

mother liquor an additional 20 mg. was obtained. Paper chromatography of the sodium acetate failed to show any propionate or butyrate.

**Degradation of the Conhydrine.**—The radioactive conhydrine from the plant was diluted with natural (+)-conhydrine.

**erythro-Octane-3,4-diol.**—A solution of conhydrine (200 mg.) in a mixture of ethanol (10 ml.) and methyl iodide (3 ml.) was refluxed in the presence of sodium bicarbonate (0.4 g.) for 24 hr. The filtered reaction mixture was evaporated to small bulk when N-methylconhydrine methiodide separated (390 mg.), m.p. 221–223° (lit.<sup>18</sup> 221°). This methiodide (380 mg.) was dissolved in warm water (20 ml.) and stirred with silver hydroxide (from 0.4 g. of silver nitrate) for 10 min. The filtered solution was evaporated and the residue distilled (200°, 0.01 mm.). The distillate was dissolved in ethanol (20 ml.) and methyl iodide (3 ml.) was added. After standing overnight at room temperature the solution was evaporated and the residue crystallized from a mixture of ethanol and ethyl acetate affording colorless needles of 1-dimethylamino-5,6-epoxyoctane methiodide (331 mg.), m.p. 134–135° (lit.<sup>18</sup> 134–135°). This methiodide (300 mg.) was subjected to a Hofmann elimination using the same conditions as those described for the N-methylconhydrine methiodide. The distillate from the elimination was washed out with methanol (10 ml.) and diluted with water (20 ml.). The solution was made

acidic with a few drops of perchloric acid and then stirred at room temperature for 3 days. The solution was then extracted with ether which was dried and evaporated. The residue was dissolved in methanol (10 ml.) and hydrogenated in the presence of platinum oxide (50 mg.) at 40 p.s.i. for 45 min. Evaporation of the filtered methanol solution yielded a solid residue which was crystallized from petroleum ether affording colorless plates of erythro-octane-3,4-diol (77 mg., 46% yield from conhydrine), m.p. 96–97° (lit.<sup>19</sup> 98°).

**Oxidation of erythro-Octane-3,4-diol.**—The diol (73 mg.) was dissolved in water (50 ml.) containing potassium permanganate (158 mg.) and shaken at 35° for 16 hr. The mixture was then filtered and the filtrate acidified with sulfuric acid and distilled. The distillate was titrated with 0.1 N sodium hydroxide (9.7 ml. required) and then evaporated to dryness. The residual sodium salts of valeric and propionic acid were separated by chromatography on silicic acid.<sup>17</sup> Schmidt reactions were carried out on the two acids using sodium azide and concentrated sulfuric acid as previously described. A Kuhn–Roth oxidation was carried out on the valeric acid using the conditions described for the oxidation of coniine, except that the mixture was refluxed for 3 hr. before distillation was carried out. A Kuhn–Roth oxidation of conhydrine using these conditions also afforded only acetic acid.

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## COMMUNICATIONS TO THE EDITOR

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### The Zeeman Effect of Nuclear Quadrupole Resonance in Single Crystals of Sodium Bromate and *p*-Dibromobenzene

Sir:

In a preceding paper,<sup>1</sup> a spectrometer for the study of the Zeeman effect of the n.q.r. in the range 100–400 Mc.p.s. was described.

This spectrometer was first tested by measurements on a single crystal of NaBrO<sub>3</sub>, then *p*-dibromobenzene was studied.

**NaBrO<sub>3</sub>.**—This substance has a cubic cell<sup>2</sup> with four pyramidal BrO<sub>3</sub><sup>-</sup> groups, each having a ternary symmetry axis through the Br atom, arranged parallel to the four body diagonals of the cube. The Na<sup>+</sup> ions lie also on these axes on the Br side. A single crystal of NaBrO<sub>3</sub> should then show, by Zeeman effect, four electric field gradients, all with the same value of  $q_{zz}$  and with  $\eta = 0$ , but with distinct orientations making tetrahedral angles. The single crystals of NaBrO<sub>3</sub> were prepared by slowly cooling (0.5° per day) an aqueous saturated solution. The measurements were carried out, at 23°, by a technique already described<sup>3,4</sup>

and have fully confirmed the provision, giving, for the unique resonance frequency ( $\sim 178.9$  Mc.p.s.) of <sup>79</sup>Br, four directions of Z-axis of the electric field gradient all making experimental angles of  $109^\circ 28' \pm 9'$  and a value of  $\eta = 0.001 \pm 0.001$ , *i.e.*, zero. These results show the absence of any disturbance in the direction and homogeneity of the external magnetic field which might arise from the heavy brass shielding which contains the sample and the radiofrequency coil.

***p*-Dibromobenzene.**—Two values of the asymmetry parameter  $\eta$  are found in the literature: the first,  $0.12 \pm 0.01$ , reported by Kojima<sup>5</sup> and the second,  $0.05 \pm 0.01$ , given by Shimomura.<sup>6</sup> The crystal structure was determined by Croatto and Bezzi<sup>7</sup> in 1949 by X-ray diffraction. They concluded that *p*-dibromobenzene in the stable phase at room temperature is isomorphous with *p*-dichlorobenzene in the  $\alpha$ -phase. It is then monoclinic with two molecules per unit cell. The large discrepancy between the two reported values of  $\eta$  induced us to study again this substance. A single crystal of *p*-dibromobenzene was easily obtained by sealing the melted substance in a glass tube (diameter 12 mm.) terminating with a 5–10 cm. long capillary, as generally used, and letting it

(1) P. Bucci, P. Cecchi, and A. Colligiani, *Ric. Sci.*, in press.

(2) R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., Chapter VII, p. 5.

(3) P. Bucci, P. Cecchi, and E. Scrocco, *Ric. Sci.*, **34**, (IIA) 129 (1964).

(4) P. Bucci and P. Cecchi, *ibid.*, in press.

(5) S. Kojima, K. Tsukada, and Y. Hinaga, *J. Phys. Soc. Japan*, **10**, 498 (1955).

(6) K. Shimomura, *ibid.*, **14**, 235 (1959).

(7) U. Croatto and S. Bezzi, *Gazz. chim. ital.*, **79**, 240 (1949).

descend slowly into a cylindrical furnace at the temperature of about 100° and having its lower part cooled to create a temperature gradient of at least 7°/cm. in the melting zone.

Such a crystal was cut to 14 mm. length and placed in a thin-walled cylindrical container made of Plexiglas. The measurements were carried out as already described in ref. 3 and 4. Two series of measurements were made at about 23°, at the frequencies of 223.8 and 267.9 Mc.p.s. for <sup>81</sup>Br and <sup>79</sup>Br, respectively. The asymmetry parameter was  $\eta' = 0.045 \pm 0.002$  for both the isotopes, in substantial agreement with Shimomura's value. The results concerning the crystal structure confirmed the data of Croatto and Bezzi. In fact, we found two nonequivalent directions of the Z-axis of the electric field gradient, which we identified with the Br-Br directions of the two molecules contained in the unit cell. The angle between these two directions, as well as the dihedral angle between the planes of the two molecules, calculated assuming that the X-axis of the electric field gradient is perpendicular to the plane of the molecule, is reported in Table I, together with the values calculated from the data of Croatto and Bezzi.

TABLE I

	Croatto and Bezzi	This work
Angle between the two Br-Br directions	71° 30'	72° 15' ± 10'
Dihedral angle between the two molecular planes	120°	118° ± 2°

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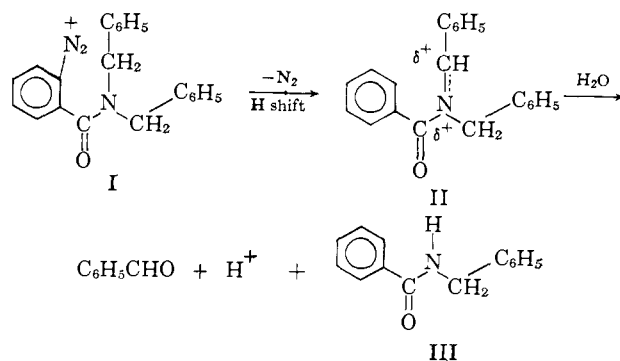
### A New Type of Cationic Intermediate from an Intramolecular Hydrogen Transfer Reaction<sup>1</sup>

Sir:

It has recently been reported<sup>2,3</sup> that thermal decomposition of the diazonium ion I derived from *o*-amino-N,N-dibenzylbenzamide produces, among other products, benzaldehyde and N-benzylbenzamide (III). Similar dealkylations have been observed in analogous cases in which the benzyl groups are replaced by methyl<sup>2</sup> and by cyclohexyl<sup>4</sup> groups and in related systems.<sup>5</sup>

It has been postulated<sup>2,3</sup> that the benzene carbonium ion generated by loss of nitrogen from I suffers an

intramolecular hydride ion transfer to produce the new and more stable cation II, which is rapidly cleaved to aldehyde and amide. Confirmation of the presence of such an intermediate, particularly in view of the previous exclusion<sup>8</sup> of a radical-chain path, would provide strong evidence for the proposed<sup>2,3</sup> hydride ion transfer process.<sup>6</sup> Furthermore, since the species II is representative of a new class of unstable cationic intermediates, its properties would be of considerable general interest.



We now wish to report the identification of the intermediate II in this reaction, its independent preparation, and some of its chemical properties. Decomposition of the hexafluorophosphate salt of I at 60° in dry ethylene chloride solution produced a tan solution, the infrared spectrum of which exhibited absorption at 1745 cm.<sup>-1</sup>. This band, which is present neither in the diazonium ion nor in the products obtained by adding water to the reaction mixture (see below), is assigned to the carbonyl group of II.<sup>8</sup> The n.m.r. spectrum of the solution exhibited a weak singlet at  $\tau$  0.53 p.p.m. (half-width = 4 c.p.s.) which is attributed to the aldehydic type proton of the -CH=N< system, and another singlet at  $\tau$  4.45 p.p.m. (half-width = 3 c.p.s.) which is attributed to the benzylic methylene group.<sup>9</sup> The characteristic spectral properties of II disappeared upon addition of chloride ion in the form of tribenzylamine hydrochloride or of water. In the latter case, benzaldehyde absorption immediately appeared at  $\tau$  0.10 p.p.m. As expected, the hydrogen transfer product N-benzylbenzamide (III, 18% yield) was identified as one of the compounds obtained from the hydrolyzed reaction mixture. Two other products were benzoic acid and benzylidenebenzylamine (IV), obtained in equivalent quantities (15% yield).

The first step of the independent preparation of II involved the treatment of benzylidenebenzylamine (IV) with 1 equiv. of benzoyl chloride to produce the  $\alpha$ -chloroamide V.<sup>10,11</sup> The latter in ethylene chloride ex-

(6) An alternative hydrogen atom transfer has been suggested as one possibility for this type of reaction.<sup>7</sup>

(7) D. N. Brown, D. H. Hey, and C. W. Rees, *J. Chem. Soc.*, 3873 (1961).

(8) As expected, it is shifted about 100 cm.<sup>-1</sup> to higher frequency than the carbonyl absorption of the uncharged N,N-dibenzylbenzamide.

(9) These assignments are based on the spectrum of the independently prepared specimen; see below. A comparison of the intensities of the two peaks was not possible because the high-field peak overlapped with benzoyl peaks of other products of the reaction.<sup>8</sup>

(10) T. C. James and C. W. Judd, *J. Chem. Soc.*, 105, 1427 (1914).

(11) The infrared spectrum of the adduct V always exhibited a very weak band for the carbonyl group of unreacted benzoyl chloride. The adduct formation is thus presumably reversible.

(1) Supported by the National Science Foundation through Grant NSF G-23705.

(2) T. Cohen, R. M. Moran, and G. Sowiński, *J. Org. Chem.*, **26**, 1 (1961).

(3) T. Cohen, A. H. Dinwoodie, and L. D. McKeever, *ibid.*, **27**, 3385 (1962).

(4) J. Lipowitz, unpublished results.

(5) For pertinent references, see the first paper in this series.<sup>2</sup>