

EVIDENCE FOR AN S_N2 CONTRIBUTION IN THE SOLVOLYSIS OF BENZHYDRYL

p-NITROBENZOATE

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It is contended by Snee that direct nucleophilic attack on covalent carbon via the traditional concerted S_N2 mechanism¹ has not been established, and that the kinetic and stereochemical characteristics usually associated with the process can better be explained in terms of nucleophilic attack on pre-formed ion-pairs.² We now present evidence which strongly suggests that there exists a pathway in the solvolysis of benzhydryl p-nitrobenzoate ($Ph_2CHOPNB$) that does not involve the intermediacy of an ion-pair or carbonium ion.³

TABLE 1

Product proportions and ratios in the solvolysis of $Ph_2CHOPNB$
 in 50% Me_2CO , ^a $x\%$ EtOH, and (50- x)% H_2O at 104°C.

Solvent		Products ^b		R ^c
% EtOH	% H_2O	% Ph_2CHOEt	% Ph_2CHOH	
25	25	67.1	32.9	2.04
30	20	70.2	29.8	2.36
35	15	71.1	28.9	2.46
40	10	76.7	23.3	3.30

^a Volume percentages. ^b By g.l.c. on an OV-17 column. No other products detected. Ether and alcohol were not significantly interconverted under the reaction conditions. ^c Product ratio: $[Ph_2CHOEt]/[Ph_2CHOH]$. [Ester]₀ ca. 0.01 M.

In Table 1 we show the product proportions for the ester solvolysis in 50% acetone, $x\%$ EtOH and (50- x)% H_2O , the presence of acetone being necessary for solubility reasons. If a pre-formed ion-pair or a spectrum of ion-pairs are the sole precursors of the solvolytic products, it follows that generation of the same ion-pairs from a different source in the same solvents will give rise to identical product ratios.

Diphenyldiazomethane (Ph_2CN_2) has been allowed to react with HOPNB in the same solvents at 0°C and 25°C . In Table 2 we show the proportions and the product ratios for the solvolytic products (ether and alcohol). Ester Ph_2CHOPNB comprised about 70% of the overall product mixture, but did not solvolyse at these temperatures. Benzophenone was a minor contaminant whose concentration could be minimized by deoxygenation of solutions prior to mixing. Results are in Table 2.

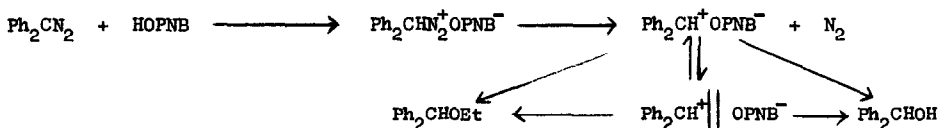
Table 2

Proportions and ratios of solvolysis products from the reaction of Ph_2CN_2 (ca. 0.03 M) with HOPNB (ca. 0.06 M) in solvents containing 50% Me_2CO , x% EtOH and (50-x)% H_2O .

Solvent		Products (0°C) ^a			Products (25°C) ^a		
% EtOH	% H_2O	% Ph_2CHOEt ^b	% Ph_2CHOH ^b	\bar{R}	% Ph_2CHOEt ^b	% Ph_2CHOH ^b	\bar{R}
25	25	51.9	48.1	1.08	52.0	48.0	1.08
30	20	59.1	40.9	1.45	59.3	40.7	1.46
35	15	66.9	33.1	2.03	67.0	33.0	2.03
40	10	75.5	24.5	3.08	75.7	24.3	3.11

^a As a percentage of total solvolysis products. Ph_2CHOPNB comprised 70-74% of total products, based on $[\text{Ph}_2\text{CN}_2]_0$ and amounts of ether and alcohol obtained. ^b Yields in this Table and in Table 1 have a maximum uncertainty of $\pm 0.2\%$.

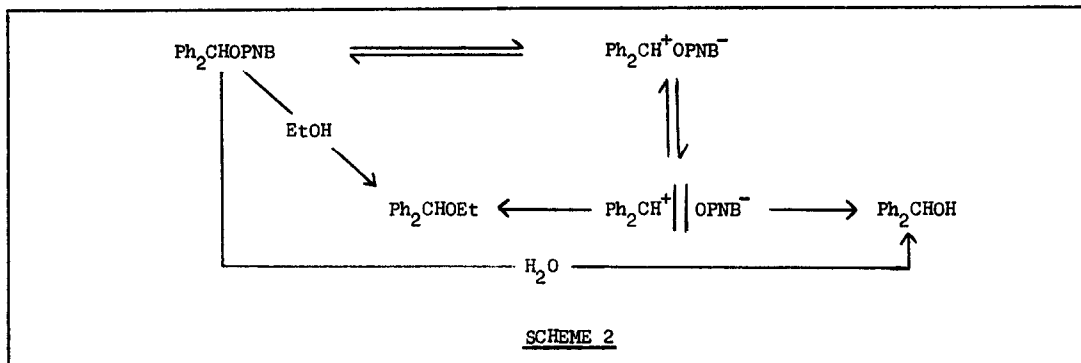
The accepted mechanism⁴ for the Ph_2CN_2 -HOPNB reaction is shown in Scheme 1. The product ratios in Table 2 are thus measures of the relative rates of attack of EtOH and H_2O on ion-pairs alone. The ratios in the two Tables are not directly equated to rate constant ratios, as the former are not linear functions of various measures of solvent composition.



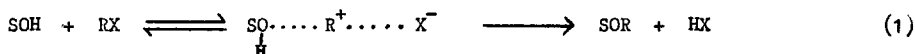
SCHEME 1

It is immediately clear that the product ratios arising from the two reactions are not identical in any solvent. All discrepancies are well outside experimental error and are not explained by a temperature effect (Table 2). The conclusion is that there exists a further product precursor other than the ion-pairs $\text{Ph}_2\text{CH}^+\text{OPNB}^-$ (intimate) and/or $\text{Ph}_2\text{CH}^+ \parallel \text{OPNB}^-$ (solvent-separated) in the solvolysis of Ph_2CHOPNB . Covalent ester reacting by an $\text{S}_{\text{N}}2$ route is an obvious

possibility, and the suggested pathways are shown in Scheme 2. We omit dissociated carbonium ions from the Schemes for the reason that external return is negligible in the ester solvolysis.⁵



The nucleophiles are more selective in the ester solvolysis than in the $\text{Ph}_2\text{CN}_2 - \text{HOPNB}$ reaction, which suggests that a product precursor of lower energy than the ion-pairs in Scheme 1 is involved competitively in the solvolysis. Ethanol and water are nucleophilic solvents⁶ and ethanol is generally the better of the two, as is found here. The Grunwald-Winstein m -value for ($p\text{-ClC}_6\text{H}_4$) PhCHOPNB solvolysis in aqueous acetone is⁷ 0.8 which is far enough from the limiting value pertaining to unassisted solvolysis via ion-pairs (ca. 1.2)⁸ to allow serious consideration of a solvent-assisted pathway in the overall solvolysis. While solvent-assisted formation of a specifically solvated ion-pair (equation 1) cannot be directly excluded from the



solvolysis scheme, it is worth noting that this process degenerates into the classical concerted $\text{S}_{\text{N}}2$ mechanism as the lifetime of the ion-pair becomes infinitely short. We emphasize the claimed² covalent interaction in such as ion-pair in pointing out that the difference between it and an $\text{S}_{\text{N}}2$ transition state is more semantic than chemical.

Other miscellaneous points having no strong bearing on the $\text{S}_{\text{N}}2$ vs. ion-pair controversy may be noted. The lack of temperature dependence of the product ratios in Table 2 implies that the nucleophiles attack high energy intermediates (but not the diazonium ion).⁹ The $\text{EtOH} > \text{H}_2\text{O}$ nucleophilicity order is apparently not in accordance with attack solely on $\text{Ph}_2\text{CH}^+ \parallel \text{OPNB}^-$ in the stepwise ester solvolysis route, as the opposite order is thought to prevail for attack on solvent-separated ion-pairs.¹⁰ However, other related observations have been explained in terms of solvent capture by external ion-pairs in the Ph_2CHOPNB system.¹¹ Small but significant discrepancies between the fraction of internal return as separately estimated from the solvolysis and ¹⁸0 equilibration rates of Ph_2CHOPNB in 90% aqueous acetone on one hand, and on the fraction

of covalent ester formed in the Ph_2CN_2 -HOPNB reaction in the same solvent on the other,⁹ suggest non-identity of routes in the two reactions. The discrepancy is in such a direction as to allow consideration of a route in the solvolysis which does not involve ion-pairs, and an $\text{S}_{\text{N}}2$ process is a possibility.

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