for 15 h, and the bath temperature was 80 °C. The crystalline product was washed with some hexane and dried. The product was analyzed by mass spectrometry at 20 and 70 eV.

Thermal Decomposition of Diazidomalonamide (14). A solution of diazidomalonamide (**14**) (100 mg, 0.5 mmol) in dodecane (1.0 g) was heated to 140–142 °C in an oil bath for 2 h. At the end of given time the reaction was cooled and the white solid separated, which was washed with hexane (5 mL) to give 50 mg (89%) of 5-carbamoyltetrazole (**15**): mp 230–232 °C (lit.[1] mp 231–232 °C); IR (Nujol) 1700 (C=O) cm^{-1}; NMR (Me_2SO-d_6) δ 4.5 (2 H, s, NH_2), 8.3 (1 H, s, NH); MS, *m/z* (relative intensity) 113 (M^+, 35), 86 (7), 85 (58), 71 (100), 70 (16), 69 (10), 60 (41), 57 (12), 44 (58), 42 (33).

Thermal Decomposition of *N,N'*-Dimethyldiazidomalonamide (16). *N,N'*-dimethyldiazidomalonamide (**16**) (150 mg, 0.7 mmol) in dodecane (1.0 g) was heated in an oil bath to 140–144 °C for 3 h. On cooling the reaction mixture, a white solid separated, which was filtered, washed with hexane (15 mL), and dried to give 80 mg (90%) of 5-(methylcarbamoyl)tetrazole (**17**): mp 233–235 °C (lit.[1] mp 235–236 °C); IR (Nujol) 1665 (C=O) cm^{-1}; NMR (Me_2SO-d_6) δ 2.4 (3 H, s, CH_3), 4.3 (1 H, s, $NHCH_3$), 8.3 (1 H, s, NH); MS, *m/z* (relative intensity) 127 (M^+, 20), 99 (18), 98 (4), 85 (16), 84 (8), 70 (16), 69 (12), 58 (100), 56 (38), 55 (10), 44 (15), 43 (44), 42 (30).

5-Carbomethoxytetrazole (22). Dimethyl tetrazole-1,5-dicarboxylate (**3**)[1] (372 mg, 2.0 mmol) was dissolved in 3% aqueous potassium hydroxide solution (5 mL) and methanol (10 mL), and the reaction mixture was stirred at room temperature for 6 h. It was diluted with water (20 mL), neutralized with acetic acid, and extracted with chloroform (3 × 10 mL). The combined chloroform extracts were washed with saturated sodium bicarbonate solution and then with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in vacuo to give 75 mg of 5-carbomethoxytetrazole (**22**): mp 96–98 °C; IR (Nujol) 3405 (NH), 1740 ($COOCH_3$) cm^{-1}; NMR ($CDCl_3$) δ 4.16 (3 H, s, CH_3). Anal. Calcd for $C_3H_4N_4O_2$: C, 28.12; H, 3.12. Found: C, 28.43; H, 3.23.

Thermal Decomposition of Dimethyl Diazidomalonate (1) in the Presence of the Lithium Salt of 5-Carbomethoxytetrazole (13-Li). A solution of 5-carbomethoxytetrazole (**22**) (64 mg, 0.5 mmol) in dry tetrahydrofuran (5 mL) was cooled to −78 °C, and to this was added dropwise a solution of *n*-butyllithium (0.5 mL, 2.5 M) in dry tetrahydrofuran (5 mL) under nitrogen. The reaction mixture was stirred at −78 °C for 1 h, and then it was slowly brought to room temperature. After the mixture was stirred 0.5 h at room temperature, a solution of dimethyl diazidomalonate (**1**) (1.0 g, 4.6 mmol) in dodecane (2.0 g) was added at once, and the reaction mixture was heated in an oil bath to 104–106 °C for 2 days. The reaction mixture was cooled to room temperature, and the dodecane was decanted from a black oil. The oil was washed with hexane (2 × 5 mL): IR (Nujol) 1745 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 4.1 (3 H, s, CH_3), 4.51 (3 H, s, CH_3). The NMR of the crude product shows 10% of the 5-carbomethoxy-1-methyltetrazole.

Thermal Decomposition of Diazidomalonamide (14) in the Presence of the Lithium Salt of 5-Carbamoyltetrazole (15-Li). To a cold solution of 5-carbamoyltetrazole (**15**) (56.5 mg, 0.5 mmol)[1] in dry tetrahydrofuran (10 mL) at −78 °C was added dropwise a solution of *n*-butyllithium (1.5 mL, 2.5 M) in dry tetrahydrofuran (10 mL) under nitrogen. The reaction mixture was allowed to stir at −78 °C for 1 h, and then it was slowly brought to room temperature and was stirred for 2 h. To this was added a suspension of diazidomalonamide (**14**) (500 mg, 2.5 mmol) in dodecane (1 g), and the reaction mixture was heated at 70–75 °C for 15 h. The reaction mixture was cooled, and the solid was filtered, washed with water and then with hexane, and dried to give 200 mg (81%) of 5-carbamoyltetrazole (**15**): mp 240–242 °C; IR (KBr) 1700 (C=O) cm^{-1}.

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Registry No. **1**, 19132-24-2; **1**-d_6, 97763-82-1; **2**, 32366-17-9; **2**-d_3, 97752-03-9; **2'**-d_3, 97752-04-0; **2**-d_6, 97752-05-1; **3**, 16932-76-6; **13-Li**, 97752-06-2; **14**, 32366-18-0; **15**, 32366-22-6; **15-Li**, 97752-07-3; **16**, 32366-19-1; **17**, 32366-23-7; **22**, 97752-08-4.

Reaction of *gem*-Dibromocyclopropanes with Potassium Dimethyl Phosphite in Liquid Ammonia. A Highly Stereoselective Reduction

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Although *gem*-dibromocyclopropanes undergo substitution with other $S_{RN}1$ nucleophiles in liquid ammonia solution stimulated by "350 nm" light, only reduction is observed with dimethyl phosphite ion. This reduction proceeds in the absence of light and involves nonradical intermediates. It gives high yields of the trans monobromides **4** with little or no contamination by the cis isomers **5** or the direduced products **6**. *gem*-Dichlorocyclopropanes are inert under the reaction conditions. The reaction is suited to preparative work.

It has recently been reported that *gem*-dibromocyclopropanes undergo a photostimulated reaction with certain nucleophiles to afford disubstituted products.[1] The reactions bear apparent similarity to the well-known $S_{RN}1$ reaction in that they are retarded by radical inhibitors and do not occur in the dark. Nucleophiles which have been shown to react with *gem*-dibromocyclopropanes,[1] such as thiophenoxide ion, pinacolone enolate, and cyanomethyl anion, are all effective $S_{RN}1$ nucleophiles on aromatic systems.[2,3]

However, diphenylphosphide ion, a very reactive nucleophile in aromatic $S_{RN}1$ chemistry,[4] undergoes a reaction with *gem*-dibromocyclopropanes in which the first step is *reduction* to the monobromide, followed by a substitution of the remaining bromine to form cyclopropyldiphenylphosphines.[5,6] We sought, therefore, to examine the behavior of other phosphorus nucleophiles under conditions believed to promote substitution.

Dialkyl phosphite ions are also effective aromatic $S_{RN}1$ nucleophiles,[7] although they are somewhat less reactive

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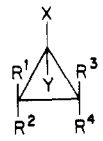
(6) See, also: Rossi, R. A.; Santiago, A. N.; Palacios, S. M. *J. Org. Chem.* **1984**, *49*, 3387–88.

0022-3263/85/1950-3713$01.50/0

Chart I



1, X = Y = Br
2, X = Y = $PO(OMe)_2$
3, X = H; Y = $PO(OMe)_2$; or X = $PO(OMe)_2$; Y = H
4, X = H; Y = Br
5, X = Br; Y = H
6, X = Y = H
7, X = Y = Cl
8, X = :⁻; Y = Br
9, X = Br; Y = :⁻
10, X = H; Y = :⁻

a, $R^1,R^3 = -(CH_2)_4-$; R^2,R^4 = H
b, $R^1,R^3 = -(CH_2)_6-$; R^2,R^4 = H
c, R^1 = Ph; R^2,R^3,R^4 = H
d, $R^1 = CH_3(CH_2)_5$; R^2,R^3,R^4 = H
e, $R^1 = CH_3(CH_2)_3$; R^2,R^3,R^4 = H
f, $R^1 = (CH_3)_3C$; R^2,R^3,R^4 = H
g, R^1,R^2,R^3,R^4 = H
h, $R^1,R^2,R^3,R^4 = CH_3$
i, $R^1,R^2,R^3 = CH_3$; R^4 = H
j, $R^1 = CH_3$; R^2 = CN; R^3,R^4 = H
k, $R^1 = CH_3$; $R^2 = CO_2CH_3$; R^3,R^4 = H

than diphenylphosphide ion.[4] We report now the results of a detailed investigation of the reaction of dimethyl phosphite ion with *gem*-dibromocyclopropanes.

Results

UV Irradiation. Dibromide **1a** was irradiated for 4 h in a Rayonet apparatus equipped with 16 "350 nm" lamps in liquid ammonia with an excess of dimethyl phosphite ion, formed from the reaction of potassium *tert*-butoxide and dimethyl phosphonate.[4] Although these conditions were thought likely to promote substitution, the expected products **2a** or **3a**, however, were not detected (Chart I). Instead, the monobromide **4a** was obtained in virtually quantitative yield. Less than 1% of its isomer **5a** was formed. Similarly, irradiation of **1c** in the presence of dimethyl phosphite ion gave **4c** (96%). The remainder was **5c**; no phosphorus-containing cyclopropyl derivatives could be detected. Irradiation of **1h** in liquid ammonia returned only starting material, although it was noted that **1h** was not completely soluble in the reaction mixture. Addition of THF (25%) gave a homogeneous solution, but 4-h irradiation yielded only 31% of **4h** accompanied by starting **1h** (64%). The substitution products **2h** or **3h** were not detected. Evidently, photostimulated $S_{RN}1$ substitution of cyclopropyl bromides is not a favored process under the reaction conditions with dimethyl phosphite ion.

A phenomenon useful for initiating certain sluggish $S_{RN}1$ reactions is entrainment,[3] where a small amount of a quite reactive substrate is added to the compound under investigation; the resultant radical chains initiated by the reactive substrate often serve to initiate the slower reaction. Iodobenzene is known to be quite reactive with dimethyl phosphite ion under photostimulation.[7] However, addition of 5 mol % of iodobenzene to the reaction mixture containing **1a**, followed by 4-h irradiation, failed to stimulate the production of **2a** or **3a**, even though the iodobenzene had been fully consumed. We did not search further for examples of photostimulated substitution with potassium dialkyl phosphites but chose to investigate the nature of the reduction reaction.

"Dark" Reactions. Treatment of **1a** for 4 h in the dark with excess potassium dimethyl phosphite in refluxing liquid ammonia again gave the isomerically pure monobromide **4a** in quantitative yield. Significantly, no direduction to the cyclopropane **6a** occurred. It was discovered that the reaction was complete after 1 h; even after 5 min, appreciable (82%) quantities of the starting material had been consumed. Diethyl phosphite ion was equally effective in reducing **1a**, giving essentially the same results (100% **4a** after 4 h) as its dimethyl analogue. Dimethyl phosphonate, itself, however, was a rather ineffective reducing agent; after 4 h of stirring in liquid ammonia with **1a** in the dark, **4a** was formed in only 20% yield accompanied by **5a** (2%). The remainder of the reaction was starting material.

Table I. Dark Reactions of 1 with Dimethyl Phosphite Ion in Liquid Ammonia

substrate	substrate remaining, %	4, %	5, %	isolated and distilled (4 + 5), %
1a	0	100	0	91
1b	10	82	0	71
1c	2	96	4	96
1d	0	92	4.5	94
1e	0	91	8	60[c]
1f	0	98	2	88
1g	0	98		n.d.[b]
1h	93	4		n.d.
1h[a]	73	19		n.d.
1i	21	67	7	31[d]
1j	0	76	24	83
1k	0	49	48	74

[a] Using THF/liquid NH_3 (1:3) as solvent. [b] n.d. = not determined. [c] Some thermal decomposition appeared to occur on distillation. [d] Extreme volatility made the isolation of **1i** difficult.

Table I details the results, as determined by calibrated GLC, of the reaction of potassium dimethyl phosphite with a series of cyclopropyl dibromides in refluxing liquid ammonia in the absence of light for 1 h.

In every case, except **1h**, the yield of reduced material was high. With **1h**, as in the irradiated experiments, the low solubility evidently played a part in decreasing the reaction rate, but this was apparently not the only factor since, with cosolvent, unreacted **1h** still remained.

The dibromobicyclononane **1b** gave a high stereochemical preference toward the trans monobromide **4b**; not even a trace of **5b** could be detected in the reaction mixture. With **1c**, the preference for the formation of the trans monobromide over the cis was 24:1. The *n*-alkyl-substituted dibromocyclopropanes **1d** and **1e** both were reduced cleanly, giving 19- and 10-fold excesses of the trans monobromides **4d** and **4e**, respectively.

The *tert*-butyl-substituted cyclopropyl dibromide **1f** exhibited a 50-fold preference toward reduction to the trans monobromide. The unsubstituted compound **1g** was reduced virtually quantitatively. Even **1i** showed a good (9×) selectivity toward giving the trans product **4i**.

Compounds **1j** and **1k**, in which there is substitution on both sides of the ring, did not show a great preference toward dehalogenation from either side, giving mixtures of **4j** and **5j**, and **4k** and **5k**, respectively.

The *gem*-dichlorides **7a** or **7e** were completely inert to dimethyl phosphite ion under the reaction conditions.

Table I also records the yields of isolated, distilled material and demonstrates the preparative utility of the reaction. In contrast to some other preparative methods of reduction, in all cases, no trace of direduced product could be detected in the reaction mixtures.

Table II shows that debromination was markedly slower in THF than in liquid ammonia. Even at room temperature, the reaction returned appreciable amounts of starting material. The reaction in THF using sodium or potassium hydride as base to generate the phosphite ion failed, even though deprotonation of the phosphonate had clearly oc-

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Table II. Dimethyl Phosphite Reductions in Other Solvents[a]

substrate	temp, °C	solvent	base	substrate remaining, %	4, %	5, %
1a	−33	THF	KOBu-*t*	45	51	2
1a	−33	THF/Bu-*t*-OH (3:1)	KOBu-*t*	75	17	1
1a	−33	THF	NaH	96	0	0
1a	−33	THF	KH	100	0	0
1a	25	THF/Bu-*t*-OH (3:1)	KOBu-*t*	38	60	1
1a	25	Me_2SO	KOBu-*t*	0	96	1
1h	25	Me_2SO	KOBu-*t*	0	83[b]	

[a] The reaction time in all cases, except for **1h**, was 1 h. [b] 17% of **6h** was also formed; the reaction time in this case was 4 h.

curred, as evidenced by the temperature of the reaction mixture rising and the liberation of hydrogen. Apparently, a little *tert*-butyl alcohol, formed from the butoxide deprotonation of the phosphonate, is necessary for the reaction to proceed in THF. A vast excess appears to decrease the reaction rate. However, in liquid ammonia, there was essentially no difference in the reaction outcome, whether potassium *tert*-butoxide or sodium hydride was used as the base to deprotonate the phosphonate. Potassium *tert*-butoxide without dimethyl phosphonate caused extensive decomposition of **1a** and no **4a** or **5a** could be detected.

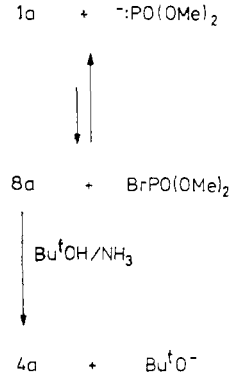
The stereoselectivity was lower in THF and in Me_2SO than in liquid ammonia. The high stereoselectivity in liquid ammonia was not associated with the low reaction temperature, since, in THF, reaction at −33 °C did not give improved stereoselectivity over reaction at 25 °C. Interestingly, **1h**, which was reduced poorly in liquid ammonia, even with cosolvent, debrominated at 25 °C in Me_2SO. The longer reaction time required, however, led to some overreduction of **4h**.

Mechanistic Studies. To exclude the possibility of reaction occurring by single electron transfer or homolytic pathways,[8] the following experiments were carried out.

Dibromide **1a** was treated for 5 min in the dark with dimethyl phosphite ion in liquid ammonia under an atmosphere of oxygen. The yield of **4a** (75%) essentially remained the same as when the reaction was carried out under nitrogen. Similarly, the radical inhibitor, di-*tert*-butyl nitroxide (20 mol %), or *m*-dinitrobenzene (20 mol %), an electron scavenger, had no significant effect on the yields (95% and 92%, respectively, after 45 min) of **4a** in the dark, compared with an identical experiment without inhibitors (yield 92%). These results point to nonradical intermediates. Confirmation that the reducing hydrogen is not derived from dimethyl phosphite's methyl groups was gained by treating $(CD_3O)_2PO^-$ with **1a**; the resultant sample of **4a** had no detectable incorporation of deuterium.

Assignment of Stereochemistry. The identities of the reduced products **4** and **5** were established by comparing their GLC retention times with those of "authentic" samples prepared, except as noted below, by tributyltin hydride reduction of the dibromides **1**.[10] In all such cases, except for **1f**, the major isomer from the phosphite reduction had the same retention time as the minor isomer from the tin hydride reduction, previously assigned[10] to the trans compound and vice versa for the cis compound. The monobromide **4f** was the major product from tributyltin hydride reduction of **1f**, as previously reported.[11]

Scheme I



Its stereochemistry was further confirmed from analysis of its ^1H NMR spectrum.[11] Dibromide **1b** was reported not to afford **4b** on tin hydride reduction;[10] the sample assigned the structure **4b** was shown to be identical with the minor isomer formed on Zn/HOAc reduction of **1b**.[12]

Compounds **4j**, **4k**, **5j**, and **5k** were identified by comparison with samples prepared by zinc reduction of **1j** and **1k**.[13] Their ^1H NMR spectra were in reasonable agreement with that previously reported.[13]

All isolated compounds had ^1H NMR spectral data consistent with their structure, or in agreement with those reported. ^1H coupling constants, J_{trans}, which were all in the range 3.5–3.9 Hz, were derived either directly or from decoupling experiments at 300 MHz for all trans isomers **4**.

Discussion

Lack of Reactivity toward Substitution. The reasons for the lack of reactivity of dimethyl phosphite toward substitution with **1** under the reaction conditions are unclear. Diethyl phosphite ion is, however, some 4–16 times less reactive than diphenylphosphide ion with respect to $S_{RN}1$ substitution with iodo and bromo aromatics.[4] Compounds **1** are clearly rapidly converted to monobromides **4**, which are less reactive to substitution than **1**.[1] Evidently the monobromides, although reactive to diphenylphosphide ion,[5,6] are comparatively inert to potassium dimethyl phosphite. There are, however, insufficient data to speculate on which of the $S_{RN}1$ chain steps is necessarily inefficient with dimethyl phosphite ion and **4**.

Mechanism of Reduction. The experimental results point to an ionic pathway of reduction, the most likely of which seems to be nucleophilic attack *on* bromine by the phosphite ion. Such a nucleophilic displacement process has considerable precedent for phosphanions.[14,15] A

(8) A suggestion has recently been made[9] that 1-iodoadamantane is reduced with diethyl phosphite ion by a process involving single electron transfer.

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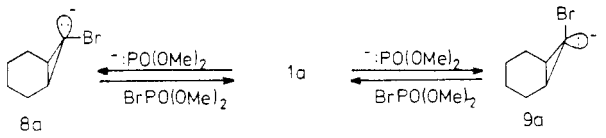
(15) Gillespie, D. G.; Walker, B. J. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1689–95.

Scheme II



pathway consistent with the available data is given in Scheme I, drawn for the reactions of **1a**.

We suggest that the equilibrium between phosphite ion and **1a** lies toward the starting materials as evidenced by the failure of **1a** to react in THF in the complete absence of a proton source. However, when a proton source is present, the anion **8a** can be irreversibly protonated, in effect, pushing the equilibrium toward product formation. Undoubtedly too, in the presence of nucleophilic solvents $BrPO(OCH_3)_2$ undergoes further reaction removing it from the equilibrium. The trans monobromide **4a** is visualized as arising from the anion **8a**. Evidence exists to suggest that **8a** is the thermodynamically preferred anion.[16-18]

It is interesting to note that treatment of **1a** with Me_2SO carbanion, a reaction also reported to involve nucleophilic displacement *on* bromine, results in a similar strong preference toward the formation of the trans isomer **4a**.[19]

We suspect that under the reaction conditions the exo anion **9a** is either not formed to any great extent or that it equilibrates to anion **8a**. We tend to prefer[20] the latter suggestion, but we note that it relies on the assumption that the rate of protonation of carbenoids **8a** and **9a** under the reaction conditions is slow compared with the equilibration of **9a** to **8a**. Such equilibration might occur either by a pathway involving displacement with another molecule of **1a**[16] or by the equilibria shown in Scheme II.

The absence of direduction is presumably a result of the lack of stabilisation of anion **10a** by bromine, and its consequent inaccessibility.

We suggest that similar processes lead to the other monobromides **4b-k**.[21]

Synthetic Utility. The results demonstrate the preparative utility of the procedure. As well as giving high stereoselectivity and freedom from overreduction, the reaction is convenient to perform in the laboratory and the isolation of products is straightforward. It occurs under mild conditions and the phosphorus-containing byproducts can be removed in an aqueous workup. Little or no further purification is required. The reduction offers substantially more stereoselectivity than that presented in a previous report[23] using diethyl phosphonate in boiling triethylamine for longer periods—a reaction which may proceed by a similar pathway.

The present procedure is envisaged to have application in synthesis when coupled with stereospecific modes of alkylation.[24]

Experimental Section

General Methods. Analytical GLC was performed on a Perkin-Elmer 990 gas chromatograph equipped with a flame ionization detector. The column used was a 55 m × 0.5 mm SP 2100 SCOT capillary, temperature programmed between 80 and 240 °C. All ^1H NMR spectra were recorded on either a JEOL JNM-PMX 60 (60 MHz) or a Bruker CXP-300 (300 MHz) spectrometer.

Starting Materials. *gem*-Dihalocyclopropanes were prepared by phase-transfer methods as previously described.[25-29] 1,1-Dibromocyclopropane was prepared by a Hunsdieker–Cristol reaction.[30] Ammonia was distilled from sodium prior to use. Me_2SO was distilled from calcium hydride and stored over 4A molecular sieves under an atmosphere of nitrogen. Tetrahydrofuran was freshly distilled from benzophenone ketyl before use. In the initial experiments, potassium *tert*-butoxide was freshly sublimed before use; the experiments in Table I, however, were conducted without resubliming the commercial material. Dialkyl phosphonates (Fluka) were redistilled. Other starting materials were commercially available and further purified only where necessary.

Typical Procedure. Dimethyl phosphonate (660 mg, 6.0 mmol) was added to a solution of potassium *tert*-butoxide (673 mg, 6.0 mmol) in redistilled anhydrous liquid ammonia (40 mL) at reflux under N_2. After 5 min of stirring, 1,1-dibromo-2,2,3,3-tetramethylcyclopropane (242 mg, 1.0 mmol) was added. The mixture was allowed to stir for 1 h, and then chilled ether (−40 °C) was added and the reaction mixture was quenched by the cautious addition of ammonium nitrate (0.75 g). The ammonia was allowed to evaporate and the mixture was diluted with water (20 mL). The phases were separated and the aqueous phase was extracted with ether (20 mL). After the addition of internal standards [7,7-dibromobicyclo[4.1.0]heptane and 2-bromotoluene (1.0 mmol each)] and drying, the combined organic phases were quantitatively examined by GLC. All yields were corrected for the detector responses. Sometimes, where appropriate, the internal standard(s) were added after quenching and before workup. For reactions in THF, the total solvent volume was kept to 40 mL; in the Me_2SO experiments, the solvent volume was 10 mL.

For preparative experiments, the reaction was then repeated on a larger scale, typically using 10 mmol of the dibromide in 100 mL of liquid ammonia. Under these conditions the standard reaction time was 2.5 h. Internal standards were not added and the reaction mixture was worked up as before and dried ($MgSO_4$). The combined extracts were fractionally distilled to afford the monobromide which was examined spectroscopically. In the case of **1i**, traces of residual *tert*-butyl alcohol were not readily removed. The use of sodium hydride to generate the phosphite ion obviated this problem. However, isolation of **1i** was still difficult because of its extreme volatility.

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Registry No. **1a**, 2415-79-4; **1b**, 32644-18-1; **1c**, 3234-51-3; **1d**, 41848-90-2; **1e**, 5398-70-9; **1f**, 52730-96-8; **1g**, 3591-34-2; **1h**, 22715-57-7; **1i**, 21960-71-4; **1j**, 63262-97-5; **1k**, 39647-01-3; **4a**, 1121-41-1; **4b**, 1551-94-6; **4c**, 32523-77-6; **4d**, 34780-91-1; **4e**, 32816-30-1; **4f**, 32728-88-4; **4g**, 4333-56-6; **4h**, 3815-06-3; **4i**, 3815-08-5; **4j**, 78004-15-6; **4k**, 58683-51-5; **5a**, 1121-40-0; **5c**, 32523-76-5; **5d**, 34780-90-0; **5e**, 57234-70-5; **5f**, 35756-66-2; **5i**, 3815-07-4; **5j**, 78004-14-5; **5k**, 58683-50-4; **6h**, 4127-47-3; $HPO(OMe)_2$, 868-85-9; *t*-BuOH, 75-65-0; $PO(OME_2)^-$, 19437-82-2.

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