spectra confirmatory of the structures presented, and satisfactory elementary analyses have been obtained for all except those utilized without isolation.

We wish to express our warm appreciation to the National Institutes of Health, the National Science Foundation, and Research Corporation for generous support, to Chas. Pfizer and Co., Inc., for support and invaluable assistance in preparation of primary intermediates in quantity, to Professor Dr. Arthur Stoll and Sandoz A. G. for a handsome gift of methyl phaeophorbide *a*, and to Drs. Stephan Sallay and Wolfgang H. F. Sasse for their coöperation in certain phases of our work.

R. B. WOODWARD
W. A. AYER
J. M. BEATON
F. BICKELHAUPT
R. BONNETT
P. BUCHSCHACHER
G. L. CLOSS
H. DUTLER
J. HANNAH
F. P. HAUCK
S. ITÔ
A. LANGEMANN
E. LE GOFF
W. LEIMGRUBER
W. LWOWSKI
J. SAUER
Z. VALENTA
H. VOLZ
CONVERSE MEMORIAL LAB., HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.

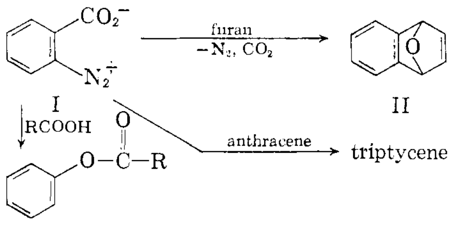
RECEIVED JUNE 29, 1960

DECOMPOSITION OF BENZENEDIAZONIUM-2-CARBOXYLATE

Sir:

Benzenediazonium-2-carboxylate (I) was prepared by Hantzsch and Davidson,[1] who reported only that its aqueous solution decomposed to furnish salicylic acid in unspecified yield. Recent experiments, here reported, indicate that the decomposition may take an entirely different course in other media.

Freshly prepared samples of the anhydrous crystalline salt are soluble in water (λ_{max} 257 and 302, log ϵ 3.87 and 3.43, respectively), insoluble in nonpolar solvents, and possess sharp peaks at 2283, 1652, and 1624 cm.$^{-1}$ (Nujol mull). The crystalline substance is therefore better represented by the zwitterion formula (I) than by alternative[2] cyclic structures.



Aqueous solutions of I lose nitrogen slowly at room temperature and rapidly upon heating. At 45° during 36 hours an 88% yield of salicylic acid was produced.

Heating suspensions of the inner salt (I) in benzene or toluene results in the evolution of both nitrogen and carbon dioxide, the yield of the latter depending somewhat upon conditions. At 39° during 48 hours in benzene the yield of nitrogen was 100% and of carbon dioxide 59%. The product of decomposition under these conditions is a complex mixture, largely polymeric, which has not been resolved.

Refluxing a suspension of I in furan for 64 hours led to a 55% yield of 1,4-dihydronaphthalene-1,4-endoxide (II),[3] m.p. 55–56°, which was identified by conversion to 1-naphthol (81%) in methanolic hydrochloric acid.[3] Similar decomposition of I in a benzene solution of anthracene gave triptycene (30%).[4] Although direct evidence for an intermediate is lacking, these products are readily visualized as derived from benzyne.[5]

Decomposition of I in the presence of carboxylic acids leads to phenyl esters. Heating the salt to 45–55° with a slight excess of benzoic acid in either benzene or *p*-xylene solution yielded phenyl benzoate (25% and 22%, resp.). Similar reaction with *m*-toluic acid gave phenyl *m*-toluate.[6] Since benzoylsalicylic acid is not measurably decarboxylated under these conditions, and since the rate of decomposition of I at any given temperature is not strongly dependent upon the nature of the other reactant, the postulation of benzyne or an equivalent intermediate in this transformation is also attractive. The types of bonds which are broken in the decomposition of I are sufficiently different from those in molecules which are currently believed to yield benzyne[5] that critical study will be required to determine whether the reaction intermediates are structurally similar. In particular it must be emphasized that there is no necessity in the present case for postulating an intermediate with the symmetry properties which have been demonstrated[7] for the intermediate in the reaction of halobenzenes with various strong bases. Current work aims at testing this point.

The reactions outlined here may find some use in synthesis because of the ease of preparing I,[1] and its compatibility with a wide variety of reagents. A major limitation is the hazard associated with handling large quantities of the substance, owing to its sensitivity to heat and shock.[8]

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN
MARTIN STILES
ROY G. MILLER

RECEIVED MAY 23, 1960

---

(1) A. Hantzsch and W. B. Davidson, *Ber.*, **29**, 1535 (1896).

(2) A. Hantzsch and R. Glogauer, *ibid.*, **30**, 2548 (1897).

(3) G. Wittig and L. Pohmer, *Chem. Ber.*, **89**, 1334 (1956).

(4) G. Wittig, *Org. Syn.*, **39**, 75 (1959).

(5) For recent reviews see: (a) G. Wittig, *Angew. Chem.*, **69**, 245 (1957); (b) J. D. Roberts, *Chemical Society (London) Special Publication No. 12*, 115 (1958); (c) R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960).

(6) These three experiments, involving variation of both the aromatic solvent and the acid reactant, indicate that the aryl esters are derived from both I and the acid, and eliminate mechanisms in which benzoate radicals form phenyl benzoate by partial decarboxylation or by attack upon solvent.

(7) J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith and C. W. Vaughan, THIS JOURNAL, **75**, 3290 (1953); J. D. Roberts, D. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *ibid.*, **78**, 601 (1956); A. T. Bottini and J. D. Roberts, *ibid.*, **79**, 1458 (1957); E. Jenny and J. D. Roberts, *Helv. Chim. Acta*, **38**, 1248 (1955).

(8) Of some twenty preparations of the compound, two were encountered which detonated upon being scraped against the surface of a porcelain funnel.