The Decomposition of N-Nitroso-N-benzhydrylbenzamides and Its Relation to Product Partitioning of Benzhydryldiazonium and Diphenylcarbonium Benzoate Ion Pairs in Hydroxylic Solvents[1a]

E. R. Stedronsky,[1b] Joseph Gal, R. A. More O'Ferrall, and Sidney I. Miller[1c]

Contribution from the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616. *Received September 11, 1967*

Abstract: Three N-nitroso-N-benzhydrylbenzamides were allowed to decompose in 15 hydroxylic solvents and the fraction (R) of ester in the product (ester + ether) was measured. R was not sensitive to temperature (40–60°), the *para* substituents of the nitrosoamide, or the insolubility of the nitrosoamide in some solvents. R did change with solvent, from 0.24 in methanol to 0.78 in *t*-butyl alcohol, decreasing roughly as the polarity of the solvent increased. We propose that product partitioning occurs after the nitroso compounds rearrange to a diazo ester intermediate; in the *syn* form, this intermediate can give benzhydryl benzoate directly or benzhydryldiazonium benzoate ion pair; in the favored *anti* form, the intermediate probably gives more solvent-separated than contact ion pairs. The R values for our decomposition are lower than those for two related reactions, diphenyldiazomethane with carboxylic acid and benzhydryl benzoate solvolyses. Although several of the decomposition routes of the nitroso compounds merge with those from these two reactions at benzhydryldiazonium and diphenylcarbonium benzoate ion pairs, others branch off earlier and make the mechanistic pattern more complex.

Organic ions and ion pairs are often postulated as reaction intermediates,[2] but these species, which are often necessary to elucidate or refine a mechanism, may also make for loss of definition and focus. Where they are transients, it is usually difficult to "see," trap, or otherwise characterize solvated ions without perturbing them. In this paper, we consider two such elusive and ephemeral ion pairs, benzhydryldiazonium benzoate and diphenylcarbonium benzoate.

Ion pairs involving benzhydryl cations have been formed in a variety of reactions from the corresponding halides,[3] thiocyanate,[4] arenesulfonate,[5] nitrate,[6a] alcohol,[6b] thionbenzoate,[7] carbene,[8] etc. Unlike these, it appeared that the diphenylcarbonium benzoate pair could be generated in three different reactions:[9] diphenyldiazomethane (DDM) and benzoic acid; benzhydryl benzoate solvolysis; N-nitroso-N-benzhydrylbenzamide decomposition. If, in fact, the *same* ion pair were produced under the *same* conditions, three discrete processes should produce identical products along paths that led from the common ion pair. On the other hand, differences in the products would indicate mechanistic variations at some stage in the three reactions.[9] These mechanistic possibilities have been reviewed critically.[2]

Roberts, *et al.*,[10] Chapman, *et al.*,[11] and our group have provided data on ion pairs from the DDM reaction, under certain conditions (Chart II).[9] Goering, *et al.*, have provided data on ion pairs formed by benzhydryl benzoate solvolysis, under other conditions (Chart III).[12] White,[13] Huisgen,[14] Heyns,[15] and their coworkers have provided data on the decomposition of N-nitrosoamides, which however, did not involve the benzhydryl cation. Recognizing that the critical comparisons required identical ion pairs, several groups began to fill in the gaps: Winstein, *et al.*, looked at ester solvolysis;[16] White, *et al.*,[17] and our group examined the decomposition of N-nitroso-N-benzhydrylbenzamides (eq 1). Thus, it appeared that a detailed examination of the fate of their common ions would provide a fine probe of the mechanisms of three interesting processes as well as insight into the detailed behavior of an important ion pair, diphenylcarbonium benzoate. Since the benzhydryldiazonium ion could be involved with benzoate in two of the processes, this pair would also be considered. When we began this

$$p\text{-}XC_6H_4(C_6H_5)CHN(NO)COC_6H_4Z\text{-}p \xrightarrow[-N_2]{SOH} \underset{\mathbf{1}}{} \qquad (1)$$

$$p\text{-}XC_6H_4(C_6H_5)CHOOCC_6H_4Z\text{-}p \;(\mathbf{3}) + p\text{-}XC_6H_4(C_6H_5)CHOS \;(\mathbf{7})$$

a, X = Z = H; **b**, X = H; Z = NO_2; **c**, X = Cl; Z = NO_2

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work, some of the evidence for the three mechanisms was plausible, if incomplete, while other evidence was speculative.[2] Now, we are inclined to believe that two mechanisms overlap substantially but merge only partially with the third, as indicated in Charts I–III.

Experimental Section[18]

All of the inorganic chemicals and many of the solvents were reagent grade; other solvents were distilled before use. Boiling and melting points are uncorrected. Infrared (ir) spectra were taken on a Beckman IR 8 spectrophotometer; for quantitative ir analysis, we used a Perkin-Elmer Model 21 spectrophotometer. Micro-Tech Laboratories, Skokie, Ill., provided our elemental analyses.

The Schotten–Baumann procedure was used to prepare three amides: N-benzhydrylbenzamide, ν_{NH} 3304 and ν_{CO} 1633 cm^{-1}, mp 170–172° (lit.[6a] mp 174–176°); N-benzhydryl-*p*-nitrobenzamide, ν_{NH} 3318 and ν_{CO} 1622 cm^{-1}, mp 225–226° (*Anal.* Calcd for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85. Found: C, 72.42; H, 4.92); N-*p*-chlorobenzhydryl-*p*-nitrobenzamide, ν_{NH} 3393 and ν_{CO} 1638 cm^{-1}, mp 230–231° (*Anal.* Calcd for $C_{20}H_{15}ClN_2O_3$: C, 65.49; H, 4.12. Found: C, 65.52; H, 4.38). The appropriate acid chlorides and alcohols led to the three esters: benzhydryl benzoate, ν_{CO} 1710 cm^{-1}, mp 90–91° (lit.[19] 91.5°); benzhydryl *p*-nitrobenzoate, ν_{CO} 1718 cm^{-1}, mp 132–133° (lit.[20a] 131–133°); *p*-chlorobenzhydryl *p*-nitrobenzoate, ν_{CO} 1716 cm^{-1}, mp 120–121.5° (lit.[20a] 120–123°). Treatment of the appropriate carbinol with an excess of the lower alcohol and a few milliliters of concentrated sulfuric acid led to the ethers: benzhydryl ethyl ether, bp 94–96° (0.1 mm) (lit.[6a] 128–132° (1.2–1.4 mm)); benzhydryl methyl ether, bp 172–174° (33 mm) (lit.[20b] 86–90° (0.3 mm)); *p*-chlorobenzhydryl ethyl ether, bp 108° (0.15 mm) (*Anal.* Calcd for $C_{15}H_{15}ClO$: C, 73.02; H, 6.13. Found: C, 72.64; H, 5.94); *p*-chlorobenzhydryl methyl ether, bp 100° (0.2 mm) (*Anal.* Calcd for $C_{14}H_{13}ClO$: C, 72.26; H, 5.62. Found: C, 72.15; H, 5.40).

The preparation of one of three nitroso compounds (**1**) by a modification of White's procedure[13f] will be described. N-Benzhydryl-*p*-nitrobenzamide (5.0 g, 0.015 mol), anhydrous sodium acetate (5.0 g, 0.06 mol), and dichloromethane (50 ml) were placed in a three-necked, 500-ml flask, fitted with a mechanical stirrer and a thermometer, and cooled in an ice–water slush to *ca.* 0°. Dichloromethane (200 ml) was added to dinitrogen tetroxide (10 g, 0.11 mol), condensed in a trap at *ca.* −70°. This solution was added to the flask, and the mixture was stirred for *ca.* 1 hr at 0–5° and then poured into a filtration flask. The solvent was evaporated in a stream of dry air, or in a rotary evaporator. The yellow residue was triturated with 0.1 *M* sodium hydroxide (50 ml) and filtered. After three such treatments, the solid was washed with water until free of alkali, sucked free of excess water, and then air dried at *ca.* 25° for 2 hr. This material often contained some of the starting amide and the ester formed by decomposition, but it could be stored for several days at −10° without further decomposition. (The samples were not dried under vacuum, since this appeared to promote decomposition to the ester.) In general, it was found that reaction for 1 hr gave the best balance between the rate of formation and the rate of decomposition of the nitroso compound in solution. This compromise or "optimization" gave the following best samples: N-nitroso-N-benzhydrylbenzamide (ν_{CO} 1700 and ν_{NO} 1514 cm^{-1}) (**1a**), 89.8%; N-nitroso-N-benzhydryl-*p*-nitrobenzamide (ν_{CO} 1700 and ν_{NO} 1513 cm^{-1}) (**1b**), 80.1%; N-nitroso-N-(*p*-chlorobenzhydryl)-*p*-nitrobenzamide (ν_{CO} 1710 and ν_{NO} 1514 cm^{-1}) (**1c**), 74.8%.

Although we were able to separate **1b** from the amide by recrystallization, the yield was low (*ca.* 20%). The crude product was dissolved in a minimum of ether at 0°, diluted with an equal volume of Skellysolve B, and cooled to *ca.* −60°. Precipitation of the solid was slow and three fractions were taken. According to its ir spectrum, the middle fraction was free of amide but not of ester.

Analysis of N-Nitrosoamides.[18] Dimethylformamide (25 ml) was placed in an electrolytic beaker (250 ml), fitted with a three-hole stopper through which passed a buret tip, a gas inlet, and gas outlet tube. The outlet tube was connected to an oil bubbler. All operations were carried out under gently streaming prepurified nitrogen. After the system was flushed with nitrogen, potassium iodide (3 g) and concentrated hydrochloric acid (5 ml) were added to the beaker, and magnetic stirring was started. The solution was cooled to *ca.* 5° and a weighed sample of nitrosoamide was introduced. After 5 min, 20% aqueous sodium acetate (25 ml) was added, and the liberated iodine was determined with standard 0.01 *N* sodium thiosulfate. The "dead-stop" technique was used to determine the end point.[21]

$$Ar_2CHN(NO)COAr + HI \longrightarrow Ar_2CHNHCOAr + 0.5I_2 + NO \quad (2)$$

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

Duplicate determinations on *ca.* 0.1-g samples of **1** gave satisfactory precision: for **1a**, 89.8, 90.2, and 89.4%; for **1b**, 66.1 and 67.1%; for **1c**, 74.6 and 75.1%. The weight of ester plus amide could be estimated at this stage.

In an improved version of the basic method of analysis, the reaction medium consisted of glacial acetic acid, potassium iodide, and dissolved hydrogen chloride gas; the weighed sample was held in a "spoon" above the acid solution during the preliminary nitrogen sweep. It was then lowered into the solution where reaction took place; any nitrogen oxide generated was swept out, and the titration was completed. At no time was the beaker opened during these operations, for even traces of air (oxygen) could raise the iodine titer, according to the sequence

$$NO \xrightarrow{O_2} NO_2 \xrightarrow{HI} I_2 \quad (3)$$

Because the decomposition step in eq 2 was completed in <2 min, thermal decomposition according to eq 1 was probably negligible. A complete description of the preferred analytical method for N-nitroso compounds is given elsewhere.[22]

The composition of the starting material was found in the following way. Residues from the titrimetric determinations of the nitrosoamides were collected and treated with more water, and the solids were filtered off. The solids were dried, weighed, and made up to standard volume in chloroform. The weights of ester and amide in this solution were determined by ir analysis, in which the carbonyl absorptions of pure amide and ester were used to establish reference transmissions. The compositions of known mixtures of amide and ester were determined in this way and gave satisfactory checks on the analytical method. Taking into account the losses during the separation, that is, the discrepancy between the calculated *vs.* the weighed quantity of total solid, the individual percentages could be estimated. Thus, **1a**, which analyzed for 89.8% nitroso compound titrimetrically, showed 2.7% amide and 10.2% ester, or 102.7% total; **1b** analyzed for 66.6% nitroso compound, 15.5% amide, 16.5% ester, or 98.6% total. (Because of solubility problems with **1c** and related compounds, ir analysis could not be carried out.)

Decomposition of the Nitrosobenzamides. As indicated in eq 1 the thermal rearrangement and decomposition of the N-nitroso compounds leads to ester and ether, when the solvent is an alcohol, or ester and carbinol, when the solvent is water. Barring other decomposition routes and other products, we can define

$$R = \frac{[\text{ester}]}{[\text{nitrosoamide}]} = \frac{[\text{nitrosoamide}] - [\text{acid}]}{[\text{nitrosoamide}]} \quad (4)$$

For decomposition runs, a tared glass tube, sealed at one end, was filled with nitrosoamide (*ca.* 0.1 g) and weighed. The tube was dropped into an ampoule, which was cooled to *ca.* −60°. The desired solvent (10.0 ml at *ca.* 25°) was added to the ampoule. The ampoule was sealed, placed in a constant-temperature bath, and shaken vigorously for 3 min. Initially, the nitrosoamide solutions were deep yellow; after 20 min at 40°, the solutions turned pale yellow and gas evolution ceased. The ampoules were left in

(18) Most of this work was done once by E. R. S. In attempting to make our method of analysis general for *other* N-nitroso compounds than **1**, he encountered problems of reproducibility. J. G. was able to adapt the basic method of analysis, with variations, to several stable N-nitroso compounds; he then repeated much of the work done by E. R. S. and obtained essential agreement. Some minor differences can reasonably be traced to the analyses of our N-nitroso compounds. For this reason, we are inclined to weigh the results of J. G. more heavily than those of E. R. S., where they overlap. However, the data of E. R. S. is internally consistent and suitable for internal comparison.

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Table I. The Product Ratio, R, in the Decomposition of Three Nitrosoamides, p-$XC_6H_4(C_6H_5)CHN(NO)COC_6H_4Z$-$p$, in Several Solvents[a]

Code	Solvent	Temp, °C[b]	X = H, Z = H[c]	X = H, Z = NO_2[d]	X = Cl, Z = NO_2[e]	X = H, Z = NO_2[m]
1	CH_3OH	39.2	0.237[j]	0.256[j,k]	0.270[j,k]	0.238[n] (0.122)
2	C_2H_5OH	25.0	0.43[l]			
		39.2	0.387[g,k]	0.433[f,j,k]	0.464[k]	0.416[o] (0.341[p])
		60.0	0.387[g,k]	0.421[k]	0.461[k]	
3	80% CH_3COCH_3[h]	39.2	0.505[k]	0.485[k]	0.500[k]	0.460[q]
		60.0		0.469[k]	0.503[k]	
4	80% CH_3COCH_3[i]	39.2		0.550[k]		0.539[q]
		60.0		0.565[k]		
5	$C_6H_5CH_2OH$	39.2	0.536[g]	0.609	0.625	0.573[q]
		60.0	0.538[g]			
6	t-C_4H_9OH	39.2	0.765[g,j]	0.806[j]	0.849[j]	0.780[r] (0.674)
		60.0	0.762[g]			
7	sec-C_4H_9OH	39.2	0.623			0.637[r]
8	i-C_4H_9OH	39.2	0.557			0.576[q]
9	n-C_4H_9OH	39.2	0.522			0.540[q]
10	$C_6H_5CH_2CH_2OH$	39.2	0.600			
11	n-C_3H_7OH	39.2		0.517[f]		0.474[r] (0.426)
12	i-C_3H_7OH	39.2		0.622[f,j]		0.601[q]
13	$CH_3OCH_2CH_2OH$	39.2	0.428[g]	0.484		0.433[s]
14	$HOCH_2CH_2OH$	39.2		0.537[f,j]		0.548[s]
15	$CH_3CH(OH)CH_2OH$	39.2		0.531[f,j]		0.533[q]
16	CH_3COOH	25.0	0.40[l]			
17	CH_3COOD	25.0	0.42[l]			

[a] Each R, precise to ±0.03, is the mean of at least two to four separate determinations. The last column of R values was obtained by J. G.; the other columns of R values were obtained by E. R. S. and are considered to be self-consistent.[18] [b] The temperature was kept constant (±0.1°) in any given run, but the variation about the indicated temperature in different runs was 38.6–39.8 and 59.9–60.0°. [c] 89.8% nitrosoamide. [d] 66.6% nitrosoamide. [e] 74.8% nitrosoamide. [f] Also includes runs based on 80.1% nitrosoamide. [g] Also includes runs based on 55.4% nitrosoamide. [h] Acetone–water (v/v 80:20). [i] Acetone–water (v/v 90:10). [j] Heterogeneous decompositions. [k] The products were analyzed by tlc. [l] Reference 17. [m] The low values in parentheses derive from one preparation consisting of *ca.* 37% nitroso compound, except as indicated. [n] 71.5% nitrosoamide. [o] 61.2, 67.96, and 71.46% samples of nitrosoamide. [p] 59.7% nitrosoamide. [q] 68.0% nitrosoamide. [r] 71.5% nitrosoamide. [s] 61.2% nitrosoamide.

the bath for 3–4 hr more, then cooled to *ca.* 25° and opened; their contents were washed out completely with ethanol (10 ml) into a beaker.

The amount of acid in the product was determined by titration with standard 0.01 N sodium hydroxide; the end point was obtained electrometrically (Beckman Model G pH meter). Knowing the nitrosoamide content of our starting material, we obtained R from eq 4. All of the R values are given in Table I. Each R is the mean of at least two to four determinations for a given set of conditions.

In some of the solvents, the nitrosoamide was only partially dissolved. If the product ratio from the solid differed from that in solution, then the observed R should vary with the size of the sample. On the other hand, if the decomposition took place only in solution, then R should be independent of the size of the sample. In Table II are listed the results of decompositions where heterogeneity was apparent and where a range in sample size was examined. It is quite clear that R is essentially invariant in our runs, even though the nitrosoamide was present in two phases, solid and solution.

Table II. The Decomposition of Partially Dissolved Nitrosobenzhydryl Amides, p-$XC_6H_4(C_6H_5)CHN(NO)COC_6H_4Z$-$p$

Nitrosoamide	Solvent	Temp, °C	Sample wt, g	R
X = H, Z = NO_2	t-C_4H_9OH	39.0	0.10644	0.806
			0.09468	0.799
			0.15997	0.806
			0.12818	0.810
	CH_3OH	39.0	0.07867	0.257
			0.08758	0.255
			0.11951	0.256
	2-$CH_3OC_2H_4OH$	39.0	0.11089	0.489
			0.12626	0.482
			0.10325	0.481
X = H, Z = H	t-C_4H_9OH	59.9	0.09024	0.762
			0.08223	0.767
		39.5	0.08139	0.766
			0.06683	0.766

Products from the Decomposition of the Nitrosobenzamides. In order to be certain that only ester, acid, and ether (or carbinol) were produced, according to eq 1, we analyzed the product residues by thin layer chromatography (tlc). After neutralization of the acid by titration, the mixtures from runs under the same conditions were combined, sometimes acidified, often not. These were extracted exhaustively with dichloromethane. This solution was dried and evaporated. The oily residues were taken up in acetone (*ca.* 1 ml) and spotted on tlc plates coated with Brinkmann's aluminum oxide G. The plates were developed with benzene and the spots were located with an ultraviolet lamp.

The results of the tlc analyses are both uniform and simple. In no case was an extraneous spot observed on any plate. That is, we found the compounds, acid, carbinol, amide, ester, and ether, in order of increasing R_f values and properly matched to the reference compounds. For each tlc analysis, appropriate reference amides, esters, ethers, acids, amines, etc., were run simultaneously. Although not every solvent was analyzed in this way, all three nitrosoamides were checked under several conditions; the specific cases are given in Table I.

With regard to the sensitivity of the tlc analyses, we believe we could have detected any impurity at the 3% level, provided, of course, it responded to our tlc method. To determine this limit, 1 ml of an acetone solution of minor component (0.001 g) was added to 0.1 g of major component. Acetone was added or removed by evaporation until the solution was saturated in the major component. The results on tlc tests of this and similar solutions are shown in Table III.

As a further check, we took ir spectra of the products used in the tlc analysis. To the extent that there were no absorptions beyond those expected from the four compounds detected by tlc, the applicability of our quantitative analyses to process 1 may be taken as confirmed.

Decompositions in the Presence of Sodium Iodide and Sodium Azide. Sodium iodide (0.033 M) and **1b** in ethanol were treated in the usual way at 39°. Some free iodine developed, possibly according to eq 2 or by reaction with oxidant. By correcting for the acid consumed in eq 2 ($2H^+ \equiv I_2$), a corrected value of R = 0.40 was obtained. Evidently, the iodide ion had little if any effect on R.

Sodium azide (0.1384 M) and **1c** in 80% acetone were used for

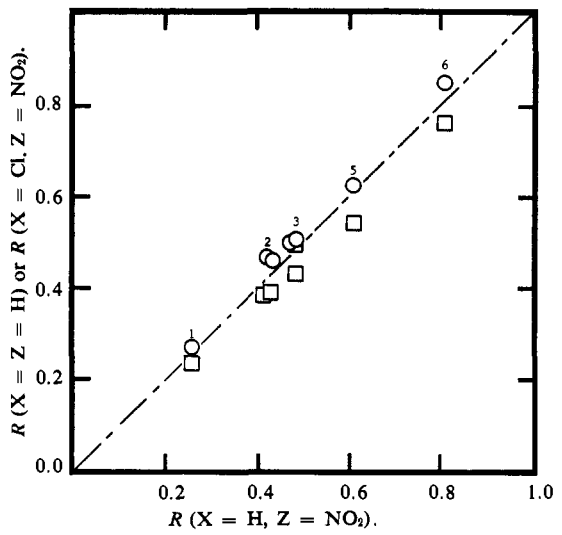


Figure 1. The product ratio, R, in the decomposition of three nitrosoamides, p-$XC_6H_4(C_6H_5)CHN(NO)COC_6H_4Z$-$p$, in several solvents. The dashed line is of unit slope. The squares are for R (X = Z = H) *vs.* R (X = H, Z = NO_2); the circles are for R (X = Cl, Z = NO_2) *vs.* R (X = H, Z = NO_2).

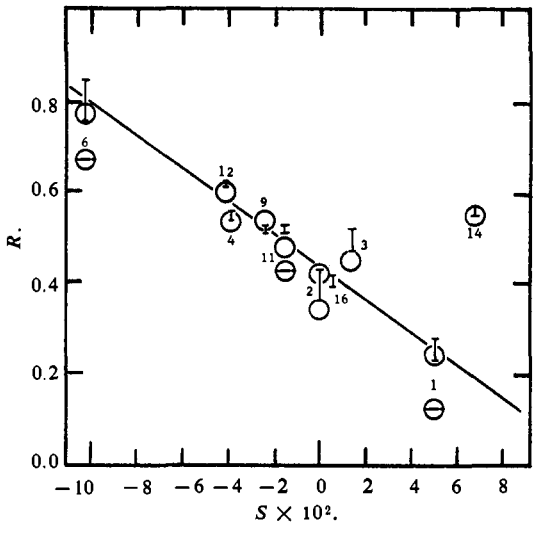


Figure 2. The effect of the solvent polarity on product partitioning, R, in the decomposition of N-nitroso-N-benzhydrylbenzamide in hydroxylic solvents (solvent polarity prameter, S, from ref 24; R values and solvents are given in Table I). Vertical bars, data of E. R. S.; circles, data of J. G.; circles with horizonal bars derive from the 37% sample (see Table I, footnote *m*).

runs at 39.5 and 60.0°. Compared to similar runs in which azide was absent, the end points in the acid titrations were ill defined and only *ca.* 20% of the theoretical amount of acid, based on nitrosoamide, was observed. Decompositions with azide present generated *p*-nitroaniline, the *p*-nitrobenzoate ester, *p*-chlorobenzhydryl alcohol, and *p*-chlorobenzhydryl azide (*p*-nitrobenzamide from the starting material was also found). Tlc analysis was used to identify the *p*-nitroaniline, -benzoate, and -benzamide; a faint spot between the aniline and ester was observed, but was not identified. Ir analysis of the product mixture indicated *p*-chlorobenzhydrol, ν_{OH} 3200–2600 cm^{-1}, and *p*-chlorobenzhydryl azide, ν_{N_3} 2100 cm^{-1} (our crude reference sample of benzhydryl azide had ν_{N_3} 2095 cm^{-1} (lit.[8] ν_{N_3} 2104 cm^{-1})).

Table III

Solution	Amide	Ester	Ether
Amide[c] (1%), ether[b] (99%)	+		+
Amide[c] (1%), ester[a] (1%), ether (98%)	+	+	+
Ether[b] (3%), amide[c] (97%)	+		+
Ether[b] (3%), amide[d] (97%)	+		+
Amide[d] (3%), ether[b] (97%)	+		+

[a] Benzhydryl *p*-nitrobenzoate. [b] Benzhydryl methyl ether. [c] N-Benzhydryl-*p*-nitrobenzamide. [d] N-Benzhydrylbenzamide.

Results

Although we learned how to make the N-nitrosoamides, our samples were impure, since a decomposition product (ester) was always present and the starting material (amide) was usually present. However, once we devised a method for estimating nitrosoamide quantitatively, our work could proceed. This analytical technique depended on the observation that strong acid denitrosates nitrosoamides and produces nitrosonium ion, which can oxidize iodide (eq 2).[22]

The N-nitrosobenzhydrylbenzamides decompose in hydroxylic solvents (SOH) according to eq 1. Of necessity, equivalent quantities of ether (or carbinol) and acid are produced. By estimating the quantity of nitrosoamide before reaction and the quantity of acid produced after reaction, we could obtain a measure of the product partitioning in eq 1. This is given by R, the fraction of starting compound converted to ester (eq 4).

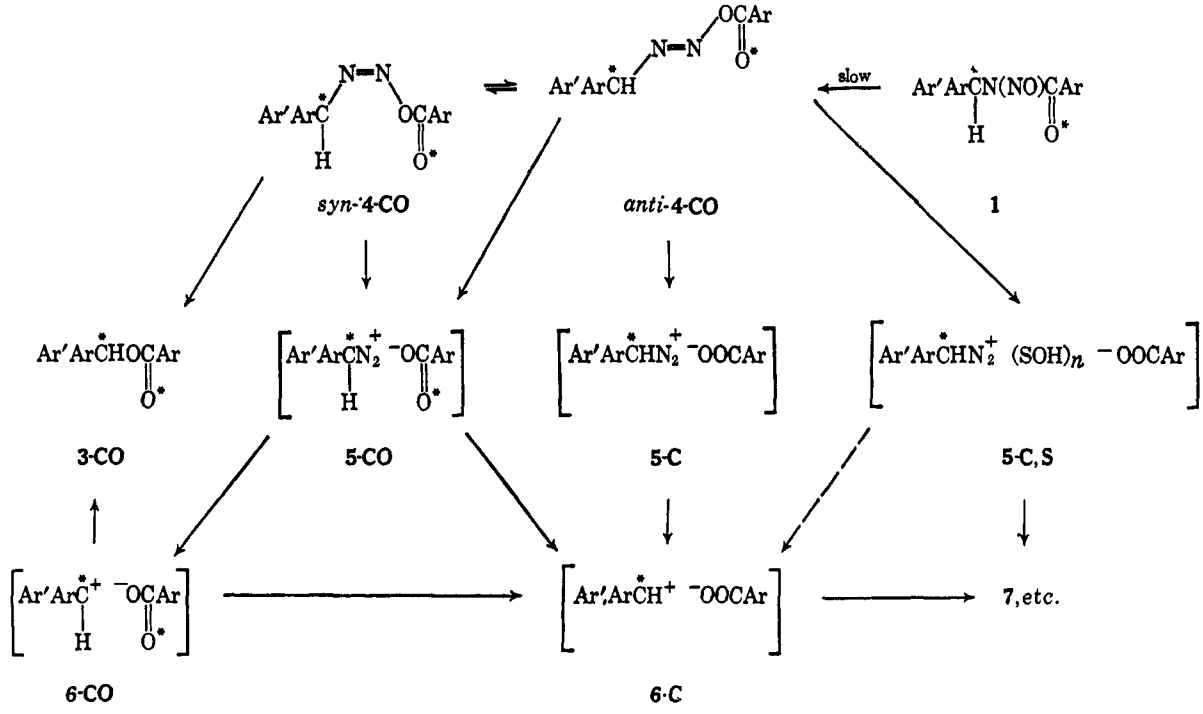
In order that both ratios in eq 4 be identical and apply to decomposition 1, it is necessary that paths to other products be excluded. For the decompositions in methanol, ethanol and aqueous acetone, tlc analyses of the products turned up no extraneous materials. In addition, infrared analysis of our products disclosed no unaccountable absorptions. Therefore, we have confidence in our R values.

Concerning decomposition 1 and R, we find that there is no sensitivity to the concentration of excess carboxylic acid present in the product, there is little if any temperature dependence, there is a barely perceptible structure dependence, but there is a substantial solvent dependence. Consider Table I. For a 20° variation, R is constant for the three compounds in six solvents, within experimental error. The structural variations in the nitrosoamides are remote from the reaction center, so that the absence of strong substituent effects on R is plausible. However, if one compares the first three columns of R values in Table I,[18] one will notice slight increases in R as the nitro group is put into the benzoate and the chlorine atom put into the benzhydryl portion. That this substituent effect is real, albeit marginal, is illustrated in Figure 1, by the deviations from the line.

Taking the values in Table I as a whole, there is a change of 0.24 to 0.8 or a factor of 3–4 in R with change in hydroxylic solvent. Although we have compared R with a variety of solvent properties or functions, *e.g.*, boiling point (bp), molecular weight (M), molar volume (V), pK,[23] viscosity (η), dielectric constant (ϵ), $(\epsilon - 1)/(2\epsilon + 1)V$, η/ϵ, etc., no general relation was found. A few limited correlations were apparent, *e.g.*, R was linear in boiling point, V, etc., for a few of the solvents, but the best correlation (Figure 2) was with Brownstein's S.[24] (Since other solvent polarity param-

(23) J. Hine and M. Hine, *J. Amer. Chem. Soc.*, 74, 5266 (1952).
(24) S. Brownstein, *Can. J. Chem.*, 38, 1590 (1960).

Chart I. For Continuation See Charts II and III; Ar ≡ C_6H_5 or p-C_6H_4; C, Optically Active; O, Oxygen-18



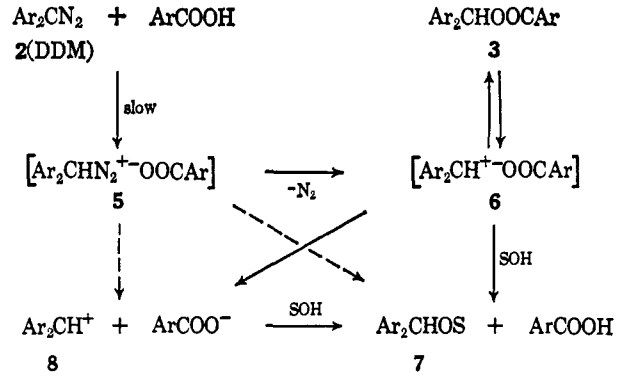
eters, *e.g.*, E_T, Z, δ, Ω, etc., are linearly related to S, correlations with these would also be expected.)[25] S is best characterized as a solvent polarity function, initially based on solvolytic rate data and spectral transition energies, but which has also been applied to equilibrium, ir, and pmr data.[24,25] It is not at all clear whether any detailed interpretation of our correlation is possible or why the most polar solvent, glycol (code 14), should deviate so markedly.

Discussion

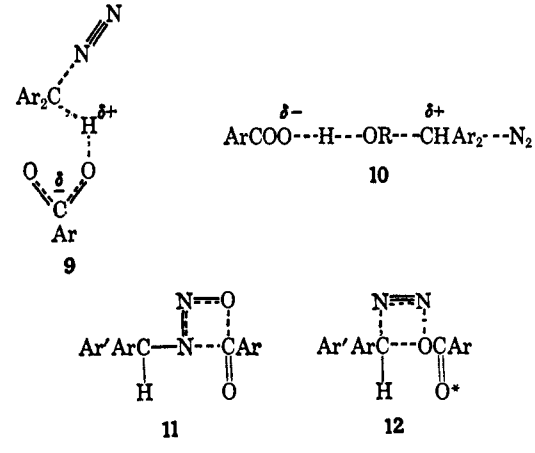
After reviewing the evidence for the mechanisms in Charts I–III and indicating some alternatives, we shall consider the question of their common paths and intermediates. By setting out the detailed mechanisms in these charts, we do not mean to imply that these are the exclusive or the generally accepted paths. They are perhaps best regarded as a partly speculative framework, which we favor and find useful for the specific systems at hand. Since dramatic changes in the character of closely related reactions may be observed with changes in solvent, structure, etc.,[2,26–29] our discussion will be limited to heterolytic processes usually involving diphenylcarbonium and carboxylate ions in hydroxylic solvents.

DDM Reaction (Chart II). It seems generally agreed that the first step involves a slow proton transfer from acid to the DDM,[2,9–11] as in **9**. Subsequent product partitioning (R) in ethanol shows little or no temperature dependence, isotope effect (k_H/k_D), or sensitivity to added benzoate, thiocyanate, or iodide.[9,10] In

Chart II. Ar ≡ C_6H_5



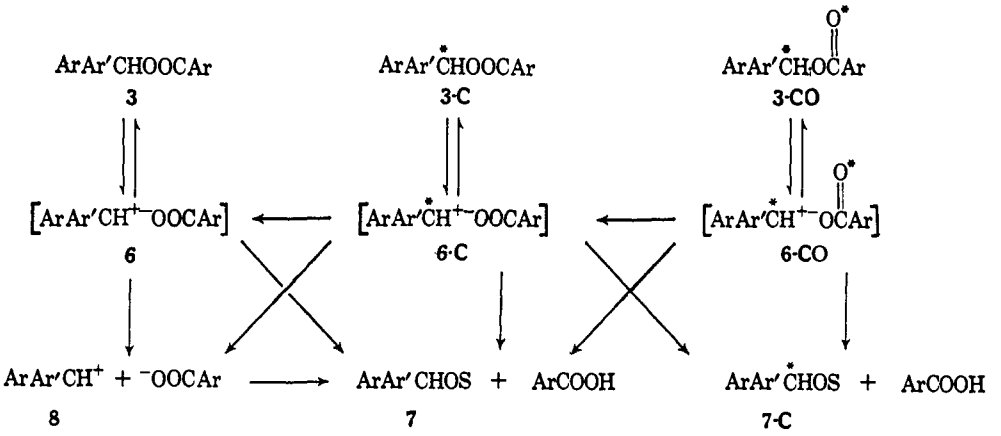
ethanol, variations in the structure of the attacking acid, with few exceptions, produce only small changes in partitioning, *e.g.*, benzoic R = 0.63, acetic R = 0.67, 2,6-dinitrophenol R = 0.68.[9] The R values do change from one alcohol to another, and sometimes show a much stronger dependence on the attacking acid, *e.g.*, in *t*-butyl alcohol.[11] For these reasons, it appeared that product



partitioning involved extremely fast, low-energy processes. To minimize any discrimination effects on R,

(25) H. F. Herbrandson and F. R. Neufeld, *J. Org. Chem.*, 31, 1140 (1966); C. Reichardt, *Angew. Chem. Intern. Ed. Engl.*, 4, 29 (1965).
(26) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, Chapter 12; C. G. Overberger, J. P. Anselme, and J. G. Lombardo, "Organic Compounds with Nitrogen–Nitrogen Bonds," The Ronald Press Co., New York, N. Y., 1966, Chapter 4.
(27) W. Kirmse and K. Horn, *Tetrahedron Letters*, 1827 (1967).
(28) M. C. Whiting, *Chem. Brit.*, 482 (1966).
(29) J. H. Bayless and L. Freedman, *J. Amer. Chem. Soc.*, 89, 147 (1967).

Chart III. Ar ≡ C_6H_5 or p-C_6H_4; C, Optically Active; O, Oxygen-18 Label



which would arise if several intermediates were involved in partitioning, we proposed that product proportions were controlled by the rate of diffusion of the paired diphenylcarbonium carboxylate ions out of their solvent cage.[9] It was also recognized that several solvent properties, *e.g.*, polarity, nucleophilicity, acidity, did influence R, but the over-all effect was complex.

An alternative product-partitioning mechanism has been proposed by Chapman, *et al.*[11] These workers favored product formation from a solvated benzhydryldiazonium carboxylate ion pair, in which nitrogen is ejected in SN2-like transition states, giving ester **3** or ether **7**. In this mechanism, because a proton is transfered in **10**, we would anticipate a substantial deuterium isotope effect on R which is not observed in ethanol.[9] Because of the SN2-like mechanism, we would also expect R to be sensitive to steric restraints on the acid site, yet 2-*t*-butylbenzoic acid, benzoic acid, and 2,6-dinitrophenol give similar R values in ethanol.[9,11] Thus, while we do not preclude product formation at the diazonium ion stage, we believe that less structured, but oriented transition states are more consistent with the observations in ethanol. However, where there is exceptional partitioning, *e.g.*, R = 0.8 for formic acid in ethanol,[9] or structural sensitivity, *e.g.*, R = 0.62–0.77 for benzoic acids in benzyl alcohols,[11] these objections no longer apply. Then, the possible formation of products directly from the benzhydryldiazonium carboxylate ion pair cannot be ignored.

Ester Solvolysis (Chart III). This reaction allows for finer distinction in the structure of ion pairs. By using optically active *p*-chlorobenzhydryl benzoate or ester labeled with oxygen-18 at the carbonyl, two groups have measured the over-all rate of solvolysis (k_s), the rate of racemization in the ester (k_{rac}), and the rate of oxygen-18 equilibration or scrambling in the two oxygen positions of benzoate (k_e).[12,16]

Although our scheme in Chart III appears to be somewhat more detailed than that used by Goering and Winstein, it is essentially theirs, except that we prefer to refine the notions of orientation and solvent separation.[30] In 80% acetone at 99.6°, both in the presence and absence of azide ion, the first-order constants (10^3 hr^{-1}) are[12a]

k_s	4.41	k_e	6.5	k_{rac}	2.76
$k_2(N_3^-)$	30	$k_e(N_3^-)$	5.9	k_{rac}	0

In this system, the partitioning is given by

$$R \leq k_e/(k_s + k_e) \quad (5)$$

This ratio is only a lower limit, because "identity" collapse from the doubly oriented ion pair (**6-CO**) without racemization or oxygen scrambling is unobservable. Since oxygen-18 scrambling is the fastest process ($k_e/k_{rac} > 1$), it has been taken as independent of the others (Chart III). Racemization and solvolysis are slower and have been assumed to involve prior or simultaneous oxygen-18 equilibration. It is worth noting that there is some retention of optical activity in the ether. This suggests that some ether must be formed from oriented ion pairs.[30] In the runs which included azide ion, *p*-chlorobenzhydrol and *p*-chlorobenzhydryl azide were produced with some retention of optical activity. Again, at least some of these products must be formed before racemization is complete. Since added azide had little effect on the scrambling process and an enormous effect on the subsequent steps, Goering, *et al.*, suggested that the azide intercepts a singly oriented, solvent-separated ion pair,[12a] perhaps

$$[\text{L-Ar'Ar}\overset{*}{\text{C}}\text{H}^+ (\text{SOH})_n\ ^-\text{OOCAr}]$$
6-C,S

Although we have used **6-C** at this stage, it appears to us that a choice between **6-C** and **6-C,S** is not yet possible.

N-Nitrosoamide Reaction (Chart I). This reaction is first order in N-nitrosoamide.[13a] Based on White's stereochemical and tracer studies of products, certain observations require mechanistic explanation. Recognizing that the data are scanty, and considering only the N-nitroso-N-(*sec*-alkyl)amides, *e.g.*, cyclohexyl, *dl*-phenylethyl, *sec*-butyl, and benzhydryl, we find:[13c,e,17] R varies with the *sec*-alkyl structure; only occasionally is R or the kind of ester product influenced by the presence of added carboxylic acid; R varies with the temperature; incomplete retention of optical activity and the labeled carbonyl oxygen is typical, but the per cent of retention of optical activity is usually greater in the ester; retention of optical activity and the labeled carbonyl oxygen in the ester is greater in polar solvents, *e.g.*, ethanol and acetic acid, than in nonpolar solvents, *e.g.*, methylene chloride; although retention of optical activity is observed in the ether,[7c] this is usually less than in the ester **3C**; the formation of diazo

(30) We shall use the term singly oriented to indicate that one of the partners of an ion pair is of known configuration, *e.g.*, [R^+−OC(=O*)-Ar] or [L-Ar'ArC*H+Cl−]; in the doubly oriented pair, both partners have defined configurations, *e.g.*, [L-Ar'ArC*H+−OC(=O*)Ar]. Solvent-separated pairs such as [$R^+(SOH)_nX^-$] may be oriented as in **5-C,S**.[12]

or carbene intermediates appears to be ruled out in polar solvents.[17] If we now consider only the N-nitrosobenzhydrylamides we find a curious, possibly accidental trend.[17] Although R varies drastically for a miscellaneous group of solvents, *e.g.*, methylene chloride, toluene, acetic acid, ethanol, the degree of retention of oxygen-18 and of optical activity in the product ester, which covered a rather narrow range (*ca.* 15%), was the same for any given solvent. Such a result would seem to require a rather simple reaction scheme: at the critical point, a choice is made between retention or no retention in the ester.

The pattern of product partitioning in our work, *i.e.*, the low sensitivity of R to "extra" carboxylic acid (Table II), to added sodium iodide (0.033 M), to the nitrosoamide structure, and to temperature change, and the high susceptibility of R to the solvolytic power of the solvent, **S**, complements that of White, *et al.*[13] In the presence of sodium azide (0.14 M) in 80% acetone,[31] there is evidence for *p*-nitroaniline and probably *p*-chlorobenzhydryl azide in the product, and the yields of ester, carbinol, and carboxylic acid are reduced. Presumably, the attack of azide on the nitrosoamide or the diazo ester could lead to *p*-nitroaniline through *p*-nitrobenzoyl azide in a series of steps; for this product at least, attack on ion pairs involving benzoate

$$\begin{matrix} Ar_2CHN(NO)COAr'' \\ \text{or} \\ Ar_2CHN{=}NOOCAr'' \end{matrix} + 2N_3^- \xrightarrow{H_2O} Ar_2CHN_3 + 2N_2 + Ar''NH_2 + CO_3^{2-} \quad (6)$$

ion is unlikely. To resolve the alternatives explicit in eq 6 further rate and product determinations are needed.[31]

The scheme given in Chart I differs in some details from those previously proposed. As Huisgen suggested, a slow four-center rearrangement of **1** yields diazoester, which breaks up rapidly. Certainly, such an ester is a plausible intermediate *en route* to the products; moreover, it makes a good analogy with the related decompositions of nitroamides in which N-oxydiazo esters can be isolated.[13a] It is interesting that the diazo ester, as it is first formed, is in the *anti* conformation, similar to **11** with respect to the diazo bond. The *anti* form of course is likely to be more stable than the *syn* form.[32]

A four-center reaction of the *syn*-diazo ester **4-CO** with ejection of nitrogen would yield the doubly labeled ester **3-CO** directly. Such a four-membered transition state (**12**) has precedent in the decomposition of diazonium anhydrides[33] or azoalkanes.[26] The one-step path on the left of Chart I might be termed the *stereospecific extreme.* Previous workers, including ourselves, have favored ionization (SN1) paths to the ester: **4-CO** → **5-CO** → **6-CO** → **3-CO**. Both kinds of route can lead to ester in stereospecific fashion. Thus, the stereospecific extreme is interesting and plausible, but not essential.

Now, the *anti* form (**4-CO**) could dissociate in the *anti* sense to give the solvent-separated ion pair (**5-C,S**), or fragment directly with possible help from the solvent, to give ether **7**, or solvent-separated ions **8**. This is the path along the right side of Chart I, which might be termed the *dissociation extreme.* It is not clear how much of the ether **7** is formed along the dissociation extreme, but since not all of the ether **7** is racemic,[17] it appears that some **7** must arise from paths to the left of the dissociation extreme.

In assigning a mechanism to the decomposition of the N-nitroso compounds, we face an interesting dilemma. In its gross features, this mechanism should have much in common with the other two reactions (Charts II and III). The products are the same, the effect of added ions seems similar, etc. It seems reasonable to suppose, therefore, that the *syn*, *anti*, and intermediate conformations of the diazo ester ionize to give diazonium ion pairs.[13c,14a] Down the middle paths of Chart I, the carboxylate ion *may* remain oriented within the diazonium ion pair, but it is highly probable that the oxygen atoms will become equivalent by the time nitrogen has departed.[13a] At this stage, this mechanism merges with those in Charts II and III. It is clear, however, that whatever the path, the degree of retention of optical activity always equals or exceeds the degree of scrambling of oxygen-18 in the ester.

In polar solvents, ionization of **4-CO** and dissociation of the ion pairs will be favored. This will cut down on the fraction of ester formed, as we have observed. Consequently, the retention of label in ester (**3-CO**) will be greater,[17] even though the total amount of ester will be less in the polar solvents. Although both the left- and right-hand paths in Chart I are of low energy, it might be expected that variations in the structure of the ions and in the temperature of the decompositions should produce some changes in R. All of these observations have been noted above.

One, Two, or Three Mechanisms. In Table IV and Figure 3 we compare R values obtained by different research groups. On the basis of nearly equal R values for ester solvolysis and the DDM reaction, Winstein and Diaz concluded that "the diazoalkane route for generating ion pairs leads to essentially the same ion pairs or spectrum of ion pairs in solvolysis."[16] Because their R values for the DDM reaction should probably be increased by a few per cent,[34] we believe that only the rough equality of the R values was demonstrated. In any case, it is recognized that the experimental R value for ester solvolysis must be equal to or lower (eq 4) than that for DDM, if the product forming steps are identical.[12,16,17] Nevertheless, the R values for ethanol and 80% acetone are close and have the proper relative magnitudes. Therefore, the existence of common product-partitioning steps for these two processes seems probable, although firmer evidence would be desirable.

If the preceding is true, there are at least two important consequences. As has been pointed out by us and

(31) Our chief purpose in using azide in our work was to have a comparison with Goering's ester data.[12a] It is curious that benzoyl azide is a postulated intermediate in both systems, but leads to *p*-nitroaniline only in ours.

(32) (a) The possibility that the diazo ester could give the ester in a concerted six-center process was considered some time ago.[15] We feel that this is not at all likely here, chiefly because it would lead to an ester with the labeled oxygen wholly in the ether position, which has never been found. There does not appear to be any strong theoretical objection to it, however, and insofar as nitrogen is lost from a six-membered ring in an oxadiazinone,[32b] there may be even a rough analogy for it. (b) M. Rosenblum and H. Moltzan, *Chem. Ind.* (London), 1480 (1956).

(33) C. Rüchardt and B. Freudenberg, *Tetrahedron Letters*, 3623 (1964).

(34) R(DDM) in ethanol of Winstein and Diaz shows a larger temperature dependence[16] than that reported previously;[11] it is also a few per cent lower than that reported by several groups.[9,11,17] The value of $\epsilon^{EtOH}_{525\,m\mu}$ 94.8 for DDM is lower than the 102 reported by us.

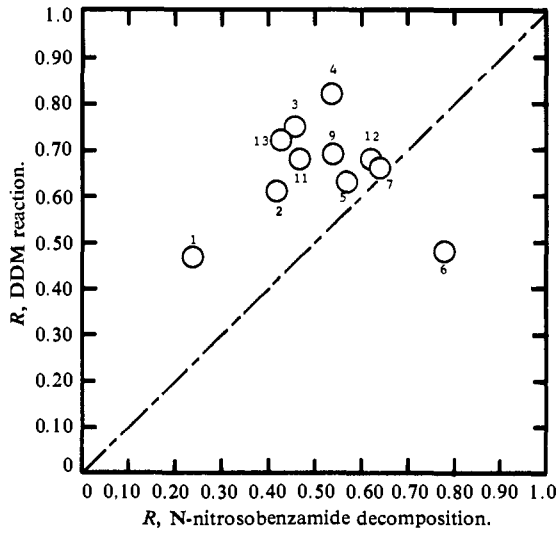


Figure 3. Product partitioning, R, in the DDM reaction and N-nitroso-N-benzhydrylbenzamide decomposition. R values and the solvent code are given in Table I. The DDM data are chiefly those of Chapman, *et al.*, privately communicated.[11]

by Winstein and Diaz, the benzhydryldiazonium ion is not involved in the product-determining steps.[9,16] Second, hot, or vibrationally excited, carbonium ions, which are often called upon to explain puzzling points of mechanism,[17] do not seem to be necessary.

Table IV. Product Partitioning, R, in the Reactions of Three Benzhydryl Molecules in Hydroxylic Solvents[a]

Code	Solvent	$Ar_2CHN(NO)$-COAr[b]	Ar_2CN_2, HOOCAr	Ar_2-CHOOCAr
1	CH_3OH	0.24	0.46–0.49[e]	
2	C_2H_5OH	0.42[c]	0.58–0.63[d,e]	0.47[f]
3	80% CH_3COCH_3	0.46	0.75[f]	
4	90% CH_3COCH_3	0.54	0.82[f]	0.745[g]
5	$C_6H_5CH_2OH$	0.57	0.63[e]	
6	*t*-C_4H_9OH	0.78	0.45–0.50[e]	
7	*sec*-C_4H_9OH	0.64	0.66[e]	
9	*n*-C_4H_9OH	0.54	0.69[e]	
11	*n*-C_3H_7OH	0.47	0.68[e]	
12	*i*-C_3H_7OH	0.62	0.68[e]	
13	$CH_3OCH_2CH_2OH$	0.43	0.70–0.75[e]	

[a] R is defined in eq 4. The R values were often determined for different temperatures or *para* substituents in the aryl moiety, but the dependence on these factors appears to be insignificant for the present comparison. For the course of these reactions, see Charts I–III. [b] Data from Table I. [c] $R = 0.42$.[17] [d] Reference 9. [e] Reference 11. [f] Reference 16. [g] Reference 12c.

Our present data will permit a three-way comparison, parts of which have already been made in preliminary communications.[16,17] In the two solvents for which ester solvolysis and nitrosoamide decomposition data are available, the R values are different, and the discrepancy can only increase if the ester value were increased (eq 4). Then, White and Elliger showed that the extents of oxygen-18 equilibration and racemization in the ester product from these two processes are different: k_{eq}/k_{rac} = 40/31 for nitrosoamide decomposition[17] and 6.5/2.8 for ester solvolysis.[12a] Clearly, the product-forming steps in these two processes are different.

Noting low R values for the decomposition of **1** in ethanol (Table III), White and Elliger concluded that the nitrosoamide decomposition and the DDM reaction produced different ion pairs, or, if the intermediates were the same, the proportions were different, and the product ratios would also be different.[17] Our data for several solvents show definitely that R values for the two reactions are independent (Figure 3). Indeed, these are rarely close, for any given solvent, and they do not appear to be related. Now, as we have already pointed out, partitioning steps at the benzhydryldiazonium ion pair stage, whether this is "hot" or "cold," does not seem applicable here. The production of different ratios of similar ions (**6**, **8**, **11**), each one of which has its characteristic partitioning ratio, could lead to different R values for **1** and **2**, but one would be compelled to place the whole burden of variable R values on the slight structural difference of **6-CO** from **6-C** and **6**. We must therefore seek product-forming steps for the mechanism of nitrosoamide decomposition which differ from those in the DDM reaction. It is generally accepted that the first ion pair **5** from DDM must be oriented as in **9**.[9,11,17] White and Elliger point out that the ions would be farther away from one another when formed from **4-CO** and this would lead to less ester (lower R) from N-nitrosoamide decomposition.[17] Our mechanism in Chart I is fairly explicit as to how this could take place. If the left and right extreme paths from **4-CO** were excluded, the mechanisms from N-nitrosoamide and DDM would essentially merge, unless memory effects and/or hereditary differences were transmitted through similar ion pairs. It seems improbable that such effects could persist beyond the diazonium ion pairs. As we have seen, the left-hand branch in Chart I is not a required part of the mechanism; the right-hand branch from the *anti* form does seem essential because it permits one to differentiate the nitrosoamide decomposition mechanism from the other two by lowering the yield of ester. It is also consistent with the trend in R with solvent polarity (Figure 2). How useful this idea will be remains to be seen.

Acknowledgment. We wish to thank Professor Chapman and his colleagues for making their DDM results available to us.[11]