

THE INTERACTION OF ARYL AZIDES AND DICHLOROCARBENE

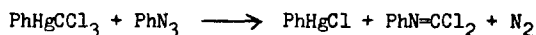
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Our interest in the interaction of organic azides and reactive intermediates¹ has led us to a study of systems involving aryl azides and carbene intermediates. There have been several reports concerning reactions of azides which generate products that might have resulted from the interaction of azides and a reactant containing divalent carbon.² However, the resulting products also can be rationalized using reaction schemes devoid of reagents containing divalent carbon. We wish to report the results of stoichiometric and kinetic studies that bear directly on the question of the reactivity of an organic azide with a carbene intermediate.

Phenyl azide is decomposed in degassed dimethoxyethane (DME) at 80° in the presence of phenyl(trichloromethyl)mercury. Product studies indicate that the starting mercury compound generates a quantitative yield of phenylmercuric chloride after 90 hr. at 80° and that a 70% yield (based on decomposed azide) of the nitrogen-containing product, phenylcarbonimidoyl dichloride (1)³, is generated from the azide. We observed that phenylcarbonimidoyl dichloride

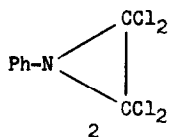


1

(PCD) also may be generated either by the pyrolysis of sodium trichloroacetate in DME or by the action of sodium methoxide on ethyl trichloroacetate in hexane in the presence of phenyl azide. The latter method is similar to that employed by Baldwin^{2c} in the conversion of n-octyl azide to the corresponding anil.

Although PCD is thermally stable and does not react with phenyl azide in solution at 80°, it decomposes at 80° in the presence of phenyl(trichloromethyl)mercury. The major product isolated from this reaction yields infrared and mass spectra consistent with the structure of

1-phenyl,2,2,3,3-tetrachloroethylenimine (2)⁴.



The rates of decomposition of phenyl azide in the presence of phenyl(trichloromethyl)mercury are most conveniently expressed in terms of an initial pseudo-first-order rate constant, k_{obs} . Linearity of the first-order plots for phenyl azide decomposition (with initial concentrations of the azide and mercury being 0.06 M and 0.30 M, respectively) is observed through only about ten hours, or until about 10% of the azide is decomposed. All recorded values of k_{obs} were determined within this range. The progress of the azide decomposition was followed by measuring the intensity of the azide band at 2110 cm^{-1} . Table I shows the results of some of our measurements of k_{obs} in runs with varied initial concentrations of azide and mercury compound. The value of k_{obs} shows a first-order dependence on the initial concentration of phenyl-(trichloromethyl)mercury, while higher initial concentrations of azide lower the value of the rate constant.

Table I

Pseudo-first-order Rate Constants for Phenyl Azide Decomposition in DME at 80.0°

Azide concn, M	Mercury ^a concn, M	$10^6 k_{\text{obs}}$, sec ⁻¹
0.061	0.300	19 \pm 1.0 ^b
0.060	0.202	12 \pm 0.6
0.062	0.150	8.8 \pm 0.5
0.604	0.304	2.8 \pm 0.2
0.400	0.300	3.5 \pm 0.2
0.122	0.301	13 \pm 0.7
0.031	0.149	11 \pm 0.6

^aPhenyl(trichloromethyl)mercury. ^bAverage value of 5 runs.

The addition of water, phenylmercuric chloride, or PCD to the reaction mixture decreases the value of k_{obs} . Oxygen apparently does not affect the rate since the value of k_{obs} is the same in a run that is incompletely degassed (one freeze-degas-thaw cycle) as in a carefully degassed run (four cycles). Table II lists the observed rate constants for some substituted aryl azides in 0.30 M solutions of phenyl(trichloromethyl)mercury in DME at 80.0° . The initial concentrations of the azide were 0.06 M.

Table II

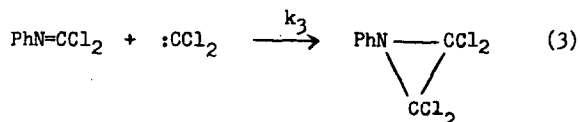
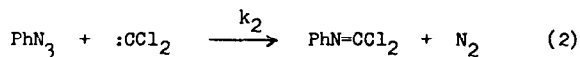
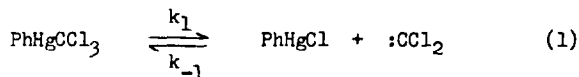
Pseudo-first-order Rate Constants for Decomposition of Substituted Aryl Azides

Substituent	$10^6 k_{\text{obs}}, \text{sec}^{-1}$	Substituent	$10^6 k_{\text{obs}}, \text{sec}^{-1}$
p-CH ₃ O	25 ± 1.2	o-phenyl	11 ± 0.6
H	19 ± 1.0	2,6-dimethyl	21 ± 1.1
p-Cl	16 ± 0.8		

In a related experiment, a limiting amount of ethyl trichloroacetate was treated with sodium methoxide in the presence of equimolar amounts of phenyl and p-chlorophenyl azide. Vapor phase chromatographic analysis indicated the phenyl azide to be more reactive than the p-chlorophenyl azide by a factor of 1.20. This parallels the ratio of the pseudo-first-order rate constants for these same azides, 1.2 (Table II).

Scheme I best explains the observed results:

Scheme I



Application of the steady-state approximation to Scheme I gives an initial rate law as shown (4), and yields a pseudo-first-order rate constant of a form (5) consistent with the observed rate data.

$$\frac{-d(\text{PhN}_3)}{dt} = \frac{k_2 k_1 (\text{PhHgCCl}_3) (\text{PhN}_3)}{k_{-1} (\text{PhHgCl}) + k_2 (\text{PhN}_3) + k_3 (\text{PCD})} \quad (4)$$

$$k_{\text{obs}} = \frac{k_2 k_1 (\text{PhHgCCl}_3)}{k_{-1} (\text{PhHgCl}) + k_2 (\text{PhN}_3) + k_3 (\text{PCD})} \quad (5)$$

Phenyl azide may interact with intact phenyl(trichloromethyl)mercury or with some intermediate generated from the mercury compound to produce the observed PCD. That this product can be generated from two other sources and that the value of the k_{obs} is decreased by added phenylmercuric chloride suggest that the azide is attacked by some intermediate reversibly formed from the mercury compound. As discussed by previous workers⁵, the nature of this intermediate may be free dichlorocarbene ($:CCl_2$), a carbene complexed to the phenylmercuric chloride ($PhHgCl \rightarrow :CCl_2$) or solvent ($S \rightarrow :CCl_2$), a radical ($PhHgCl_2C\cdot$, $Cl_3C\cdot$), a carbonium ion ($PhHgCl_2^+$, CCl_3^+), or an anion (CCl_3^-). Radical and anionic intermediates appear to be unlikely suspects because of the insensitivity of the observed rate constant to the presence of oxygen and the relative reactivities of the para-substituted azides. A similar electrophilic intermediate is generated from the mercury compound and the ethyl trichloroacetate, as supported by the product as well as the relative reactivity studies with the aryl azides. That intermediate, free or complexed dichlorocarbene, reacts with phenyl azide to yield PCD, and with the PCD to yield 1-phenyl,2,2,3,3-tetrachloroethylenimine. Further study of steric and solvent effects will indicate whether the intermediate generated from the mercury compound is a free or complexed carbene.

References

1. J. E. Leffler and H. H. Gibson, Jr., J. Am. Chem. Soc., 90, 4117 (1968).
2. (a) P. A. S. Smith, The Chemistry of Open Chain Nitrogen Compounds, Vol. I, W. O. Benjamin, Inc., New York, N. Y., 1965, p. 248; (b) L. Horner, A. Christmann, and A. Gross, Chem. Ber., 96, 399 (1963); (c) J. E. Baldwin and J. E. Patrick, Chem. Commun., 968 (1968).
3. J. B. Murphy, J. Org. Chem., 29, 1613 (1964).
4. D. Seyferth and W. Tronich, J. Organometal. Chem., 21, P3 (1970).
5. D. Seyferth, J. Yick-Pui Mui, and J. Burlitch, J. Am. Chem. Soc., 89, 4953 (1967).

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