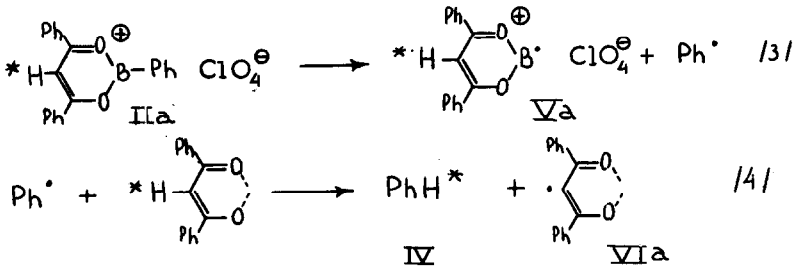
III IV

a, R' = R" = Ph ; b, R' = R" = An ; c, R' = Me, R" = Ph.

The decomposition /2/ of 2-phenyl-1,3,2-dioxaborinium perchlorates II takes place at ca. 100° in solid state or in an inert solvent. If the decomposition of IIa is effected in toluene in the presence of diphenylpicrylhydrazyl, the violet colour of the radical disappears rapidly.

A plausibile mechanism of the reaction /2/ in the absence of hydrogen donors involves the homolytical breaking

of the carbon-boron bond in II. Such processes are known.[2] The resulting phenyl radical then abstracts a hydrogen atom from the ligand molecule (either from the phenyl rings, or as shown in reaction /4/ from the central atom of the 1,3-diketone).



The last stages of the process leading to III from two fragments V are not yet clear.

In the present paper we report the study of the thermal decomposition of isotopically labeled IIa. Dibenzoylmethane (Ia) was tritiated at the metylene group by refluxing for one hour in ethanol with tritiated water, followed by recrystallization. This product was then converted into IIa by stirring at 0° for 4 hrs the reagents of reaction /1/ in dry dichloromethane ; after filtration, washing with dichloromethane and drying in vacuum at room temperature, 2,4,6-triphenyl-5-t-1,3,2-dioxaborinium perchlorate (IIa) was obtained in 82 % yield.

The thermal decomposition /2/ was performed by heating for 40 min. 2 g IIa at 100° in an evacuated vial (8 mm pressure) and condensing the volatile products in a trap cooled at -50°. Preparative gas chromatography of

these products after drying over sodium from water formed in the decomposition shows that they consist in 95 % benzene (IV) (yield ca. 90 %) and 5 % a more volatile product, whose separation does not modify the activity of the volatile fraction. The residue IIIa is recrystallized from dry acetonitrile (yield 27 %).

The activities of Ia, IIa, IIIa and IV were determined by combustion and by conversion of the condensed water into hydrogen over $LiAlH_4$. The hydrogen activity was determined with two GM counters compensated in length.[3] The results of two experiments are shown below. The precision of the measurements is ± 1 %.

Substance	Ia	IIa	IIIa	IV
Specific activity, mCi/mole	10	5.5	5.2	0.5
	10	4.4	5.9	0.4
Average ratios to the activity of Ia	1	0.50	0.55	0.045
Calculated activity ratios	1	0.50	1.00	0.045

If in the hydrogen abstraction /4/ all hydrogens of the ligand are equivalent, the activities of Ia, IIa, IIIa and IV should be proportional to 22 : 11 : 22 : 1. These figures lead to the calculated activity ratios shown in the table. The agreement with the observed values for IIa and IV is excellent. The activity of IIIa is smaller than the calculated value, probably owing to detritiations subsequent to reaction /4/.

References

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3. C. Măntescu and M. Fiti, Studii şi Cercetări Fiz., Acad.R.P.R., 11, 788 (1960).