Product-determining Steps in the Reaction of Diaryldiazomethanes with Acids in Acetonitrile

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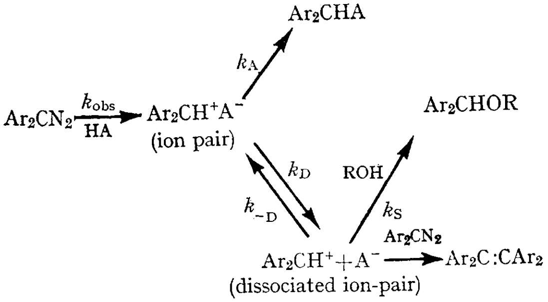
THE reaction of diphenyldiazomethane with carboxylic acids, both in aprotic solvents (*e.g.*, toluene) where the product is the corresponding diphenylmethyl ester and in alcoholic media where ester and ether are formed, has been widely used in the study of substituent effects on reactivity.[1] In hydroxylic solvents, despite considerable study, the product-determining steps are not well understood.[2] The principal feature is the low sensitivity of the product ratio, P (=[Ester]/[Ether]), to the chemical nature of the carboxylic acid and nucleophilic solvent. We now report the results of our extension of earlier work[3] on the acid-catalysed decomposition of diaryldiazomethanes in acetonitrile to the reaction of 4,4′-dichlorodiphenyldiazomethane with benzoic acid in the presence of a number of alcohols, which, we believe, throws new light on the problem.

The rate of decomposition of the diazo-compound by an excess of benzoic acid (HA) in acetonitrile containing up to 8M-hydroxylic nucleophile (ROH) was followed spectrometrically.[3] The reaction was accurately first-order in the diazo-compound and showed an apparent order somewhat greater than one in benzoic acid. Product analysis, by thin-layer chromatography on fluorescent silica gel, was accurate to ±1%. Essentially all the product was ester or ether with only traces (< 1%) of tetra-arylethylene.

The kinetic and product studies were inconsistent with mechanisms involving (a) separate routes for the formation of ester and ether, and (b) partitioning of a single intermediate to form the products. For all alcohols, P tended to unity at very high nucleophile concentration but varied widely at low concentration.

Adopting the reaction scheme in the Chart as being of minimal complexity, and applying the steady state hypothesis, $P = (k_A/k_D)\ \{1 + (k_{-D}[A^-]/k_S[ROH])\}$. However, k_D is expected to be constant only for fixed values of [HA] and [ROH]. Benzoic acid is known to react with benzoate ion (A^-) to form HA_2^- in acetonitrile[4] and, indeed, P *decreased* with increasing [HA] but was only slightly dependent upon [A^-]. Furthermore, k_D refers to ion-pair dissociation and is thus dependent upon the dissociating power of the solvent which is in turn dependent upon [ROH]. This was allowed for, at constant [HA] (0·1 M), by use of the equation $\log (k_D/k_D{}^0) = \varrho\Delta Z$, where



k_D^0 refers to dissociation in pure acetonitrile, ΔZ is the difference in Z-value[5] between acetonitrile and the solvent in question, and Q is a constant. For large [ROH], $P = k_A/k_D$ and $\log P = \log (k_A/k_D^0) - Q\Delta Z$. Plots of $\log P$ against ΔZ for the alcohols studied tended to linearity for $\Delta Z > ca.$ 3, giving $k_A/k_D^0 = 4{\cdot}6$ and $Q = 0{\cdot}067$, using points for methanol, ethanol, n-propanol and s-butanol. Assuming constancy for all the alcohols, the expression for P becomes $P \times$ antilog $(Q\Delta Z)$. $k_D^0/k_A = 1 + k_{-D}[A^-])/(k_S[ROH])$. Experimental values of $P \times$ antilog $(Q\Delta Z)$. k_D^0/k_A were found to be linearly dependent upon $[ROH]^{-1}$ with intercepts close to unity. From the slopes, values of k_S relative to methanol were evaluated and compared with the relative nucleophilic activities of the alcohols in the perchloric and toluene-p-sulphonic acid-catalysed decompositions, derived as previously described.[3]

TABLE

Relative nucleophilic reactivities of alcohols toward 4,4′-*dichlorodiphenylmethyl cations in acetonitrile at* 30°

ROH	$C_6H_5\cdot CO_2H$	p-Me·$C_6H_4\cdot SO_3H$*	$HClO_4$*
Methanol	(1·0)	(1·0)	(1·0)
Ethanol	0·21	0·56	0·52
n-Propanol	0·11	0·59	—
s-Butyl alcohol	0·077	0·19	0·14
t-Butyl alcohol	0·027	0·040	0·023
p-Methylbenzyl alcohol	0·3	0·43	0·29
p-Chlorobenzyl alcohol	0·2	0·22	0·12

* From r-values[3] extrapolated to [ROH] = 0.

Clearly the alcohols show a wide (∼40-fold) variation in nucleophilic reactivity in the carboxylic acid reaction, but the pattern of results is similar to that for the reactions with the stronger acids, where the products are determined by competition between the alcohol and unchanged diazo-compound for a single carbonium ion intermediate. The differences between values in the Table for different catalysts suggest that the species which reacts with the alcohol may be a second type of ion-pair, rather than a free ion as depicted in the Chart.

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[4] J. F. Coetzee and G. P. Cunningham, *J. Amer. Chem. Soc.*, 1965, **87**, 2534.

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