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Anion-catalyzed Phase-transfer Catalysis. II. Effects of Anionic Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate Catalyst in Phase-transfer-catalyzed Sulfonium Ylide Formation

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Synopsis. Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) ion as an anionic phase-transfer catalyst promoted the formation of oxirane from various carbonyl substrates and trimethylsulfonium chloride in a two-phase mixture of dichloromethane and concentrated aqueous sodium hydroxide.

Sulfonium methylide can be conveniently generated in a hydrophobic organic medium under phase-transfer catalytic (PTC) conditions by use of a cationic catalyst which functions to incorporate hydroxide ions into the hydrophobic organic medium.1) An anionic catalyst might also be useful for the same purpose, where the catalyst would help to incorporate the sulfonium ions into the organic phase. We have developed a highly lipophilic tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) ion2) as an anionic phase-transfer catalyst.3) This note is to describe the catalytic behavior of TFPB toward the formation of sulfonium methylide in an aqueous-organic two-phase system.

Results and Discussion

In the formation of phenyloxirane from benzaldehyde and trimethylsulfonium iodide under PTC conditions (see Table 1) the addition of a TFPB catalyst caused the reaction rate to approximately double, but still it took 9.5 h for the reaction to attain a quantitative yield. A similar catalytic effect seemed likely in some ketone reactions, though it would not be effective enough for preparative use.

Reactions involving reactive trimethylsulfonium chloride4,5) with various carbonyl substrates are also summarized in Table 1. Benzaldehyde was completely converted to phenyloxirane within half an hour, irrespective of the presence or absence of a TFPB catalyst. The yield of phenyloxirane was quantitative when catalyzed with TFPB, while the yield without the catalyst was somewhat lower. Cyclohexanone, acetophenone, and benzophenone afforded corresponding oxirane products in quantitative yields within 4 h. Without a TFPB catalyst a reaction mixture of the former two ketones formed an emulsion and suffered some difficulties in product separation. The last ketone was less reactive and gave the oxirane in a lower yield (71%) without the catalyst.

The concentration of the aqueous alkali was required to be as high as 50 w/w% for a satisfactory yield of oxirane.5)

An increasing amount of the TFPB catalyst correspondingly accelerated the reaction rate, but also caused a decreased conversion of benzaldehyde. When the reaction started with equimolar amounts of trimethylsulfonium iodide and benzaldehyde, the conversion of benzaldehyde stopped at a stage where approximately an equimolar amount of benzaldehyde remained with the TFPB catalyst; *e. g.* when 25 and 50 mol% of sodium TFPB were added, the reactions stopped within 1.7 and 1 h with 25 and 55% of the benzaldehyde remaining unreacted, respectively.6)

When an equimolar amount of sodium TFPB was added to the sulfonium salt, neither oxirane formation nor a Cannizzaro reaction occurred, even under prolonged vigorous agitation. This indicated that a 1:1 binary ion pair of trimethylsulfonium and TFPB ions was so stable as not to yield the sulfonium methylide in the two-phase system.

TFPB salts were found to disperse in the form of aggregates in solution phases.7) The particle sizes of aggregates varied with the counter cation and the solvent. Also the sizes of sodium TFPB particles were measured using a light-scattering method.8) Aggregates of 200 and 20 molecules were found in water and dichloromethane, respectively. The catalytic behavior of TFPB in the present PTC system might have some connection with the aggregation of TFPB and related ionic species.

Table 1. Yields of oxiranes in PTC reaction of sulfonium halides

Halide	Reaction conditions[a)]	Yield[b)]/% (Reaction time/h)			
		PhCHO	$cy\text{-}C_6H_{10}$=O	PhMeC=O	Ph_2C=O
Cl	(A)	97 (0.5)	Quant. (4)	Quant. (4)	Quant. (4)
Cl	(B)	91 (0.5)	Quant. (3)	Quant. (4)	71 (4)
I	(A)	98 (9.5)[c)]	24 (48)	23 (48)	8 (48)
I	(B)	59 (9.5)	13 (48)	12 (48)	7 (48)

a) Reaction conditions (A); catalyzed with sodium TFPB (10 mol%). (B); without the catalyst. b) By GLC analyses of the reaction mixture. c) The use of 40 and 25 w/w% aqueous alkali afforded the phenyloxirane in the yields of 70% (22-h reaction) and 10% (19-h reaction), respectively, under the similar conditions.

TFPB salts were also shown to cause a suppression of the Cannizzaro reaction of benzaldehyde. In a separate run without the sulfonium salt under similar two-phase conditions, the addition of sodium TFPB reduced the yield of benzyl alcohol in the Cannizzaro reaction of benzaldehyde to one forth of that without the catalyst. Trimethylsulfonium TFPB was also effective in retarding the Cannizzaro reaction, though to a somewhat smaller extent than the sodium salt.

Thus, the anionic TFPB catalyst appeared to function in a similar way as the cationic ones in promoting oxirane formation with trimethylsulfonium halides under PTC conditions.

Experimental

Reaction of a Carbonyl Compound with Trimethylsulfonium Halide under PTC Conditions. A mixture of trimethylsulfonium chloride[9] (2.4 mmol), the aldehyde or ketone (1.6 mmol), 50 w/w% aqueous sodium hydroxide (20 cm^3), dichloromethane (20 cm^3) and an internal standard for GLC analysis (biphenyl for the reactions of benzaldehyde and benzophenone and tetradecane for those of cyclohexanone and acetophenone) was stirred at 1000 rpm by a mechanical stirrer at room temperature in both the presence and absence of sodium TFPB (0.24 mmol, (10 mol%)). The reaction was followed by GLC analyses of aliquots from the dichloromethane layer with reference to an internal standard. Results are summarized in Table 1.

The reaction products were characterized as follows: 1-Oxaspiro[2.5]octane; a colorless oil, IR and ^{1}H-NMR spectral comparisons with that of the authentic specimen separately prepared:[10] 1-Methyl-1-phenyloxirane; a colorless oil, ^{1}H-NMR (CDCl$_3$, TMS): 1.648 (d, J_{CH_3-H}=0.74 Hz, 3H of CH$_3$), 2.689 (d.q., J_{H-H}=5.61 Hz, J_{H-CH_3}=0.74 Hz, 1H of CH$_2$), 2.871 (d, J_{H-H}=5.61 Hz, 1H of CH$_2$), and 7.275 (m, 5H). (lit[11]: 1.63 (s, CH$_3$), 2.58 and 2.77 (two d. J=6 Hz, CH$_2$), 7.27 (s, ArH)): 1,1-Diphenyloxirane; colorless solid melting at 54—56 °C (lit,[12] mp 55—56 °C). ^{1}H-NMR (CDCl$_3$, TMS): 3.250 (s, 2H of CH$_2$) and 7.314 (s, 10H of ArH). (lit[12] 3.14 (CH$_2$) and 7.36 (ArH)).

Reactions of trimethylsulfonium iodide were carried out under similar PTC conditions.

Cannizzaro Reaction of Benzaldehyde in a Two-phase System. A mixture of benzaldehyde (2.3 mmol) in dichloromethane (20 cm^3) and 50 w/w% aqueous sodium hydroxide (20 cm^3) was stirred in a similar manner with or without the addition of a 10 mol% TFPB salt. The reaction was followed by GLC in a similar manner. After a 23-h reaction without a TFPB salt, 40% of the benzaldehyde was converted to give benzyl alcohol in a 19% yield. With the addition of sodium TFPB and trimethylsulfonium TFPB, 23-h reactions converted 10 and 21% of the aldehyde to form benzyl alcohol in yields of 5 and 11%, respectively.

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6) Reaction conditions; the sulfonium iodide (0.16 mmol) and benzaldehyde (0.16 mmol) in a two-phase mixture of dichloromethane (20 cm^3) and 50% aqueous sodium hydroxide (20 cm^3) at room temp.

7) Regarding the aggregation behaviors of TFPB salts, see also T. Takada, T. Sonoda, and H. Kobayashi, *Bunseki Kagaku*, **32**, E191 (1983).

8) The light-scattering measurement facilities were afforded by Professor Toyoki Kunitake in the Department of Organic Synthesis, Kyushu University, to whom the authors are grateful.

9) A. Brändström, "Preparative Ion Pair Extraction. An Introduction to Theory and Practice," Apotekarsocieteten/Hässle Lakemedel, Stockholm, (1976), p. 153. Trimethylsulfonium chloride for preparative use was conveniently prepared by treating aqueous trimethylsulfonium iodide with 0.3% chlorine water. Liberated iodine was removed by decantation and ether-extraction. The resulting aqueous solution was adjusted to pH 7—8 with sodium hydrogencarbonate and evaporated to dryness.

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