ratio of 1.1:1.0:3.5, respectively, with *p*-chloronitrobenzene as a standard in 10 mL of acetone was added 2.5 g of sodium bromide. The mixture was refluxed, and after 40 h **8a** was converted to **8b** in 74% yield. Products **3a** and **5a** did not react under these conditions.

Reaction of Methyl Hypochlorite with *cis,trans*-Ethyl Sorbate Under Molecule-Induced Homolysis Conditions. To 215 mg (1.53 mmol) of *cis,trans*-ethyl sorbate[11] at 0 °C in the dark was added 0.7 mL of 0.495 M methyl hypochlorite solution in carbon tetrachloride.[12] After 3 h at 0 °C, VPC analysis on column C at 50 °C showed that only 1.8% of **1** was formed from *cis,trans*-ethyl sorbate during this reaction. This experiment shows that return to the starting diene from intermediates **11b** and **11d** is a very minor component in this reaction pathway. Therefore, the product percentages in Table I very nearly represent the kinetic product ratio for these radical reactions. Analysis on column C at 105 °C gave products (38% yield) **8a**, **3a**, and *cis*-**5a** in a ratio of 4.5:1.0:1.6, respectively.[13] Products **8a** and *cis*-**5a** were a 60:40 ratio of erythro–threo isomers. Compound **3a** was a broad peak in the VPC analysis, but the erythro–threo isomers were not resolved under these conditions.

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Registry No.—1, 5941-48-0; *cis,trans*-**1**, 53282-25-0; **2a,** 66017-96-7; **2b,** 65996-25-0; **3a,** 65996-26-1; **3b,** 65996-27-2; **4a,** 65996-28-3; **4b,** 65996-29-4; *erythro*-**5a,** 65996-30-7; *threo*-**5a,** 65996-31-8; (*Z*)-*erythro*-**5a,** 65996-32-9; (*Z*)-*threo*-**5a,** 65996-33-0; *erythro*-**5b,** 65996-34-1; *threo*-**5b,** 65996-35-2; **6b,** 65996-36-3; **7b,** 62006-45-5; *erythro*-**8a,** 65996-37-4; *threo*-**8a,** 65996-38-5; **8b,** 65996-39-6.

References and Notes

(1) (a) Point Loma College; (b) Bethany Nazarene College.

(2) D. F. Shellhamer, V. L. Heasley, J. E. Foster, J. K. Luttrull, and G. E. Heasley, *J. Org. Chem.*, **42**, 2141 (1977).

(3) Alkyl hypochlorites and hypobromites react by an ionic process in a protic solvent or in a nonpolar aprotic solvent when an acid catalyst is used. In aprotic solvents without an acid catalyst, or in neat olefin or diene, a rapid radical reaction (molecule-induced homolysis) is observed. See (a) G. E. Heasley, V. L. Heasley, D. F. Shellhamer, W. E. Emery III, R. Hinton, and S. L. Rodgers, *J. Org. Chem.*, in press; (b) G. E. Heasley, V. M. McCully, R. T. Wiegman, V. L. Heasley, and R. A. Skidgel, *ibid.*, **41**, 644 (1976); (c) C. Walling and R. T. Clark, *ibid.*, **39**, 1962 (1974); (d) D. F. Shellhamer, D. B. McKee, and C. T. Leach, *ibid.*, **41**, 1972 (1976).

(4) (a) The IR stretching frequency of a double bond in conjugation with a carbonyl is very strong; see R. T. Conley, "Infrared Spectroscopy", Allyn and Bacon, Boston, Mass., 1966, p 99. The nonconjugated double-bond frequency was too weak to be observed at normal concentration of the products. (b) NMR spectral shifts of the β-vinyl hydrogen on the α,β-unsaturated products **4a,b**, **5a,b**, and **6a,b** appear at 0.4–0.9 ppm downfield relative to the α-vinyl protons in these products. Our data show that the protons of a methyl group on the δ carbon in the NMR spectrum resonate at 1.2–1.3 ppm when a methoxy substituent is on the δ carbon, while a halogen on that carbon lowers the chemical shift to 1.4–1.8 ppm. A vinyl methyl appears at 1.28 ppm.

(5) Bimolecular substitution is greatly accelerated when a carbonyl is α to the leaving group; see E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston, New York, N.Y., 1959, p 284.

(6) The absence of any 1,2 product (**3a**) from addition of chlorine electrophiles to **1** is curious. Addition of chlorine to butadiene in methanol gives only ca. 30% of 1,4 products, while addition to the 1,2 bond in *cis*- and *trans*-1,3-pentadienes gives predominately 1,4 products. See ref 3b.

(7) M. L. Poutsma, *J. Org. Chem.*, **31**, 4167 (1966). See ref 3a.

(8) The 4% of **4b** formed with methyl hypobromite may be due to a minor ionic component in this reaction.

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(11) *cis,trans*-Sorbic acid was donated by Keith H. Hollenback, University of Oklahoma. The acid was treated with ethanol and boron trifluoride as catalyst to give *cis,trans*-ethyl sorbate.

(12) The *cis,trans*-ethyl sorbate was chosen since the intermediate **11b** destroys a cis α,β bond and would therefore be a sensitive test for a reversible intermediate. Return to the starting diene from **11b** gives back the resonance stabilization energy of a diene to a carbonyl. This molecule-induced homolysis reaction was done in the dark because UV illumination isomerized *cis,trans*-ethyl sorbate to **1**. Reaction of neat **1** with or without UV illumination did not change the product ratio.

(13) Compound **8a** rather than **5a** is the major product when methyl hypochlorite is added to *cis,trans*-ethyl sorbate. Perhaps the cis α,β bond is more reactive than the trans α,β bond of **1**.

Solid–Liquid Phase-Transfer Catalysis by a Quaternary Ammonium Salt. A Comparison with Crown Ethers and Polyalkylamines

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Aliquat 336, a quaternary ammonium salt, has been used as a phase-transfer catalyst for the solid–liquid interface. A comparison of its catalytic ability with that of 18-crown-6 ether and tetramethylethylenediamine has been made. The quaternary ammonium salt is equivalent to and in many cases markedly superior to both crown ether and tetramethylethylenediamine for catalyzing acetate, fluoride, and adeninyl anion displacement reactions. However, the cyanide anion reacts at least 100 times faster when catalyzed by crown ether relative to the quaternary salt.

Crown ethers,[1] polyamines,[2] and ammonium and phosphonium salts[3] have been established as unique and effective catalysts for anionic reactions during the last 10 years. All three of these types of catalysts derive synthetic utility from their ability to solubilize inorganic reagents (and salts) in aprotic nonpolar organic solvents. The anions of these solubilized salts possess tremendous nucleophilicity as a result of a high degree of ionic dissociation[4] and at the same time they lack any significant solute–solvent interaction. The result of this phenomenon is the ability to use inorganic reagents in organic solvents to perform a variety of synthetic reactions[1–3] which would otherwise require more drastic, less desirable conditions.

Although the principles for the catalytic ability of these classes of compounds are similar, the application of each class has until now been different. The crown ethers and polyamines function by complexing with an insoluble reagent rendering the entire entity soluble. The quaternary ammonium salts have traditionally only been used to extract the anions of salts from an aqueous solution into an organic phase for subsequent reaction with a dissolved electrophile. Herein we report our results on the ability of a quaternary ammonium salt (Aliquat 336, Q^+)[5] to function as a phase-transfer catalyst

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Table I. A Comparison of the Ability of Q^+, 18-Crown-6, and TMEDA to Catalyze the Reaction

$$\underset{(1\ M)}{PhCH_2Cl + KN} \xrightarrow[\text{acetonitrile}]{\text{catalyst}} PhCH_2N + KCl$$

N^- (2.0 equiv)	Registry no.	Catalyst (0.1 equiv)	Registry no.	Half-life, h
CH_3CO_2 (rt)	71-50-1	Q^+	5137-55-3	0.75
		CE	17455-13-9	1.15
		TMEDA	110-18-9	1.30
CN (83 °C)[b]	57-12-5	Q^+		2.2
		CE		0.03
		TMEDA		1.1
F (83 °C)[b]	16984-48-8	Q^+		42
		CE		147
		TMEDA		107
Ad[a] (rt)	50339-88-3	Q^+		1.18
		CE		6.63
		TMEDA		3.23
		NONE		41

[a] Ad^- is the adeninyl anion prepared from adenine and potassium hydroxide. The products obtained from the alkylation of the adeninyl anion under such conditions will be discussed in a forthcoming publication. [b] These reactions also proceed well at room temperature and the trends do not change.

Table II. A Comparison of the Ability of Q^+, 18-Crown-6, and TMEDA to Catalyze the Reaction

$$\underset{(1.0\ M)}{CH_3(CH_2)_4CH_2Br + KN} \xrightarrow[\text{acetonitrile}]{\text{catalyst}} CH_3(CH_2)_4CH_2N + KBr$$

N^- (2.0 equiv)	Catalyst (0.1 equiv)	Half-life, h
CH_3CO_2 (83 °C)[b]	Q^+	0.11
	CE	0.13
	TMEDA	0.15
CN (83 °C)[b]	Q^+	0.98
	CE	0.57
	TMEDA	1.26
Ad[a] (83 °C)	Q^+	0.33
	CE	0.42
	TMEDA	0.54

[a,b] See footnotes *a* and *b* for Table I.

between a *solid–liquid* interface. In this regard it is performing "crown ether type" chemistry.

We have also compared the catalytic efficiency of Q^+ with that of 18-crown-6 (CE) and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA)[2a] for transporting the acetate,[2a,6] fluoride,[7] cyanide,[2a,8] and adeninyl anions from the crystalline state into an organic solvent. *The data indicate that Q^+ is equivalent to, and in most cases markedly superior to, both CE and TMEDA* (see Tables I and II). However, this trend is dramatically reversed in the case of the cyanide anion.[9,10]

The function of Q^+ in these reactions is to exchange the alkali metal cation for a soluble quaternary ammonium ion. The new quaternary ammonium salt is much more dissociated in the organic phase than the alkali metal salt and therefore much more reactive for displacement reactions. After the chemical reaction occurs, a new Q^+X^- is formed and available for another catalytic performance. The reason for the faster reactions with Q^+ vs. CE and TMEDA is either an enhanced nucleophilicity of the dissolved anion or a greater efficiency in transporting the anion into the organic phase (or both) and must be established experimentally.

Q^+ offers the flexibility of catalyzing reactions in both liquid–liquid and solid–liquid systems at least as well as crown ethers. Furthermore, it overcomes all of the disadvantages accompanying crown ether catalysis. For example, the catalytic ability of Q^+ *is applicable to all cationic species* whereas a specific crown should be chosen for each cation[11] (15-crown-5 for Li^+, 16-crown-5 for Na^+, 18-crown-6 for K^+, etc.) for optimum performance. For those reactions which are particularly slow, greater amounts of Q^+ may be employed since it is soluble in all proportions in all organic solvents; most crown ethers have solubility limits in several solvents. Finally, Q^+ is cheap[5] (3¢/10 g vs. $15/10 g of 18-crown-6) and perhaps most important it is nontoxic.[12] For these reasons we consider Q^+ the phase-transfer catalyst of choice and hope to see many new applications of this versatile catalyst.

Experimental Section

All reactions within a series were done under identical conditions. All products were shown to be stable to the reaction conditions. The certainty of anhydrous conditions, and thus a truly solid–liquid system, was assured by slurrying the potassium salt (predried), catalyst, and solvent (sieve dried) with powdered 4A molecular sieves for 24 h prior to adding the alkylating agent. This procedure also ensured that the particle size of the salts was uniformly fine. The values for the half-lives were obtained by removing a small aliquot from the reaction mixture, centrifuging the sample, and analyzing the centrifugate for both starting material and product[13] by GC.[14] A few samples around the 50% conversion point were taken and the half-life was determined by assuming that pseudo-first-order kinetics was operative. Values obtained in this fashion were quite consistent with each other and varied by less than 10%. Conversions greater than 95% and yields above 90% were obtained for those reactions which were continued to completion. Only substitution reactions were observed for hexyl bromide with all three catalysts; elimination did not compete to any significant degree.

A typical procedure follows: A 25-mL flask was charged with 10 mL of acetonitrile containing 1.0 mmol of phase-transfer catalyst (from a 0.1 M stock solution stored over 4A molecular sieves), 20 mmol of potassium OAc^-, CN^-, F^-, or Ad^- (oven dried, vacuum desiccator stored), and 0.5 g of powdered 4A molecular sieves (<3% loss on drying). The vessel was sealed and the mixture was magnetically stirred for 24 h and then the alkylating agent was charged. GC analysis, as described, was used to determine the half-life for conversion of the starting material to product. Replicate experiments were always within ±10%; half-life data are found in Tables I and II.

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(5) A mixture of $(n\text{-}C_8\text{-}C_{12})_3NCH_3{}^+Cl^-$ average molecular weight ~500; available from McKerson Corp., Minneapolis, Minn. 55408, approximately $9 per gallon. Our sample had a molecular weight of 520 by Cl^- titration.
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(9) The difference in the catalytic ability is even more pronounced at 25 °C: Q^+, $t_{1/2} = 34$ h; TMEDA, $t_{1/2} = 27$ h; CE, $t_{1/2} = 0.33$ h! A possible explanation for the slower rates with cyanide and Q^+ is the low efficiency of the quaternary ammonium salt to solubilize cyanide relative to other nucleophiles. The K_{eq} for Q^+Cl^- and KOAc is 1.76×10^{-2} and K_{eq} for Q^+Cl and KCN is 0.25×10^{-2}. These values were determined by slurrying the reaction mixture (minus alkyl halide) for 1 h, filtering, and titrating the filtrate for chloride.
(10) Other workers have reported that tetrabutylammonium halides are about as reactive as crown ether complexed halides. See D. J. Sam and H. E. Simmons, *J. Am. Chem. Soc.*, **96**, 2252 (1974).

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(13) Except for the adenine alkylations where the product was not volatile. In those examples mesitylene was used as an internal standard and the rate of alkylation was determined only by monitoring the disappearance of alkylating agent.

(14) Analyses were performed on a Hewlett-Packard Gas Chromatograph Model 5830A using a 6-ft column packed with 3% SE-30.

Ozonation of Nucleophiles. 8. Secondary Amines[1]

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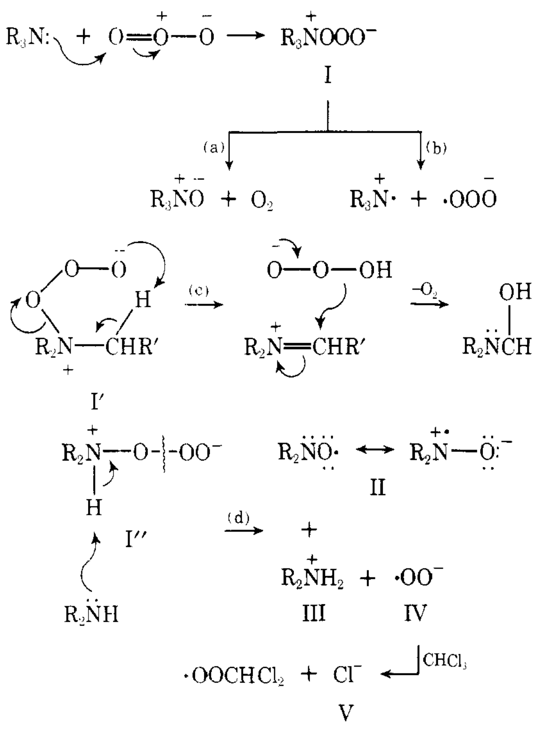
Secondary amines react with ozone via two major routes, one involving nitroxide and ammonium salt formation and the other involving side-chain oxidation. The first appears to be the only reaction type with di-*tert*-butylamine and the major route with diisopropylamine. Side-chain oxidation is the major route with di-*n*-butylamine. Detailed mechanisms are proposed based on present findings and theories developed in earlier studies with primary, secondary, and tertiary amines bearing primary, secondary, and/or tertiary alkyl groups.

Previous papers in this series have been concerned with ozonations of various primary, secondary, and tertiary amines,[2-7] as well as with a similar study regarding certain dialkyl sulfides.[1] Studies with primary amines having primary, secondary, and tertiary alkyl substituents have been published,[2,4,7] but the only secondary and tertiary amines so far included are di-*tert*-butylamine,[5] tri-*n*-butylamine,[2,3] and 1-di-*n*-butylamino-2-butanone.[3] These investigations have led to the proposal of four competing fates (Scheme I) for the initially formed ozone–amine adduct (I). The equations representing these fates (a–d, Scheme I) depict only the initial steps; additional reactions generally follow.

The present paper describes ozonations of diisopropylamine and di-*n*-butylamine and completes and summarizes our studies concerning secondary amines possessing primary, secondary, and tertiary alkyl substituents, as did our earlier paper[7] with primary amines.

The ozonations of diisopropylamine were performed with 1 mol of amine in chloroform (at −65 °C), methylene chloride (−78 °C) and carbon tetrachloride (−20 °C). Ozone reacted quantitatively and the molar ratio of ozone to amine reacting was approximately 2 in the chloroform and methylene chloride reactions and 1 in the carbon tetrachloride reaction. The molecular oxygen yield was 0.7–0.9 mol/mol of ozone reacting. These and other results are shown in Table I, along with results from ozonation of diisopropylhydroxylamine.

Scheme I



The results in chloroform solvent (experiment 1, Table I) were similar to those obtained with di-*tert*-butylamine in the same solvent,[5] with the exception that the nitroalkane yield was only about half as high as with di-*tert*-butylamine and that obvious side-chain oxidation products were obtained. A major product was diisopropylammonium chloride, analogous to findings with di-*tert*-butylamine[5] (as well as with primary amines[7]). However, the ratio of salt to nitro compound was greater than 1 with diisopropylamine but less than 1 with di-*tert*-butylamine.[5] The origin of the salt was shown to be fate d (Scheme I, R = *i*-Pr), as found also for di-*tert*-butylamine,[5] rather than the cation radical–ozonate anion radical route (fate b, Scheme I) characteristic of primary amines.[7] EPR studies, in pentane at −100 °C, Freon 11 at −120 °C, or the neat amine at −70 °C, gave no indication of the ozonate anion radical but showed a strong nine-line signal characteristic of diisopropyl nitroxide (II, Scheme I, R = *i*-Pr)[8] (cf. ref 5). Other workers also have shown that dialkyl or diaryl nitroxides are produced in the first stage of ozonation of secondary amines.[9]

The ozonations of di-*tert*-butylamine in chloroform, to give di-*tert*-butyl nitroxide (II, R = *t*-Bu) and di-*tert*-butylammonium chloride (III + V, Scheme I, R = *t*-Bu), and of di-*tert*-butyl nitroxide to give 2-methyl-2-nitropropane and other products, were described in previous papers.[5,6] Equation 1 describes the overall results.[5]

$$\begin{aligned}8t\text{-}Bu_2NH + 14O_3 + 6CHCl_3 &\rightarrow 4t\text{-}BuNO_2 + 4t\text{-}Bu_2NH_2^+Cl^- \\ &+ 2t\text{-}BuOH + 2Me_2C{=}O + 6Cl_2C{=}O \\ &+ Cl_2 + CH_3OH + H_2C{=}O + 2H_2O + 10O_2 \quad (1)\end{aligned}$$

Reactions analogous to most of those leading to eq 1 (eq 7–10, ref 5 and 6–8, ref 6) would also be expected to occur during ozonations of diisopropylamine and diisopropyl nitroxide, with, however, different weightings and certain additions, the principal one of which has to do with the difference in stabilities of the dialkyl nitroxides involved. Dialkyl nitroxides

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