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THE WITTIG REARRANGEMENT OF FLUORENYL ETHERS IN TWO-PHASE SYSTEM

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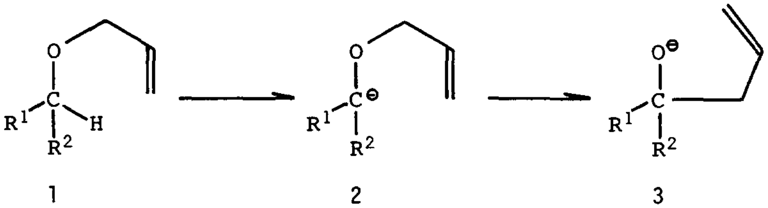
Summary: The Wittig rearrangement of fluorenyl ethers by the use of potassium hydroxide as base in solid phase was readily effected by crown ethers and onium salts, while diamines moderately catalyzed the reaction.

Phase transfer catalysis (PTC) has grown into a versatile preparative means for substitution, alkylation, carbene formation, oxidation, reduction, and so on.$^{1)}$ However, the rearrangement reaction under PTC conditions has been scarcely investigated so far. We now describe the catalytic ability of crown ethers, onium salts, and diamine for the Wittig rearrangement.



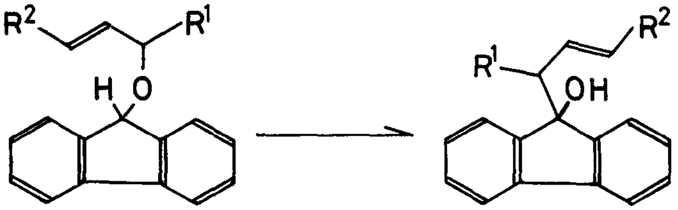
1 2 3

Anionic species 2 can readily rearrange to alkoxide 3 which is categorized in [2,3]sigmatropic rearrangement.$^{2)}$ The proton abstraction from ether 1 has been effected by the use of an equimolar amount of strong bases such as phenyllithium to give the carbanion 2.$^{3)}$ In the present study, fluorenyl ethers were subjected to the rearrangement under PTC conditions.

The fluorenyl ethers 4-7 were submitted to the action of potassium hydroxide which was by itself incapable of producing the carbanion.[4)] In solid-liquid system, crown ethers and ammonium and phosphonium salts were found to exhibit excellent catalytic ability (Table 1). As predicted from the complexing ability, dibenzo-18-crown-6 was inferior to the other crown ethers (run 4). The reaction should be conducted in a sealed tube for the reactants to be protected against atmospheric oxygen. Performance in an open vessel resulted in a reduced yield of 8 by the formation of fluorenone presumably due to the attack of molecular oxygen on the carbanion (run 2).[5)] These catalysts were not effective for promoting the reaction under liquid-liquid condition using 20% aqueous potassium hydroxide. The finding suggests that the proton abstraction from very weak carbon acids should be carried out in the absence of water. The rearrangement was not realized when potassium hydroxide was replaced by potassium carbonate, bicarbonate, and fluoride as the solid base which have been reported to be efficient enough for carbon acids much more susceptible to proton abstraction.[6)] Benzyl allyl ether turned out to be such a weak acid that deprotonation does not occur under the PTC condition using potassium hydroxide.

It is noticed that the diamines showed moderate catalytic ability (runs 7 and 8). Although the quaternary ammonium salt formed from the amine in the reaction medium was considered to be the actually operating catalyst,[7)] the present finding proved that the diamines as such have considerable catalytic ability even though not so good as the ammonium salts because any alkylating agents were not available in the system. The possibility was also ruled out experimentally that the diamines might act as a base to deprotonate the ether 4.

It is known that [2,3]sigmatropic rearrangement is often accompanied by a second pathway via a radical-pair mechanism.[8)] The formation of 10 and 9 from 5 and 6 respectively indicates the intervention of the by-path. The lower the temperature, the less the formation of the product through the radical pathway (runs 9-12). Therefore, the reaction could be easily directed to afford the desired products with high selectivity with the sole exception that the ether 7 possessing cinnamyl moiety always rearranged via the radical pathway (run 13).[9)]



4: R^1=H; R^2=H
5: R^1=H; R^2=CH_3
6: R^1=CH_3; R^2=H
7: R^1=H; R^2=Ph

8: R^1=H; R^2=H
9: R^1=CH_3; R^2=H
10: R^1=H; R^2=CH_3
11: R^1=H; R^2=Ph

Table 1: The Wittig Rearrangement of Fluorenyl Ethers.

run	ether	catalyst[a]	temp./time	solvent	product	%yield
1	4	18-C-6	R.T./6 hr	C_6H_6	8	89
2[b]	4	18-C-6	R.T./6 hr	C_6H_6	8	47
3	4	DC-18-C-6	R.T./6 hr	C_6H_6	8	90
4	4	DB-18-C-6	R.T./6 hr	C_6H_6	8	55
5	4	TBAB	R.T./6 hr	C_6H_6	8	93
6	4	TBPB	R.T./6 hr	C_6H_6	8	87
7	4	TED	R.T./6 hr	C_6H_6	8	34
8	4	TMED	R.T./6 hr	C_6H_6	8	26
9	5	18-C-6	R.T./6 hr	C_6H_6	9:10[c] (89:11)[d]	97
10	5	18-C-6[e]	-20°C/24 hr	CH_2Cl_2	9	80
11	6	18-C-6	R.T./6 hr	C_6H_6	9:10[c] (8:92)[d]	96
12	6	18-C-6[e]	-20°C/24 hr	CH_2Cl_2	9:10[c] (5:95)[d]	79
13	7	18-C-6[e]	-20°C/24 hr	CH_2Cl_2	11[c]	78

a: 18-C-6, 18-crown-6; DC-18-C-6, dicyclohexyl-18-C-6; DB-18-C-6, dibenzo-18-C-6; TBAB, tetrabutylammonium bromide; TBPB, tetrabutylphosphonium bromide; TED, triethylenediamine; TMED, *N,N,N',N'*-tetramethylethylenediamine. *b*: The reaction was carried out in an open vessel. *c*· The geometry around the double bond was proved to be *E* and the *Z* counterpart was not detected. *d*: The product distribution was assessed by ^1H nmr spectroscopy. *e*: 0.1 mmol.

General Procedure for the Rearrangement

To pulverized potassium hydroxide (1.0 mmol) was added the solution of fluorenyl ether (1.0 mmol) and the catalyst (0.01 mmol) in the solvent (5 ml). The mixture was stirred in a sealed tube under the specified conditions in Table 1, then subjected to column chromatography (silica gel, benzene as eluent). For all compounds prepared herein, correct elemental analyses and ^{1}H nmr and ir spectra were obtained.

References and Notes

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2) R.B.Woodward and R.Hoffmann, 'The Conservation of Orbital Symmetry', Verlag Chemie, Weinheim, 1970.

3) G.Wittig, H.Döser, and I.Lorenz, *Liebigs Ann.Chem.*, 562, 192 (1949), U. Schöllkoph and K.Fellenberger, *ibid.*, 698, 80 (1966)

4) The [2,3]rearrangement of *S*-methyl-*S*,*S*-bis(3,3-dimethylallyl)sulfonium fluoroborate via the ylide was effected readily even in the absence of catalysts. Slight acceleration of reaction was observed when 18-crown-6 (10 mol%) was added. The Horner-Wittig reaction by phosphonates was also reported to take place in the absence of a typical phase transfer catalyst; M.Mikolajczyk, S. Grzejszczak, W.Midura, and A.Zatorski, *Synthesis*, 1976, 396.

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6) M.Fedoryński, K.Wojciechowski, Z.Matacz, and M.Makosza, *J.Org.Chem.*, 43, 4682 (1978), I.Belsky, *Chem.Commun.*, 1977, 237

7) W.P.Weber and G.W.Gokel, 'Phase Transfer Catalysis in Organic Synthesis', Springer-Verlag, Berlin, 1977, p7.

8) J.E.Baldwin and J.E.Patrick, *J.Am.Chem.Soc.*, 93, 3556 (1971)

9) The molecule containing a cinnamyl moiety is prone to homolytic fission. We also observed *N*,*N*-dimethylcinnamylamine oxide rearranged through radical-pair under any conditions; Y.Yamamoto unpublished data, cf. Y.Yamamoto, J.Oda, and Y.Inouye, *J.Org.Chem.*, 41, 303 (1976).

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