

Fabric Softeners as Phase Transfer Catalyst in Organic Synthesis

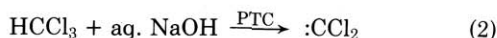
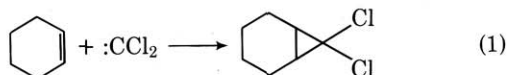
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Phase transfer catalysis (PTC) is an invaluable technique in organic synthesis (1). Many heterogeneous reactions can be carried out with reasonable success only using PTC. The principle and the applications of PTC are now commonly covered in organic textbooks (2). Laboratory experiments involving PTC are also designed for the undergraduate level (3).

Various kinds of onium salts such as ammonium, phosphonium, and sulfonium salts (4) have been used as the catalysts. Among them, quarternary ammonium salts with long alkyl chains are the most commonly used phase transfer agents. Because of their antistatic and surface-active properties, quaternary ammonium compounds are also the active component of many commercial fabric softeners (5). Their concentration in household fabric softeners can be up to 5%.

In this article we describe a PTC experiment using fabric softeners as the phase transfer agent for the addition of dichlorocarbene to an olefin (eq 1). It has long been known that dichlorocarbene can be generated when chloroform is in contact with a strong base. This very reactive carbene can add to olefin to form a cyclopropane ring. Traditionally, the generation of dichlorocarbene was carried out in a homogeneous phase using *tert*-butanol as the solvent and potassium *tert*-butoxide as the base. Makosza (6) and Starks (7) had independently discovered a PTC modification of the procedure. Dichlorocarbene can be generated in a two-phase sodium hydroxide/chloroform system using quaternary ammonium salts as the phase transfer agent (eq 2)



Experimental

Handling precautions: Chloroform is a flammable, hazardous, and carcinogenic chemical. All operations involving the transfer of solutions of chloroform should be carried out in a ventilation hood.

To 10 mL of 50% (W/W) aqueous sodium hydroxide solution in a 100-mL round-bottom flask was added 5 mL of cyclohexene and 20 mL of chloroform. Then 2 mL of the fabric softener to be tested was added to the mixture. The stoppered two-phase mixture was stirred magnetically at ~1000 rpm using a 1-in. Teflon-coated stirring bar. The reaction mixture turned turbid as some white emulsion started to form after 15 to 20 min.

The reaction was monitored by GC at 15- to 20-min time intervals (Fig. 1). The stirrer was turned off, and 1-mL GC samples were taken from the *top* organic layer of reaction mixture. The samples were passed through some anhydrous sodium sulfate packed in a Pasteur pipet to remove any of

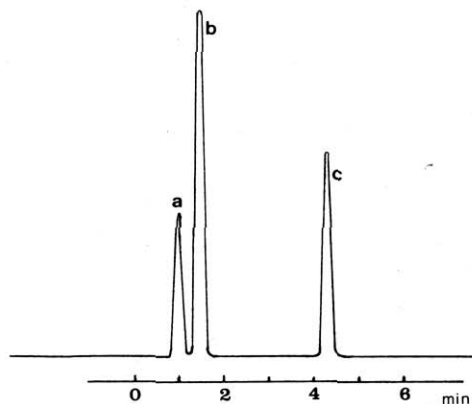


Figure 1. Typical GC trace of the reaction mixtures (injector temperature: 200 °C; initial temperature: 70 °C, temperature ramp: 7.5 °C/min for the first 3 min, then 100 °C/min) a: chloroform, b: cyclohexene, c: 7,7-dichlorobicyclo [4.1.0]-heptane.

the white emulsion and moisture. The GC experiments were carried out using a 3 mm × 1 m SE-30 column installed in a Hitachi 163 gas chromatograph with flame ionization detector and a Hitachi 561 recorder. In a larger scale experiment, 15 mL of the sodium hydroxide solution, 20 mL of chloroform, 20 mL of cyclohexene, and 8 mL of the fabric softener were stirred for 5 h as above. After simple work up and distillation (collected between 192–198 °C), NMR pure (Fig. 2) 7,7-dichlorobicyclo [4.1.0] heptane was obtained in 51% Yield¹.

Results and Discussion

The reaction times of each fabric softener used were summarized in the table. For 2 mL of the fabric softeners used, the reactions were completed within 2 h with the exception of one brand (run 4, table). Two control experiments were also carried out. Without the fabric softener, the reaction did not proceed as indicated by GC. When a typical phase transfer catalyst, Aliquat 336 (methyltriocylammonium chloride, 2 mol % to cyclohexene) was used in the reaction, the reaction was also completed in 2 h. This indicated that the

Fabric Softeners as Phase Transfer Catalyst

Fabric Softener	Place of manufacture	cents/mL	Reaction time (h)
1. Soft Greet	Japan	0.14	1.50
2. Comfort	UK	0.16	1.33
3. Concentrated Comfort	UK	0.23	1.33
4. Bonnie Hubbard	Canada	0.12	>4 ^a
5. Softlan	US	0.13	2.00
6. Park'n	Hong Kong	0.11	1.00

¹ We thank C. W. Chan in carrying out this experiment.

^a Reaction was not complete after 4 h.

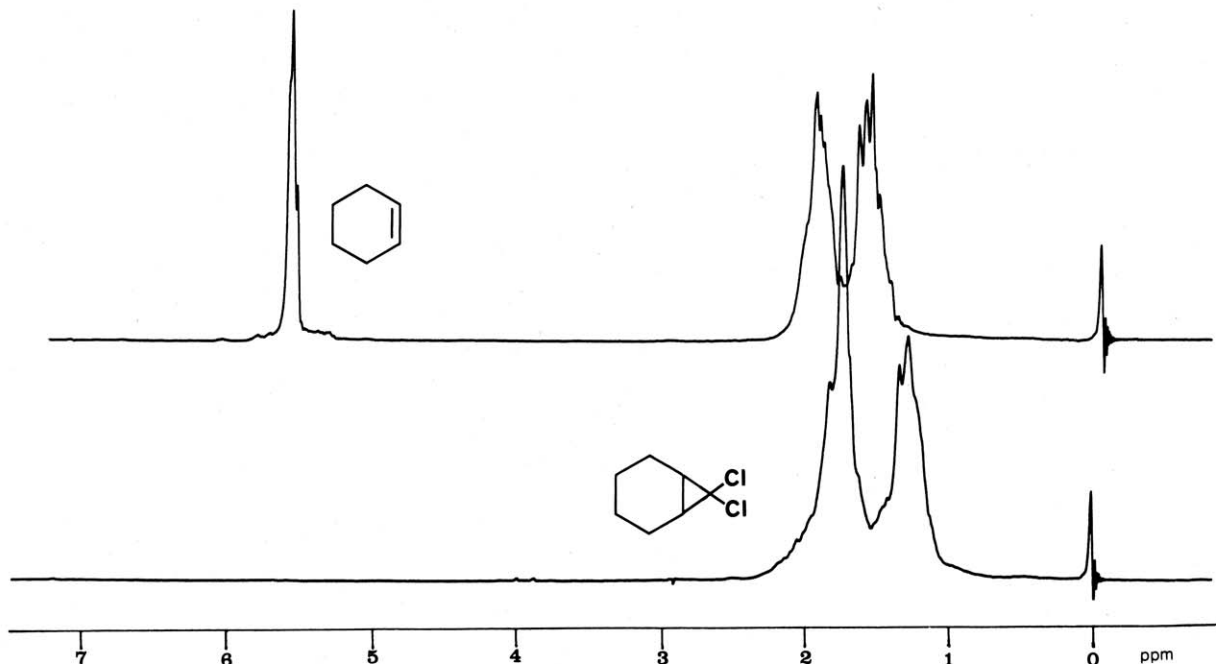


Figure 2. NMR spectra of starting material and product.

effect of 2 mL of fabric softener was roughly equivalent to that of 2 mol % of a typical phase transfer catalyst.

One sample tried did not work well as a phase transfer agent (run 4, table). It may be due to the fact that another active ingredient such as noncationic softening agent was used in the formula. It is also worth noting that the concentrated formula (run 3) did not work better as a phase transfer agent than the regular formula (run 2).

The idea of the incorporation of consumer products in the teaching of chemistry has been discussed (8). Household chemicals such as calcium hypochlorite (9) and "swimming pool chlorine" (10) had been used as oxidizing agents to replace more expensive research-grade chemicals. In this experiment we have demonstrated that fabric softener can be used effectively as a phase transfer agent in the generation of dichlorocarbene. The yield and reaction time are comparable to using standard phase transfer catalyst such as Aliquat 336.

Literature Cited

- (a) Starks, C. M.; Liotta, C. *Phase Transfer Catalysis—Principles and Techniques*; Academic: New York, 1978. (b) Gokel, G. W.; Weber, W. P. *J. Chem. Educ.* **1978**, *55*, 350 and 429. (c) Dehmlow, E. V.; Dehmlow, S. *Phase Transfer Catalysis*, 2nd ed., VCH: Weinheim, 1983.
- (a) Streitwieser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 3rd ed.; Macmillan: New York, 1985; p 696; (b) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 5th ed.; Allyn and Bacon: Boston, 1987; p 238; (c) Pine, S. H. *Organic Chemistry*, 5th ed.; McGraw-Hill: New York, 1987; p 386.
- For examples, see: (a) Ault, A. *Techniques and Experiments for Organic Chemistry*, 4th ed.; Allyn and Bacon: London, 1983; p 361; (b) Roberts, R. M.; Gilbert, J. C.; Rodewald, L. B.; Wingrove, A. S. *Modern Experimental Organic Chemistry*, 4th ed.; Saunders: New York, 1985; p 368.
- Kondo, S.; Takeda, Y.; Tsuda, K. *Synthesis* **1988**, 403.
- (a) Davidson, A.; Milwidsky, B. M. *Synthetic Detergents*, 6th ed.; Wiley: New York, 1978; p 24; (b) Cocktel, R. F. "Surfactants in Textile Processing", In Karsa, D. R., Ed. *Industrial Applications of Surfactants*; Royal Society of Chemistry: 1987; p 195.
- Makosza, M.; Wawrzyniewicz, M. *Tetrahedron Lett.* **1969**, 4659.
- Stark, C. M. *J. Am. Chem. Soc.* **1971**, *93*, 195.
- (a) Lieu, V. T.; Kalbus, G. E. *J. Chem. Educ.* **1988**, *65*, 207. (b) Miller, J. A. *ibid.*, 210.
- Hill, J. W.; Jenson, J. A.; Henke, C. F.; Yaritz, J. G.; Pedersen, R. L. *J. Chem. Educ.* **1984**, *61*, 1118.
- (a) Zuczek, N. M.; Furth, P. S. *J. Chem. Educ.* **1981**, *58*, 824. (b) Kauffman, J. M.; McKee, J. R. *J. Chem. Educ.* **1982**, *59*, 882.