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THE HYDROLYSIS OF *ALPHA*-NITROBENZHYDRYL CHLORIDE

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The effect in nucleophilic displacement reactions of a nitro group attached to the reaction center has received little attention. At present there is a single description of reaction kinetics for an *alpha*-nitrohalo system (2). Neither 2-bromo- nor 2-chloro-2-nitropropane undergoes S_N1 solvolysis in the absence of silver ion at 95°, but both react cleanly with hydroxide ion. Although these substances resemble geometrically the corresponding *t*-butyl halides, the presence of the nitro group apparently so inhibits carbonium ion formation that the S_N2 pathway becomes the preferred reaction course.

Of further interest in this connection are nucleophilic displacements on compounds in which a nitro group is separated from the reaction center by a phenyl group, which can efficiently relay electronic demands. Baker (3) found relative rates of 1.0 and 0.044 for the S_N1 solvolysis of benzyl chloride and *p*-nitrobenzyl chloride, respectively, in 48% ethanol at 30°. Likewise, Nishida (4) reports relative rates of 1.0 and 0.00079 for ethanolysis at 25° of benzhydryl chloride and *p*-nitrobenzhydryl chloride, respectively. In these instances, also, the nitro group clearly inhibits carbonium ion formation.

To elaborate on this effect, we studied the hydrolysis of *alpha*-nitrobenzhydryl chloride, **1**. Compound **1**, m.p. 61.0-61.5° and satisfactory elemental analysis, was synthesized by nitration of diphenylmethane (5), followed by conversion of the product to the potassium salt and subsequent chlorination of the salt in aqueous solution. This substance undergoes quantitative hydrolysis in neutral or alkaline 80% ethanol to form benzophenone, chloride ion, and nitrite ion. The rate of formation of benzophenone can be conveniently followed spectrophotometrically using its intense absorption at 252 mμ. First-order rate constants at

49.6° are collected in the Table. It is apparent that the rate is independent of the hydroxide ion concentration. In addition, the rate constants are insensitive to hydroquinone, a free radical inhibitor, and to whether or not the reaction vessel is protected from light. Thus, despite the presence of the nitro group attached to the reaction center, this hydrolysis proceeds *via* the S_N1 mechanism.

TABLE

First-Order Rate Constants At 49.6° in 80% Aqueous Ethanol

Run No.	$[RX] \times 10^2$	$[OH^-] \times 10^2$	$k_1 \times 10^3$ hr^{-1}
1	1.100	-	83.2
2	1.100	-	79.0
3	1.000	2.000	79.3
4	1.190	3.692	79.6
5	1.190	3.692	87.0
6	1.190	3.692	78.5
7	1.000	4.000	77.0
		Avg.	80.5

Interestingly, application of the Winstein-Grunwald (6) *m* value for benzhydryl chloride and *Y* value for 100% ethanol to the rate constant of Nishida (4) for the ethanolysis of *p*-nitrobenzhydryl chloride predicts a rate constant of 1.416×10^{-3} hr^{-1} at 50° in 80% ethanol. Carbonium ion formation is therefore apparently more favorable from 1 than from *p*-nitrobenzhydryl chloride. Whether this unanticipated finding is primarily a consequence of ground state or transition state effects is under study.

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