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Deamination of Aliphatic Amines in Ethanol

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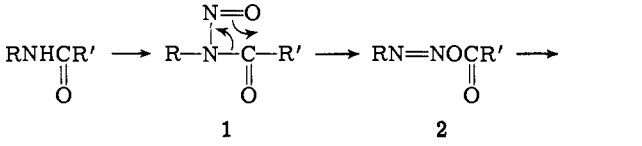
Abstract: The methyl and ethyl *N*-butyl-*N*-nitrocarbamates based on *n*-butylamine, *sec*-butylamine, and *tert*-butylamine were decomposed in ethanol and in other solvents, and the product distributions were measured. These results and those from related nitrocarbamates are discussed in terms of inert gas-separated ion-pair intermediates that appear to be characteristic of deamination reactions. The product distributions indicate a gradual change in mechanism with carbonium ion stability; discontinuities as a function of the substituent were not seen.

Deamination reactions, in which carbonium ions are formed by the loss of nitrogen or nitrous oxide from diazonium ion-like intermediates, are profoundly different from their solvolysis counterparts.[1,2] The present study involving the decomposition of a series of nitrocarbamates in ethanol was undertaken to elucidate these differences and also to clarify results reported for the deamination of primary and secondary alkylamines in acetic acid.

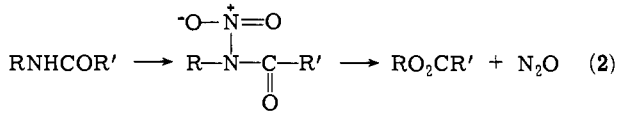
We chose the general "nitrosoamide" approach to deamination[1,3] rather than the triazene[1,4] or nitrous acid[1,2] methods because of the clean, unimolecular nature of the reaction. In the nitrosoamide approach, the reactant (**1**) is "primed" in that it bears a nitroso group, which together with the nitrogen of the amine (or amide) forms the nitrogen gas that is produced (eq 1); thus, no other reagent need



1 **2**

$$(R^+, N_2, R'CO_2^-) \longrightarrow N_2 + ROCR' \quad (1)$$

be present in the reaction mixture. *N*-Nitroamides (**3**) are also "primed"; these derivatives yield nitrous oxide and the corresponding esters (eq 2).[5] Specifically, we used *N*-nitro-



$$RNHCOR' \longrightarrow R{-}N(NO){-}C(=O){-}R' \longrightarrow RO_2CR' + N_2O \quad (2)$$

3, R′ = alkyl or O-alkyl

carbamates (**3**, R′ = O-alkyl) as the primed molecules[5b,6,7,8] in this study, because all members of the series R = primary, secondary, and tertiary are stable enough to be isolated and purified; in no other "primed" series investigated is this true.

A reactive solvent was used to act as a scavenger for carbonium ion intermediates. Solvent-derived products were expected from carbonium ions that had escaped domination by the counterion, whereas the carbonate ester product (eq 2) was expected from noninterceptible carboxylate ion pairs (Chart I).[1,7] Although acetic acid has been used as a scavenger in the past,[1] we used ethanol in this study because of a serious side reaction of acetic acid. Acidic solvents, in general, exchange with the counterion of reaction intermediates (e.g., **7**) in proportion to their acidities (frontside exchange).[1,3d] Thus, the decomposition of a nitrosobenzamide (eq 1, R′ = C_6H_5) in acetic acid yields a benzoate ester (the intramolecular product) and also an acetate ester; the latter stems in part from frontside exchange and in part from a scavenging of the carbonium ions, e.g., from **8**, by the solvent.[1,3d] Ethanol as the solvent functions only, or largely, in the latter capacity because of its relatively low acidity.

In the present study, the methyl *N*-nitrocarbamates[6b] of *n*-butylamine (**4a**), *sec*-butylamine (**4b**), and *tert*-butylamine (**4c**) (Chart I) and also the corresponding ethyl esters (**5a–c**) were decomposed in ethanol and in other solvents (Table I).

Discussion

Products. The decomposition of methyl *N*-nitrocarbamates **4a–c** in inert solvents yields the corresponding carbonate esters, olefins, nitrous oxide, carbon dioxide, and methanol (Chart I, Table I).[5a,6b] In a reactive solvent such as ethanol, in addition to the above products (which constitute the intramolecular portion of the reaction), solvent-derived products are formed, namely the butyl ethyl ethers. Prolonged reaction times are required for the decomposition of the *n*-butyl derivatives (**4a** and **5a**) and, in these cases, ester

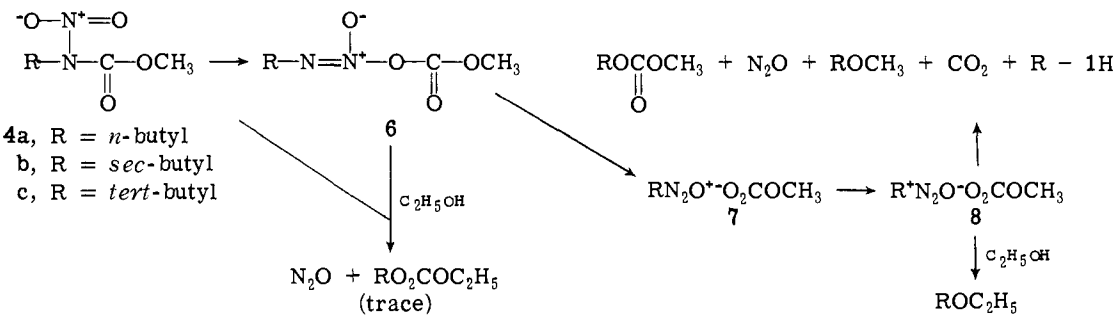
Table I. Decomposition of *N*-Alkyl *N*-Nitrocarbamates at 105°[a]

Runs	Compd	R′	Solvent	R″	Isomers	Products, %[b] $C_4H_9OCO_2R''$	C_4H_9OR''	C_4H_8
			Series A					
1	n-$C_4H_9N(NO_2)CO_2R'$	Methyl (4a)	Ethanol	Methyl	(*n*-Butyl)[c]	19, 19	0.1, 0.1	32, 34
					(*sec*-Butyl)	3, 4	<0.1, <0.1	
				Ethyl	(*n*-Butyl)	0.1, 0.2	18, 16	
					(*sec*-Butyl)	<0.1, <0.1	28, 26	
2		Ethyl (5a)	Ethanol	Ethyl	(*n*-Butyl)[d]	19	18	32
					(*sec*-Butyl)	3	28	
							sec-Butyl Products	
3	sec-$C_4H_9N(NO_2)CO_2R'$[e]	Methyl (4b)	Ethanol	Methyl		15, 15	0.4, 0.4	61, 59
				Ethyl		*f*	23, 25	
4		Ethyl (5b)	Ethanol	Ethyl		13, 14	24, 23	63, 63
							tert-Butyl Products	
5	t-$C_4H_9N(NO_2)CO_2R'$[e]	Methyl (4c)	Ethanol	Methyl		2, 2	<0.1, <0.1	65, 65
				Ethyl		*f*	33, 32	
6		Ethyl (5c)	Ethanol[g]	Ethyl		4, 2	29, 29	67, 69
7		Ethyl (5c)	Methanol	Methyl			55, 53	43, 44
				Ethyl		2, 3	<0.1, <0.1	
8		Ethyl (5c)	Dichloromethane	Ethyl		1.4, 1.4	<0.1, <0.1	98, 98
9		Ethyl (5c)	Nitrobenzene[h]	Ethyl		7, 8	*f*	93, 92
10		Ethyl (5c)	Acetonitrile[i]	Ethyl			3.0	65

Compd	Series B (Ethanol Solvent) Products, %[b]	
N-(1-Norbornyl)-$N(NO_2)CO_2C_2H_5$[j] (5d)	1-Norbornyl-OCO-C_2H_5 16	1-Norbornyl-O-C_2H_5 84
N-(1-Adamantyl)-$N(NO_2)CO_2C_2H_5$[j] (5e)	1-Adamantyl-OCO-C_2H_5 23	1-Adamantyl-O-C_2H_5 77
N-Benzhydryl-N(NO)COC_6H_5[k] (9)	Benzhydryl-OCC_6H_5 43	Benzhydryl-O-C_2H_5 57

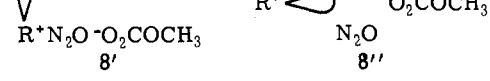
[a] Decomposition conditions, additional products, and absolute recoveries are tabulated in the Experimental Section. [b] Normalized to 100%. [c] Methyl ethyl carbonate (14, 17%) was also formed. [d] Diethyl carbonate (12%) was also formed. [e] No isomerization of the butyl group was detected in the ether or carbonate ester, and no methyl ethyl carbonate or diethyl carbonate was detected (<0.01%). [f] Not detected by GLC analysis. [g] Similar results were obtained by procedures A and B (Experimental Section). [h] Several minor (<1.0%) unidentified materials were observed. [i] *N*-*tert*-Butylacetamide (31.5%) also formed. [j] Reference 8. [k] E. H. White and C. A. Elliger, *J. Am. Chem. Soc.*, 89, 165 (1967).

Chart I



interchange products are also formed. The butyl ethyl carbonates, methyl ethyl carbonate, and diethyl carbonate that are formed (Table I) presumably arise via "ester interchange" with species **4**, and less likely with **6**. The butyl methyl and butyl ethyl carbonates themselves are stable in ethanol under the reaction conditions.

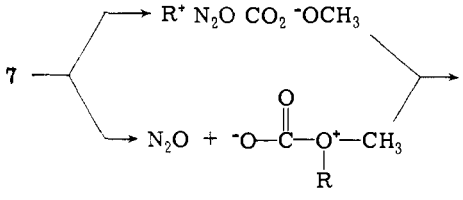
Reaction Intermediates. It is our view that most of the reaction products stem from the inert gas-separated ion pair **8**[7] (an additional pathway is available for primary systems, see below) and that considerable disorder exists in the solvent cage containing **8**.[1,8,9] It is convenient to treat **8** as a mixture of species ranging from sets of ions fully separated by inert gas molecules and with the carbonium ion oriented toward interaction with the solvent (**8′**) to sets in which the inert gas molecule is off the carbonium ion-counterion axis, and the carbonium ion is oriented to give ion-pair interactions (**8″**).[8] The latter sets appear to be noninterceptible,



yielding the corresponding esters even in reactive solvents.[8] Species **8′** in the present case would lead to the butyl ethyl ethers and also to olefins. In the case of the decomposition of ethyl *N*-nitro-*N*-(1-adamantyl)carbamate (**5e**) in a solvent such as dichloromethane (where the carbonium ion-solvent interactions are weak) all of the **8′** sets can apparently rearrange to **8″** sets eventually to form the ester.[8] This interconversion does not appear to be possible when olefins

can be formed. For example, in the present system, the decomposition of the *tert*-butyl derivative **5c** in dichloromethane (Table I) yielded mostly isobutylene (98%) accompanied by ~1.5% of *tert*-butyl ethyl carbonate.[6b] In ethanol (Table I), an additional product, *tert*-butyl ethyl ether (29%), was formed—at the expense of the isobutylene (67%). The yield of ester at 2-4% was not sensibly different from the yield in the dichloromethane run, and it was also similar to the yield in nitrobenzene, a more polar solvent than ethanol.[10] It thus appears that the solvent-derived product (ether) and the olefin arise from a common intermediate (suggested to be **8'**) which, in nonreactive solvents, leads only to the olefin.

The decomposition of the methyl nitrocarbamates (**4**) in ethanol led to small amounts of the butyl methyl ethers; these products stem from either a "2-gas" deamination, or more probably from attack of the carbonium ion at the second nucleophilic site of the counterion (eq 3). Ample evi-



$$ROCH_3 + N_2O + CO_2 \quad (3)$$

dence exists which indicates that carbonium ions formed in deamination are highly reactive and nonselective.[1,8]

In the *n*-butyl series (**4a** and **5a**), considerable *sec*-butyl products are formed (Table I). The solvent-derived products contain a far larger ratio of *sec*-butyl to *n*-butyl products (1.6) than the intramolecularly formed esters (0.19). Similarly, it had been noted before that the solvent-derived products in deamination were formed more highly racemized than the intramolecularly derived products.[3b,11,12] Apparently the intermediates escaping domination by the counterion have longer lifetimes or are less stabilized by interactions with nearest neighbors (and thus have more positive character) than intermediates leading to intramolecular products.

Solvent Effects. The decomposition of methyl *N*-nitro-*N*-*tert*-butylcarbamate (**4c**) in ethanol [a solvent in which a portion of the inert gas-separated ion pairs (**8'**) was scavenged by the solvent to form *tert*-butyl ethyl ether] was outlined in the previous section. A "reverse" experiment was also carried out (Table I) in which ethyl *N*-nitro-*N*-*tert*-butylcarbamate was decomposed in methanol. The same suite of products was formed as before, but the ether yields were much higher (54 vs. 29%). The lower olefin yields in methanol relative to ethanol probably are a result of the greater solvent polarity,[13] although the smaller size of the methanol molecule may also enhance the rate of ether formation. Finally, acetonitrile as the solvent proved to be fairly reactive, scavenging ~32% of the carbonium ions to form *N*-*tert*-butylacetamide.

Quantitative Results. To better detect trends in the effect of structure on product distribution, the total ester yields (intramolecularly formed products), the total ether yields (solvent-derived products), and the total olefin yields were tabulated (Table II). In most studies of this type, the ratios of products are discussed as a function of some regular change in the structure of the reactants.[14] In the present case, as an example, the ester/ether ratios for the 1, 2, and 3° butyl systems are 0.5/0.6/0.07. A rigorous interpretation of trends in product ratios is impossible at the present time. The trends could be interpreted if the ratios were derived from the absolute rate constants of various competing

Table II. Decomposition of Methyl Nitrocarbamates 4a–c in Ethanol at 105°

Compd	Products, %		
	Total ester	Total ether	Total olefin
4a	23	44	33
4b	15	25	60
4c	2	33	65

paths; however, in no case of solvolysis or deamination have the absolute rates been determined. In the present case, the change in the ester/ether ratio from 0.5 for *n*-butyl to 0.07 for *tert*-butyl could arise from a decrease in the rate of ester formation, an increase in the rate of ether formation, a selective diversion of intermediates from ester formation to olefin formation, etc. Where only two products are formed, the trends can usually be interpreted rationally; when three or more products are formed, about the only attack available is a qualitative examination of the data (e.g., as in Figure 1).

The most obvious trend in Figure 1 is the increase in olefin production in the series 1, 2, 3° butyl. Such trends are common,[15] and presumably they stem from the increasing number of β hydrogens in the series, the increase in the stability of the olefins formed, and the increase in the steric requirements for ester and ether production. The only unusual feature in the data (Figure 1) is the minimum in the ether yield for **4b**. This observation is almost certainly an artifact of the abnormally high ether yield in the primary butyl case, a result of the occurrence of a new reaction pathway in the primary case—a displacement reaction. Evidence for the displacement reaction in primary systems is the overall inversion of configuration observed in the butyl acetate obtained from the deamination of 1-deuterio-1-butylamine in aetic acid (~84% inversion, 16% retention).[16] Such a reaction mode is especially favored in the primary case because of the longer lifetime of intermediates and for steric reasons. Presumably a displacement by the solvent on species **6** or **7** is involved.[17]

The above results and discussion are relevant to conclusions that have been drawn from the deamination of 1-octyl and 4-octylamines by Whiting et al.[18] The amines were deaminated in acetic acid via the nitrous acid, nitrosobutyramide, and triazene approaches. Intramolecularly formed products were observed in addition to solvent-derived products. The ratio of these products was 0.04 for 1-octyl and 0.7 for 2-octyl in the nitrosobutyramide series, for example. The authors interpreted the change in these ratios in terms of the relative rates of bond breaking to the nitrogens (eq 4 and 5). They proposed that in the secondary case, the R–N

$$\text{(pri)}\ R{-}N{=}N{-}X \longrightarrow R{-}N^{+}{\equiv}N + X^{-} \longrightarrow R^{+} + N_2 + X^{-} \longrightarrow \text{products} \quad (4)$$

$$\text{(sec)}\ R{-}N{=}N{-}X \longrightarrow R^{+} + N_2 + X^{-} \longrightarrow \text{products} \quad (5)$$

and N–X bonds cleave synchronously, and "the R^+ fragment is liberated close to X^-, and bears different relationships to X^- and to an analogous external nucleophile Y^-" whereas, in the primary case, "diffusion must equate X^- and Y^-". In our opinion, the trend in the ratios (0.04 → 0.7) does not support these conclusions. In the first place, trends in ratios cannot be rigorously interpreted, especially when three or more products are formed (earlier discussion). Secondly, acetic acid was used in this study, and the occurrence of "frontside" exchange[1,3d] with acidic solvents will complicate matters in that the acidity of the solvent is a variable. Finally, the lower value for the primary system is almost certainly a result of the occurrence of a displacement reaction (see earlier discussion). In the present study—the decomposition of nitrocarbamates of *n*-, *sec*-, and *tert*-

butylamine in ethanol—the product distribution changes continuously over the range of alkyl groups examined, indicating a gradual change of reaction mechanism.

In systems forming only two products, the ratios of product yields are easier to interpret since only two rates are involved: the rate of formation of the intramolecular product and the rate of formation of the solvent-derived products. The ester/ether ratios for compounds of this type based on 1-norbornylamine, 1-adamantylamine, and benzhydrylamine show a trend of increasing values for this series (Table I, series B),[19a] probably a result of the greater selectivity of the more stable carbonium ions. The trend is highly damped, however, a result which supports the view that the deamination reaction is insensitive to the nature of the carbonium ion formed, relative to the situation in solvolysis.[1,19b] Earlier results leading to this conclusion were the insensitivity of stereochemical and O-18 scrambling results to the nature of the carbonium ions formed. This insensitivity is reasonable in view of the low activation energy expected for reactions in which nitrogen is the leaving group.[1,2,20]

In our view, it is reasonable that the breaking of the two bonds to nitrogen in deamination becomes more synchronous as the carbonium ion stability increases, but it appears that the trend is a weak one, and that there are no discontinuities in the series studied to date.

$$R{-}N{=}N{-}X \longrightarrow R{-}N^{+}{\equiv}N\ X^{-} \longrightarrow R^{+}N_2X^{-} \longrightarrow \text{products}$$

Experimental Section

Analytical Procedures. Infrared spectra were obtained with a Perkin-Elmer Infracord (Model 337) and NMR spectra with a Varian A-60 instrument with tetramethylsilane as an internal standard. The decomposition reactions were analyzed via quantitative gas chromatography (Disc integrator) on a Varian Aerograph (Model 1800) instrument equipped with the following columns: (A) 12 ft × 0.13 in., Carbowax 20M (10%) on Chromosorb W (60–80 mesh); injector 125°, detector 150°, column isothermal 50° (4 min) then programmed to 140° (4°/min); flow rate 30 ml/min (He). (B) 150 ft × 0.01 in., stainless steel, Ucon LB-550-X (R) Perkin-Elmer wall-coated tubular column; injector 125°, detector 150°, column 25°, flow rate 30 ml/min. Column A was used to obtain the yield data, column B afforded separation of the *n*-, *sec*-, and *tert*-butyl methyl and ethyl ethers. The quantitative GLC data for each component in the reaction mixture were obtained from calibration curves by plotting the area ratio of the product:naphthalene (internal standard) vs. the weight ratio of product:naphthalene. The identity of each decomposition product was established through GLC analysis on two different columns, supported by peak enhancement with authentic materials. A qualitative infrared analysis of a *N*-*tert*-butylnitrocarbamate decomposition mixture (vide infra) confirmed the presence of the products detected by GLC. The isomeric nitrocarbamates and their decomposition products were found to be stable under the GLC conditions used. Melting points (Thomas-Hoover capillary apparatus) and boiling points are uncorrected.

Materials. Dinitrogen tetroxide, 2-methylpropene, and nitrous oxide were obtained from Matheson Gas Products and potassium *tert*-butoxide from Alfa Products. The isomeric butyl methyl and ethyl ethers were obtained from Fluka AG or Eastman Organic Chemicals. Methyl and ethyl chloroformate were also obtained from Eastman and used as received. The nitric acid (red fuming, sp gr 1.59–1.60) was purchased from Fisher Scientific Co. and acetic anhydride and anhydrous methanol from Baker Chemical Co. The absolute ethanol was used as received from Publicker Industries Inc.

Methyl and Ethyl Carbamates. The *N*-*n*-, *sec*-, and *tert*-butyl derivatives of methyl and ethyl carbamate were prepared from the requisite amines and methyl or ethyl chloroformate by standard literature procedures.[21]

Ethyl *N*-Nitro-*N*-*tert*-butylcarbamate.[22] Nitric acid (red fuming) (15.0 g) was added dropwise to acetic anhydride (20 ml, 0.21 mol) at ca. −60°. Ethyl *tert*-butylcarbamate (5.0 g, 0.034 mol) in acetic anhydride (20 ml, 0.21 mol) was added dropwise to the stirred acid solution over a 20-min period at the same temperature.

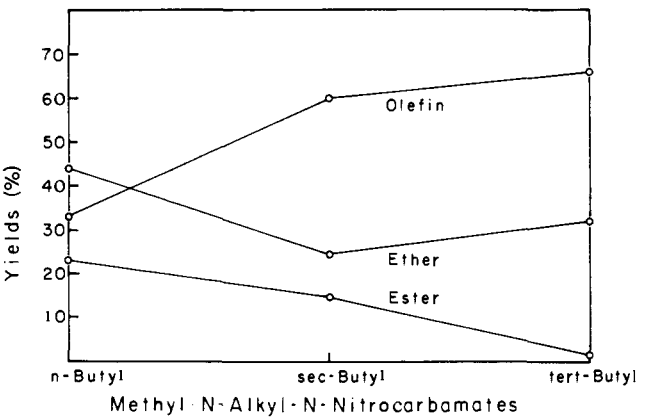


Figure 1. Yields of products for the decomposition of a series of methyl *N*-butyl-*N*-nitrocarbamates in ethanol at 105°.

After addition, the temperature of the mixture was allowed to rise to 0°, and the yellow solution was stirred for an additional 20–30 min. The mixture was poured into 300 ml of ice–water, and the yellow oil was extracted with 3 × 50-ml portions of ether. The combined ether layers were washed with 4 × 50-ml portions of cold 10% sodium carbonate solution and 3 × 25-ml portions of cold distilled water. After drying over sodium sulfate, the ether was removed by rotary evaporation, and the yellow residue was distilled (4.2 g, 0.022 mol, 64%): bp 49–51° (0.4 mm) [lit.[6c] 56° (2 mm)]; λ_{max} (95% C_2H_5OH) 237 nm (ϵ 2430) and 328 (21) [lit.[6d] λ_{max} (C_2H_5OH) 239 nm (ϵ 2690)]; ir (CCl_4) 1773 and 1748 (C=O)[23] and 1603 and 1557 cm^{-1} (N-NO_2); NMR ($CDCl_3$) δ 1.32 (t, 2.9 H, J = 7.3 Hz, CH_2CH_3), 1.53 [s, 9.1 $C(CH_3)_3$], and 4.34 (q, 2.0, J = 7.3 Hz, CH_2CH_3).

Methyl *N*-Nitro-*N*-*tert*-butylcarbamate. This methyl ester was prepared in 91% yield by the procedure used for the ethyl derivative: bp 23° (0.045 mm) [lit.[23] 32° (0.1 mm)]; ir (CH_2Cl_2) 1785 and 1760 (C=O) and 1605 and 1550 cm^{-1} (N-NO_2).

Ethyl *N*-Nitro-*N*-*sec*-butylcarbamate. The compound was prepared in 73% yield by the method given above for the tertiary isomer: bp 37° (0.15 mm); ir (CCl_4) 1765 and 1740 (C=O) and 1680 and 1660 cm^{-1} (N-NO_2); NMR ($CDCl_3$) δ 0.95 (t, 3.0 H, J = 7.5 Hz, OCH_2CH_3), 1.26–2.12 (m, 8.4, $CH_3CH_2CHCH_3$), 4.4 (q, 2.0, J = 7.5 Hz, OCH_2CH_3), and 4.57 (m, 1.0, CHN).

Ethyl *N*-nitro-*N*-*n*-butylcarbamate was prepared in 81% yield by the method described above for the tertiary isomer: bp 50–51° (0.025 mm); ir (CCl_4) 1775 and 1735 (C=O) and 1580 cm^{-1} (N-NO_2).

Ethyl *tert*-Butyl Carbonate. A solution of ethyl chloroformate (8.7 ml, 0.091 mol) in 250 ml of ether (distilled from $LiAlH_4$) was cooled to 0° with stirring. Potassium *tert*-butoxide (6.8 g, 0.061 mol) was added portionwise to the stirred solution over a period of 2.5 hr, a slow nitrogen purge was applied throughout the reaction. After filtration and solvent removal, distillation afforded the desired material (4.0 g, 0.027 mol, 45%): bp 139–140° (lit.[24] 140–143°); ir (CCl_4) 1738 cm^{-1} (C=O); NMR (CCl_4) δ 1.25 (t, 2.7 H, J = 7.0 Hz, OCH_2CH_3), 1.45 [s, 10.8, $C(CH_3)_3$], 4.03 (q, 2.0, J = 7 Hz, OCH_2CH_3).

Methyl Ethyl Carbonate. A solution of methyl chloroformate (9.5 g, 7.7 ml, 0.1 mol) in 50 ml of anhydrous ether was added dropwise with stirring to a solution of pyridine (7.9 g, 8.0 ml, 0.1 mol) and ethanol (4.6 g, 5.8 ml, 0.1 mol) in 200 ml of anhydrous ether at 0°. After additional stirring, work-up, and distillation, GLC analysis revealed that a small amount (ca. 4%) of diethyl carbonate had also formed. Preparative GLC (column A) yielded the desired material: bp 103–104° (lit.[25] 107°); ir (CCl_4) 1750 cm^{-1} (C=O); NMR (CCl_4) δ 1.26 (t, 3.0 H, J = 7 Hz, CH_2CH_3), 3.7 (s, 3.0, OCH_3), and 4.12 (q, 2.1, J = 7 Hz, OCH_2CH_3).

Authentic samples of ethyl *sec*-butyl carbonate and ethyl *n*-butyl carbonate were prepared as described for ethyl *tert*-butyl carbonate. After distillation, each carbonate was purified further via preparative GLC (column A).

Decomposition Methods. Decomposition of Alkyl *N*-Nitro-*N*-*n*-, *sec*-, and *tert*-butylcarbamates. General Procedure A. The nitrocarbamate (ca. 0.2 mmol) was placed in a predried (120°) glass tube with 2.0 ml of the appropriate solvent. The solution was degassed

during three freeze–pump–thaw cycles at ca. 0.05 mm. After sealing in vacuo, the tube was placed in a preheated oil bath at the requisite temperature for a specified period of time. After the decomposition was complete, the solution was chilled (Dry Ice–acetone bath), and the tube was opened. A solution of naphthalene, the GLC internal standard, was added, the reaction tube was sealed with a rubber septum, and the reaction mixture was analyzed via quantitative GLC.

General Procedure B. The dried reaction tube was charged with a 1.0-ml aliquot of the nitrocarbamate (ca. 0.02 *M*) and naphthalene, the GLC standard, in the appropriate solvent. Except for the addition of the internal standard, procedure A was followed for the remainder of the decomposition and analysis.

Control reactions revealed that all the ethers and carbonates produced during the decompositions of the *N*-nitrocarbamates were stable in ethanol at 105° for at least the time duration of the requisite decompositions.

Half-Life Determinations for the *N*-Nitro-*N*-*n*-, -*sec*-, and -*tert*-butylcarbamates. The nitrocarbamates were decomposed as described in general procedure B; however, the decompositions were not taken to completion. The initial GLC nitrocarbamate:naphthalene ratios were compared with the ratios obtained after partial decomposition. The half-lives for the nitrocarbamates were [solvent, temperature (deg), and half-life]: (ethyl *N*-nitro-*N*-*tert*-butylcarbamate) ethanol, 105 ± 2°, 10.5 ± 1.0 min; ethanol, 78°, 2.7 hr; ethanol, 50°, 80.4 hr; methanol, 105 ± 2°, 12.3 ± 1.0 min; dichloromethane, 105 ± 2°, 14.6 ± 0.3 min; (ethyl *N*-nitro-*N*-*sec*-butylcarbamate) ethanol, 105 ± 2°, 6.8 hr; (ethyl *N*-nitro-*N*-*n*-butylcarbamate) ethanol, 105 ± 2°, 67.3 hr. The half-life calculations are based on first-order kinetics for the decompositions.[6b] The rate constants (sec^{-1}) for the decomposition of the nitrocarbamates in ethanol at 105° were *tert*-butyl, 1.1×10^{-3}; *sec*-butyl, 2.8×10^{-5}; *n*-butyl, 2.7×10^{-6}. These constants compare favorably with the values obtained from an extrapolated Arrhenius plot of literature data[6b] from the decomposition of *O*-methyl nitrocarbamates in decane: *tert*-butyl, 4.0×10^{-4}; *sec*-butyl, 9.33×10^{-6}; *n*-butyl, 4.0×10^{-7}.

Decomposition of Alkyl *N*-Nitro-*N*-*tert*-butylcarbamates. Qualitative Analysis. An infrared analysis of a typical ethyl *N*-nitro-*N*-*tert*-butylcarbamate–ethanol reaction mixture (run neat) revealed the presence of nitrous oxide (2220 cm^{-1}) and carbon dioxide (2330 cm^{-1}). After quenching the reaction mixture in water, extraction with carbon tetrachloride and analysis revealed the presence of *tert*-butyl ethyl ether (957 cm^{-1}), *tert*-butyl ethyl carbonate (1740 cm^{-1}), and 2-methylpropene (3070, 1655, and 890 cm^{-1}), bands for carbon dioxide and nitrous oxide were also present.

Quantitative Analysis. The data obtained from decompositions in several solvents under various reaction parameters are summarized in Table I, or else below in the following order: solvent, temperature, general procedure, molarity of decomposition solution, time, absolute percent recovery, and miscellaneous products not reported in Table I.

Methyl *N*-Nitro-*N*-*n*-butylcarbamate (Run 1). Duplicates: ethanol, 105 ± 2°, A; 0.249, 0.287; 288, 290 hr; 100, 85. Methyl ethyl carbonate (14 and 17%, respectively) and methyl *N*-*n*-butylcarbamate (5 and 4%) were also formed.

Ethyl *N*-Nitro-*N*-*n*-butylcarbamate (Run 2). Ethanol; 105 ± 2°; B; 0.03; 471 hr; 87. Diethyl carbonate (12.0%) and ethyl *N*-*n*-butylcarbamate (4%) were also formed.

Methyl *N*-Nitro-*N*-*sec*-butylcarbamate (Run 3). Duplicates: ethanol; 105 ± 2°; A; 0.263, 0.199; 46, 48 hr; 93, 101. Methyl *N*-*sec*-butylcarbamate (1.9 and 1.4%) was also formed.

Ethyl *N*-Nitro-*N*-*sec*-butylcarbamate (Run 4). Duplicates: ethanol; 105 ± 2°; B; 0.031; 61.4 hr; 86, 77. No ethyl *N*-*sec*-butylcarbamate could be detected (<0.01%) by GLC analysis.

Methyl *N*-Nitro-*N*-*tert*-butylcarbamate (Run 5). Duplicates: ethanol; 105 ± 2°; B; 0.063; 1.5 hr; 79, 77. Methyl *N*-*tert*-butylcarbamate (1.1 and 0.7%) was also formed.

Ethyl *N*-Nitro-*N*-*tert*-butylcarbamate (Run 6). Duplicates: ethanol; 105 ± 2°; B; 0.03; 1.5 hr; 88, 90. Ethyl *N*-*tert*-butylcarbamate (1.1 and 1.2%) was also formed. By procedure A, a 0.157 *M* solution in 1.5 hr at 105° led to 76% of products. Other runs: (A) Ethanol; 105 ± 2°; A; 0.232, 0.18 hr; ethyl *tert*-butyl carbonate (5), ethyl *tert*-butyl ether (24), 2-methylpropene (72), ethyl *N*-*tert*-butylcarbamate (0.7); 63. Because of insufficient reaction time, starting material (ca. 10%) was also present. (B) This decomposition was similar to run A except that the stirred solution contained sodium carbonate (0.632 mmol): ethanol; 105 ± 2°; A; 0.106; 0.18 hr; ethyl *tert*-butyl carbonate (4), ethyl *t*-butyl ether (24), 2-methylpropene (72), ethyl *N*-*tert*-butylcarbamate (0.7); 64. Because of insufficient reaction time, starting material (ca. 10%) was also present. (C) Ethanol; 78°; B; 0.229; 24 hr; ethyl *tert*-butyl carbonate (6), ethyl *tert*-butyl ether (37), 2-methylpropene (58), ethyl *N*-*tert*-butylcarbamate (0.6); 60. (D) Ethanol; 50°; B; 0.229; 648 hr; ethyl *tert*-butyl carbonate (5), ethyl *tert*-butyl ether (32), 2-methylpropene (63), ethyl *N*-*tert*-butylcarbamate (0.5), 80. In ethanol solvent the *N*-nitro-*N*-*tert*-butylcarbamate decompositions afforded, in addition to the products listed, 2-methyl-2-propanol (<0.5%).

Ethyl *N*-Nitro-*N*-*tert*-butylcarbamate in Methanol (Run 7). Duplicates: methanol; 105 ± 2°; B; 0.038; 1.5 hr; 99, 99. Ethyl *N*-*tert*-butylcarbamate (1.5 and 0.8%) was also formed.

Ethyl *N*-Nitro-*N*-*tert*-butylcarbamate in Dichloromethane (Run 8). Duplicates: dichloromethane; 105 ± 2°; B; 0.033; 1.5 hr, 98, 102. 2-Methyl-2-propanol and 2-chloro-2-methylpropane were not detected; however, ethyl *N*-*tert*-butylcarbamate (0.5 and 0.3%) was formed.

Ethyl *N*-Nitro-*N*-*tert*-butylcarbamate in Nitrobenzene (Run 9). Duplicates: nitrobenzene; 105 ± 2°; A; 0.039; 1.5 hr, 81, 85.0. 2-Methyl-2-propanol and ethyl *N*-*tert*-butylcarbamate were not detected; however, several minor (<1.0% each) materials were observed.

Ethyl *N*-Nitro-*N*-*tert*-butylcarbamate in Acetonitrile (Run 10). 105 ± 2°; A; 0.28; 48 hr; 71. Ethyl *tert*-butylcarbamate (0.1%) was formed. Ethyl *tert*-butyl carbonate was not detected; however, if formed, it may have decomposed during the extended reaction time. A run on a larger scale (acetonitrile; 105 ± 2°; A; 0.2) afforded, after removal of volatile materials, *tert*-butylacetamide (20%, mp 95–96.5°) [lit.[26] 96.5–97.5°].

Control Reactions. Ethyl *tert*-Butyl Ether Formation. A solution of 2-methylpropene (0.178 mmol) and ethanol (1.0 ml) was placed in a tube (general procedure A) and heated for 1.5 hr at 105 ± 2°. GLC analysis revealed only the presence of solvent and alkene, no ethyl *tert*-butyl ether was detected.

In an analogous experiment, a trace of ethyl *N*-nitro-*N*-*tert*-butylcarbamate was added to the 2-methylpropene–ethanol solution. After 1.5 hr at 105 ± 2°, no ethyl *tert*-butyl ether could be detected by GLC analysis.

Similarly, a reaction between 2-methylpropene (0.027 mmol), nitrous oxide (0.027 mmol) and ethanol (1.0 ml) at 105 ± 2° for 1.5 hr failed to produce any detectable ethyl *tert*-butyl ether.

Ethyl *tert*-Butylcarbonate Stability. Ethyl *N*-nitro-*N*-*tert*-butylcarbamate (0.307 mmol), *tert*-butyl ethyl carbonate (0.218 mmol), and ethanol (2.0 ml) were sealed in a tube, as in procedure A, and heated for 0.10 hr at 105 ± 2°. GLC analysis showed that the carbonate was stable under the reaction conditions.

A second series of control reactions utilizing procedure B, in which a specified amount of ethyl *tert*-butyl carbonate was added to previously analyzed decomposition mixtures, revealed that, after 1.65 and 3.3 hr at 105 ± 2°, no carbonate decomposition had occurred (101 and 97% recovery, respectively). Albeit the above control reactions suggest that ethyl *tert*-butyl carbonate is stable under the reaction conditions; a half-life determination for the carbonate in ethanol revealed that decomposition does occur under prolonged heating. Solutions of ethyl *tert*-butyl carbonate and ethanol were prepared as in general procedure A, then placed in an oil bath (105 ± 2°) for a specified period of time (0.5, 1.0, 3.0, 6.0, 24, and 48 hr). After the addition of the internal standard, GLC analysis (column A) afforded the weight of carbonate remaining after decomposition and a plot of $\ln [a/(a - x)]$ vs. time ultimately gave the carbonate half-life (3.3 hr). After 48 hr at 105°, no carbonate could be detected; the decomposition products were ethyl *tert*-butyl ether (81%) and 2-methylpropene (19%). The yield of ethyl *tert*-butyl carbonate from the nitrocarbamate decompositions is low (<5%) with typical reaction times of 1.5 hr or less; thus, a correction for the carbonate half-life is not significant.

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Radiationless Decay in the Azabenzenes as Studied by Opto-Acoustic Spectroscopy

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Abstract: In the broadest terms, two classes of relaxation behavior are observed in the azabenzenes. (i) In pyridine, pyridazine, *sym*-tetrazine, and probably *sym*-triazine, the relaxation rates to the ground state following $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitations are equally fast on our time scale ($k \geq 10^6$ sec^{-1}). In the presence of biacetyl, the relaxations from the $^1(n,\pi^*)$ states of pyridine and *sym*-triazine are noticeably slowed, but not those in *sym*-tetrazine or pyridazine. Relaxation from the $^1(\pi,\pi^*)$ states are not affected by the addition of biacetyl. (ii) In pyrazine, pyrimidine, and 2,6-dimethylpyrazine, the $^1(n,\pi^*)$ relaxation rate is significantly slower than that from $^1(\pi,\pi^*)$ and becomes even slower in the presence of biacetyl. However, in the presence of oxygen, the two rates are both very fast, except in the case of 2,6-dimethylpyrazine. Tetramethylpyrazine probably belongs in this second class. It is clear in the optical spectra of the diazines that a new relaxation channel opens up within the S_1 band envelope; this new channel is tentatively identified as $S_1 \rightarrow T_3$ relaxation. In all cases, it appears that the $S_2(\pi,\pi^*)$ state relaxes rapidly and avoids the S_1, T_2, T_1 levels on its way to the ground state. There is some evidence that symmetry-determined spin–orbit matrix elements are important in determining the rates of $^1(n,\pi^*)$ relaxation in certain of these compounds.

The azabenzenes, from pyridine to tetrazine, have been the objects of spectroscopic and photochemical studies for many years, and deservedly so.[1,2] Paralleling this experimental work on the excited states are several dozens of theoretical calculations on spectral excitation energies, intensities, etc., in these systems. Clearly, the azabenzenes have become a cornerstone of molecular spectroscopic research. As in almost all polyatomic molecules, that area of azabenzene spectroscopy still in great need of study involves the paths by which these excited molecules relax, in particular, the paths for radiationless relaxation. To this end, we have performed a low-resolution study of the azabenzenes and some of their derivatives in the 7000–2200 Å region using the relatively new technique of opto-acoustic spectroscopy.

Following the act of absorption, that fraction of the molecules electing radiationless decay cascade down the myriad electronic–vibrational–rotational ladders to the ground state thereby releasing heat. By opto-acoustic spectroscopy, one is able to measure the relative amounts of heat released and the relative temporal relationships between heats re-