COMMUNICATION

LETTERS

Convenient Preparation of Sulfonium Salts

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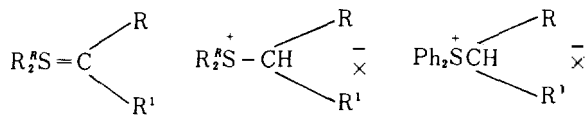
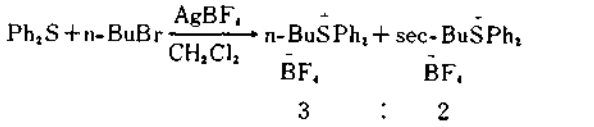
Sulfonium ylides 1, which are efficient alkylidene transfer reagents to various carbonyl compounds,[2] are usually prepared by deprotonation of the corresponding sulfonium salts 2.



1 2 3

However, the choice of residual alkyl group (R^R), in 1 is dictated by the fact that in the ensuing deprotonation of 2, R^R should contain significantly less acidic protons as compared to those in the transferrable alkyl groups in 2. Otherwise, a mixture of ylides would result. In this regard, phenyl groups as residual alkyl groups, R^R, are an ideal choice, which would allow unambigous deprotonation of sulfonium salts, 2 to ylides, 1 regardless of the nature of the transferrable alkyl groups. In fact, there exist presently several routes to alkyldiphenylsulfonium salts, 3 with silver-assisted alkylation of diphenyl sulfide with alkyl halides being the most general. However, the transferrable alkyl group is limited to ones with lower alkyl groups since under the reaction condition which more or less generates carbonium ion species by silver cation, rearrangement interferes seriously.[2]

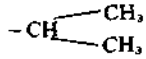


For this reason, sec-alkyldiphenylsulfonium salts are best prepared in multi-steps by alkylation of alkylidene ylide (1 R = alkyl, R′ = H) with R′X.[3]

We have been concerned with simple preparation of alkyldiphenylsulfonium salts, 3 by direct phenylation of alkyl phenyl sulfides readily available from alkyl halides.[6] Among the various candidates for this transformation, the highly reactive hypervalent diphenyliodonium ion seems to be appropriate since these reagent are known to phenylate diaryl sulfides.[4,5]

Consequently, various alkyl phenyl sulfides[6] were treated with 1.2 equiv. of diphenyliodonium tetrafluoroborate[4] in tetrachloroethylene (1 mmol/10 m*l*) in the presence of copper (II) acetate (4 mole %). After refluxing for 3-8 hr (TLC monitoring) and cooling to room temperature, enough ether was added. The resulting solid was washed with ether several times and recrystallized (ethanol). However, sulfides with relatively bulky alkyl groups resisted phenylation presumably due to decomposition to alkyl fluoride. Thus, diphenyliodonium triflate (mp 161-3°C, 75%) was prepared in an analogous manner simply

TABLE 1: Preparation of Alkyldiphenylsulfonium Salts

R	X	yield (%)	mp (lit)°C	nmr (δ, TMS ref)
$-CH_2CH_3$	BF_4	96	75-78(78-80)	7.3-8.3(m, 10H), 4.1(q, 2H), 1.2(t, 3H)
$-CH_2CH_2CH_2Cl$	BF_4	95	104-107(104-107)	7.5-8.2(m, 10H), 4.3(t, 2H), 3.75(t, 2H), 2.3(m, 2H)
	BF_4	98	137-139(137-139)	7.5-8.2(m, 10H), 3.5(m, 1H), 1.4-1.75(m, 4H)
	OSO_2CF_3	93	a	7.1-7.9(m, 10H), 3.3(m, 1H), 1.3(d, 6H)
	OSO_2CF_3	81	a	7.1-7.9(m, 10H), 3.0-3.2(m, 1H), 1.1-1.2(m, 10H)

a; semisolids were obtained.

by substituting triflic acid for tetrafluoroboric acid and the both iodonium compounds served for the purpose.

As can be seen in Table 1, excellent yields of diphenylsulfonium salts were obtained from readily available starting materials. The mechanism of the present reaction may only be tentative, but it is tempting to speculate that the course of reaction was governed by oxidative addition-reductive elimination chemistry. Further efforts for the utility of the ylides generated from the above sulfonium salts are being planned.

References

(1) Undergraduate Research Participant, 1982–83, Present Address; Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul, Korea.

(2) (a) B.M. Trost and M.S. Melvin, "Sulfur Ylides", New York, Academic Press, 1975; (b) H.O. House, "Modern Synthetic Reactions", 2nd ed., Benjamin, 1972, Chapt. 9; (c) C.J.M. Stirling, "Organic Chemistry of Sulfur", S. Oae. ed., Plenum Press, 1977, Chapt. 9.

(3) E.J. Corey, M. Jautlelat, and W. Oppolzer, *Tetranedron Lett.*, 2325 (1967).

(4) For a review of hypervalent iodine compounds, A. Varvoglis, Synthesis, 709 (1984); (a) J.V. Crivello and J.H.W. Lam, *J. Oro. Chem.*, **43**, 3065 (1978); (b) idem., *ibid.*, *Synth. Commun.*, **9**, 151 (1979).

(5) Recently, after completion of this study, an arylation procedure was developed in which alkyl phenyl sulfides are treated with p-benzoquinone followed by methylation (40–65% yields). See B.J. McBride, M.E. Garst, and M.Hopkins, *J. Oro. Chem.*, **49**, 1824 (1984).

(6) D. Landini and F. Rolla, *Oro. Synth.*, **58**, 143 (1978).

(7) B.M. Trost and M.J. Bogdanowicz, *J. Amer. Chem. Soc.*, **93**, 3733 (1971), **95**, 5321 (1973); *Oro. Synth.*, **54**, 27 (1974).

Preparation of *cis*-(2S, 3R)-Epoxy-1-butanol; The Unexpected Regiocontrol

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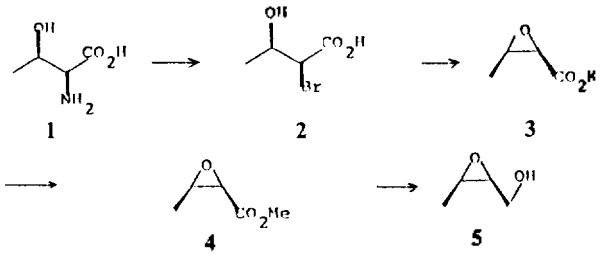
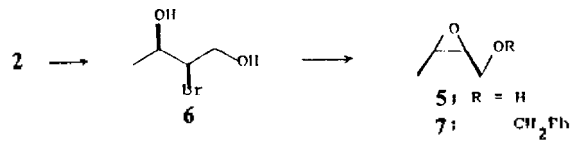
For on-going projects in these laboratories, large quantities optically active (2S, 3R)-epoxy-1-butanol was required, the preparation of which seemed to be quite straightforward in view of the well established asymmetric epoxidation by Sharpless.[1] Unfortunately, even with modified work-up available for water-soluble epoxy alcohols,[2] the chemical yield in large-scale reactions was not so high to be synthetically useful. Consequently, recourse was made to utilize other chiral C-4 fragments. In this regard L-threonine seemed to be appropriate. In fact, it was transformed to the epoxy alcohol by Djerassi *et al.* following the route shown below.[3]



Thus, L-threonine was diazotized (1.5 equiv $NaNO_2$ in 2.5 M H_2SO_4) in the presence of 3.5 equiv potassium bromide (1.5 hr at 0°C, 2 hr at rt) to give a 86% yield of bromo acid 2,[4] which was treated with aqueous KOH to effect cyclization and concurrent formation of the salt 3. Water was stripped off to a white solid of the salt, which was subsequently methylated with a large excess of methyl iodide in DMF. The resulting methyl ester 4 was reduced with sodium borohydride in a 50% aqueous methanol to furnish the cis epoxy alcohol in fair yields.[3]

Indeed, the synthesis worked moderately well with preliminary small scales, but attempted large-scale reactions encountered three major difficulties: Evaporative drying of the salt 3 from large amount of water was tedious, moreover the methyl ester 4 obtained was often contaminated with its C-2 epimer (NMR(δ) of 4, 1.34 (d, J=7, 3H), 3.75 (S, 3H); of the trans isomer of 4, 1.20 (d, J=7, 3H), 3.68 (S, 3H), which would speak for isomerization during salt formation and/or methylation, and finally the reduction of the ester with $NaBH_4$ was not entirely chemoselective, thus necessiating a premature work-up and chromatography before all the starting ester was consumed.

Consequently, the bromo acid 2 was reduced with borane methyl sulfide (2.5 equiv) in THF at rt for 24 hr to give, after aqueous work-up, easily manageable pure diol 6 in 79% yield. The idea here was that after some form of selective protection of the primary OH in 6 ring closure and subsequent deprotection would furnish the *cis*-epoxy alcohol 5. However, direct treatment of the bromo diol 6 with anhydrous K_2CO_3 in methanol (0°C for 1 hr and rt for 7 hr) surprisingly afforded a 65% yield of *cis*-(2S, 3R)-epoxy-1-butanol 5 bp 78–84°C/20 mm (lit. 55–57°C/5 mm).[3] Although expensive, 1.5 equiv DBU in THF (0°C for 0.5 hr, rt for 18 hr) was more effective in terms of purity and yield (80%).



Optical rotation of the alcohol 5 was erratic with variation of water contents in the sample but that of the corresponding ben-