

TABLE II

	a, cm. <sup>-1</sup>	b, cm. <sup>-1</sup>	Av. dev., cm. <sup>-1</sup>
CoCl <sub>2</sub> in HCl <sup>a</sup>	14302	416	68
C <sub>5</sub> H <sub>5</sub> CoCl <sub>5</sub>	14225	393	57
C <sub>5</sub> H <sub>5</sub> CoCl <sub>4</sub>	14231	391	69
(PyH) <sub>2</sub> CoCl <sub>4</sub>	14304	390	73
(QuH) <sub>2</sub> CoCl <sub>4</sub>	14236	391	64
(QuH) <sub>2</sub> CoCl <sub>4</sub> ·H <sub>2</sub> O	14282	389	74

<sup>a</sup> Analysis based on the data of Kiss and Gerendas.<sup>5</sup>

stants, together with the average deviations between the calculated and experimental values of  $\nu$ , are listed in Table II. The latter are somewhat larger than the experimental uncertainties in the wave number values of the bands but are of the same order of magnitude. Since the bands are from 100 to 300 cm.<sup>-1</sup> in width, the deviation might be due, in part, to slight systematic errors in picking out the band maxima.

In view of these regularities, following a suggestion made recently by one of us<sup>9</sup> for several other complex ions, these spectra may be interpreted as having originated in electronic transitions for which vibrational structure characteristic of the CoCl<sub>4</sub><sup>2-</sup> complex ion is developed. It may be noted that the average frequency for the complex in solution, 413 cm.<sup>-1</sup>, differs by 22 cm.<sup>-1</sup> from the average value of the crystals, 391 cm.<sup>-1</sup>. Since the frequencies of the normal vibrations of the complex depend on the force constant of the cobalt-chlorine bond and since the frequency found here is probably that of the totally symmetric vibration, the existence of this difference indicates that the binding energy of the complex ion in the crystal is smaller than in solution.

(9) M. L. Schultz, *J. Chem. Phys.*, **10**, 194 (1942).

Although each observed band in the spectra of the crystals (and in the solution as well) is represented by an integral value of  $n$ , not all values of  $n$  represent observed bands. This, together with the somewhat unsatisfactory fit of the group of bands at 22,000 cm.<sup>-1</sup> into the suggested analysis, indicates that this analysis is too simple. Probably several electronic transitions, each with its associated vibrational structure, occur. With the data at present available, no reliable energy level diagram can be constructed. It is the intention in this Laboratory to study the spectra of these crystals at low temperatures in order to obtain information which might permit the construction of such a diagram and also in order to study in more detail the effect of the environment upon the spectrum.

### Summary

1. The absorption spectra of crystals of two cesium cobaltous chlorides, dipyridinium cobaltous chloride, diquinolinium cobaltous chloride and diquinolinium cobaltous chloride monohydrate have been measured.

2. Comparison of the spectra of these crystals with the spectrum of the solution of cobaltous chloride in concentrated hydrochloric acid shows that the same complex ion, CoCl<sub>4</sub><sup>2-</sup>, is present in all.

3. A tentative analysis of the spectra of the crystals has been made. This analysis suggests that the spectra may be considered to originate in coupled electronic-vibrational transitions.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

## Some Boron Trifluoride Catalyzed Alkylations of Halobenzenes<sup>1</sup>

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### Introduction

Previous work in this Laboratory has shown that boron trifluoride, in the presence of a strong dehydrating agent such as phosphoric anhydride or sulfuric acid, is an excellent catalyst for the alkylation of benzene<sup>2</sup> and its homologs<sup>3</sup> with alcohols. This method was extended in the present work to the halobenzenes.

(1) Paper XXVII on organic reactions with boron trifluoride; XXXVI delayed in press; XXV, *THIS JOURNAL*, **63**, 2603 (1941).

(2) Toussaint and Hennion, *ibid.*, **62**, 1145 (1940).

(3) Welsh and Hennion, *ibid.*, **63**, 2603 (1941).

In many respects boron trifluoride has been found superior to aluminum chloride for these alkylations. With aluminum chloride there may be considerable halogen migration to produce benzene, dihalobenzene and alkylbenzene as well as the desired alkylhalobenzene.<sup>4,5</sup> Furthermore, the aluminum chloride methods result in both meta and para substitution,<sup>6,7</sup> thus giving an

(4) Dumreicher, *Ber.*, **15**, 1866 (1882).

(5) Berry and Reid, *THIS JOURNAL*, **49**, 3146 (1927).

(6) Tsukervanik, *J. Gen. Chem. (U. S. S. R.)*, **8**, 1512 (1938); *C. A.*, **33**, 4587 (1939).

(7) Dreisbach, Britton and Perkins, U. S. Patent 2,193,760 (1940).

TABLE I  
 PHYSICAL CONSTANTS AND ANALYSES OF *p*-*s*-ALKYLHALOBENZENES

Compound	Yield, %	°C.	B. p., Mm.	$n_D^{20}$	$d_4^{20}$	Mol. wt.		% Halogen	
						Calcd.	Obsd. <sup>a</sup>	Calcd.	Obsd. <sup>b</sup>
2- <i>p</i> -Chlorophenylpropane	63.0 <sup>c</sup>	66-72	11	1.5109	1.0190	152.5	150.5	23.30	22.77
2- <i>p</i> -Chlorophenylbutane	66.4	81-82	8	1.5095	1.0122	166.5	167	21.29	21.28
2- <i>p</i> -Chlorophenylpentane	35.0	93-96	9	1.5040	0.9951	180.5	173	19.65	19.30
3- <i>p</i> -Chlorophenylpentane	33.6	95	10	1.5049	0.9934	180.5	177	19.65	19.50
<i>p</i> -Chlorophenylcyclohexane	34.0	145-7	19	1.5585	1.0753	194.5	192	18.34	18.20
2- <i>p</i> -Chlorophenyloctane	45.0	106-8	3	1.4971	0.9553	223.5	220	15.88	15.75
2- <i>p</i> -Bromophenylpropane	31.7	58-60	3	1.5379	1.2936	197	195	40.61	40.54
2- <i>p</i> -Bromophenylbutane	35.3	96-98	8	1.5290	1.2225	211	211	36.92	36.70
2- <i>p</i> -Bromophenylpentane	27.3	68-72	3	1.5240	1.1988	225	219	36.00	35.90
2- <i>p</i> -Iodophenylbutane	31.7	92-94	3	1.5651	1.4438	258	260	49.30	48.90
2- <i>p</i> -Iodophenylpentane	19.1	94-97	3	1.5538	1.3636	272	268	46.67	46.20

<sup>a</sup> Cryoscopic in cyclohexane. <sup>b</sup> Sodium-liquid ammonia method. <sup>c</sup> Polyalkylation product 15.1%.

undesirable mixture. Boron trifluoride is a less drastic catalyst. No migrations of the halogen on the benzene nucleus were observed, nor were any dehalogenated products isolated. Moreover, oxidation of the alkylhalobenzenes to the *p*-halobenzoic acids reveals that the orientation of the product is entirely para when boron trifluoride is used as a catalyst.

The reactions were found to proceed analogously to those described in previous papers.<sup>2,3</sup> The yields decrease with the increasing molecular weight of the alcohol or halobenzene used, and with the increasing tendency of the alcohol toward dehydration. Isomeric primary and secondary alcohols were found to give the same product, *p*-*s*-alkylhalobenzene. This was proved by the reaction of *p*-*s*-butylchlorobenzene (from *n*-butyl alcohol) with sodium in liquid ammonia at  $-34^\circ$ , which gave a 10% yield of *p*-*s*-butylaniline and a 50% yield of *s*-butylbenzene. The various reaction products are described in Table I.

### Experimental

**Procedure.**—The halobenzene was weighed into a one-liter, three-neck, round-bottom flask, equipped with an efficient oil-sealed stirrer, a reflux condenser and a thermometer. The alcohol was then added and mixed with the halobenzene. The flask was cooled in ice-water and boron

trifluoride introduced below the liquid surface until the appearance of white fumes above the condenser indicated that the reactants were saturated. It was found, in every case, that the mixture at this point had absorbed one mole of boron trifluoride per mole of alcohol. Phosphorus pentoxide (0.25 mole per mole of alcohol) was then added as quickly as possible. The temperature was raised slowly to about  $75-85^\circ$  and maintained there for about six hours. The heating was then stopped, the mixture cooled with ice-water and then poured into a separatory funnel. The lower layer was discarded and the upper washed with water, twice with 10% solution of sodium carbonate, and finally with water. After drying with calcium chloride the material was distilled through an efficient column. The yields in Table I represent products of narrow refractive index range after two distillations.

**Oxidation.**—Small samples (0.2 to 0.3 g.) were oxidized with sodium dichromate (3.5 g.) and sulfuric acid (5.0 ml.) in (6.0 ml.) acetic acid solution at  $70-75^\circ$ . Melting points of the *p*-halobenzoic acids agree with literature values: *p*-chloro,  $242^\circ$ ; *p*-bromo,  $252^\circ$ ; *p*-iodo,  $269-270^\circ$ .

### Summary

1. Boron trifluoride, with phosphoric anhydride as an adjunct, has been shown to be an effective catalyst in the condensation of alcohols with chloro-, bromo- and iodobenzenes.

2. Satisfactory yields of *p*-*s*-alkylhalobenzenes are readily obtained in this manner.

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