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THE REACTION OF IONIC AZIDE WITH 3-HALO-4-PHENYLCYCLOBUTENEDIONES
A NOVEL ROUTE TO PHENYLCYANOKETENE

Roy C. De Selms
Research Laboratories, Eastman Kodak Company,
Rochester, New York 14650, U.S.A.

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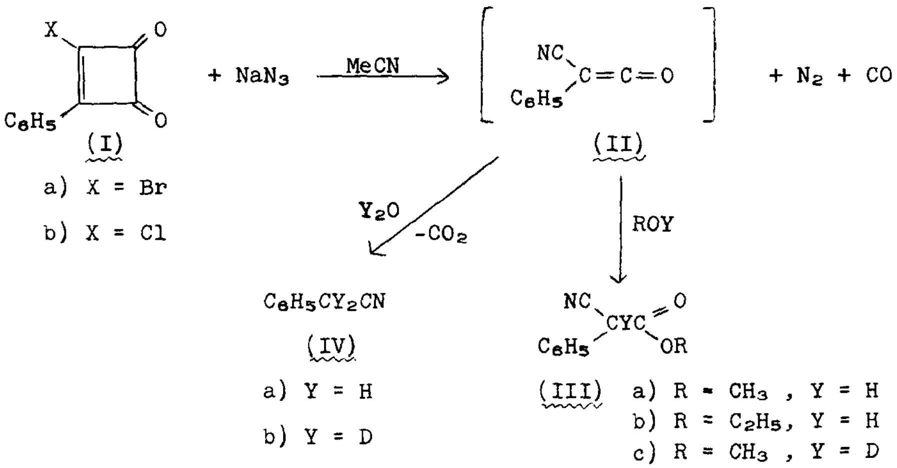
We wish to report a novel degradation leading to phenylcyanoketene (II). At ambient temperatures, the evolution of two molar equivalents of gas (N_2 and CO by glc analysis) is simultaneous with the gradual addition of a solution of 3-halo-4-phenylcyclobutenedione (I) (1) in acetonitrile to a vigorously stirred suspension of NaN_3 in acetonitrile. If the reaction is carried out in the presence of hydroxylic compounds (*i.e.*, alcohols, H_2O) *or* with their subsequent addition, products such as III (2) or IV arise. This is interpreted to mean that bond reorganization of the intermediate fragment occurs rapidly yielding II.



When the reaction is carried out in the presence of D_2O or CH_3OD, the cleanly deuterated products IVb (86% yield) and IIIc (89% yield), respectively, are obtained. However, under conditions of nonexchange, formation of II in CH_3CN or CD_3CN with subsequent addition of D_2O or H_2O, respectively, (30 min after cessation of gas evolution) leads in both cases to lower yields of mixtures containing equal amounts of IVa and IVb with less than 10% C_6H_5CHDCN. These data indicate that in the absence of ketene reactive substances, II undergoes free radical reaction and decomposition.

While the competition for I greatly favors azide ion in the presence of hydroxylic substances, more nucleophilic agents such as amines are favored over azide. Thus, the amides corresponding to III can not be prepared in the presence of amines. Furthermore, free radical decomposition of II at room temperature apparently competes effectively with potential cycloaddition and does not lead to formation of adducts with cyclopentadiene, cyclopentene, cyclohexene, diphenylacetylene, and benzalaniline.

The method described here constitutes a novel route to the rare cyanoketenes. Only the putative formation of cyanoketene itself is suggested in the literature (3,4) heretofore.

Footnotes and References

1. E. J. Smutny, M. C. Caserio, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 1793 (1960).

2. IIIa: Analysis found: C, 69.1; H, 5.1; N, 8.3%. $C_{10}H_9NO_2$ requires: C, 68.6; H, 5.2; N, 8.0%. Ms showed expected parent at m/e 175. Nmr at 60 MHz ($CDCl_3$) exhibited singlets at 3.66 (OMe), 4.83 (methinyl) and 7.31 δ (phenyl). IIIb: Identical to Aldrich Chemical Co., E4520-1.

3. A. K. Bose, B. Anjaneyulu, S. K. Bhattacharya, and M. S. Manhas, *Tetrahedron*, **23**, 4769 (1967).

4. *Cf*., H. Böhme, S. Ebel, and K. Hartke, *Ber*., **98**, 1463 (1965).