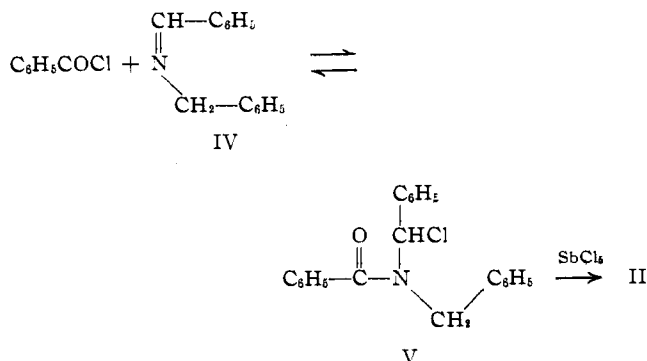


hibited carbonyl absorption at 1658 cm^{-1} and benzylic methylene absorption at $\tau\ 5.45$ p.p.m. (half-width = 2 c.p.s.). The benzylic proton on the chlorine-bearing carbon atom absorbed in the aromatic region. Integration of the n.m.r. spectrum indicated that there are 16 protons in the aromatic 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) ($-\text{CH}^{\delta+}=\text{N}^{\delta+}$) in its infrared spectrum and at $\tau\ 0.48$ (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 $\tau\ 0.52$ 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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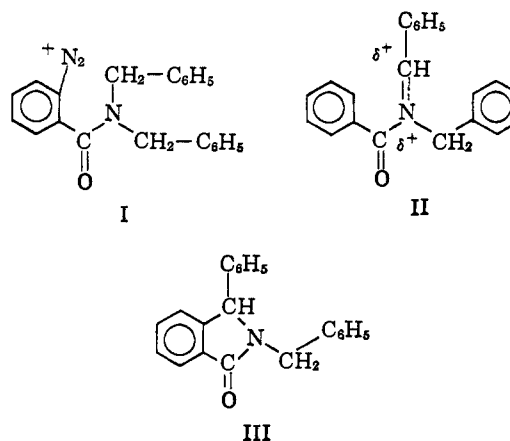
THEODORE COHEN
JONATHAN LIPOWITZ

RECEIVED APRIL 6, 1964

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).

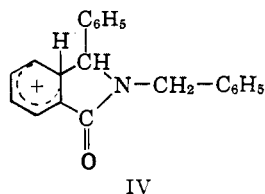
(5) The N,N-dimethyl analog of I gives substantial quantities of 2-methylphthalimidine even in aqueous solution.³

(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. Skell and I. Starer, *ibid.*, **84**, 3962 (1962).

availability of the rather stable σ -complex IV as an intermediate. This species, which could be formed by an "insertion"⁹ of the benzene carbonium ion into the C-H bond, is of course the same intermediate that would be involved if III were formed from II. It is in fact conceivable that the cation II could also be formed from IV rather than by a more direct 1,5-hydride ion transfer. The possibility of such an "insertion" reaction takes cognizance of the similarity between benzene carbonium ions and carbenes.^{11,15}



The independent preparation of the cation II⁴ now makes it possible to study its intramolecular electrophilic substitution reactions. In dry ethylene chloride, II has been found to be stable with respect to five-member ring formation for 24 hr. at room temperature. In the presence of the base tribenzylamine, the phthalimidine III is formed in detectable quantities (n.m.r.) at the end of 10 min. at the same temperature.¹⁷ This remarkable finding probably indicates that the proton removal from the presumed intermediate IV is the rate-determining step in this electrophilic substitution.

In the absence of added base, phthalimidine III was produced in 6% yield at the end of 1 week at room temperature and in 14% yield when the solution was heated at 70° for 1.5 hr. None of the 1-phenyl-2-benzoylisoindoline² which would result by substitution into the benzyl ring could be detected by gas chromatography. Thus, it is evident that this electrophilic ring closure reaction is controlled exclusively by the stereoelectronically imposed proximity of the reacting centers rather than by the electron availability on the ring in which substitution occurs.

The low rate of the intramolecular electrophilic substitution makes it appear doubtful that ring closure could compete with solvolytic cleavage of the cation II. A direct study of this competition was performed by injecting 1 ml. (0.7 mmole) of an ethylene chloride solution of the hexachloroantimonate salt of II into the acetic-sulfuric acid reaction mixture (50 ml.) at the temperature (steam bath) of the previous² diazonium

(9) This "insertion" reaction would require attack of the cationic carbon on the carbon-hydrogen bond in a direction perpendicular to it. This would presumably involve a transition state of the very same type as that suggested¹⁰ on experimental and theoretical grounds for hydride transfer reactions.

(10) M. F. Hawthorne and E. S. Lewis, *J. Am. Chem. Soc.*, **80**, 4296 (1958).

(11) Both have only two σ -bonds and are thus capable of forming two more. Both are very unselective.¹² The existence of both singlet and triplet carbenes¹³ might also have an analogy in this system since evidence has recently been put forth that such cations may exist in triplet states.¹⁴

(12) E. S. Lewis, *J. Am. Chem. Soc.*, **80**, 1371 (1958); W. E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *ibid.*, **78**, 3224 (1956).

(13) G. Herzberg and J. Shoosmith, *Nature*, **183**, 1801 (1959).

(14) R. W. Taft, *J. Am. Chem. Soc.*, **83**, 3350 (1961).

(15) The benzene carbonium ion may or may not be associated with a molecule of nitrogen.¹⁶

(16) E. S. Lewis and J. M. Insole, *J. Am. Chem. Soc.*, **86**, 34 (1964).

(17) Competing with phthalimidine formation in this case is a hydride transfer from tribenzylamine to II.⁴

ion decomposition in this solvent and examining the hydrolysis product by gas chromatography for the phthalimidine III. None was found. If III were indeed formed from the cation II in the diazonium ion decomposition, a simple calculation based on the previous data² indicates that about 9% of this cation should be converted to phthalimidine III under these conditions.

Although this cannot be taken as rigorous proof that the phthalimidine is formed by direct attack of the benzene carbonium ion on the benzylic carbon atom (or on the C-H bond), it is certainly suggestive of this type of mechanism.¹⁸ Experiments now under way should throw more light on this question.

(18) Many of the products that have been reported in diazonium ion decompositions can be explained, although not uniquely, by the "insertion" process. For example, this path is much more attractive than a radical combination mechanism for the production of *m*- and *p*-nitrophenylethanols in the photolytic decomposition of the corresponding diazonium ions in ethanol.¹⁹ The formation of fluorenes, in one case quantitatively, upon deamination of 2-amino-2'-alkylbiphenyls²⁰ is another example. Finally, the reductions that frequently occur when diazonium ions are heated in alcohol solutions could be brought about by insertion of the benzene carbonium ion into the carbinol C-H bond to form a σ -complex followed by loss of a proton and an aldehyde or ketone.

(19) W. E. Lee, J. G. Calvert, and E. W. Malmberg, *J. Am. Chem. Soc.*, **83**, 1928 (1961).

(20) L. Mascarelli and B. Longo, *Gazz. chim. ital.*, **67**, 812 (1937); *Chem. Abstr.*, **32**, 4564 (1938); L. Mascarelli and A. Angeletti, *Gazz. chim. ital.*, **68**, 29 (1938); *Chem. Abstr.*, **32**, 4565 (1938); L. Mascarelli and B. Longo, *Gazz. chim. ital.*, **68**, 121 (1938); *Chem. Abstr.*, **32**, 6235 (1938).

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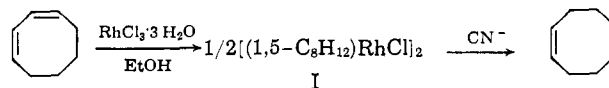
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The Isomerization of 1,3-Cyclooctadiene to 1,5-Cyclooctadiene via the Rhodium(I) π -Complex

Sir:

Recent reports on the isomerization of cyclooctadiene by iron carbonyl¹ and by potassium *t*-butoxide in dimethyl sulfoxide² have demonstrated that 1,3-cyclooctadiene is thermodynamically the most stable of the isomeric cyclooctadienes. By each method, 1,5-cyclooctadiene is isomerized quantitatively to 1,3-cyclooctadiene.

We wish to report that $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, which forms π -complexes preferentially with chelating 1,5 dienes,³ under conditions which isomerize other olefins,⁴ isomerizes 1,3-cyclooctadiene to I, the dimer of rhodium(I) chloride-1,5-cyclooctadiene.^{5,6} Analytically pure 1,5-cyclooctadiene is obtained by treating I with aqueous KCN.



(1) J. E. Arnet and R. Pettit, *J. Am. Chem. Soc.*, **83**, 2954 (1961).

(2) D. Devaprabhakara, C. G. Cardenas, and P. D. Gardner, *ibid.*, **85**, 1553 (1963).

(3) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

(4) R. E. Rinehart, H. P. Smith, H. S. Witt, and H. Romeyn, Jr., *J. Am. Chem. Soc.*, **84**, 4145 (1962).