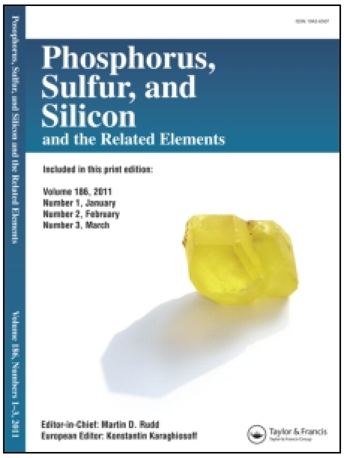

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MECHANISM OF THE REACTION OF DIPHENYL *N*-BROMOSULFILIMINE WITH SULFIDES, PHOSPHINES AND TERTIARY AMINES

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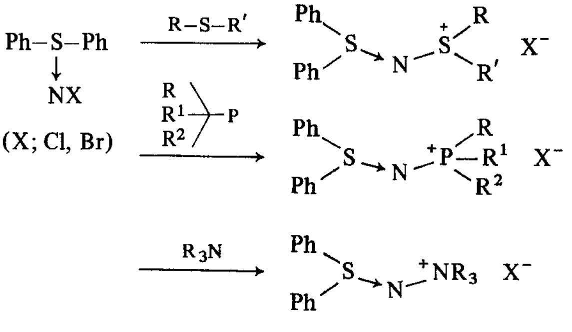
The mechanism of the reactions of diphenyl *N*-bromosulfilimine (I) with such nucleophiles as sulfides, phosphines and tertiary amines was investigated. In the presence of water, (I) reacts with sulfides or phosphines to afford the corresponding sulfoxides or the phosphine oxides in moderate yields; however, the reaction with tertiary amine gave only the *N*-t-aminosulfilimine derivative. The effect of ring size in the reaction with cyclic sulfides suggests that the reaction proceeds via initial bromine transfer from the nitrogen atom to the sulfur atom of the cyclic sulfides followed by S_N2 type substitution of bromide on the sulfur atom of the cyclic sulfide with the sulfilimino group. The phosphine oxide obtained in the reaction of (I) with optically active methyl *n*-propyl phenyl phosphine was racemized but retained a small portion of the optical activity. In the case of tertiary amines, even 1,4-diazabicyclo-(2,2,2)-octane (DABCO), in which the back side of the nitrogen atom is blocked, reacted smoothly to afford the corresponding ammonium salts, suggesting the reaction to be of S_N2 type on the nitrogen atom of the sulfilimine.

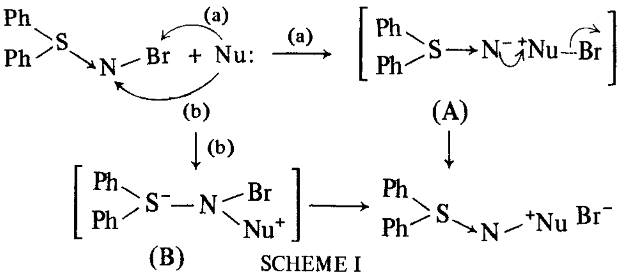
INTRODUCTION

Recently we found a convenient and versatile procedure to prepare *N*-unsubstituted diarylsulfilimine (free sulfilimine) by treating the corresponding *N*-*p*-tosylsulfilimine with conc. sulfuric acid.[1,2] The free sulfilimine is a key compound which opened a new field of chemistry of trivalent sulfur compounds. Various diaryl *N*-acylsulfilimines were prepared by treating diphenyl free sulfilimine with acylating agents[2,3] and the Michael addition of the free sulfilimine to electrophilic alkenes was found to afford aziridine rings.[4,5] Meanwhile, when free sulfilimines were treated with halogenating reagents, the corresponding *N*-halosulfilimines were obtained in high yields.



Earlier we reported that the *N*-halosulfilimine reacts readily with such nucleophiles as sulfides, phosphines and tertiary amines affording the sulfonium, phosphonium and ammonium derivatives as shown below.[6]

Although the mechanisms for these reactions have not been explored, the reactions of the *N*-halosulfilimine with nucleophiles appear to proceed via nucleophilic substitution on the iminonitrogen atom. However, when the reactions of diphenyl *N*-bromosulfilimine with sulfides or phosphines were carried out in the presence of a small amount of water, the corresponding sulfoxides of phosphine oxides were obtained. Thus, the reactions do not seem to proceed by way of the S_N2 process (route (b)) on the nitrogen atom but by an initial attack of the sulfides or phosphines on the bromine atom to form the halosulfonium or the halophosphonium salts as intermediates, namely via route (a), as illustrated in Scheme I.



SCHEME I

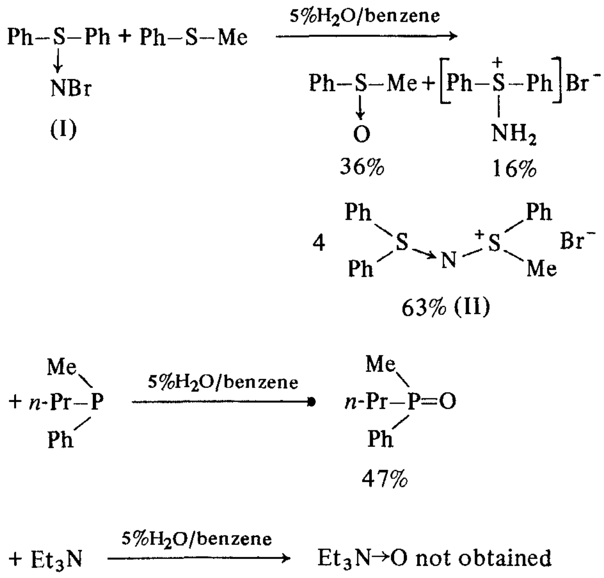
In order to understand the mechanisms of these reactions, we have carried out the reactions of (I) with (i) sulfides, phosphines and tertiary amines in the presence of water, (ii) cyclic sulfides, (iii) an optically active phosphine and (iv) bicyclic tertiary amines.

This paper describes in detail the mechanisms of the reactions of *N*-halosulfilimine with such nucleophiles as sulfides, phosphines and tertiary amines.

RESULTS AND DISCUSSION

Reaction of (I) in the Presence of Water

Generally, sulfides (or phosphines and tertiary amines) reacted with (I) in anhydrous media (e.g., benzene) at room temperature to afford the corresponding diphenylsulfiliminosulfonium salts (or phosphonium salts and ammonium salts) in quantitative yields.[6] However, when (I) was treated with methyl phenyl sulfide in a benzene solution containing 5% water, methyl phenyl sulfoxide was obtained in 36% yield together with methyl phenyl (diphenylsulfilimino)sulfonium bromide (II) in 63% yield. Similarly, in the case of methyl *n*-propyl phenyl phosphine, the corresponding phosphine oxide was obtained, whereas triethylamine did not afford the corresponding amine *N*-oxide but the ammonium salt.

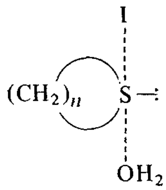


The oxidation of either sulfides or phosphines to the corresponding sulfoxides or phosphine oxides with *N*-bromo-succinimide or bromine-pyridine complex is known to proceed via an initial formation of bromosulfonium or bromophosphonium salts which are readily hydrolyzed to afford the corresponding sulfoxides[7] or phosphine oxides.[8] Similarly, when the reaction of (I) with nucleophiles was carried out in tetrahydrofuran, another less polar solvent, sulfoxides were obtained in moderate yields. These results suggest that the reactions proceed via the initial formation of the bromosulfonium salts, which are readily hydrolyzed with water to afford the corresponding sulfoxides. Thus, sulfides and phosphines are considered to attack the bromine atom of the *N*-bromosulfilimine, affording initially the bromosulfonium or the phosphonium salts (A), followed by an intramolecular substitution on the sulfur or phosphorus atom to replace bromide by imino-nitrogen, eventually yielding (II). Unlike the two previous reactions, there was no formation of t-amine oxide in the reaction of (I) with tertiary amines, nor was there any indication of the formation of the *N*-bromoammonium salts which upon treatment with aqueous alkali would give olefins and/or secondary amines.[9, 10] Thus, the reaction of (I) with tertiary amines appears to undergo reaction via route (b), namely, a direct nucleophilic substitution (S_N2) on the nitrogen atom of the sulfilimine (B) by amines, as we shall discuss later.

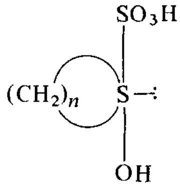
The Effect of Ring Size on the Reaction of (I) with Cyclic Sulfides

In order to shed further light on the mechanisms of diphenylsulfiliminosulfonium salt formation, we carried out the reactions of (I) with cyclic sulfides at −1.5°C in chloroform and obtained the corresponding cyclic diphenylsulfiliminosulfonium salts in quantitative yields.

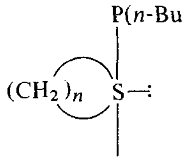
The effect of ring size on the S_N2 displacement reactions on the trivalent sulfur atoms revealed[11] that the relative rates of the reactions generally fall in the following order: 5- > 7- > 6-membered cyclic sulfur compounds in the acid-catalyzed reduction of cyclic sulfoxides with iodide ion; tetramethylene sulfoxide is reduced 700 times faster than pentamethylene sulfoxide.[11a] Johnson and his coworkers[11b] also observed a similar trend in the reduction of cyclic sulfoxides by sodium hydrogen sulfite, and proposed (IV) as either the transition state complex or an energetically contiguous intermediate. Recently, we reported that the relative rates of the reduction of cyclic *N*-*p*-tosylsulfilimine with such nucleophiles as cyanide ion or tri-*n*-butyl phosphine fall in a similar rate sequence.[11c] This reaction is considered also to involve the tetravalent intermediate (V), as shown below. These rate sequences seem to be correlated with the steric strains



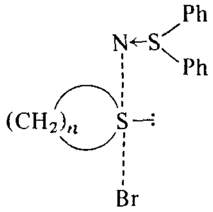
(III)



(IV)



(V)



(VI)

of the transition complexes. Further, when sulfides act as nucleophiles and attack the electrophilic center at the transition state, the relative rates of the cyclic sulfides do not change markedly with the change of the ring size as illustrated in the reaction of cyclic sulfides with iodine[12a] or hydrogen peroxide.[12b] If the reaction of (I) with cyclic sulfides proceeds through the initial fast formation of the sulfonium salts followed by the rate-determining nucleophilic attack of the sulfilimino group on the trivalent sulfur atom, the transition complex (VI) would have a similar structure to that of (III)-(V). Therefore, the effect of ring size should also resemble that of the acid-catalyzed reduction of sulfoxides with iodide or sodium hydrogen sulfite or the reaction of N-p-tosylsulfilimine with cyanide ion or phosphines. The actual rates of the reactions were measured by the use of an electric conductometer and the relative rates thus obtained are summarized in Table I. The relative reactivities of cyclic sulfides with (I) observed in this experiment show a similar trend to those of other reactions which are considered to proceed via the S_N2 type displacement on the trivalent sulfur atom.[11] Therefore, we believe that the reaction of (I) with sulfides proceeds via route (a).

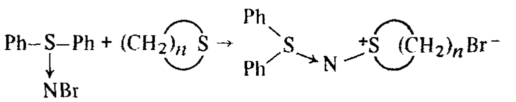
The Reaction of (I) with Optically Active Phosphine

(+)–(S)–Methyl n-propyl phenyl phosphine ((+)–(S)–(VII)) was prepared according to the method developed by Mislow.[13] The reaction of (I) with (+)–(S)–(VII) was carried out in benzene solution under ice-cooling for 1 hr. After washing the reaction mixture with n-hexane and evaporating the solvent, methyl n-propyl phenyl(diphenylsulfilimino)phosphonium bromide (VIII) was obtained in good yield. Without further purification, (VIII) was hydrolyzed with aqueous sodium hydroxide solution to afford (+)–(R)–methyl n-propyl phenyl phosphine oxide (IX) in good yield as shown in Table II.

The hydrolysis of phosphonium salts is known to proceed with inversion of configuration around the phosphorus atom.[14, 15] If the reaction of (I) with (VII) would proceed via route (a), the phosphine oxide obtained by the hydrolysis of (III) should retain its configuration, since both route (a) and the hydrolysis of (VIII) are inversion processes. Thus, (+)–(S)–(VII)

TABLE I

The reaction of (I) with cyclic sulfides (at −1.5°C)

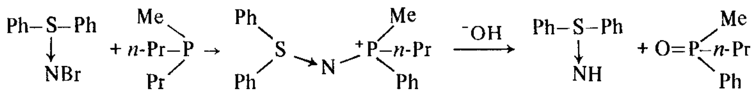


Sulfide	$k_2 \times 10^3$ (l/mol sec)	k_{rel}	Sulfoxide		Sulfilimine[a]	Relative rates for the reaction with I_2[b]	H_2O_2[c]
$(CH_2)_4S$	53.9	17.8	717[d]	6.3[e]	25.0	1.60	1.80
$(CH_2)_5S$	3.03	1	1	1	1	1	1
$(CH_2)_6S$	1.56	0.51	9.9	3.3	10.0	–	0.96

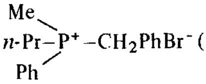
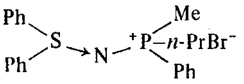
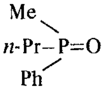
[a] Relative rates of the reaction of cyclic N-p-tosylsulfilimine with tri-n-butylphosphine; Ref. 11c.
[b] Ref. 12a.
[c] Ref. 12b.
[d] Relative rates of the reduction of cyclic sulfoxides with iodide ion; Ref. 11a.
[e] Relative rates of the reduction of cyclic sulfoxides with sodium hydrogen sulfite; Ref. 11b.

TABLE II

The reaction of (I) with (+)-(S)-(VII)



(I) (VII) (VIII) (IX)

	$[\alpha]^{25}_{589}$ (MeOH)	
 (X)	+29.2° (op, 79.3%)	+31.7°
 (VIII)	(−0.7°)	–
 (IX)	+0.4° (oy, 2.5%)	–
Benzyl bromide salt of recovered phosphine	–	+32.8°

should give (+)–(R)–(IX). On the other hand, if the reaction proceeds via route (b), the configuration of the phosphine oxide should be inverted, since the initial addition of (VII) to (I) is a retention process and the subsequent reaction is an S_N2 path. Thus, (+)–(S)–(VII) should afford (–)–(S)–(IX). The stereochemical results shown in Table II, indicate that though the optical yields of both (VIII) and (IX) are quite small, suggesting that the stereochemical course for the reaction is racemization, the phosphine oxide has partially retained the configuration which is quite significant. Furthermore, when we used (–)–(R)–(VII) instead of (+)–(S)–(VII), the resulted (IX) was found to have (–)–(S) configuration with a small magnitude of $[\alpha]_D$ indicating that the reaction proceeds via the route (a) giving the partially retained phosphine oxide though it racemizes substantially due mainly to the interaction between the phosphine and a small amount of bromine. The optically active phosphine did not racemize under these reaction conditions since the recovered phosphine retained exactly the same sign and magnitude of $[\alpha]_D$ as the starting material. In order to check the effect of temperature in this racemization, the reaction was carried out at −65 to −70°C; however, the phosphine oxide obtained likewise had very little optical activity. On the other hand, when the optically active phosphine was treated with molecular bromine at the same temperature, the phosphine oxide obtained was found to be racemized completely. Horner reported that the adduct of the phosphine and halogen exists as an equilibrium mixture between the pentacovalent and the ionic states, and hence optically active phosphines are racemized very readily by this reaction.[16] These observations suggest that the small magnitude of the optical activity of the resulting phosphine oxide is due mainly to the rapid racemization of initially formed bromophosphonium salt ($\geqslant P^+–Br\ ^-N\leftarrow S<^{Ph}_{Ph}$) by the interaction with a trace of bromide ion generated by the decomposition of (I) in the reaction mixture.[17]

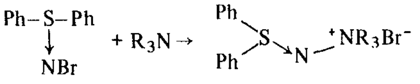
The Reaction of (I) with Tertiary Amines

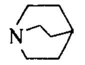
The products obtained in the reaction of (I) with several tertiary amines are shown in Table III.

If the reactions of (I) with tertiary amines proceed via the initial attack of tertiary amine on bromine of (I), as in the case of sulfides or phosphines (route (a)), the intermediates thus formed should be *N*-bromoammonium salts (quaternary ammonium salts) which would afford the olefins or α-substituted products upon treatment with hydroxide. However, there was no indication of *N*-bromoammonium salt formation, and the products obtained are the nucleophilic substitution products of (I) with tertiary amines by the Menshutkin-type reaction.[9] Consequently, the mechanism of the reaction of

TABLE III

The reaction of (I) with tertiary amines



Amine	Counter ion	mp	nmr (δ, ppm)	Elemental analysis Calcd. C; H; N; Found. C; H; N;
Et_3N[a]	ClO_4^-	128–9 (dec)	7.60–7.82 (m, 4H) 7.35–7.60 (m, 6H) 3.54 (q, 6H, CH_2) 1.20 (t, 9H, CH_3)	–
	ClO_4^-	195–9 (dec)	7.40–7.90 (m, 10H) 3.33–3.75 (m, 6H) 2.80–3.33 (m, 10H)	52.49 5.38 10.20 52.20 5.36 10.16
	Br^-	195–6 (dec)	7.63–7.95 (m, 4H) 7.36–7.63 (m, 6H) 3.57–4.10 (m, 6H) 1.90–2.35 (m, 7H)	58.31 5.92 7.16 58.13 5.92 7.18

[a] Ref. 6.

(I) with tertiary amine is assumed to proceed not via route (a) but via route (b). This argument seems to be supported by the facile reaction of (I) with DABCO or quinuclidine in which the S_N2 type reaction on the nitrogen atom of the N-bromoammonium salt of DABCO or quinuclidine cannot take place since the back side of the nitrogen atom is blocked.

Consequently, although the reactions of (I) with such nucleophiles as sulfides, phosphines and tertiary amines afforded structurally similar products, the reactions of sulfides and phosphines which proceed via route (a) are different from those with tertiary amines (route (b)). The difference of attacking site due to the change of nucleophile may be due partly to the softer nature of both sulfides and phosphines than amines[18] and partly to a special affinity between nitrogen atoms in substitution.

EXPERIMENTAL

All melting points are uncorrected. The ir spectra were recorded on a Hitachi 215 Spectrometer. The nmr spectra were recorded by a Hitachi R-24A High Resolution nmr Spectrometer in deuterated chloroform using tetramethylsilane as the internal standard, and the optical rotations were determined with Union OR-50D Automatic Digital Polarimeter and JASCO J-20 Automatic Recording Spectropolarimeter.

Diphenyl N-bromosulfilimine (I) was prepared according to the procedure reported earlier.[6]

The Reaction of (I) with Sulfide, Phosphine and tertiary Amine in the Presence of Water

Diphenyl N-bromosulfilimine (I) (2 mmol) and an equimolar amount of methyl phenyl sulfide were dissolved in 10 ml of benzene containing 5% water, and the solution was vigorously stirred at room temperature for 24 hr. After the reaction, benzene was evaporated under reduced pressure. The residue was dissolved with water and the aqueous solution was extracted with chloroform, and the chloroform solution was dried over anhydrous magnesium sulfate. The chloroform was evaporated and the residue was chromatographed through a column packed with silica gel using chloroform as an eluent. Methyl phenyl sulfoxide, methyl phenyl(diphenylsulfilimino)sulfonium bromide, diphenylaminosulfonium bromide and diphenyl sulfide were obtained in 36, 63, 16 and 8% yields, respectively. The structure of the isolated products was determined by comparing the spectra with those of authentic samples. Similarly, in 5% aqueous tetrahydrofuran, methyl phenyl sulfoxide was obtained in 25% yield (GLC).

Methyl n-propyl phenyl phosphine (VII) (0.7 mmol) was treated similarly with (I) (0.7 mmol) in 7 ml of benzene containing 5% water at room temperature for 1 hr. By the usual work up, the corresponding phosphine oxide (IX), methyl-n-propylphenyl(diphenylsulfilimino)phosphonium bromide and diphenylaminosulfonium bromide were obtained in 47, 38 and 15% yields, respectively. In the case of triethylamine, the corresponding amine N-oxide was not detected by ir spectra.

Preparation of Cyclic Diphenylsulfiliminosulfonium Bromides

Tetramethylene- and pentamethylene(diphenylsulfilimino)sulfonium bromides were prepared according to the procedure reported earlier.[19] Hexamethylene(diphenylsulfilimino)sulfonium bromide was prepared by the reaction of (I) with

1.2 molar amount of hexamethylene sulfide in 82% yield. The sulfonium bromide was converted to the corresponding perchlorate by treating the bromide with aqueous sodium perchlorate; mp, 157-8°C, elemental analysis; $C_{18}H_{22}ClO_4NS_2$, calcd., C: 51.98, H: 5.33, found., C: 52.24, H: 5.18.

Kinetic Measurements

A typical run was as follows. The kinetic measurement to determine the rate constants was carried out by observing the change of the electric conductivity of the reaction mixture directly in the reaction cell using a liquid-specific electric conductometer. Platinum electrodes were sealed into the reaction cell in which 6 ml of chloroform containing pentamethylene sulfide (1.52×10^{-3} mol) was placed. After the cell was placed in a thermostated bath for a sufficient length of time to equilibrate the temperature of the chloroform solution with that of the bath, (I) (5.05×10^{-5} mol) was added at once. The change of the electric conductivity was directly recorded until the change of conductivity was no longer observed. The second-order-rate constants (k_2) were computed by the usual method. The results obtained are summarized in Table I.

The Reaction of (I) with Optically Active Phosphine

Optically active methyl *n*-propyl phenyl phosphine (VII) was prepared according to the method developed by Mislow.[13] In order to determine the optical purity (VII) was converted to the corresponding phosphonium salt ((+)-(S)-(X)) by treatment with a tenfold excess of benzyl bromide in acetonitrile at 50°C for 2 hr.[13] (+)-(S)-(X); 89% yield mp, 192-6°C, $[\alpha]^{25}_{589}$ = +29.2° (c, 1.70, MeOH, op, 79.3%) (Ref. 19) mp, 201°C, $[\alpha]_D$ = 36.8° (c, 1.507, MeOH)).

Reaction of (I) with (+)-(S)-(VII): (+)-(S)-(VII) (1.8 mmol) was added to the benzene solution of (I) (1.5 mmol) and the reaction was carried out with vigorous stirring in an ice-water bath for 1 hr. After the reaction, the solvent was evaporated under reduced pressure to afford an oily product. The product was purified only by washing 5 times with *n*-hexane. Diphenylsulfiliminophosphonium bromide (VIII) was obtained in 90% yield. (VIII) (oil); $[\alpha]^{25}_{589}$ = −0.7° (c, 3.55, MeOH), ir (cm^{-1}), 920, 1080, 1100, nmr (δ, ppm), 0.97 (t, 3H), 1.22-1.75 (m, 2H), 2.38 (d, 3H, $J_{P\text{-}H}$ = 13 cps), 2.10–3.0 (m, 2H), 7.35-8.20 (m, 15H).

Alkaline Hydrolysis of (VIII)

The hydrolysis of (VIII) was carried out with 10% aqueous sodium hydroxide solution in an ice-water bath for 1 hr. Then the reaction mixture was poured into water. The aqueous solution was extracted with methylene chloride and the methylene chloride extract was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the products obtained were separated by preparative thin layer chromatography performed with silica gel using chloroform–methanol as the eluent. The free sulfilimine and the phosphine oxide (IX) were obtained in 70 and 82% yields, respectively. (IX) (oil); $[\alpha]^{25}_{589}$ = +0.4° (c, 1.88, MeOH), oy, 2.5%, ir (cm^{-1}), 1175 (P=O), (Ref. 21) $[\alpha]_D$ = 20.0° (MeOH)).

The Reaction of (I) with Excess of (VII)

The *N*-bromosulfilimine (I) (0.56 mmol) reacted with a twofold excess of (VII) [benzyl bromide salt, $[\alpha]^{25}_D$ = +31.7° (c, 1.64, MeOH), op, 86.1%, mp, 192–5°C] with the procedure described above. After the reaction the solvent was evaporated and the oily residue was washed with *n*-hexane. The phosphine was recovered from *n*-hexane solution in 41% yield. This phosphine was converted to the corresponding phosphonium salt [$[\alpha]^{25}_D$ = +32.8° (c, 2.38, MeOH), op, 89.1%, mp, 193–6°C].

The Reaction of (I) with Optically Active (VII) at Low Temperature

The methylene chloride solution of (I) (1 mmol) and (+)–(S)–(VII) 1.2 mmol, op, 86.1%) was treated with 10% sodium hydroxide solution of water-methanol under vigorous stirring at −65 to −70°C for 5 min. Then the reaction mixture was poured into water and extracted with methylene chloride. The methylene chloride solution was dried over anhydrous magnesium sulfate. After evaporating the solvent, the oily residue was separated by preparative thin layer chromatography with chloroform as an eluent. Phosphine oxide (IX) was obtained in 44% yield, but the optical activity, measured using the D line, was found to be very small [$[\alpha]^{25}_D$ = +0.4° (c, 0.79, MeOH)].

The Reaction of Optically Active (VII) with Bromine

A methylene chloride solution of (+)–(S)–(VII) (0.66 mmol, op, 86.1%) was cooled at −65 to −70°C and methylene chloride solution of bromine (0.66 mmol) was added dropwise with stirring for 15 min. Then the reaction mixture was hydrolyzed with a 10% sodium hydroxide solution in water–methanol at the same temperature. After the usual work up, the corresponding phosphine oxide (IX) was obtained in 75% yield, but was found to be completely racemized.

The Reaction of (I) with Tertiary Amines

A typical run was as follows. DABCO (2 mmol) was added to the benzene solution of (I) (2 mmol) under vigorous stirring at room temperature and kept for 12 hr. The 1 : 1 adduct deposited in 81.6% yield. Then this ammonium bromide was converted to the corresponding perchlorate by treating with aqueous sodium perchlorate solution. The results obtained are shown in Table II.

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