Interception of Deaminatively Generated Benzyl Carbenium Ions by Acetone

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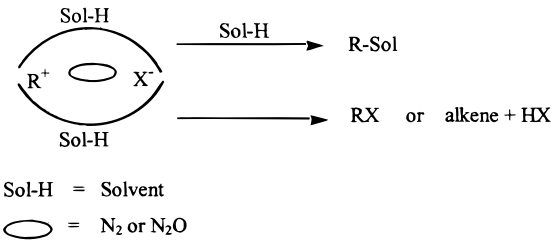
Essentially free benzyl carbenium ions were generated via protonation of phenyldiazomethane with benzoic acid in acetone. Interestingly, no proton transfer occurred below −20 °C. After protonation and dediazoniation of the diazoalkane at −20 °C, the solvent was found to intercept the deaminatively generated carbocations to yield initially the corresponding *O*-benzyl oxonium ion and benzyl benzoate. The onium ion, however, was labile under the reaction conditions, and decomposed into a cascade of products whose concentrations as a function of time were used to trace the reaction pathway. Thus, the *O*-benzyl oxonium ion reacted with benzoate ion to yield (2-benzyloxy)isopropyl benzoate; subsequent decomposition of this *O*-benzyl-*O*-benzoyl ketal produced 2,2-dibenzyloxypropane (a dibenzyl ketal), 2-benzyloxypropene, and benzyl alcohol. In a related study, benzyl cations were generated via thermolyses of *N*-benzyl-*N*-nitroso-*O*-benzoyl hydroxylamine at 0 and −70 °C. The product distributions were found to be temperature-dependent and different from that in the $PhCHN_2 + PhCO_2H$ case.

Introduction

Quite recently, a number of articles[1] have appeared in the literature concerning the reactivity, synthetic and mechanistic utility, and stereochemistry of deaminatively generated carbocations. These carbocations, formed as part of a nitrogenous-molecule separated ion-pair (NSIP), may be produced via several precursors[1b] and may represent the most reactive carbocations accessible in the solution phase.[1b,c] The high reactivity[1] of deaminatively generated carbocations is due, in part, to the low activation energy required for the loss of nitrogen (or of N_2O) that allows the cation to be formed with minimal solvent participation.[1] Additionally, the temporary screening of the cation from its counterion by the sheer physical presence of the nitrogenous molecule results in the maximal positive charge at the electron-deficient center.[1]

These exceedingly reactive cations can be chosen so that β-eliminations and rearrangements are not possible and reaction with nucleophiles is their only fate. The nucleophiles available to them are the counterion and the solvent. Cation−solvent reactions must occur before diffusion of the nitrogenous molecule from between the ions as the latter process leads to internal collapse of the ion-pair to form the corresponding ester. The yield of solvent-derived products (SDPs) is increased by conditions that decrease the diffusion rate of the nitrogenous molecule,[1b,2] by use of large mole fractions of highly nucleophilic solvents,[1b,d−f] and through use of poorly nucleophilic counterions.[1b,d,e] Alkenes can also form from the cation−counterion reaction if the former possesses a removable β-hydrogen (eq 1) and if the basicity of the latter is at or above some threshold level.



(1)

Two previous studies[1d,e] have dealt with the interception of deaminatively generated benzyl carbenium ions by acetonitrile in the presence of counterions of low nucleophilicity (triflate)[1d] and of modest nucleophilicity (pivalate)[1e] ($n_{pivalate} \approx 2.7$; $n_{triflate} < 0$)[3]. In those cases, thermolyses of *N*-benzyl-*N*-nitrosoamides at 25 °C were used to generate the benzyl carbenium ion. In the present work in acetone, benzyl carbenium ions originated via protonation of phenyldiazomethane with benzoic acid at −20 °C (eq 2a) and via nitrosation of *N*-benzyl-*O*-benzoyl hydroxylamine at 0 and −70 °C (eq 2b). The product distributions from these runs were used to determine the prevailing reaction mechanisms.

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‡ This paper is dedicated to the memory of Professor Emil H. White, 1926-1999.

(1) (a) White, E. H.; Field, K. W.; Hendrickson, W. H.; Dzadzic, P.; Roswell, D. F.; Paik, S.; Mullen, P. W. *J. Am. Chem. Soc.* **1992**, *114*, 8023. (b) Darbeau, R. W.; White, E. H.; Song, F.; Darbeau, N. R.; Chou, J. C. *J. Org. Chem.* **1999**, *64*(16), 5966. (c) White, E. H.; Darbeau, R. W.; Chen, Y.; Chen, D.; Chen, S. *J. Org. Chem.* **1996**, *61*, 7986. (d) White, E. H.; De Pinto, J. T.; Polito, A. J.; Bauer, I.; Roswell, D. F. *J. Am. Chem. Soc.* **1988**, *110*, 3708. (e) Darbeau, R. W.; White, E. H.; Nunez, N. P.; Coit, B. C.; Daigle, M. A. *J. Org. Chem.* **2000**, *65*, 1115. (f) Darbeau, R. W.; White, E. H. *J. Org. Chem.* **1997**, *62*, 8091. (g) Song, F.; St. Hilaire, V. R.; White, E. H. *Org. Lett.* **1999**, *1 (12)*, 1957. (h) Wiberg, K. B.; Osterle, C. G. *J. Org. Chem.* **1999**, *64*, 7756. (i) Wiberg, K. B.; Osterle, C. G. *J. Org. Chem.* **1999**, *64*, 7763. (j) Wiberg, K. B.; Shobe, D. S. *J. Org. Chem.* **1999**, *64*, 7768. (k) Darbeau, R. W.; Delaney, M. S.; Ramelow, U.; James, K. R. *Org. Lett.* **1999**, *1*(5), 761.

(2) The yield of SDP also rises with decreasing temperature and to a lesser extent as the nitrogenous molecule is changed from N_2 to N_2O.[1b]

(3) Swain, C. G.; Scott, C. B. *J. Am. Chem. Soc.* **1953**, *75*, 141.

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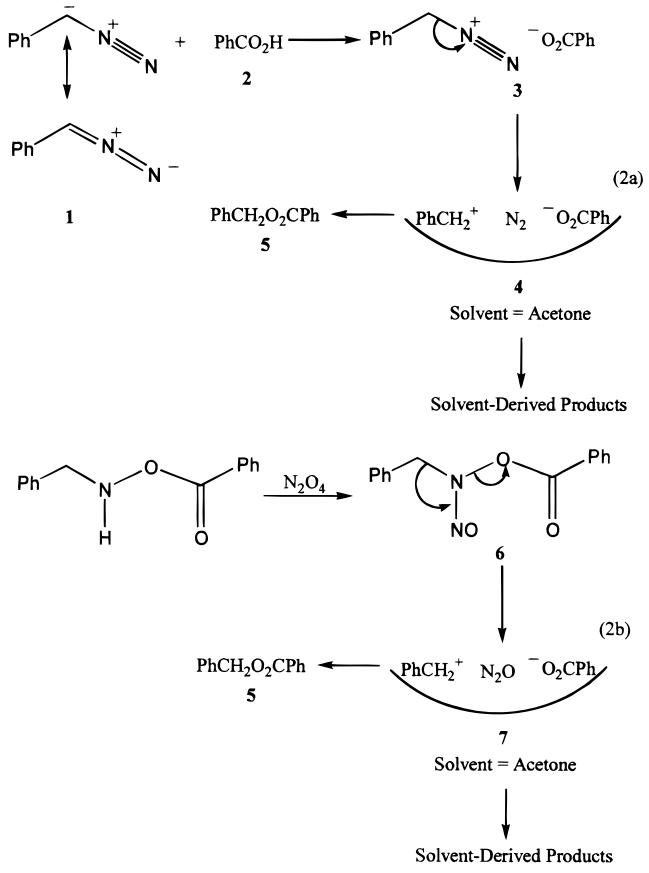


Results and Discussion

Acidification of phenyldiazomethane (eq 2a) and nitrosation of *N*-benzyl-*O*-benzoyl hydroxylamine (eq 2b) were employed here because of the high speed of these reactions in producing the cations (vide infra). The former reaction is completed after ~3 h at −20 °C whereas the latter is essentially instantaneous even at −78 °C.[1b] These rapid decompositions permit spectroscopic observation of thermolabile, transient intermediates. With few exceptions, runs were performed in acetone-d_6 (99%) in NMR tubes to allow direct ^{1}H NMR analyses of the products.

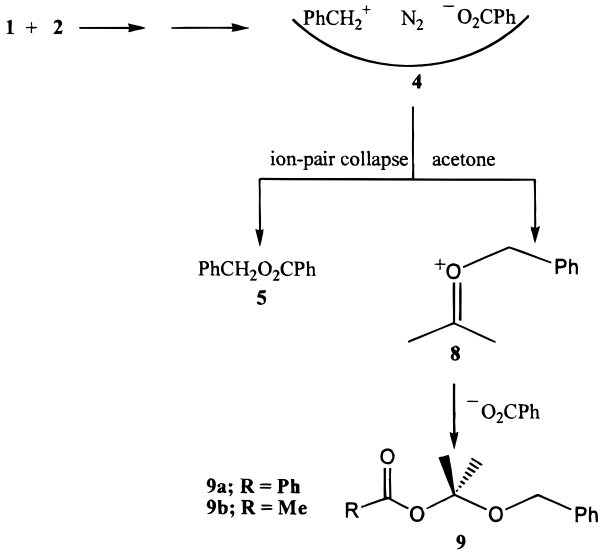
Reaction of Phenyldiazomethane with Benzoic Acid in Acetone. Separate solutions of benzoic acid and phenyldiazomethane in acetone-d_6/acetone-h_6 (9:1, vol/vol) were allowed to equilibrate at −78 °C. The benzoic acid solution was injected via a septum, with stirring, into a round-bottom flask containing the solution of phenyldiazomethane at −78 °C. No reaction occurred as evidenced by the persistence of the red color of the phenyldiazomethane and the absence of N_2 evolution (i.e., effervescence). The sample was allowed to warm to −20 °C and was kept at that temperature until the reaction ceased. The reaction products were analyzed immediately after the reaction. The ^{1}H NMR spectrum showed that the reaction afforded benzyl benzoate (**5**; 56%), (2-benzyloxy)isopropyl benzoate (**9a**; 41%) (vide infra for product identification), 2-benzyloxypropene (**12**; 1%), and benzyl alcohol (**10**; 2%) (Table 1, Schemes 1 and 2). After complete reaction, the product mixture was stored at 4 °C for 23 h; ^{1}H NMR (acetone-d_6) showed 58% of **5**, 33% of **9a**, 5% of **12**, and 4% of **10** (Table 1, Schemes 1 and 2). After a further 3 days at 4 °C, the solvent was removed in vacuo. The ^{1}H NMR spectrum (in $CDCl_3$) showed 60% of **5**, 16% of **9a**, 13% of **12**, 5% of 2,2-dibenzyloxypropane (**11**), and 6% of **10** (Table 1, Schemes 1 and 2).

Table 1. Product Distribution[a] from the Reaction of Phenyldiazomethane with Benzoic Acid in Acetone

	product distribution				
run no.	5	9a	10	11	12
1[b,c]	58	33	4	0	5
1[b,d]	60	16	6	13	5
2[e,f]	54	13	9	7	17
3[g]	56	41	2	0	1

[a] Standard deviation ~0.5. [b]Runs performed in acetone-d_6/acetone-h_6 (9:1; vol/vol) and started at −78 °C. [c]Sample stored at 4 °C for 23 h after completion of run. [d]Solvent removed in vacuo and residue redissolved in $CDCl_3$. [e]Runs performed in acetone-h_6 at −20 °C; data obtained in $CDCl_3$ after solvent removal in vacuo; preferential loss and some hydrolysis were likely. [f]Sample stored at 4 °C for 4 days after completion of run. [g]Runs performed in acetone-d_6 at −20 °C.

Scheme 1. Proposed Mechanism for the Formation of (2-Benzyloxy)isopropyl Benzoate

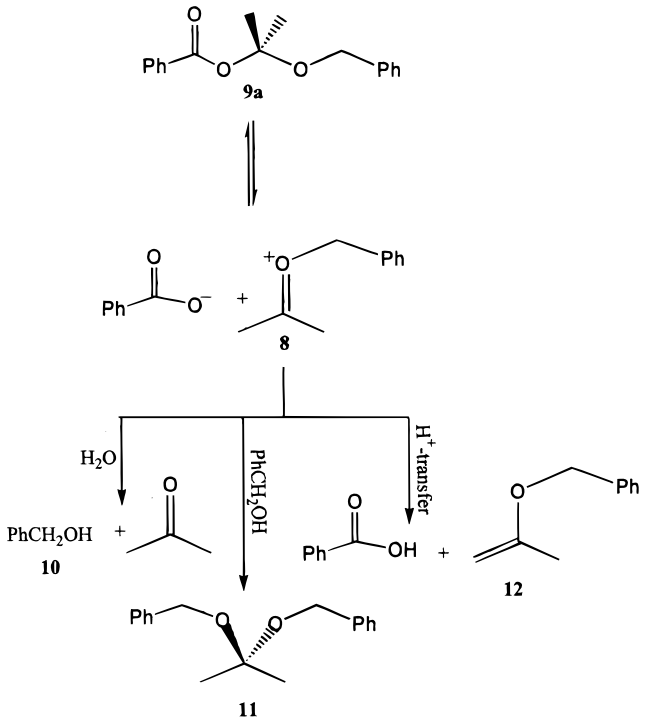


The Lability of the Onium Ion and a Case of Slow Proton Transfer. In an attempt to detect the putative oxonium ion, **8**, a solution of benzoic acid in acetone-d_6/acetone-h_6 (1/9, v/v) at −78 °C was added to phenyldiazomethane in the same solvent system at the same temperature. The ^{1}H NMR spectrum showed that no reaction had occurred in over 20 min at −78 °C. When the mixture was warmed stepwise in 10 °C increments (10 min per ramp and a 10 min hold time), reaction was observed to begin only at −20 °C (vide supra) as evidenced by the appearance of product peaks at δ 5.42 from benzyl benzoate and at δ 4.88 from **9a**.[4]

On the basis of this NMR study, it appears that (1) protonation of phenyldiazomethane with benzoic acid at temperatures <−20 °C is quite slow and (2) the onium ion is undetected by NMR spectroscopy at −20 °C. This observation may arise because **8** is too labile under these conditions or because of the slow kinetics of phenyldiazomethane decomposition by benzoic acid <−20 °C. However, (3) **8** must persist long enough and be present in a sufficient steady-state concentration to effect bimolecular reactions.

It may be that detection of **8** is possible at temperatures well below −20 °C (vide infra), but this would be contingent upon the successful acidification of phenyl-

Scheme 2. Possible Decomposition Pathways of (2-Benzyloxy)isopropyl Benzoate



diazomethane at significantly lower temperatures (possibly via triflic acid).[1d] The issue of the slow proton transfer is not unusual for acid−base reactions involving carbon bases (or carbon acids) and is well documented in the acid decompositions of diazoalkanes that undergo esterification with carboxylic acids.[5a] In these cases, the protonation of the diazomethane is rate-limiting.[5a,b] In the present study, the reaction between benzoic acid and phenyldiazomethane would then be expected to be even slower because of the lower basicity of phenyldiazomethane (vs diazomethane)[5c] and the inherent low rates of diffusion and reactivity at depressed temperatures. It should be pointed out that the rate-limiting protonation of the phenyldiazomethane would be succeeded by rapid dediazoniation because of the facility of the loss of N_2, the inherent stability of the benzyl cation, and the formation of the ion-pair in a polar solvent.

Identification of Intermediates and Products. Partial proof of the structure of compound **9a** was obtained by model studies involving preparation of the analogous compound **9b** by the reaction of phenyldiazomethane with acetic acid in acetone at −20 °C. The ^{1}H NMR and IR spectra (vide infra) are consistent with the assigned structure of 2-benzyloxyisopropyl acetate.[4] Additionally, when D_2O was added to **9b**, the latter hydrolyzed to the expected products: acetic acid, acetone, and compounds **12** and **10**.

Identification of compound **11** was based on the comparison of the ^{1}H NMR signals in the product with that of an authentic sample prepared via "trans-etherification" of 2,2-dimethoxypropane with benzyl alcohol under reflux in the presence of catalytic quantities of *p*-toluenesulfonic acid.[6a] Compound **12** was identified in a similar fashion: in this case, **12** was independently prepared by elimination of benzyl alcohol from 2,2-dibenzoxypropane with P_2O_5 in the presence of quinoline at 120 °C.[6b] The identities of **10** and **5** were deduced by comparison with spectra of commercial samples and by spiking.

The Reaction Mechanism. The formation of **9a** is believed to occur via trapping of the benzyl carbenium ion of the NSIP by acetone to form the metastable onium ion, **8** (Scheme 1). The latter then reacted with the benzoate (or acetate for **9b**) counterion to produce **9** (Scheme 1).[7a] 2-Benzyloxypropene is believed to have arisen from *β*-deprotonation of **8** by benzoate (Scheme 2),[7b] whereas **11** ostensibly formed from attack on **8** by **10** (Scheme 2).

Some benzyl alcohol was probably formed by reaction between trace moisture and the first-formed benzyl cation. The low mole fraction of water in acetone, however, makes this source of the alcohol, somewhat poorly competitive with other routes (vide infra).[1b] However, during storage of the product mixture for 4 days at 4 °C, compound **9a** evidently underwent slow decomposition to produce compounds **10**, **11**, and **12** (vide supra). The implication therefore is that **9a** must be in equilibrium with an ion pair containing an onium ion and benzoate (**4′**) [although it is formed irreversibly from the NSIP (**4**)].[8] Hence, on standing, **9a** generates a steady-state concentration of **4′**, the onium ion of which is reversibly attacked by benzoate (to regenerate **9a**) and reversibly attacked by water to yield a labile hemiacetal that fragments to acetone and benzyl alcohol (Scheme 2). The onium ion can also be attacked by benzyl alcohol to form **11** (Scheme 2). As with the first generation of

(4) (a) The structure assignment of compound **9a** was based on comparison of the chemical shifts observed in the products with the expected (estimated) value for the methyl signal based on the following considerations. From the chemical shifts of the methyl groups in ethyl benzoate (δ 1.42)[4b] and in benzyl ethyl ether (δ 1.20)[4c] the $\Delta\delta = 0.22$ presumably due to the differences in the inductive effects of the benzyloxy and benzoate groups on the Me group. Assuming that the effect is transferable then the Me group of **9** would be expected to be at δ 1.76, i.e., 0.22 ppm higher than the Me group of **11** (known to be δ 1.54). The Me peaks for **9** (δ 1.88 for **9a** and δ 1.73 for **9b**) are close to the expected value along with a corresponding benzylic signal (δ 4.79 for **9a** and δ 4.66 for **9b**). On the basis of known values for 2,2-dimethoxypropane [δ 3.20, $C(CH_3)_2$][4b] and 1-methoxy-1-acetoxy ethane [δ 3.30, $C(CH_3)_2$],[4d] an acetoxy group and a methyloxy group differ by 0.10 ppm in their effects on the chemical shift on Me. Assuming that the acetate (similarly benzoate) and methyloxy (similarly benzyloxy) groups would exert a similar difference in **9**, a benzylic peak at δ 4.68 (the benzyloxy peak is at δ 4.58 in **11**) was expected for the corresponding signal in compound **9**. This estimated chemical shift is also close to the observed values (δ 4.79 for **9a** and δ 4.66 for **9b**). (b) *The Aldrich Library of NMR Spectra*, 2nd ed.; Aldrich: Milwaukee, 1983; Vol. 2, p 281. (c) Barleunga, J.; Alonso-Cires, L.; Campos, P. J.; Asensio, G. *Synthesis* **1983**, 53. (d) Pihlaja, K.; Lampi, A. *Acta Chem. Scand.* **1986**, *40B*, 196.

(5) (a) Isaacs, N. In *Physical Organic Chemistry*, 2nd ed.; John Wiley & Sons: New York, 1995; p 407. (b) More O'Ferrall, R. A. *Adv. Phys. Org. Chem.* **1967**, *5*, 331. (c) We have been unable to find the pK_b values of diazoalkanes. However, resonance interaction involving the lone pair of electrons on the benzylic group with both the adjacent diazonium group and the aromatic ring would be expected to lower the basicity of phenyldiazomethane below that of diazomethane. (d) Isaacs, N. In *Physical Organic Chemistry*, 2nd ed.; John Wiley & Sons: New York, 1995; p 239.

(6) (a) Lorette, N. B.; Howard, W. L. *J. Org. Chem.* **1960**, *25*, 521. (b) Crocker, H. P.; Hall, R. H. *J. Chem. Soc.* **1954**, 2052. (c) Borkovec, A. B. *J. Org. Chem.* **1961**, *26*, 4866−4868. (d) Anderson, C.; Larson, J.; Hallberg, A. *J. Org. Chem.* **1990**, *55*, 5757.

(7) (a) This reaction is analogous to the attack by pivalate on the sp-hybridized carbon of the *N*-benzylnitrilium ion derived from acetonitrile.[1e] (b) No deprotonation of the acetonitrilium ion by pivalate to form the ketimine was observed.[1e] This mechanistic divergence is probably related to the inherent differences in product stability between the cummulated product and the monovinyl species.

(8) The onium ion in the ion-pair, **4′**, is expected to be less reactive than that produced initially during the encounter between the NSIP, **4**, and acetone. Additionally, **4′** is almost surely a spectrum of intimate and solvent-separated ion-pairs.

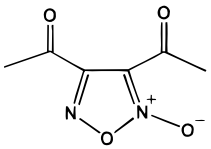
onium ions, these onium ions generated by ionization of **9a**[8] are also apparently deprotonated to yield compound **12**.

Nitrosation of *N*-Benzyl-*O*-benzoylhydroxylamine in Acetone-h_6. *N*-Benzyl-*O*-benzoylhydroxylamine was nitrosated in acetone at −70 °C, and the solvent was removed in vacuo. The product consisted only of **5** (50%), **10** (40%), **11** (6%), and 4-hydroxy-4-methyl-2-pentanone (4%; from acid-catalyzed aldol-type reaction of acetone). When nitrosation was performed at 0 °C and the solvent was removed as above, the product contained **5** and diacetylfuroxan (**13**) (from the reaction of acetone with N_2O_4)[9] in a ratio of 6/5, respectively. Surprisingly, compounds **10**, **11**, and **12** accounted for less than 10% of the product mixture.

The formation of **5** from these runs is evidence of the formation and decomposition of *N*-benzyl-*N*-nitroso-O-benzoylhydroxylamine and the generation of the NSIP, which on internal collapse produces the observed ester (eq 2b).[1b] However, despite the intermediacy of the deaminatively generated benzyl cation, only trace amounts of the other intermediates and products observed in the $PhCHN_2$ + $PhCO_2H$ case were detected here. Thus, although both deamination methods used in this study successfully generate the benzyl cation, SDPs are not readily accessible via hydroxylamine nitrosation (eq 2b).

It would appear then that in both cases a fraction of the benzyl cations were intercepted by acetone to generate the undetectable electrophilic oxonium ion **8**. In the $PhCHN_2$ + $PhCO_2H$ system, no acid stronger than benzoic acid was present during the reaction. As a result, the modestly nucleophilic benzoate ion (generated as the conjugate base after protonation of the diazoalkane) was available to enter into bimolecular reactions with **8** giving the array of products observed in that case. However, HNO_3 is a side product of X−H (X = C, heteroatom) nitrosation via N_2O_4. Indeed, if moisture is present in the system then both HNO_2 and HNO_3 are generated (facile oxidation of the former by air, e.g., yields the stronger, latter acid). Under these more strongly acidic conditions, most of the benzoate ions presumably exist largely in the protonated and much less nucleophilic form, i.e., as benzoic acid and are thus less adept at intercepting the onium ion.[10] Consequently, the products **10**, **11**, and **12** observed in the $PhCHN_2$ + $PhCO_2H$ system are generated here in only trace amounts because the nucleophile from which they are formed was significantly deactivated.

Nitric acid's role in the diminished yield of benzyl derived products may extend beyond inhibition of their formation through deactivation of benzoate. It may also be involved in hydrolyses of labile benzyl species. Thus, acid-catalyzed hydrolysis of labile **9a** in particular, as well as of other intermediates and products ostensibly resulted in the significantly larger yield of benzyl alcohol observed. Theoretically, only 1 equiv of water would be sufficient to effect the observed hydrolyses. Typically, $\sim 10^{-4}$ moles of hydroxylamine in 2 mL of acetone were used in these runs (vide infra); thus, only ~1 mg of water would be sufficient to produce the observed results. The absence of the furoxan, **13**, would appear to indicate that the N_2O_4−acetone reaction is not competitive at depressed temperatures.



13

Summary and Conclusion

Acetone intercepts deaminatively generated benzyl cations to form an electrophilic onium ion that is competitively scavenged by the benzoate counterion in an equilibrium with (2-benzyloxy)isopropyl benzoate. Two generations of onium ions are apparently formed: the first originates as an ion-pair containing the benzoate ion derived from capture of the deaminatively generated carbocation; the second arises from simple solvolysis of the labile (2-benzyloxy)isopropyl benzoate.

Proton transfer between benzoic acid and phenyldiazomethane is very slow below −20 °C presumably because of the feeble acidity and basicity of $PhCO_2H$ and $PhCHN_2$, respectively, as well as the low rates of diffusions and reactions at depressed temperatures.

When strong acids are present, the benzoate ion is apparently converted to benzoic acid whose nucleophilicity is too low for competitive attack on the onium ion. Consequently, limited yields of solvent-derived product are observed from nitrosation of *N*-benzyl-*O*-benzoylhydroxylamine in acetone. The more acidic conditions inherent in this approach, in tandem with adventitious moisture serve to hydrolyze many of the labile benzyl intermediates and products. Additionally, at temperatures around 0 °C, large yields of the side product **13** are observed, although this problem does not arise at depressed temperatures. The hydroxylamine nitrosation approach is therefore a poorer method of studying carbenium ion interception in acetone.

Experimental Section

Materials and Methods. All commercial reagents were reagent grade and were used without further purification. Spectra were recorded on 300 MHz FT-NMR, FT-IR, and UV−vis spectrometers.

Stability of Phenyldiazomethane and *N*-Benzyl-*O*-benzoylhydroxylamine: Handling and Storage. Phenyldiazomethane is labile and was prepared as needed. It decomposes under acidic conditions and in the presence of moisture and light. **Caution!** Phenyldiazomethane should be handled with extreme care because of its possible mutagenicity[11a] and carcinogenicity (local and systemic).[11b] *N*-Benzyl-*O*-benzoylhydroxylamine is comparatively stable, and the dry solid can be stored indefinitely under nitrogen at −25 °C. Efficient fume hoods and appropriate personal protection (chemical-resistant gloves, safety glasses, lab coat, etc.) are recommended when handling these compounds.

2,2-Dibenzyloxypropane (11). The title compound was prepared by the general procedure of Lorette and Howard:[6a] ^{1}H NMR ($CDCl_3$) δ 7.38−7.25 (m, 10H), 4.58 (s, 4H), 1.54 (s, 6H); (lit.[6c] bp 125 °C at 1 Torr).

(9) Peterson, L. I. *Tetrahedron Lett.* **1966**, 1727.

(10) (a) The pyridinium ion ($pK_a = 5.2$[10b]) probably hydrogen bonds with benzoate mitigating against the reaction of the latter with **8**. (b) Davies, D. T. In *Aromatic Heterocyclic Chemistry*, 1st ed.; Oxford University Press: New York., 1992; p 35.

(11) (a) Lee, K.; Gold, B.; Mirvish, S. *Mutat. Res.* **1977**, *48*, 131. (b) Preussman, R.; Stewart, B. W. In *Chemical Carcinogenesis*; Searle, C., Ed.; ACS Monograph No. 182; American Chemical Society: Washington, DC, 1984; pp 643−828.

2-Benzyloxypropene (12). Following the general procedure of Crocker and Hall,[6b] 2,2-dibenzyloxypropane (60 mg, 0.25 mmol) was added to a slurry of phosphorus pentoxide (36 mg, 0.25 mmol) and quinoline (32 mg, 0.25 mmol) in a flask connected to a U-tube. The mixture was heated to 120 °C at 0.1 Torr. A colorless liquid (0.10 mmol, ~15 mg) was collected in the U-tube (cooled to − 78 °C). The distillate consisted of compound **12** [^{1}H NMR ($CDCl_3$) δ 4.73 (s, 2H), 3.94 (m, 2H), 1.88 (m, 3H)] and an equimolar amount of benzyl alcohol [^{1}H NMR ($CDCl_3$) δ 4.70 (s, 2H)]; the aromatic signals were obscured in an unresolved multiplet at δ 8.90−7.17 (m). The ^{1}H NMR spectrum ($CDCl_3$) of an analogue, benzyl vinyl ether, has been reported:[5d] δ 7.4−7.3 (m), 6.60 (dd, J = 14, 7 Hz), 4.80 (s), 4.35 (dd, J = 14, 2 Hz), 4.12 (dd, J = 7, 2 Hz).

Benzaldehyde tosylhydrazone was prepared as described by Closs and Moss.[12]

Phenyldiazomethane (1). Method A.[12] To 10 mL of ethanol was added sodium (100 mg, 2.3 mmol). After the reaction was over, benzylaldehyde tosylhydrazone (549 mg, 2 mmol) was added at 25 °C. After 1 h of reaction at 60 °C, the solution became red in color. The resulting reaction mixture was treated with 40 mL of ice−water and then extracted with pentane (10 mL). The organic phase was separated, dried with Na_2SO_4, and concentrated in vacuo (20 Torr) at 0 °C. When the residue was distilled at 40 °C under vacuum (0.1 Torr), a red oil (100−200 mg) was collected in a U tube cooled to −70 °C: ^{1}H NMR ($CDCl_3$) δ 7.30−6.90 (m, 5H), 4.93 (s, 1H) (the method afforded 5−10% trans-stilbene as a impurity with δ 6.60). **Method B.** To 2.5 mL of methanol was added sodium (52 mg, 2.5 mmol) previously rinsed with pentane. After cessation of hydrogen evolution, benzylaldehyde tosylhydrazone (342 mg) was added. After dissolution, the solvent was evaporated at 0.1 Torr to give a solid that was heated at 90−100 °C with an oil bath at 0.1 Torr. A red oil (~100 mg) was collected at −70 °C in a U-tube. The red oil was distilled at 0 °C and 0.1 Torr to give phenyldiazomethane: ^{1}H NMR ($CDCl_3$) δ 7.28 (t, 2H, J = 8.1 Hz), 7.03 (t, 1H, J = 8.1 Hz), 6.92 (d, 2H, J = 8.4 Hz), 4.93 (s, 1H). No *trans*-stilbene was observed by this procedure.[1b]

(2-Benzyloxyl)isopropyl Acetate. Acetic acid (5.7 μL, 6.0 mg, 0.10 mmol) was injected into a solution of phenyldiazomethane (~12 mg, 10 mmol) in 0.5 mL of acetone in a NMR tube with a septum cooled to −70 °C. The mixture was shaken immediately and then kept at −20 °C in a freezer. After ~3 h, the solvent and volatile products were distilled at 0.1 Torr and 25 °C over ~25 min to give a colorless oil: ^{1}H NMR ($CDCl_3$) 7.36 (m, 5H), 4.66 (s, 2H), 2.03 (s, 3H), 1.73(s, 6H); IR ($CDCl_3$) 1725, 1378 and 1360 (d), 1219, 1125 cm^{-1}. The NMR spectrum of the distillate showed that (2-benzyloxyl)isopropyl acetate was also partially distilled.

Decomposition of (2-Benzyloxy)isopropyl Acetate in the Presence of D_2O. D_2O (10 μL, 10 mg, 0.55 mmol) was added to (2-benzyloxy)isopropyl acetate; after ~4 h, the ^{1}H NMR spectrum showed ~69% of decomposition to give 27% of benzyl alcohol, 24% of 2-benzyloxylpropene, 19% of acetone, 35% of acetic acid.

The Reaction of Phenyldiazomethane with Benzoic Acid. In Acetone-d_6. The ^{1}H NMR spectrum of phenyldiazomethane (2.5 mg, 0.02 mmol) in 0.25 mL of acetone-h_6/acetone-d_6 (1/9, v/v) exhibited a CH peak at δ 5.44 (s, 1 H) at 25 °C and 5.67 (s, 1H) at −78 °C. When a solution of benzoic acid (2.5 mg, 0.02 mmol) in 0.25 mL of acetone-h_6/acetone-d_6 (1/9, v/v) at −78 °C was added to this solution at −78 °C, the ^{1}H NMR spectrum was unchanged after 20 min. When the reaction mixture was warmed in the NMR probe in 10° increments (over 10 min per increment) and held for a further 10 min, no reaction was observed until at −20 °C. The ^{1}H NMR spectrum showed two new major peaks at δ 4.83 (s) (2-benzyloxy)isopropyl benzoate and δ 5.38 (s) (benzyl benzoate); 50% of the phenyldiazomethane still remained. After 23 h at 4 °C, the ^{1}H NMR spectrum showed δ 5.38 (s) (benzyl benzoate), 4.83 (s) (2-benzyloxy)isopropyl benzoate, 4.73 (s), 4.67 (s) in a ratio of 49:27:4:3. After 3 days at 4 °C, this sample was concentrated in vacuo (20 Torr); the ^{1}H NMR ($CDCl_3$) spectrum showed that the reaction afforded **5** [60% (δ 5.37)]; **9a** [16%, δ 4.79 (s) and 1.88 (s)]; **12** [13%, δ 4.73 (s, 2H), 3.95 (m, 2H), 1.89 (m, 3H)]; **11** [5%, δ 4.58 (s, 4H), 1.54 (s, 6H)]; **10** (6%, δ 4.70).

In another run, phenyldiazomethane (~10 mg, 0.082 mmol) was added to a solution of benzoic acid (11 mg, 0.090 mmol) in 1 mL of acetone at −80 °C. No reaction occurred within 30 min at −80 °C based on the persistence of the red color. More benzoic acid (6.0 mg, 0.049 mmol) was added; there was still no reaction. The sample was allowed to warm to 25 °C gradually, and the red color disappeared. The mixture was concentrated in vacuo: ^{1}H NMR ($CDCl_3$) showed **5** (63%); **9a** (4%); **12** (6%); **11** (9%); **10** (17%).

At −20 °C in Acetone-d_6. In a typical run, a solution of benzoic acid (10.2 mg, 8.4 mmol) in 50 μL of acetone-d_6 was injected into a solution of phenyldiazomethane (~12 mg, 10 mmol) in 0.5 mL of acetone-d_6 in an NMR tube with a septum cooled to −70 °C. The mixture was shaken immediately and then kept at −20 °C in a freezer. After completion of the reaction in ~3 h, the reaction products were analyzed by NMR. The ^{1}H NMR (acetone-d_6) spectrum showed benzyl benzoate (**5**, 56%); (2-benzyloxy)isopropyl benzoate (**9**, 41%); 2-benzyloxypropene (**12**, 1%); and benzyl alcohol (**10**, 2%).

Synthesis and Decomposition of *N*-Nitroso-*N*-benzyl-*O*-benzoylhydroxylamine (6) in Acetone-h_6; at 0 °C. To a stirred solution of *N*-benzyl-*O*-benzoylhydroxylamine (20 mg, 20 μL, 0.088 mmol) and pyridine (9.8 mg, 0.12 mmol) in 2 mL of acetone at 0 °C was injected gaseous dinitrogen tetroxide (2.0 mL, 0.089 mmol) with a hypodermic syringe through a septum. After being stirred for ~5 min, the resulting mixture was concentrated in vacuo (20 Torr). The ^{1}H NMR ($CDCl_3$) spectrum of the residue showed that the reaction afforded **13** [δ 2.63 (s, 3H), 2.72 (s, 3H)][9] and **5** [δ 4.70 (s, 2H)] in a ratio of 6/5, respectively, plus trace quantities amount of an unknown at δ 5.70. **At −70 °C.** To a stirred solution of *N*-benzyl-*O*-benzoylhydroxylamine (20 mg, 20 μL, 0.088 mmol) and pyridine (9.8 mg, 0.12 mmol) in 2 mL of acetone at −70 °C was injected gaseous dinitrogen tetroxide (2.0 mL, 0.089 mmol) with a hypodermic syringe through a septum. After being stirred for ~5 min, the resulting mixture was concentrated in vacuo (20 Torr). The ^{1}H NMR ($CDCl_3$) spectrum of the residue showed that the reaction afforded **5** (50%), **11** (6%), **10** (40%), and 4-hydroxy-4-methyl-2-pentanone [δ 2.62 (s, 2H), 2.17 (s, 3H), 1.25 (s, 6H), 2.5 (bs, 1H) 6%].

Diacetylfuroxan (13) from the Reaction of Acetone with N_2O_4 at 0 °C. Liquid N_2O_4 (1.5 mL, 3.93 g, 0.042 mol) was injected into acetone (1.2 g, 0.021mol) in a flask with stirring at 0 °C. After 10 min, the resulting mixture was concentrated in vacuo (20 Torr) to give 1.2 g (0.066 mmol, 31%) of diacetylfuroxan **(13)** in the form of a yellow oil: ^{1}H NMR ($CDCl_3$) δ 2.72 (s, 3H), 2.63 (s, 3H) [lit.[9] δ 2.63 (s, 3H), 2.72 (s, 3H)].

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