lends itself to matching of shapes of hosts and guests. CPK molecular models of the complexes of **2**, **13**, **14**, **6**, and **7**, which have the highest K_a values, indicate three linear $^+NH\cdots O$ bonds and three $^+N\cdots O$ interactions are possible. In no other hosts are these conditions met. Hosts **2**, **13**, and **6** particularly lend themselves to structural modification that shape the cavity for binding selectively different alkylammonium ions.

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(7) (a) Carbon and hydrogen analyses were within 0.30% of theory; (b) ^1H NMR spectra in $CDCl_3$ were as expected; (c) 70 eV mass spectra gave parent ion.

(8) In the preparation of **1–5,** a solution of 0.37 mol of diol and 0.37 mol of dibromide in dry $(CH_2)_4O$ was added (2.5 h) to a stirred mixture of 1 mol of NaH in dry $(CH_2)_4O$ at reflux under N_2. The mixture was stirred at 25° for 12 h. In the preparation of **6–11,** NaH was added to the stirred mixture of diol and ditosylate in dry $(CH_2)_4O$, and the resulting mixture was refluxed for 48 h. Products **1–8** were purified by gel permeation chromatography with a 100 Å styragel column (10 or 20 ft by ⅜ in.) packed in $(CH_2)_4O$.

(9) Treatment of *p*-cresol with K_2CO_3 and $H_2O–CH_2O$ at 50° for 3.5 h gave (45%) 2,6-bis(hydroxymethyl)-4-methylphenol, mp 123–124° (note 7), which with $(CH_3)_2SO_4$ in acetone and K_2CO_3 gave (95%) 2,6-bis(hydroxymethyl)-4-methylanisole, mp 103–104° (note 7). This diol with thionyl bromide in $CHCl_3$ at 25° gave (95%) 2,6-bis(bromomethyl)-4-methylanisole, mp 66–68° (note 7).

(10) Treatment of racemic 2,2′-bishydroxy-3,3′-bis(hydroxymethyl)-1,1′-binaphthyl (R. C. Helgeson, J. M. Timko and D. J. Cram, *J. Amer. Chem. Soc.*, **95,** 3023 (1973)) and CH_3I in acetone with K_2CO_3 at reflux (24 h) gave (90%) 2,2′-bismethoxy-3,3′-bis(hydroxymethyl)-1,1′-binaphthyl, mp 178–179° (note 7).

(11) Treatment of racemic 2,2′-bishydroxy-3,3′-bis(hydroxymethyl)-1,1′-binaphthyl with $KOC(CH_3)_3$ and $ClCH_2OCH_3$ in $(CH_2)_4O$ at 25° gave (55%) 2,2′-bis(methoxymethoxy)-1,1′-binaphthyl as an oil (note 7).

(12) The initially formed cycles were hydrolyzed in a mixture of 1:40:80 concentrated HCl, $CHCl_3$, and CH_3OH at 25° (2 h), and **9–11** were purified by silica gel chromatography and crystallization.

(13) The method was suggested by the work of C. J. Pedersen (*Fed. Proc.*, **27,** 1305 (1968)) and developed by Thomas L. Tarnowski, whom we thank. Stock solutions were prepared at 25° of 0.075 M host in $CDCl_3$, and of 0.0150 M (Li, Na, K, and NH_4 picrates) or 0.0100 M (Rb and Cs picrates) salt solutions in deionized water. In a 12-ml centrifuge tube were placed 0.10 ml of the $CDCl_3$ and 0.50 ml of the more or 0.75 ml of the less concentrated salt solutions. The mixture successively was stirred magnetically, centrifuged, stirred, and centrifuged. If very yellow, 0.010 ml, and if light yellow 0.050 ml, of the $CDCl_3$ layer was diluted to 5.0 ml with spectrograde CH_3CN (for blanks, deionized water-saturated $CDCl_3$ stock solutions were similarly diluted). The uv absorbance at 380 nm of the solutions was determined and that of the blanks (~0.003) subtracted (Beckman DU spectrophotometer, slit 0.6). The extinction coefficients in CH_3CN of standard solutions of the six picrates prepared similarly from the stock aqueous solutions were found to be 16 900 and cation and concentration independent over the range used for K_a determinations. The distribution coefficients $\times 10^3$ ($K_d = [\text{picrate in } CDCl_3]/[\text{picrate in } H_2O]$) of the six salts in the absence of host were found to be: Li, 1.42; Na, 1.74; K, 2.55; Rb, 6.37; Cs, 5.41; NH_4, 4.02. For each host and guest, values of R were determined [in H_2O-saturated $CDCl_3$ at equilibrium, R = (equivalents of guest)/(equivalents of host) = 5 (blank-corrected absorbance)/(16 900)], and ranged from 0.000 18 to 0.256. Values of K_a were calculated from the equation, $K_a = R/[K_d(a - 0.075cR)^2(1 - R)]$, where a = molarity of the stock aqueous solutions and c = (volume of $CDCl_3$ layer)/(volume of H_2O layer). Values of K_a calculated from similarly treated aliquots of the equilibrated aqueous layer gave within experimental error the same values as those determined from the $CDCl_3$ layer.

(14) Corey-Pauling-Koltun (CPK) molecular models of the hosts were fitted with a series of graded ball bearings whose diameters matched those of the alkali metal ions. We thank Professor J. M. Lehn for suggesting the use of ball bearings for this purpose.

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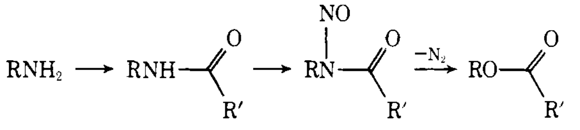
Effect of Pressure on the Stereochemistry of Ion Pair Collapse in the *N*-Nitrosamide Deamination

Sir:

The decomposition of *N*-nitrosamides (**1**) is a reaction useful for the conversion of amines into esters;[1] it involves the acylation of the amine, nitrosation of the amide, and, finally, the thermal decomposition of the nitrosamide:



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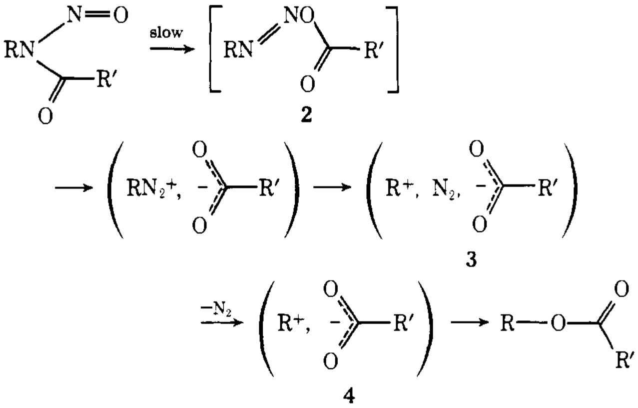
The mechanism of the last step in this sequence is thought to be formation of diazoester **2** in the rate controlling step, ionization, detachment of nitrogen to give loose (nitrogen-separated) ion-pair **3**, and, finally, collapse via the tight pair stage **4**. A variety of evidence has been amassed in support of this pathway. These studies have included the use of product and solvent studies,[1] bridgehead amino-substituted polycyclic compounds,[2] and optically active amines;[3] a comparison with the corresponding nitro derivatives;[4] ^{18}O-scrambling studies;[5] and a comparison with the same ion-pairs from other sources[6] and a comparison of secondary and tertiary amines.[3] While the reaction is characterized primarily by retention of configuration, some inversion (intramolecular[5]) does occur.[7] The inversion presumably results from rotation of the carbonium ion and circumnavigation of it by the anion prior to the ester forming step.



Pressure effects on reactions involving ion-pairs have been described in several cases. All of these studies have a single feature in common: pressure promotes the formation of tight ion pairs from neutral compounds, of loose pairs from tight ones, and of separate ions from ion-pairs. Thus, the rate of isomerization which sometimes accompanies ester solvolysis (and which presumably results from internal return) is accelerated by pressure[8] but not as much as the rate of solvolysis itself;[9] the tight-loose equilibrium of lithium fluorenide in THF is shifted toward the latter species by pressure;[10] and the N/O-alkylation ratio of the sodium salt of fluorenone oxime under pressure shifts in the direction characteristic of the free ions rather than of the pair.[11] The ionic rate[12] and equilibrium constants[13] for literally hundreds of substances have been compiled, and not a single genuine case appears to be known in which ionization is suppressed by the application of high pressures.[14]

We have now made some measurements of the effect of pressure on the degree of racemization accompanying the deamination of optically active *N*-nitroso-*N*-*p*-chlorobenzhydrylbenzamide (**5**) in methylene chloride at 25° (50–100 mg in 20 ml). These solutions were allowed to decompose for 24 h; *ir* spectra were compared before and after to

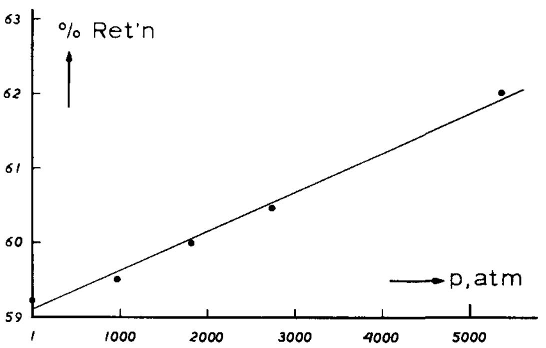
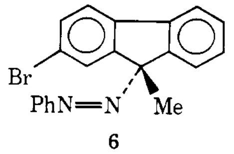


Figure 1. The effect of pressure on the stereochemistry of deamination of **5**.

ensure complete reaction, and parallel experiments were carried out in the same glassware at atmospheric pressure. On the basis of the evidence just quoted it is reasonable to assume that the lifetime of the loose pair should increase under pressure and that the rates of tight ion-pair formation and of collapse of the latter to covalent product should be retarded. Thus at face value the equilibration of the enantiomeric loose pairs should correspondingly be promoted by the application of pressure.

However, this is not the case, as is indicated by the data in Figure 1; retention is clearly favored under pressure. It can be readily shown from a steady-state treatment that $V_c^{\ddagger} - V_e^{\ddagger} = RT\,\partial \ln (100/r - 1)/\partial p$, where e and c denote equilibration and collapse of the loose pair and where r is the percent retention. When the appropriate plot is made, it is found that the transition state for inversion is 0.55 cm^3/mol *more* voluminous than that for retention. On the basis of the literature quoted above,[8-14] a large volume increase must occur when the loose pair becomes tight. This increase will be especially large in a solvent as methylene chloride: at least 10 cm^3/mol, and possibly much more.[10] The measurements reported here therefore indicate that inversion also has a large positive activation volume (larger than that of retention by 0.55 cm^3/mol).

Our interpretation of this fact is that the loose pair racemization is inhibited by viscosity increases. Pressure is known[18] to cause drastic increases in the viscosity of liquids; accordingly, diffusion controlled reactions are retarded regardless what volume changes characterize the rapid steps. Related pressure effects have been described by Neuman, who has found pressure induced increases in the ratio of cage to escape products in radical reactions;[19a] furthermore, changes were also observed in the distribution of cage products, such as recombination and disproportionation products.[19] These changes were ascribed to pressure induced viscosity changes, and their effect on rotational motions of the radicals in the cage. Independent indications that this is so are provided by work of Johnson and Seltzer,[20] who have found that the mere use of more viscous media led to increased retention in the decomposition of resolved azo compound **6**, and by results of Bartlett and McBride,[21] showing that complete retention can be ensured in the photodecomposition of **7** by the use of a solid, low temperature matrix.



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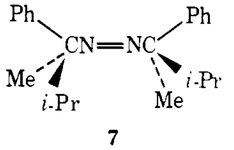

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In a similar experiment, we allowed the decomposition of **5** to occur in the solid phase (crystals) at room temperature. The product was purified, and subsequently observed to have (65.8 ± 0.10%) retained and (34.2 ± 0.10%) inverted configuration. If this point is assumed to lie on the same straight line as the high pressure results, the corresponding pressure would be about 13 000 atm. Most organic solids show a volume decrease of 5–15% on fusion, and most liquids have a compression of about 25% at 13 000 atm; it is interesting that the result in the solid phase is indeed similar to that in highly compressed methylene chloride.[22]

We may summarize our observations with the statement that they comprise the first evidence for viscosity effects on the behavior of ion pairs.

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The Intramolecular Hydrogen Bond in Malonaldehyde[1]

Sir:

Recently two quantum mechanical calculations have been published[2] dealing with the structure of the internally hydrogen-bonded form of malonaldehyde (Figure 1). We have partially analyzed the microwave spectra of a number