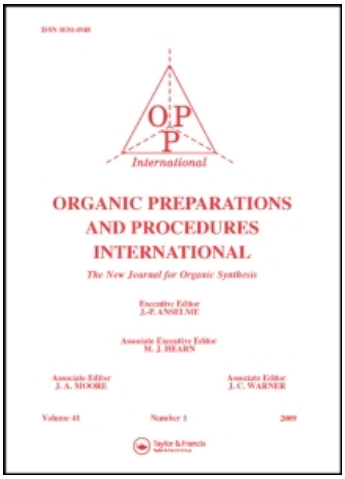

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EFFECTIVE AND PREFERENTIAL TRANSFORMATION OF COMPOUNDS HAVING 2-HALOETHYL GROUPS ON POSITIVE SULFUR INTO ETHENYL COMPOUNDS UNDER PTC CONDITIONS

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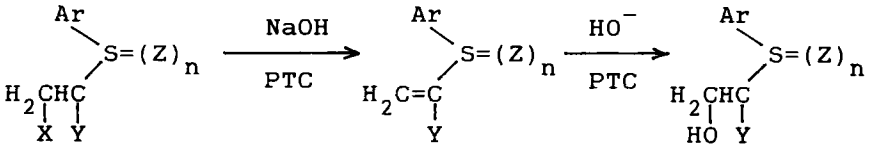
There have been many reports[1] on dehydrohalogenation using a phase-transfer catalysis (PTC) method. Since compounds having the 2-haloethyl group on positive sulfur atom, such



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as S-(2-haloethyl)sulfilimines, 2-haloethyl sulfoxides and 2-haloethyl sulfones, undergo dehydrohalogenation followed by Michael addition, the dehydrohalogenations of these compounds have been commonly carried out using non-nucleophilic organic bases and sodium hydride in organic media. In the application of dehydrohalogenation under PTC conditions to the title compounds, we have observed effective and preferential dehydrohalogenations under controlled conditions. 2-Chloroethyl phenyl sulfone (1a) was selected as the substrate to determine the best conditions. It was dehydrochlorinated with aqueous sodium hydroxide in the presence of a phase-transfer catalyst, tetrabutylammonium

TABLE 1. Dehydrochlorination of 2-Chloroethyl Phenyl Sulfone 1a under PTC Conditions[a]

Run No.	NaOH/1a (mmol/mmol)	Temp (°C)	Time (hrs)	Yield(%)[b] 2a	3a	Ratio of 2a	: 3a
1	3.0	rt	24	38	53	42	58
2	3.0	40	5	7	93	7	93
3	3.0	rt	2	96	3	97	3
4	2.0	rt	24	79	20	80	20
5	1.0	rt	24	~100	~0	100	0

a) Solvent: benzene (25 ml)-water (12 ml). TBAB: 0.015 mmol. b) Yields were estimated by NMR.

bromide (TBAB), in a two-phase system (benzene and water).

Table 1 shows that the molar ratio of NaOH to 1a, the reaction temperature and time greatly influenced the product ratio [ethenyl phenyl sulfone (2a) to Michael addition product, 2-hydroxyethyl phenyl sulfone (3a)[2]]. With a molar ratio of reactants (NaOH/1) greater than one, the ratio of 2a/3a decreased. Since a large excess of alkali metal hydroxide has generally been used in PTC dehydrohalogenations, this quantitative dehydrochlorination in the presence of a stoichiometric amount of NaOH is unusual. In the same way, the dehydrohalogention of other 2-haloethyl compounds, S-(2-chloroethyl)-S-phenyl-N-tosylsulfilimine (1b), 2-chloroethyl phenyl sulfoxide (1c), S-(2-chloroethyl)-S-(4-nitrophenyl)-N-tosylsulfilimine (1d), S-(2-chloroethyl)-S-(4-methylphenyl)-N-tosylsulfilimine (1e) and S-(1,2-dibromoethyl)-S-phenyl-N-tosylsulfilimine (1f)[3] (obtained by the bromination of 1b in situ) were carried out. Table 2 shows that these dehydrohalogenations were efficiently accomplished to give the corresponding S-ethenyl compounds 2. It is to be noted that the water unstable compound 1f[3] was dehydrobrominated almost without decomposition.

TABLE 2. Dehydrohalogenation of 2-Haloethyl Compounds 1 under PTC Conditons[a]

Run No.	1 Ar	Y	Z	n	NaOH/1 (mmol/mmol)	Temp (°C)	Time (hrs)	2 Y(%)	3 Y(%)	2 : 3	
6[b]	C_6H_5	H	NTs	1(b)	3.0	rt	24	57	41	58	42
7	C_6H_5	H	NTs	1(b)	1.0	rt	24	~100	~0	100	0
8	C_6H_5	H	O	1(c)	3.0	rt	2	98	~0	100	0
9[c]	4-$O_2NC_6H_4$	H	NTs	1(d)	1.0	rt	24	~100	~0	100	0
10	4-$CH_3C_6H_4$	H	NTs	1(e)	1.0	rt	24	98	~0	100	0
11	C_6H_5	Br	NTs	1(f)	1.0	rt	24	96	~0	100	0

a) Yields were measured by NMR. Solvent: benzene (25 ml)-water (12 ml) TBAB: 0.015 mmol. b) The presence of 3b was confirmed by IR and NMR spectra and TLC using its authentic sample.[9] c) CH_2Cl_2 (40 ml)-water (30 ml).

In conclusion, we recommend that compounds of type 2 be synthesized from type 1 compounds using a 1:1 mol ratio of NaOH/1.

EXPERIMENTAL SECTION

All melting points are uncorrected. The IR spectra were recorded on a Shimazu IR-435 spectrophotometer and ^1H NMR spectra on a JNM-PMX60 spectrometer using TMS as the internal standard. The 2-haloethyl compounds were prepared by the reported methods: 2-chloroethyl phenyl sulfone (1a) (mp. 54-55°, lit.[4] 55°), S-(2-chloroethyl)-S-phenyl-N-tosylsufilimine (1b) (mp. 101-103°, lit.[5] 101-103°), 2-chloroethyl phenyl sulfoxide (1c) by oxidizing the corresponding sulfide with sodium periodate[6] (mp. 29-30°, lit.[7] 31-32°), S-(2-

chloroethyl)-S-(4-nitrophenyl)-N-tosylsulfilimine (1d) was obtained from the reaction of 2-chloroethyl 4-nitrophenyl sulfide with chloramine T under PTC conditions.[5] [98%, mp. 114-115° (from benzene). IR (KBr): 1520 and 1344 (NO_2), 1268 and 1136 (SO_2), 990 cm^{-1} (S=N). NMR ($CDCl_3$): δ 2.35(s, 3H), 3.2-3.8(m, 4H), 7.17(d, 2H, J = 9Hz), 7.73(d, 2H, J = 9Hz), 7.93(d, 2H, J = 9Hz), 8.30(d, 2H, J = 9Hz). Calcd. for $C_{15}H_{15}ClN_2O_4S_2$: C, 45.56; H, 3.92; N, 7.24. Found: C, 45.38; H, 3.90; N, 7.17]. S-(2-chloroethyl)-S-(4-methylphenyl)-N-tosylsulfilimine (1e)[5] (mp. 124-125°, lit.[8] 125°).

General Procedure for Dehydrohalogenations.- A solution of a 2-haloethyl compound 1 (3.0 mmol) in 25 ml of benzene and a solution of NaOH (3.0, 6.0 or 9.0 mmol) and TBAB (0.015 mmol) in 12 ml of water were mixed and vigorously stirred under the reported conditions. After the reaction, the organic layer was separated, washed with water and dried over anhydrous sodium sulfate. The dried solution was evaporated to dryness and the resulting residue was purified by recrystallization or reprecipitation.

Preparation of 2a (Run No. 5).- Using the general procedure, an oily residue was obtained. The residue was purified by reprecipitation of its benzene solution with hexane to give 2a (100%), mp. 66-67°, lit.[4] 68.5°. IR(KBr): 1305 and 1142 cm^{-1} (SO_2).

Preparation of 2b (Run No. 7).- Using the general procedure, a solid residue was obtained. The residue was purified by reprecipitation of its dichloromethane solution with ether to yield 2b (100 %), mp. 111-113°, lit.[9] 111-113°. IR (KBr): 1285 and 1140 (SO_2), 958 cm^{-1} (S=N).

Preparation of 2c (Run No. 8).- Using the general procedure, an oily residue was obtained. The residue was purified by column chromatography using silica gel and dichloromethane to yield 2c (98%) as an oil, lit.[10] bp. 93-95°/0.2 mm. IR (neat): 1040 (S=O), 690 and 740 cm^{-1} (Ph). NMR ($CDCl_3$): δ 5.83(dd, 1H), 6.10(dd, 1H), 6.65(dd, 1H), 7.3-7.7(m, 5H).

Preparation of 2d (Run No. 9).- Using the general procedure, a solid residue was obtained. The residue was purified by reprecipitation of its dichloromethane solution with ether to give 2d (100%), mp. 102-103° (from CH_2Cl_2-Et_2O). IR (KBr): 1520 and 1343 (NO_2), 1300 and 1140 (SO_2), 965 cm^{-1} (S=N). NMR ($CDCl_3$): δ 2.33 (s, 3H), 5.97-6.82 (ethenyl hydrogens), 7.13 (d, 2H, J = 9Hz), 7.67 (d, 2H, J = 9Hz), 7.83 (d, 2H, J = 9Hz), 8.22 (d, 2H, J = 9Hz).

Anal. Calcd. for $C_{15}H_{14}N_2O_4S_2$: C, 51.41; H, 4.04; N, 8.00

Found: C, 51.28; H, 3.94; N, 7.96

Preparation of 2e (Run No. 10).- Using the general procedure, an oily residue was obtained. The residue was purified by reprecipitation of its dichloromethane solution with ether to yield 2e (98%), mp. 128.5-129.5°, lit.[8] 129°. IR (KBr): 1280 and 1135 (SO_2), 963 cm^{-1} (S=N).

Preparation of 2f (Run No. 11).- A dried dichloromethane solution of bromine (2.17 g, 14.0 mmol in 20 ml) was added dropwise into a stirred solution of 1b (3.05 g, 10 mmol) in dried dichloromethane (50 ml) below 20° for 0.5 hr. After stirring for 1 hr, the mixture was

evaporated to dryness under reduced pressure. The residue obtained was dissolved in dried benzene (60 ml) containing a small amount of triethylamine (ca. 0.02 g). The resulting solution was added to a solution containing sodium hydroxide (0.4 g, 10 mmol) and TBAB (0.05 mmol) in water (50 ml) and stirred vigorously at room temperature for 24 hrs. After the reaction, the organic phase was separated, washed with three 50 ml portions of water and then a saturated sodium chloride solution (50 ml), and dried over anhydrous sodium sulfate. The dried solution was evaporated to dryness under reduced pressure. The resulting solid residue was reprecipitated from its dichloromethane solution with ether to afford 2f (96%), mp. 142-144°, lit.[3] 142-144°. IR (KBr): 1282 and 1140 (SO_2), 965 cm^{-1} (S=N). NMR ($CDCl_3$): δ 2.34 (s, 3H), 6.32 (d, 1H, J = 4Hz), 7.03 (d, 1H, J = 4Hz), 7.17 (d, 2H, J = 8.6Hz), 7.2-7.9 (m, 5H), 7.77 (d, 2H, J = 8.6Hz).

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