

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 ⁸¹Br and ⁷⁹Br, 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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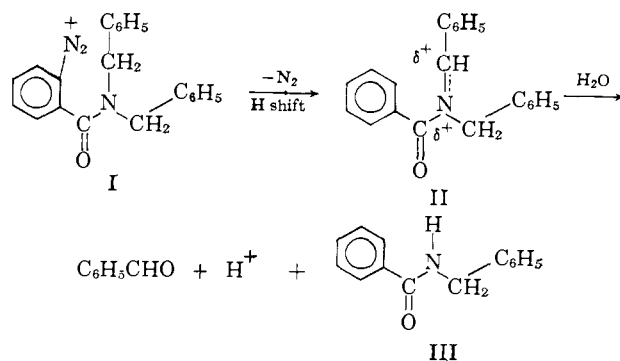
A New Type of Cationic Intermediate from an Intramolecular Hydrogen Transfer Reaction¹

Sir:

It has recently been reported^{2,3} 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 methyl² and by cyclohexyl⁴ groups and in related systems.⁵

It has been postulated^{2,3} 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 exclusion⁸ of a radical-chain path, would provide strong evidence for the proposed^{2,3} hydride ion transfer process.⁶ 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.⁻¹. 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.⁸ The n.m.r. spectrum of the solution exhibited a weak singlet at τ 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 τ 4.45 p.p.m. (half-width = 3 c.p.s.) which is attributed to the benzylic methylene group.⁹ 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 τ 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 α -chloroamide V.^{10,11} The latter in ethylene chloride ex-

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

(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.⁻¹ 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 benzylidene peaks of other products of the reaction.⁸

(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.

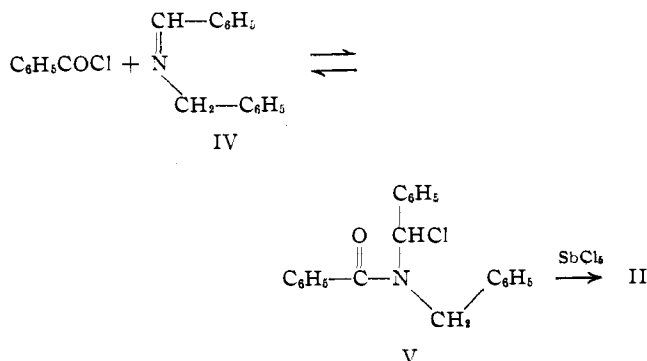
(2) T. Cohen, R. M. Moran, and G. Sowiński, *J. Org. Chem.*, **26**, 1 (1961).

(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.²

hibited carbonyl absorption at 1658 cm.^{-1} and benzylic methylene absorption at τ 5.45 p.p.m. (half-width = 2 c.p.s.). The benzylic proton on the chlorine-bearing carbon atom absorbed in the aromatic region. Integration of the n.m.r. spectrum indicated that there are 16 protons in the aromatic region and 2 in the aliphatic region.



Addition of antimony pentachloride to an ethylene chloride solution of V converted most of V into the cation II, having absorption at 1748 cm.^{-1} (s) ($\text{C}=\text{O}$) and 1585 cm.^{-1} (vs) ($-\text{CH}^+-\text{N}^+$) in its infrared spectrum and at τ 0.48 (half-width = 7 c.p.s.) and 4.30 p.p.m. (half-width = 3 c.p.s.) in its n.m.r. spectrum¹² (area ratio 1:2).

The addition of chloride ion, in the form of trimethylamine hydrochloride, to the solution of II caused the regeneration of V. Addition of water caused the cleavage of II, furnishing benzaldehyde and N-benzylbenzamide (III). The hydrolysis also produced small quantities of benzoic acid and benzylidene benzylamine (IV). The yield of the latter two products increased substantially when the hydrolysis was performed on a solution of II which had been heated at 70° for 1.5 hr.¹³ The production of the same four hydrolysis products from both the synthetic cation II, and the diazonium ion I after its thermal decomposition, provides powerful chemical evidence, in addition to the spectroscopic evidence already cited, for the existence of the cation II as an intermediate in the diazonium ion decomposition reaction.

Another interesting property of II is its conversion to N,N-dibenzylbenzamide by hydride ion abstraction from tribenzylamine.^{14,15} This reduction serves as further proof for the structure of II.

An unusual intramolecular electrophilic substitution reaction of the cation II and its mechanistic implications are discussed in the accompanying communication.¹⁶

(12) A fairly good model for II is the hydrochloride of IV, the non-aromatic protons of which absorb at τ 0.52 and 4.94 p.p.m.

(13) Upon heating, the hexachloroantimonate and hexafluorophosphate salts of II apparently decompose partially to benzoyl halide and the imine (complexed with the Lewis acid).

(14) H. Meerwein, V. Hederich, H. Morschel, and K. Wunderlich, *Ann.*, **635**, 1 (1960).

(15) The ion II failed to abstract a hydride ion from triphenylmethane under the same conditions.

(16) T. Cohen and J. Lipowitz, *J. Am. Chem. Soc.*, **86**, 2515 (1964).

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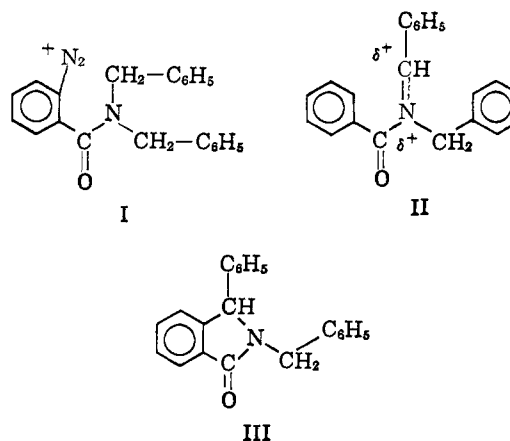
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The Question of a Benzene Cation Insertion Reaction. A Novel Intramolecular Electrophilic Substitution¹

Sir:

Three of the products obtained upon thermal decomposition of the diazonium ion I in acetic acid containing sulfuric acid have been shown to be benzaldehyde, N-benzylbenzamide, and 1-phenyl-2-benzylphthalimidine (III).² Similar products were obtained from the N,N-dimethyl analog of I.³ Evidence has been presented that the first two of these products arise from solvolytic cleavage of the cation II presumably formed by intramolecular abstraction of a hydride ion by the benzene cation which is produced by loss of nitrogen from I.⁴



One possible mode of formation of III involves an intramolecular electrophilic substitution by II. However, it is questionable whether a relatively stable cation of this type could execute an electrophilic substitution at a rate comparable to that of its solvolytic cleavage.^{5,6} Furthermore, one might expect the positive carbon atom of II to attack the benzyl ring more rapidly than it attacks the deactivated benzoyl ring. The preference for attack on the deactivated ring can, of course, be explained by invoking the argument² that the *ortho* position of the benzoyl ring is constrained by a resonance-imposed planarity of the system to a position closer to the positive carbon atom than that occupied by the *ortho* position of the benzyl ring.

Nevertheless, it is entirely possible that the ring closure to a phthalimidine only occurs because it very closely follows or is concomitant with the transfer of the hydrogen. Precedents for the formation of rings by the attack of cationic carbon on saturated carbon atoms are available.⁸ An intriguing possibility is that this type of carbon-carbon bond formation is particularly favorable in the present system because of the

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

(2) T. Cohen, A. H. Dinwoodie, and L. D. McKeever, *J. Org. Chem.*, **27**, 3385 (1962).

(3) T. Cohen, R. M. Moran, and G. Sowinski, *ibid.*, **26**, 1 (1961); A. H. Lewin, unpublished results.

(4) T. Cohen and J. Lipowitz, *J. Am. Chem. Soc.*, **86**, 2514 (1964).

(5) The N,N-dimethyl analog of I gives substantial quantities of 2-methylphthalimidine even in aqueous solution.³

(6) A somewhat similar electrophilic substitution is involved in the Pictet-Spengler reaction.⁷ In this case strong activating groups are usually required on the benzene ring being substituted.

(7) W. M. Whaley and T. R. Govindachari, *Org. Reactions*, **6**, 151 (1951).

(8) L. de Vries and S. Winstein, *J. Am. Chem. Soc.*, **82**, 5363 (1960); P. S. Skellern and I. Starer, *ibid.*, **84**, 3962 (1962).