in ethanol. The intensity could not be measured since a clear glass could not be obtained.

Photolysis of 1a at 77°K. A solution of **1a** in ethanol was prepared and its fluorescence spectrum measured as described above. Use of the phosphoroscope showed no phosphorescence from the solution. The solution, maintained at 77°K, was irradiated for 15 min using 345-nm light from the Bausch and Lomb monochromator. Remeasurement of the luminescence spectra showed a decrease in the fluorescence intensity but no phosphorescence. The glass was allowed to thaw and was then refrozen. Use of the phosphoroscope now showed the phosphorescence spectrum of **2a**.[12]

The Deamination of Bridgehead Amines *via* the Nitroso- and Nitroamide Approach[1]

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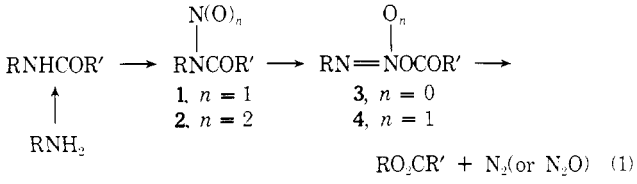
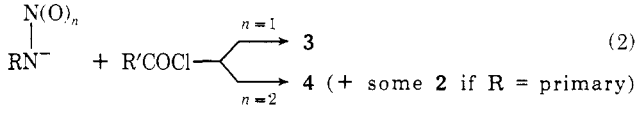
Abstract: 1-Norbornylamine, 1-apocamphylamine, and 1-adamantylamine have been deaminated using the nitroso- and nitroamide approach. The reaction yields carbonium ions that are reactive enough to abstract chloride ions from solvents such as methylene chloride, probably *via* chloronium ion species. The norbornyl ions have a much higher reactivity than the 1-adamantyl ions as shown by the higher ratio of solvent attack to reaction with the negatively charged counterion. Oxygen-18 tracer experiments are also reported. The mechanism of deamination is discussed based on these and other results.

The deamination of aliphatic amines *via* the nitroso- and nitroamide approach (eq 1) is a useful variant



(1)

of the older nitrous acid method, because of the wider range of temperatures and solvents that can be used and because of the greater control over the counterion ($R'CO_2^-$) that is possible.[2] An alternative synthesis of the reaction intermediates **3** and **4** *via* the "salt" approach (eq 2) adds to the versatility of the method.[3,4]



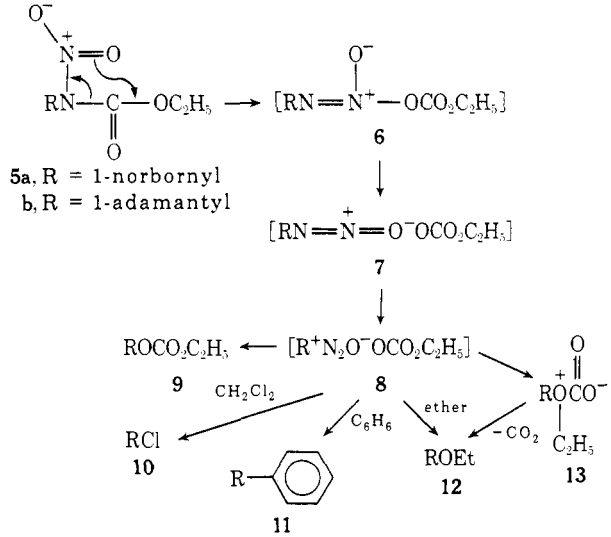
(2)

These reactions yield carbonium ions (R^+) and, typically, they not only yield esters (eq 1) but also olefins. For branched R groups the ester yields can be low, largely because of the predominance of the elimination pathway. To avoid olefin formation and also to gauge the effect of enhanced carbonium ion reactivity, we have examined the deamination of bridgehead systems.[5,6] This paper covers work on the deamination of 1-norbornylamine, 1-apocamphylamine, and 1-adamantylamine; the results reveal an extraordinarily high reactivity for the carbonium ions formed.

Procedure and Results

Nitration of ethyl *N*-1-norbornyl- and *N*-1-adamantylcarbamates with fuming nitric acid afforded *N*-nitrocarbamates **5a** and **5b** (Scheme I).[7,8] The

Scheme I



N-nitrocarbamates were decomposed at 50 and 105° to yield nitrous oxide, the corresponding carbonates, and products derived from reactions with the solvents. The products were identified by their glpc retention times and by isolation and proof of structure through spectral and analytical means. The results for the

(1) Some of the results described in this paper have appeared in preliminary form: E. H. White, H. P. Tiwari, and M. J. Todd, *J. Amer. Chem. Soc.*, **90**, 4734 (1968).

(2) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Wiley, New York, N. Y., 1968.

(3) (a) E. H. White and D. W. Grisley, Jr., *J. Amer. Chem. Soc.*, **83**, 1191 (1961); (b) R. A. Moss and K. M. Luchter, *J. Org. Chem.*, **37**, 1155 (1972).

(4) E. H. White, T. J. Ryan, and K. W. Field, *J. Amer. Chem. Soc.*, **94**, 1360 (1972).

(5) P. D. Bartlett and L. H. Knox (*ibid.*, **61**, 3184 (1939)] reported on the reaction of 1-apocamphylamine with nitrous acid and nitrosyl chloride.

(6) For a review of bridgehead reactivity and bridgehead cations *via* deamination, see R. C. Fort, Jr., and P. v. R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966).

(7) E. H. White, M. C. Chen, and L. A. Dolak, *J. Org. Chem.*, **31**, 3038 (1966).

(8) The ir spectra of **5a** and **5b** show two carbonyl peaks. For **5a** these peaks appear at 1750 and 1775 cm^{-1}, and for **5b** at 1738 and 1765 cm^{-1}. As previously noted,[7] these bands are assigned to two rotamers formed by rotation about the amide linkage.

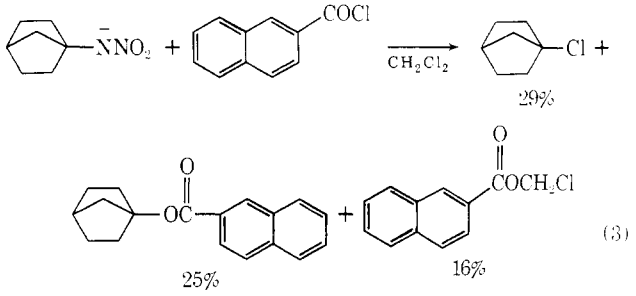
decomposition of **5** in various solvents are listed in Table I.

Table I. Decomposition of Bridgehead *N*-Nitrocarbamates[a]

	Product yields,[b] %					
	—R = 1-Norbornyl[c]—			—R = 1-Adamantyl—		
Solvent	$ROCO_2CH_2CH_3$	$ROCH_2CH_3$	RCl	$ROCO_2CH_2CH_3$	$ROCH_2CH_3$	RCl
CH_2Cl_2	37		56	83	5	2
CH_2Cl_2[d]	41	1	42			
$CHCl_3$	43		49	95	3	1
CCl_4	34		19			
CH_2BrCl	37		20[e]			
C_6H_6	31[f]			96	2	
Ether	26[g,h]	34		60	31	
EtOH	13[g]	67		21	72	

[a] Temperature = 105°, except as noted. [b] Absolute yields determined by glpc. [c] In cumene as the solvent, 20% of norbornane was found together with carbonate, which was the major product. [d] Temperature = 50°. [e] 25% of 1-Norbornyl bromide was also formed. [f] The major product was 1-phenylnorbornane (42%). [g] 8–10% yields of ethyl *N*-1-norbornylcarbamate were also found. [h] Decomposition in the presence of an excess of N_2O caused no change in the product distribution.

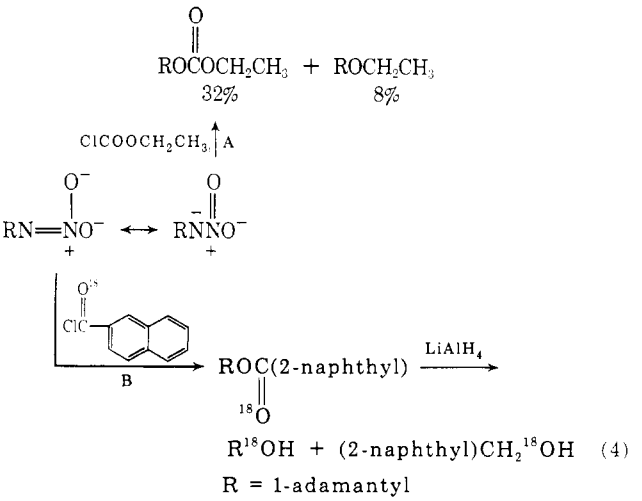
The "salt" modification of the nitroamide decomposition[3a] was also investigated (eq 2). When the sodium salt of *N*-nitro-1-norbornylamine was allowed to react in dichloromethane with 2-naphthoyl chloride (eq 3), the formation of nitrous oxide was detected at temperatures as low as −55°, illustrating the instability of **4**.[9] In further runs at 25° in dichloromethane, the same products were formed as in the thermal decomposition of **5a**; 1-norbornyl chloride and 1-norbornyl naphthoate were isolated in 29 and 25% yields, respectively, together with chloromethyl 2-naphthoate (eq 3).[10] Similarly, the sodium salt of *N*-nitro-1-adamantylamine was treated with ethyl chloroformate in diethyl ether at 25° to give 32% of ethyl 1-adamantyl carbonate and 8% of ethyl 1-adamantyl ether (eq 4A). The absolute yields are low in the "salt" reaction due to side reactions leading principally to the acid anhydride and the recovery of *N*-nitroamine. The relative yields of ester to solvent derived products are higher in these "salt" runs at 25° than in the thermal runs at 50 and 105° (Table I), but the trend for the latter reactions from 105 to 50° suggests that the lower temperature of the "salt" runs is the chief variable.



(3)

(9) Only one "diazoester" related to **3** and **4** has been identified to date. It was a hyponitrite derivative obtained from the rearrangement of *N*-benzoyl-*N*-nitroso-*O*-*tert*-butylhydroxylamine (T. Koenig, M. Deinzer, and J. A. Hoobler, *J. Amer. Chem. Soc.*, **93**, 938 (1971)).

(10) The decomposition of *N*-nitroso-*N*-(1-norbornyl)-*N'*,*N'*-dimethylurea in dichloromethane gave chloromethyl *N*,*N*-dimethylcarbamate as one of the products (detected by conversion into tetramethylurea: B. S. Hahn, unpublished results). Ethyl chloromethyl carbonate, an expected product from the decomposition of **5a** in dichloromethane, appeared unstable and it was not isolated.



(4)

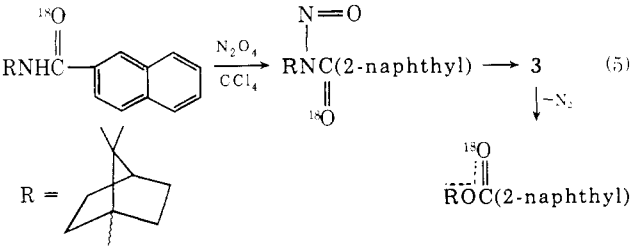
Using an ^{18}O labeled acid chloride has allowed us to introduce a labeled oxygen into intermediates **3** and **4**. The sodium salt of *N*-nitro-1-adamantylamine was treated with naphthoyl-^{18}O chloride and 1-adamantyl naphthoate-^{18}O was isolated. The ester was reduced with lithium aluminum hydride (eq 4B), the product alcohols were separated, and the oxygen-18 content of the alcohols[11] was determined. The data are summarized in Table II.

Table II. Oxygen-18 Results

Compound	Atom % excess ^{18}O[a,b,d] (R = 1-adamantyl)	Atom % excess ^{18}O[a,c,d] (R = 1-apocamphyl[13])
2-Naphthoyl chloride	0.70	0.84
R-2-Naphthoate	0.36	0.43
2-Naphthylcarbinol	0.38	0.35[e]
ROH	0.33	0.42

[a] Excess ^{18}O over natural abundance; average of two results. [b] Analysis method described in ref 11. [c] Analysis method described in ref 12. [d] Average error is probably ±10%. [e] At the low pH used (by error) in this run for the isolation of naphthylcarbinol, some exchange of the alcohol oxygen for ^{16}O from water occurred.

In a complementary study, *N*-1-apocamphyl-1-naphthamide-^{18}O was nitrosated with dinitrogen tetraoxide to give the *N*-nitrosoamide, which is much less stable than the corresponding *N*-nitrocarbamate; it decomposed at 0° to give the products shown in eq 5.



(5)

The distribution of ^{18}O in the 1-apocamphyl naphthoate was found by reducing the ester with lithium aluminum hydride, separating the alcohols, and analyzing each

(11) H. Dahn, H. Moll, and R. Menasse, *Helv. Chim. Acta*, **42**, 1225 (1959).

for ^{18}O by the method of Doering and Dorfmann.[12] The data are summarized in Table II.

Discussion

The data can be interpreted generally in terms of the reaction mechanism outlined in Scheme I.[2] A slow rearrangement of **5** (or the acylation step in the salt reaction, eq 2) leads to diazoxy ester **6**, which decomposes rapidly to form, ultimately, a carbonium ion, nitrous oxide, and a carboxylate ion.

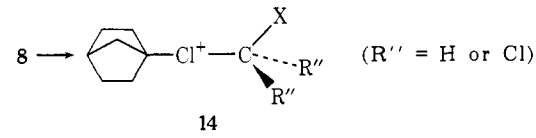
The physical characteristics of **6** are unknown in view of its high reactivity. It was hoped that **6a** might have a sufficiently long lifetime (in view of the high energy of the 1-norbornyl carbonium ion to be formed) to permit its observation at low temperatures. However, infrared spectra of reaction mixtures (eq 3) at −55° showed the immediate formation of nitrous oxide.[6]

The reaction products are formed in later stages of the reaction by the carbonium ion (Scheme I). Reactions of deaminatively formed carbonium ions with the solvent have been observed in the past but only with fairly reactive solvents such as alcohols and carboxylic acids.[2,13] In the present work, bridgehead carbonium ions are shown to react with relatively nonreactive solvents such as dichloromethane (chloride abstraction), benzene (alkylation), ether (cleavage), and cumene (hydride abstraction) (Table I).

The reactivity of the deaminatively produced 1-norbornyl carbonium ions is extremely high, as shown by the massive amounts of 1-norbornyl chloride and 1-norbornyl ethyl ether formed in chlorinated solvents and ether, respectively, and by the low discrimination noted between chloride and bromide abstraction from bromochloromethane (Table I).[14] The adamantyl carbonium ion is considerably more selective. Very little reaction with solvent occurs in halogenated solvents and in benzene. Yet in reactive solvents such as ether and ethanol, the amount of solvent-derived product approaches that found in the norbornyl case (Table I). Even in reactive solvents, however, the yield of solvent-derived product is not quantitative; it reaches a maximum at ~80% of the total product. It thus appears that in ethanol, *e.g.*, about a fifth of the carbonium ions are noninterceptible.[4,15]

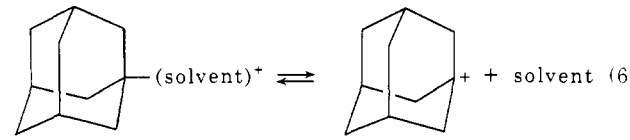
In all of the runs (Table I) the solvent is competing for the carbonium ion with a good nucleophile, the negatively charged counterion $C_2H_5O_2CO^-$. Such competition by the solvent is probably possible only because of its proximity to the carbonium ion. Since species **8** can be formed in the absence of the types of solvent participation that are found in the solvolysis reaction, it is formulated as a nonsolvated carbonium ion and counterion momentarily separated by a relatively inert molecule, N_2O in the present case. The unsolvated, highly reactive carbonium ions can apparently react with nucleophiles in the solvent cage faster than the carbonium ion and counterion can migrate around the nitrous oxide molecule to form ester.

On this basis, it is proposed that the halogen atoms—as part of the solvent cage—interact with (or solvate) the carbonium ion to give discrete halonium ion species such as **14**.[16] Similar species can be drawn for the



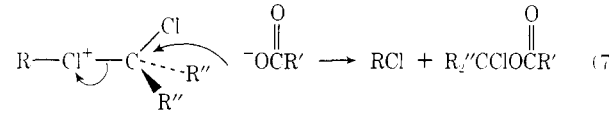
14

reactions in benzene, ether, and ethanol and also for the reactions of the adamantyl ion **15** in ether and ethanol. For adamantyl and other more stable carbonium ions[17] in the less reactive solvents such as dichloromethane, it is not clear whether discrete bonds to the solvent are formed or whether a less specific type of solvation is involved. If the former view is correct, then bond dissociation must occur to regenerate the carbonium ion (eq 6), since in most of the solvents used



15

ester was the principal product for such ions (Table I). Some regeneration of the norbornyl ion itself may be occurring, in view of the trend in yields of norbornyl chloride obtained in dichloromethane (56%), chloroform (49%), and carbon tetrachloride (19%). Such an order could result from a displacement reaction of the counterion on **14** (eq 7) in competition with dissociation (eq 6) (note the chloromethyl naphthoate formed in eq 3). The steric effect of three chlorines (*e.g.*) would decrease the rate of reaction 7, favoring ester in the product *via* process 6.[18]



R'' = H or Cl

A minor product, the bridgehead ethyl ether (**12**), was seen in all of the runs, particularly in the adamantyl series. This compound probably arises by alkylation of the alkoxy oxygen as shown in Scheme I.[13] Oxygen-18 tracer studies had shown earlier that the carbonium ion discriminates only inefficiently between the two oxygen atoms of a carboxylate group.[2]

The reactions being discussed appear to be ionic in nature. The chief evidence is the negligible amount of norbornane formed in dichloromethane (<0.5%) and the nonformation of hexachloroethane in the chloroform and carbon tetrachloride runs. Free radicals would have been expected to give these prod-

(12) W. E. Doering and E. Dorfmann, *J. Amer. Chem. Soc.*, **75**, 5595 (1953).

(13) E. H. White and C. A. Aufdermarsh, Jr., *ibid.*, **83**, 1179 (1961).

(14) High reactivity has also been noted in the alkylation of aromatic solvents by 1-apocamphyl cation generated by the silver tetrafluoroborate induced decomposition of 1-chloroformylapocamphane (P. Beak, R. J. Trancik, and D. A. Simpson, *ibid.*, **91**, 5073 (1969)).

(15) Other examples of a noninterceptible portion of the reaction have been noted in solvents such as acetic acid (ref 2).

(16) G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **91**, 2113 (1969).

(17) The relative rates of solvolysis of *tert*-butyl, 1-adamantyl, and 1-norbornyl bromides fall in the order $1:10^{-3}:10^{-13}$, *e.g.* (ref 6).

(18) The process does not appear to involve simple competitive abstraction of chloride ion by the carbonium ion since such a process should give an SN1 order of reactivity, which is the reverse of what is observed (P. Petrenko-Kritschenko and V. Opotsky, *Chem. Ber.*, **59B**, 2131 (1926), cited in J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, p 485).

ucts.[19-21] Further evidence for the minor role of radicals in these reactions was provided by the decomposition of **5a** in cumene, which is both a good hydride and a good hydrogen atom donor;[22] 20% of norbornane but less than 5% of bicumyl[23] was formed. It should be pointed out, however, that the product recovery in nonpolar solvents such as cyclohexane is low and norbornane is formed in addition to the ester; free radicals may be formed under these conditions.

In an effort to investigate the timing of the steps outlined in Scheme I, we have employed ^{18}O labeling of the carbonyl group of the reaction intermediates (eq 4 and 5). The results (Table II) show that the two oxygen atoms in the counterion have become effectively equivalent. Since we have shown that analogous labeling of nitrosoamides of acyclic secondary and tertiary carbinamines leads to preponderant retention of ^{18}O in the carbonyl group (55–74%),[13,24] some special factor must be at play in the present bridgehead systems. This factor probably is the relatively long lifetime of the diazonium or diazoxonium carboxylate ion pair (**7**), which would permit equilibration of the oxygens. The long lifetime is presumably a consequence of the relatively high activation energy expected for the formation of a high energy carbonium ion.

The high reactivity of the 1-norbornyl carbonium ion and the greater reactivity of nitrous oxide relative to nitrogen suggested that the present system (Scheme I) might be used to detect a reversal of the step in which nitrous oxide is formed (**7** $\rightleftarrows$ **8**). No difference in product yields could be detected, however, when ethyl *N*-(1-norbornyl)-*N*-nitrocarbamate was decomposed in the presence of an excess of nitrous oxide.

Conclusions

The past and present results in deamination show that considerable disorder occurs in the product-forming steps, since the product distribution is effectively the same whether syn or anti diazoesters are used and also whether nitrogen or nitrous oxide is the gas molecule formed.[4] Further, a large fraction of the carbonium ions formed escape domination by the negatively charged counterion (forming products with the solvent, *e.g.*). Only a small fraction of the carbonium ions are dominated by the counterion; these form the intramolecular ester even in reactive solvents such as acetic acid and ethanol (by a process so rapid for R = 1-phenylethyl and 2-phenylbutyl that the two oxygens in a carboxylate counterion do not become equivalent).[2] These observations can be accounted for by the formation of a range of species upon rupture of the C–N bond in the diazonium–counterion ion pairs (*e.g.*, **7**). In most of the sets of carbonium ions and counterions, the ions are separated by nitrogen (or nitrous oxide, **8**); these species lead predominantly to solvent derived products. A smaller fraction of sets arises with the nitrogen or nitrous oxide molecule to one side of the carbonium ion–counterion axis, presumably as the result of random collisions with neighboring molecules; these sets are largely noninterceptible. In a sense, the population consists of nitrogen (nitrous oxide) separated ion pairs and varieties of intimate ion pairs,[25] the former, at least, visualizable as discrete intermediates, although the activation energies may not be much larger than the barriers to diffusion.

An interesting feature of deamination is the occurrence of "intramolecular inversion"—the formation of ester from the carbonium and counterions with inversion of configuration.[2,13] A recoil action attending the rupture of the C–N bond has been proposed to account for this observation.[4] The phenomenon is not limited to diazonium ion chemistry, however, and thus the role of recoil, if any, is uncertain. The occurrence of what appears to be "intramolecular inversion" in the free radical decomposition of optically active azo compounds has been reported recently.[27]

$$\underset{L}{RN}{=}\underset{L}{NR} \xrightarrow{\Delta} R\cdot N_2\cdot R \longrightarrow RR\ (LL + DL + \text{some } DD) + N_2 \quad (8)$$

R = 1-phenylethyl

Further, it has been shown that the internal return of solvent separated benzhydryl ion pairs proceeds with some racemization (intramolecular inversion).[28] Intramolecular inversion thus appears to be the result of a more general process; presumably the rotation is a result of collisions with neighboring molecules.

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were recorded on either a Perkin-Elmer Model 337 spectrometer or a Perkin-Elmer Model 137 spectrometer. Ultraviolet spectra were taken on a Cary Model 14 spectrophotometer. The nmr spectra were recorded on either a Varian Model A-60 instrument or a Varian Model HA-100 instrument. Gas–liquid partition chromatography was carried out on either a Varian Aerograph Model 1200 instrument or a Varian Aerograph Model 800 instrument, both equipped with a Disc Chart integrator. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn., or by Mr. Joseph Walter, The Johns Hopkins University.

Ethyl *N*-1-Norbornylcarbamate. 1-Norbornanecarboxylic acid[29] (4.5 g, 31 mmol) and excess thionyl chloride (20 ml) were boiled under reflux for 2 hr. The excess thionyl chloride was removed on the rotary evaporator and the residue was distilled at 20 mm to yield the pure acid chloride (4.75 g, 30 mmol, 97%): bp 75–78°; ir (CH_2Cl_2) 1790 cm^{-1} (C=O).

The acid chloride (4.7 g, 30 mmol) was dissolved in 100 ml of chloroform which had previously been made ethanol free by passing it over a column of basic alumina. Excess sodium azide (5 g, 77 mmol) was added and the mixture was heated at reflux. The progress of the reaction was followed by ir. When the band at 1790 cm^{-1} due to the acid chloride had disappeared and was accompanied by the appearance of a band at 2260 cm^{-1} due to iso-

(19) F. G. Edwards and F. R. Mayo, *J. Amer. Chem. Soc.*, **72**, 1265 (1950).

(20) J. I. G. Cadogan, D. H. Hey, and P. G. Hibbert, *J. Chem. Soc.*, 3939 (1965).

(21) K. V. Scherer, Jr., and R. S. Lunt, III (*J. Amer. Chem. Soc.*, **88**, 2860 (1966)), have reported extensive hydrogen atom abstraction from methylene dichloride by bridgehead perchlorohomocubyl radicals.

(22) (a) M. S. Kharasch, H. C. McBay, and W. H. Urry, *J. Org. Chem.*, **10**, 401 (1945); (b) G. A. Olah and N. Friedmann, *J. Amer. Chem. Soc.*, **88**, 5330 (1966).

(23) The yields of bicumyl are high (97%) when acetyl peroxide is decomposed in cumene.[22a]

(24) E. H. White and J. E. Stuber, *J. Amer. Chem. Soc.*, **85**, 2168 (1963).

(25) Depending on the mechanism for the movement of the nitrogen (nitrous oxide) out of the solvent cage, this species could be viewed as a vibrationally excited ion pair,[26] but, in view of the speculative nature of our knowledge of these states, this is perhaps overdefining the state.

(26) E. H. White and C. A. Elliger, *J. Amer. Chem. Soc.*, **89**, 165 (1967).

(27) P. D. Bartlett and J. M. McBridge, *Pure Appl. Chem.*, **15**, 89 (1967); F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 867 (1970).

(28) H. L. Goering, R. G. Briody, and J. F. Levy, *ibid.*, **85**, 3059 (1963); H. L. Goering and J. F. Levy, *ibid.*, **86**, 120 (1964); H. L. Goering and H. Hopf, *ibid.*, **93**, 1224 (1971).

(29) R. J. Bixler and C. Niemann, *J. Org. Chem.*, **23**, 742 (1958).

cyanate formation, 10 ml of ethanol was added and the mixture was further heated at reflux for 24 hr. After this time all the isocyanate had been converted to the carbamate as shown by the disappearance of the band at 2260 cm^{-1} and the appearance of a 1730-cm^{-1} band in the ir region. Sodium azide was removed by filtration, and the solvent was stripped off on a rotary evaporator. The residue was distilled to give 3.5 g (72%) of the carbamate: bp 60–62° (10 μ); ir ($CHCl_3$) 3450 cm^{-1}, 2960, 2875, 1730, 1520, and 1160; nmr ($CDCl_3$) τ 4.56 (broad singlet, 1 H), 5.98 (q, 2 H), 7.86 (s, bridgehead H), 8.1–8.6 (m, 10 H), 8.80 (t, 3 H).

Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.25; H, 9.30; N, 7.70.

Ethyl *N*-Nitro-*N*-1-norbornylcarbamate. The procedure of White, Chen, and Dolak[7] was followed. Fuming nitric acid (90%, 12 g) was added dropwise to 60 ml of acetic anhydride cooled in a Dry Ice–acetone bath. To this nitrating mixture, 3.5 g (20 mmol) of ethyl *N*-1-norbornylcarbamate dissolved in 20 ml of acetic anhydride was added dropwise. The mixture was stirred for 1 hr while it warmed to room temperature. Then, the mixture was poured over crushed ice–water and extracted with four 50-ml portions of ether. The combined ether extracts were washed with 20% Na_2CO_3 solution and then with water, dried over $MgSO_4$, and concentrated. The residue was distilled at 68° (5 μ) to give 3.45 g (83%) of a pale yellow oil: ir (CCl_4) 2960 cm^{-1}, 2880, 1775, 1750, 1605, 1575, 1320; nmr (CCl_4) τ 5.71 (q, 2 H), 7.74 (s, bridgehead H), 7.85–8.50 (m, 10 H), 8.66 (t, 3 H).

Anal. Calcd for $C_{10}H_{16}N_2O_4$: C, 52.62; H, 7.07; N, 12.27. Found: C, 52.49; H, 7.27; N, 11.75.

Decomposition of Ethyl *N*-Nitro-*N*-1-norbornylcarbamate. General Procedure. The solvents were purified prior to use. A 0.175 *M* solution of the nitrocarbamate dissolved in the appropriate solvent was degassed and sealed under vacuum in a 10-mm o.d. tube. The tube was heated at 105 ± 2° for 48 hr. After this time it was cooled in liquid nitrogen and opened. The contents were made up to 20 ml with the reaction solvent and analyzed by glpc (10% Carbowax 20M/140°). 1-Norbornyl chloride was identified as a product from its retention time on a 10% SE-30 column and a 10% Carbowax column. Ethyl 1-norbornyl carbonate was identified by removing the solvent and chromatographing the residue on basic alumina. The first fractions eluted by light petroleum were shown by glpc to be 1-norbornyl chloride. Fractions 3 and 4 were eluted with light petroleum and 5% benzene and contained almost pure samples of ethyl 1-norbornyl carbonate: ir (CCl_4) 1750 cm^{-1} (s), 1247 (s), 1273 (s); nmr (CCl_4) τ 5.94 (q, 2 H, J = 7 Hz), 7.90 (s, bridgehead H), 8.0–9.0 (m containing t, 13 H, J = 7 Hz). From this sample the peak belonging to the carbonate in the glpc trace was identified. Norbornane and hexachloroethane (<0.5%) were not detected in the chloroform run.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.20; H, 8.75. Found: C, 65.52; H, 8.92.

When the reaction solvent was benzene, a new product was isolated by chromatography of the reaction product on a column of basic alumina. Fractions 1–3 contained the product that was identified as 1-phenylnorbornane: ir (CCl_4) 2000–1670 cm^{-1} (four weak peaks), 1598 (m), 1570 (sh), 1495 (m), 1445 (m), 697 (s); nmr (CCl_4) τ 2.7–3.0 (broad singlet, 5 H), 7.68 (s, 1 H), 8.0–8.7 (m, 10 H). This sample was used to identify 1-phenylnorbornane in the glpc trace.

Anal. Calcd for $C_{13}H_{16}$: C, 90.63; H, 9.37. Found: C, 90.81; H, 9.35.

When the solvent was ethanol, the major product was identified as ethyl 1-norbornyl ether by its isolation. The crude product was chromatographed on neutral alumina. Elution with pentane gave a series of fractions consisting mainly of ethyl 1-norbornyl ether. A pure sample was obtained by preparative glpc with a 10 ft × 0.25 in., 20% SE-30 column: ir (CCl_4) 1140 (COC); nmr (CCl_4) τ 5.62 (q, 2 H, J = 7 Hz), 8.0 (s, bridgehead H), 8.3–8.65 (m, 10 H), 8.9 (t, 3 H, J = 7 Hz). This sample was used for glpc identification purposes.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.84; H, 11.45.

The absolute yields of the reactions were determined by glpc. 2-Norbornyl chloride was used as an internal standard to calibrate 1-norbornyl chloride and ethyl 1-norbornyl ether (10% SE-30/90°). 2-Methylnaphthalene was used as an internal standard to determine the yields of ethyl 1-norbornyl carbonate (10% Carbowax/140°) and 1-phenylnorbornane (10% SE-30/140°). The results with all the solvents used are summarized in Table I.

Decomposition of Ethyl *N*-Nitro-*N*-1-norbornylcarbamate. A. In Bromochloromethane. The nitrocarbamate (0.117 g, 0.78 mmol) and bromochloromethane (5 ml) were degassed and sealed under vacuum. The tube was heated for 52 hr at 105°. After opening the tube and diluting to 20 ml, the yield of ethyl 1-norbornyl carbonate was calculated by glpc to be 37% using 2-methylnaphthalene as internal standard. 1-Norbornyl chloride and 1-norbornyl bromide were identified by glpc retention time. The yields, 20 and 25%, respectively, were determined by glpc with *exo*-2-norbornyl chloride as an internal standard.

B. In Cumene. The cumene was checked for purity by glpc and prior to use was deperoxidized by passage over a column of basic alumina.

The *N*-nitrocarbamate (0.342 g, 1.5 mmol) and cumene (6 ml) were sealed in a tube and heated at 105° for 48 hr, after which time the mixture was examined by glpc.

Using a 10% DNP column at 75° showed that norbornane was present in the reaction mixture. This finding was confirmed on another column (10% SE-30/75°). The yield was estimated to be 20%. The major product was ethyl 1-norbornyl carbonate. A small amount (<5%) of bicumyl was also detected by comparison with an authentic sample.

C. In the Presence of Excess Nitrous Oxide. A solution of the nitrocarbamate (0.07 g, 0.3 mmol) in ether (10 ml) was prepared, and an aliquot of this solution (150 μl) was introduced into a thick-walled capillary tube, attached to the vacuum line, and degassed. Nitrous oxide (*ca.* 2.5 ml, 0.11 mmol) was condensed into the tube containing the reaction mixture, and the capillary was then sealed off. The tube was heated at 105° for 48 hr and a control reaction containing no nitrous oxide was run simultaneously. On completion of heating, the tubes were cooled, opened, and examined by glpc. There was no difference in the product distribution of the two runs.

Ethyl *N*-1-Adamantylcarbamate. Commercial 1-adamantylamine hydrochloride (2 g, 0.001 mol) was mixed with 10% sodium hydroxide solution (6 ml) in a flask fitted with a dropping funnel and a stirrer. Ethyl chloroformate (1.5 g, 0.013 mol) was added dropwise with stirring while the mixture was being cooled in an ice bath. More sodium hydroxide (6 ml) was added and stirring was continued for 3 hr. The reaction mixture was then extracted with ether, the extract washed with water and dried over $MgSO_4$, and the solvent evaporated to afford a white solid (2.0 g, 84%) that was recrystallized from hexane: mp 91–92°; ir (CCl_4) 3420 cm^{-1} (w), 1720 (s); nmr (CCl_4) τ 5.60 (s, NH), 6.17 (q, 2 H), 8.0 (broad singlet, 3 H), 8.12 (s, 6 H), 8.37 (s, 6 H), 8.86 (t, 3 H).

Anal. Calcd for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48. Found: C, 70.16; H, 9.33.

Ethyl *N*-Nitro-*N*-1-adamantylcarbamate. Nitration of ethyl *N*-1-adamantylcarbamate (1.0 g, 4.5 mmol) by the usual procedure[7] afforded a yellow oil (1.1 g, 91%): ir (CCl_4) 1765 cm^{-1} (s), 1738 (s), 1599 (s), 1300 (s); nmr (CCl_4) τ 5.89 (q, 2 H), 7.91 (s, 9 H), 8.37 (s, 6 H), 8.75 (t, 3 H). A sample was purified by short path distillation in a sublimer.

Anal. Calcd for $C_{13}H_{20}N_2O_4$: C, 58.19; H, 7.51. Found: C, 58.38; H, 7.63.

Decomposition of Ethyl *N*-Nitro-*N*-1-adamantylcarbamate. General Procedure. A 0.15–0.25 *M* solution of the carbamate in the appropriate solvent was degassed by freezing and warming three times and sealed under vacuum. The reaction tube was maintained at 105 ± 2° for 48 hr. After opening the tube, the mixture was diluted with another 15 ml of solvent and examined by glpc with a 10% SE-30 column and 5% QF-1 column. 1-Adamantyl chloride and ethyl adamantyl carbonate were identified by comparison of retention times with authentic samples and from spectra of the compounds isolated by column chromatography. 1-Adamantyl chloride was prepared by the procedure of Stetter[30] and ethyl adamantyl carbonate was obtained by treating 1-adamantanol with ethyl chloroformate.

When the solvent was ethanol, the residue after removing solvent was chromatographed on a column of neutral alumina. Fractions eluted with hexane showed one compound by glpc. Distillation of the residue gave a colorless liquid: bp 40–45° (15 μ); ir (CCl_4) 1116 (s), 1091 (s); nmr (CCl_4) 6.62 (q, 2 H), 7.82 and 8.32 (broad singlets, 15 H), 8.82 (t, 3 H). The data are consistent with ethyl adamantyl ether.

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.71; H, 11.26.

1-Phenyladamantane was prepared by the procedure of Stetter.[30]

(30) H. Stetter, M. Schwarz, and A. Hirschon, *Chem. Ber.*, **92**, 1629 (1959).

The decomposition of the *N*-nitrocarbamate was carried out in benzene and the product analyzed for 1-phenyladamantane by comparing retention times with the authentic compound. There was no peak (<0.5%) indicating this compound had been formed.

The absolute yields for the products were determined by glpc (10% SE-30/150°) using 2,3,6-trimethylnaphthalene as a standard. The results are summarized in Table I.

***N*-Nitro-1-norbornylamine.** Ethyl *N*-nitro-1-norbornylcarbamate (3.4 g, 0.016 mol) was dissolved in 20 ml of anhydrous methanol and 25 ml of 10% sodium hydroxide was added. The mixture was stirred at room temperature for 4 hr. Methanol was evaporated off on a rotary evaporator, and the residue was acidified with concentrated hydrochloric acid. The white precipitate of nitroamine was extracted with chloroform. The chloroform extract was washed with water, dried, and concentrated to give a solid that was sublimed at 40° (5 μ) to afford 2.34 g of nitroamine (95%): mp 68–69°; ir ($CHCl_3$) 3380 cm^{-1}, 3250 (broad), 2950, 2860, 1595, and 1320; nmr (CCl_4) τ 0.35 (s, 1 H), 7.72 (s, 1H), 7.92–9.00 (m, 10 H).

Anal. Calcd for $C_7H_{12}N_2O_2$: C, 53.83; H, 7.74. Found: C, 55.41; H, 7.86.

***Sodium Salt of N*-Nitro-1-norbornylamine.** *N*-Nitro-1-norbornylamine (2.40 g, 0.015 mol) was dissolved in 15 ml of absolute methanol and a drop of phenolphthalein was added. This solution was titrated with 0.1 *N* sodium hydroxide solution. The end point was reached with 150.2 ml of sodium hydroxide solution. The solution was extracted with ether, and the aqueous layer was evaporated to dryness on a rotary evaporator. The white solid (2.41 g, 90%) was dried at 80° under reduced pressure and stored in a desiccator.

Reaction of the Sodium Salt of *N*-Nitro-1-norbornylamine with 2-Naphthoyl Chloride. To 1.52 g (8 mmol) of 2-naphthoyl chloride dissolved in 150 ml of dry dichloromethane was added 1.5 g of sodium sulfate, 1.56 g (9 mmol) of the sodium salt of nitroamine, and 2 drops of pyridine. The mixture was stirred at room temperature for 2 hr. A small aliquot of the mixture was withdrawn and filtered, and its ir spectrum taken. The acid chloride band at 1754 cm^{-1} had disappeared indicating that the reaction was complete. The reaction mixture was filtered and the residue triturated with small portions of dichloromethane. The solvent was stripped off and the residue was triturated with pentane and filtered. The solid was found to be 2-naphthoic anhydride (0.59 g, 22%): mp 134–135° (lit.[31] 135°); ir ($CHCl_3$) 1795 cm^{-1}, 1725, 1640, 1170, 1121, and 950; nmr ($CDCl_3$) τ 2.06 (2, 2 H), 2.51–3.68 (m, 12 H).

Concentration of the pentane filtrate gave another solid that was recrystallized from petroleum ether to give 310 mg (16%) of fine needles: mp 77°; ir (CCl_4) 1750 cm^{-1}, 1640, 1190, 1080; nmr (CCl_4) τ 1.38 (s, 1 H), 1.78–2.63 (m, 6 H), 4.00 (s, 2 H). The data are consistent with chloromethyl 2-naphthoate.

Anal. Calcd for $C_{12}H_9ClO_2$: C, 65.32; H, 4.11. Found: C, 65.54; H, 4.26.

The pentane solution obtained after filtering the above compound was chromatographed on neutral alumina. The fraction eluting with 10% ether–90% pentane was shown to be 1-norbornyl 2-napthoate (466 mg, 22%): mp 93–94°; ir ($CHCl_3$) 2960 cm^{-1}, 2875, 1725, 1640, 1290, 1280, 1255, 1225, and 1195; nmr (CCl_4) τ 1.48 (s, 1 H), 1.83–2.65 (m, 6 H), 7.65–8.65 (m, 11 H).

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.52; H, 7.03.

The reaction was repeated with 38 mg of 2-naphthoyl chloride dissolved in 20 ml of dry dichloromethane and cooled to −80° in a Dry Ice–acetone bath. The sodium salt of the nitroamine (54 mg, 0.3 mmol) and a drop of pyridine was added and the reaction mixture was stirred for 1 hr at −80°. The ir spectrum of an aliquot warmed to 25° showed that the band at 1754 cm^{-1} had disappeared and that a band assigned to N_2O had appeared at 2240 cm^{-1}.

A low temperature ir spectrum was measured at −55° immediately after mixing. This spectrum also showed the band at 2240 cm^{-1} due to N_2O and indicated that N_2O was already formed before warming to room temperature. Work-up of the reaction in the same manner as before yielded 2-naphthoic anhydride (20%), chloromethyl 2-naphthoate (15%), and 1-norbornyl 2-naphthoate (23%).

In another salt run, the filtrate from the reaction products was distilled in two stages. The dichloromethane was distilled at atmospheric pressure and the residue was distilled under vacuum at room temperature. The distillates were examined by glpc. The first distillate contained only dichloromethane, and the second fraction gave two peaks corresponding to solvent and 1-chloronorbornane. The yield of 1-norbornyl chloride was 29% as determined by glpc. The solid residue was worked up as before to afford 2-naphthoic anhydride (40%), 1-norbonyl 2-naphthoate (25%), and chloromethyl 2-naphthoate (6%). Further elution of the chromatography column gave *N*-nitro-1-norbornylamine (29%) and 2-naphthoic acid (19%).

The sodium salt of *N*-nitro-1-norbornylamine (207 mg, 1.15 mmol) was allowed to react at room temperature with 2-naphthoyl chloride (201 mg, 1.07 mmol) using chloroform as the solvent. Work-up yielded 1-norbornyl chloride (36 mg, 25%), 2-naphthoic anhydride (66%), 1-norbornyl 2-naphthoate (50 mg, 17%), *N*-nitroamine (39%), and 2-naphthoic acid (10%).

Sodium Salt of *N*-Nitro-1-adamantylamine. Ethyl *N*-nitro-*N*-1-adamantylcarbamate (2.17 g, 8.25 mmol) was dissolved in methanol (20 ml) and 15 ml of a 10% sodium hydroxide solution was added. The mixture was stirred for 6 hr at room temperature, the methanol was then removed on the rotary evaporator, and the aqueous residue made acid with concentrated hydrochloric acid. The resulting white precipitate was extracted with chloroform and the chloroform layer washed with water and dried overnight with $MgSO_4$. Evaporation of the chloroform gave a white solid that was sublimed at 120° (15 μ) to yield 1.27 g (73%) of the nitroamine: mp 144–145°; ir ($CHCl_3$) 3365 cm^{-1} (NH), 3260 (NH hydrogen bonded), 1575 (NO_2), and 1345 (NO_2).

The nitroamine (1.1 g, 5.6 mmol) was dissolved in methanol and titrated with aqueous 0.1 *N* sodium hydroxide using phenolphthalein as indicator. The solution was extracted once with ether and the aqueous layer was then evaporated to yield the nitroamine salt (1.18 g, 96%). The last traces of water were removed by pumping at 20 μ and storage in a desiccator.

Reaction of *N*-Nitro-1-adamantylamine Sodium Salt with Ethyl Chloroformate in Diethyl Ether. The sodium salt (0.475 g, 2.18 mmol) and ethyl chloroformate (0.238 g, 2.19 mmol) were mixed in dry ether and stirred at 0° for 7 hr and then overnight at room temperature. An ir spectrum of the solution showed by examination of the carbonyl region that no reaction had taken place. One drop of pyridine was then added and stirring was continued at 0° for 0.5 hr. A second ir spectrum showed the reaction was partially complete. After a further 12 hr of stirring at room temperature, the ir spectrum showed no band attributable to ethyl chloroformate. Peaks were found at 2330 cm^{-1} (w, CO_2), 2210 (w, N_2O), 1740 (s, adamantyl ethyl carbonate) and 1584 (s, *N*-nitroadamantylamine).

The solid residue was removed, the ether evaporated, and the organic residue was examined by glpc (10% SE-30). 1-Adamantol, adamantyl ethyl ether, adamantyl ethyl carbonate and an unknown compound were found. A quantitative estimate of the yields of adamantyl ethyl ether and adamantyl ethyl carbonate was obtained using 2,6-dimethylnaphthalene as internal standard. This gave a yield of 8% for adamantyl ether and 32% for adamantyl ethyl carbonate.

Reaction of the Sodium Salt of *N*-Nitro-1-adamantylamine with 2-Naphthoyl-^{18}O Chloride. The sodium salt of *N*-nitro-1-adamantylamine (1.0 g, 4.6 mmol) and the ^{18}O-labeled acid chloride (0.86 g, 4.5 mmol, 0.70 atom % excess ^{18}O), prepared by the method of White and Aufdermarsh,[18] were suspended in dry dichloromethane (100 ml). Pyridine (2 drops) was added and the mixture (protected by a drying tube) was stirred at room temperature for 3 hr. After this time, an infrared spectrum showed that the absorption of the acid chloride (1750 cm^{-1}) had completely disappeared. The mixture was then filtered and the residue shaken with warm water. Most of the residue dissolved in water. The aqueous solution was made acid with 2 *N* HCl and extracted with chloroform. The chloroform solution was dried ($MgSO_4$) and evaporated to yield 0.19 g of a white solid that was identified as *N*-nitro-1-adamantylamine by comparison of ir spectra in CCl_4.

The dichloromethane filtrate was evaporated and the residue triturated with pentane. The pentane insoluble portion was filtered to yield a white solid (0.264 g). The infrared spectrum was identical with that of an authentic sample of 2-naphthoic anhydride.

The pentane filtrate was concentrated. The ir spectrum of the residue in CCl_4 was consistent with 1-adamantyl 2-naphthoate (0.265 g, 19%). The crude material was separated from various impurities by means of preparative tlc (silica gel–benzene). An infrared spectrum (CCl_4) showed a strong carbonyl band at 1717 cm^{-1}; the nmr spectrum showed the following features: τ 1.5 (s, 1 H, 1-naphthyl proton), 1.9–2.6 (m, 6 H), 7.7 and 8.2 (singlets, 15 H).

(31) I. Heibron, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., 1953, p 559.

Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.04; H, 7.13.

Cleavage of 1-Adamantyl 2-Naphthoate-^{18}O with Lithium Aluminum Hydride. To a solution of lithium aluminum hydride (0.016 g, 0.5 mmol) in 15 ml of dry ether was added 0.215 g (0.7 mmol) of 1-adamantyl 2-naphthoate. The reaction mixture was stirred at room temperature for 3 hr and the excess hydride was decomposed with water. The mixture was filtered and the filtrate was evaporated to afford a white solid (0.208 g, 95%). Sublimation at room temperature and 10 μ onto a cold finger cooled at $-70°$ gave a solid that was shown to be 1-adamantanol. Recrystallization from pentane gave long colorless needles (35 mg).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.77; H, 10.79.

The residue from the sublimation was examined by glpc and found to be free of adamantanol. Further sublimation (45° (10 μ)) gave 2-naphthylcarbinol (mp 78–80°; lit.[32] 80–80.5°; a mixture with authentic alcohol was not depressed in melting point).

Oxygen-18 Determinations. The general method has been described previously.[11] A weighed sample of the compound to be analyzed and *O*-phenylenediamine monohydrochloride were sealed off at about 23° and 760 mm pressure and heated in a furnace for 3 hr at 300°. The reaction compartment was sealed to stopcock and cooled with a Dry Ice–acetone bath, the break seal was smashed and CO_2 was condensed into a receiver tube, and the CO_2 was analyzed by mass spectrometry. The atom per cent excess ^{18}O was calculated by the method of Dahn, Moll, and Menasse.[11] The data are summarized in Table II.

***N*-1-Apocamphyl-1-naphthamide-^{18}O.** 1-Naphthoic-^{18}O acid (4.2 g, 24.4 mmol) containing 0.862 atom per cent excess oxygen-18 was refluxed in 20 ml of thionyl chloride for 2 hr, after which the excess thionyl chloride was removed *in vacuo*. The crude acid chloride was taken up in 25 ml of anhydrous ether. 1-Aminoapocamphene·hydrochloride[5] (3.58 g, 20.3 mmol) was shaken with 75 ml of 1 *N* potassium hydroxide and 25 ml of ether. The ether solution of the acid chloride was added to this mixture. After shaking for 15 min, the layers were separated, and the aqueous phase was washed once with ether. The combined ether extracts were decolorized with charcoal, dried, and concentrated. The solid residue was recrystallized from hexane to give 5.35 g (90%) of amide: mp 140.5–142.0°. Two additional recrystallizations from hexane raised the melting point to 141.5–143.2°.

Anal. Calcd for $C_{20}H_{23}NO$: C, 81.86; H, 7.89; N, 4.77. Found: C, 82.16; H, 7.82; N, 4.52.

The amide had 0.841, 0.845 atom % excess oxygen-18.

Nitrosation of *N*-1-Apocamphyl-1-naphthamide-^{18}O. Preliminary experiments showed that this compound is quite difficult to nitrosate completely, such powerful nitrosating reagents as nitrosyl chloride being relatively ineffective. A mixture of N_2O_4 and pyridine in CCl_4 was found to give complete nitrosation, but the nitrosoamide which was formed rearranged immediately under the conditions of the reaction. The best procedure was to freeze dinitrogen tetraoxide (8.9 ml, 0.14 mol) in a flask cooled to $-80°$ in Dry Ice acetone and protected by a drying tube. A layer of carbon tetrachloride (25 ml) was frozen on top of the reagent. A solution of 5.00 g (0.017 mol) of *N*-1-apocamphyl-1-naphthamide-^{18}O (0.841, 0.845 atom % excess oxygen-18) and pyridine (16 ml) in 110 ml of carbon tetrachloride was added and the mixture was swirled while being allowed to warm to 0°. After 2 hr at 0° the initial green color had intensified and a dark precipitate appeared. The precipitate, which was collected by filtration, was water soluble and presumably consisted largely of pyridinium salts. The green CCl_4 filtrate was washed twice with water and once with 5% sodium bicarbonate and dried over anhydrous magnesium sulfate. The yellow oil obtained on removal of solvent *in vacuo* was sublimed at 0.1 mm, 70–105° to give crude 1-apocamphyl 1-naphthoate-^{18}O (1.05 g, 21%) in five fractions. The first fraction was recrystallized three times from ethanol–water mixtures and resublimed giving material melting at 94.5–95.7°.

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.59; H, 7.54. Found: C, 81.59; H, 7.49.

The remaining fractions were recrystallized from ethanol–water to give 1-apocamphyl 1-naphthoate-^{18}O (0.436, 0.439 atom % excess oxygen-18), mp 91.5–93.8°. The infrared was identical with that of the analytical sample which melted at 94.5–95.7°.

Reduction of 1-Apocamphyl 2-Naphthoate-^{18}O. A solution of the ester (590 mg, 2.00 mmol) in anhydrous ether was added dropwise with stirring to 10 ml of *ca.* 0.5 *M* lithium aluminum hydride in ether. After 10 hr of stirring, 2 ml of ice water was added carefully to destroy the excess hydride. The precipitate was dissolved by adding 3 ml of 10% sulfuric acid. The ether layer was separated and washed with an additional 3 ml of 10% sulfuric acid, water, and 5% sodium bicarbonate. After drying, the ether was removed by a stream of nitrogen to leave a slightly yellow oil which was sublimed onto a cold finger cooled with Dry Ice. Crude apocamphanol-*l*-^{18}O (215 mg, 76.8%) was collected at 35–45° (10 mm), crude 1-naphthylcarbinol (0.219 g, 69.5%) sublimed at 60–70° (1 mm). After recrystallization from 50% aqueous ethanol followed by sublimation at 60–70° (1 mm), the pure 1-naphthylcarbinol-^{18}O (0.348, 0.354 atom % excess oxygen-18), mp 63.0–63.7°, was obtained; a mixture melting point with authentic carbinol was 62.5–63.7°. The infrared spectra were identical.

A sample of the crude apocamphanol-*l*-^{18}O was recrystallized from ethanol–water, resublimed, and dried in a desiccator giving material which melted at 168–168.8° as compared with 168.7–170° observed for the alcohol obtained from deamination of 1-aminoapocamphane.[4] The infrared spectra were identical. The apocamphanol-*l*-^{18}O contained 0.418, 0.425 atom % excess oxygen-18. The ^{18}O analyses were determined by the method of Doering and Dorfman[12] and are summarized in Table II.

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(32) E. Bamberger and O. Bakmann, *Chem. Ber.*, **20**, 1118 (1887).