

## Ether Synthesis from Activated Aromatic Halides and Alkali-metal Carbonates

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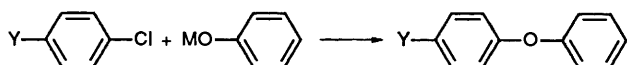
Aromatic halides activated by an electron-withdrawing group at the *ortho* or *para* position has been found to react with alkali-metal carbonates or hydrogencarbonates at elevated temperatures to form ethers. The ether yield is markedly enhanced by catalysts such as silica and aluminium silicate. The rate of the etherification is dependent on the kind of activating groups



( $Y = NO_2 > CN > ArSO_2 > ArCO$ ), halides ( $X = F > Cl \approx Br \approx I$ ) and alkali metals ( $M = K > Na > Li$ ). Cuprous and cupric compounds act as cocatalysts with silica and further promote the reaction. The reaction of *p*-chlorobenzophenone with potassium carbonate or sodium carbonate to bis(4-benzoylphenyl) ether in the presence of silica or silica-cuprous oxide catalyst was investigated in detail and the reaction mechanism is proposed. The silyl ether formed from an aromatic halide and the silanol group on the surface of silica is presumed to be the intermediate of the etherification.

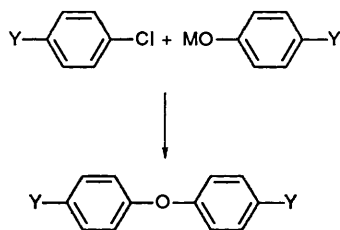
Aromatic ethers are synthesized by the nucleophilic substitution of aromatic chlorides with alkali-metal phenolates. Chlorobenzene reacts with sodium phenolate in the presence of cuprous compounds as catalysts to yield diphenyl ether. This is known as the Ullmann reaction.

The reaction proceeds more easily when aromatic chlorides are activated with electron-withdrawing groups such as nitro, cyano, sulfone and ketone at a position *para* to the chloro group,<sup>1</sup> Scheme 1. Nitro and cyano are stronger electron-

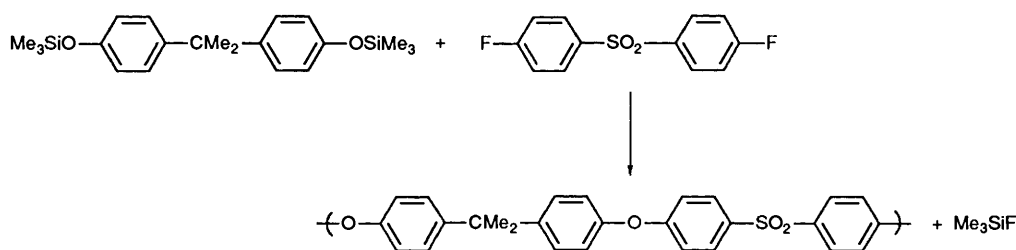


Scheme 1  $Y = NO_2, CN, C_6H_4SO_2, C_6H_4CO$  and  $M =$  alkali metal

withdrawing groups than sulfone and ketone groups. As a ketone is a weak electron-withdrawing group, a more active halogen substituent (such as an aromatic fluoro ketone) is used instead of an aromatic chloro ketone, in order to obtain an ether in high yield. Potassium phenolate is more active than sodium phenolate. The reactivity of alkali-metal phenolate is decreased by the introduction of an electron-withdrawing group. Therefore it is not easy to obtain symmetrical aromatic ethers having electron-withdrawing groups in high yield, Scheme 2.



Scheme 2



Scheme 3

Generally, the etherification reaction is accelerated by the use of an aprotic polar solvent such as *N,N*-dimethylformamide, tetrahydrothiophene 1,1-dioxide (sulfolane), *N,N*-dimethylacetamide, *N*-methyl-2-pyrrolidone (NMP) and diphenyl sulfone (PS).

There are some reports in which silyl ethers are used instead of alkali-metal phenolates and aromatic poly(ether sulfones) and aromatic poly(ether ketones) are obtained from the trimethylsilyl ether of diphenols and difluorodiphenyl sulfone (Scheme 3) or difluorobenzophenone.<sup>2,3</sup>

Aromatic fluorides activated by a nitro group at the *para* or *ortho* position are known to be converted into bis(nitrophenyl) ethers when heated with potassium carbonate in a polar aprotic solvent.<sup>4</sup> The corresponding chlorides are far less reactive and they react in the same manner only when they are further activated by cyano or trifluoromethyl groups in addition to the nitro group and in the presence of a KF catalyst.<sup>4</sup>

We found that catalysts such as silica and aluminium silicate greatly promote the reaction of an activated aromatic halide and an alkali-metal carbonate to form an ether (Scheme 4).

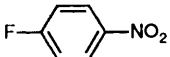
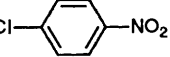
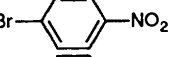
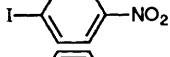
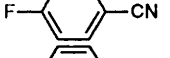
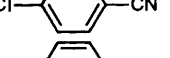
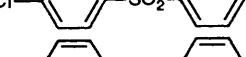
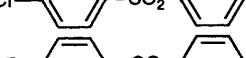
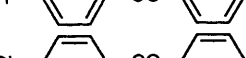
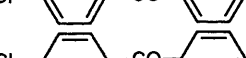

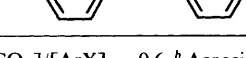


Scheme 4

In addition, cuprous and cupric compounds are found to act as cocatalysts with silica and further promote the reaction. In the presence of these catalysts, the aromatic fluoride and chloride activated by electron-withdrawing groups such as cyano, sulfonyl and carbonyl as well as those activated by the nitro group, are converted into the corresponding ethers in a high yield.

Here we report the outline of the etherification reaction and propose a reaction mechanism.

**Table 1** Reaction of aromatic halides and potassium carbonate<sup>a</sup>

ArX	Solvent	T/°C	t/h	Ether yield (%)	
				with SiO <sub>2</sub> <sup>b</sup>	without SiO <sub>2</sub>
	None	200	1	99	5
	None	200	1	11	0.4
	None	200	1	12	0.3
	None	200	1	9	0.3
	PS <sup>c</sup>	200	2	78	2
	PS	200	2	7	0.1
	PS	250	1	43	0.2
	PS	300	0.5	96	4
	PS	300	1	95	20
	PS	200	1	1	0
	PS	250	1	7	0
	PS	300	1	51	1

<sup>a</sup> ArX, 1.0 g; [K<sub>2</sub>CO<sub>3</sub>]/[ArX] = 0.6. <sup>b</sup> Aerosil 300 (Nippon Aerosil); 10 wt % to aromatic halide. <sup>c</sup> Diphenyl sulfone, same weight as ArX.

## Experimental

The aromatic halides and solvents were purified by recrystallization or distillation. Silica catalysts and their physical property data were supplied by Nippon Aerosil or Fuji Davison and these catalysts were dried at 200 °C *in vacuo* for 8 h before use. Fine powder grade (<0.2 mm) potassium carbonate and sodium carbonate, which were used throughout this work, were supplied by Nippon Soda and Takasugi Seiyaku respectively, and dried at 200 °C *in vacuo* for 8 h before use. Cuprous and cupric compounds were used without purification.

The reaction was carried out in a Pyrex test tube or in a 200 cm<sup>3</sup> Pyrex flask under a nitrogen atmosphere. After the reaction had been conducted, 100 mg of the reaction mixture was dissolved in 10 cm<sup>3</sup> NMP and analysed by high pressure liquid chromatography: apparatus, JASCO LC-800 system (Japan Spectroscopic); column; finepak SIL C<sub>18</sub>-S; eluent, methanol-water (60:40–80:20, dependent on the reaction); flow rate, 1 cm<sup>3</sup> min<sup>-1</sup>; detector, UV (254 nm).

Authentic samples of bis(4-cyanophenyl) ether, bis(benzene-4-sulfonylphenyl) ether and bis(4-benzoylphenyl) ether were synthesized by reacting 4-fluorobenzonitrile and 4-cyanophenol, 4-chlorophenyl phenyl sulfone and 4-hydroxyphenyl phenyl sulfone, and 4-fluorobenzophenone and 4-hydroxybenzophenone, respectively, in the presence of potassium carbonate.

In addition to the comparison of the liquid chromatogram, the <sup>13</sup>C NMR spectrum was measured using a JEOL FX-400 spectrometer on the reaction product from *p*-chlorobenzophenone and sodium carbonate in the presence of silica and cuprous oxide and was confirmed to be identical with that of the reaction product from *p*-fluorobenzophenone and *p*-hydroxy-

benzophenone in the presence of potassium carbonate. The spectrum had nine peaks corresponding to nine carbons in bis(4-benzoylphenyl) ether with chemical shifts of 195.2, 159.7, 137.5, 133.1, 132.4, 132.2, 129.7, 128.2 and 118.5 ppm from (CH<sub>3</sub>)<sub>4</sub>Si in 2 wt% solution in CDCl<sub>3</sub>.

## Results and Discussion

**Reactivities of Various Aromatic Halides.**—Table 1 shows the effect of silica catalyst on the ether yield from various activated halides and potassium carbonate. The silica used here is Aerosil-300 of about 7 μm particle size, manufactured by Nippon Aerosil, by the reaction of SiCl<sub>4</sub>, H<sub>2</sub> and O<sub>2</sub> in the gas phase. This silica is one of the most active catalysts for the etherification reaction described here. Silica markedly enhances the ether yield of all the reactions. The ether yield is dependent on the kind of activating groups (NO<sub>2</sub> > CN > SO<sub>2</sub>Ph > C(=O)Ph), and on the kind of halogen atoms (F > Cl ≈ Br ≈ I) present.

Aromatic fluorides activated by strong electron-withdrawing groups such as *p*-fluoronitrobenzene and *p*-fluorobenzonitrile give ethers in a high yield at rather low temperatures whereas a high reaction temperature is needed for the etherification of aromatic chlorides with weak electron-withdrawing groups such as *p*-chlorophenyl phenyl sulfone or *p*-chlorobenzophenone.

Table 2 shows the results of the etherification of some aromatic fluorides with potassium carbonate in the presence of silica. Both *o*- and *p*-fluoronitrobenzene give bis(2-nitrophenyl) ether and bis(4-nitrophenyl) ether, respectively, in a high yield whereas no reaction occurs with *meta*-nitro or non-activated

**Table 2** Etherification of aromatic fluorides<sup>a</sup>

Fluoride	Ether yield (%)
<i>p</i> -Fluoronitrobenzene	99
<i>m</i> -Fluoronitrobenzene	0
<i>o</i> -Fluoronitrobenzene	98
4-Fluorobiphenyl	0
1-Fluoronaphthalene	0

<sup>a</sup> 4 h at 200 °C; silica: Aerosil 300, 10 wt % of fluoride;  $[K_2CO_3]/[ArF] = 2.0$ .

**Table 3** Catalytic activity of various compounds on the etherification of PCBP with  $K_2CO_3$ <sup>a</sup>

Catalyst	Ether yield (%)
SiO <sub>2</sub> (Aerosil 200) <sup>b</sup>	80
SiO <sub>2</sub> (Aerosil 300) <sup>b</sup>	81
SiO <sub>2</sub> (Siloyd 244) <sup>c</sup>	82
SiO <sub>2</sub> (Aerosil R-972) <sup>b,d</sup>	21
SiO <sub>2</sub> (Aerosil R-812) <sup>b,e</sup>	24
Aluminium silicate <sup>f</sup>	78
Activated clay (S-65) <sup>g</sup>	60
Zeolite (TSZ-410-KOA) <sup>h</sup>	60
Al <sub>2</sub> O <sub>3</sub> <sup>i</sup>	40
TiO <sub>2</sub> <sup>b</sup>	48
None	2

<sup>a</sup> PCBP, 20 g (0.092 mol);  $K_2CO_3$ , 12.7 g (0.092 mol); diphenyl sulfone (solvent), 20 g; catalyst, 1.0 g; 2 h at 300 °C. <sup>b</sup> Nippon Aerosil. <sup>c</sup> Fuji Davison. <sup>d</sup> Obtained by treating Aerosil 200 with dichlorodimethylsilane. <sup>e</sup> Obtained by treating Aerosil 300 with hexamethyldisilazane. <sup>f</sup> Wako Junyaku Kogyo K.K. <sup>g</sup> Nippon Kassei Hakudo K.K. <sup>h</sup> Toyo Soda. <sup>i</sup> Rare Metallic K.K.

aryl fluorides. It is clear that an electron-withdrawing group at the *ortho* or *para* position is necessary for the etherification to occur.

The reaction of *p*-chlorobenzophenone (PCBP) to bis(4-benzoylphenyl) ether (BBPE) was investigated in detail (Scheme 5). This reaction is interesting as a model reaction for the aromatic poly(ether ketone) which recently has received much attention as a high-performance engineering plastic (Scheme 6).

**Catalysts and Cocatalysts.**—Table 3 shows the effect of various catalysts on the BBPE yield from PCBP and  $K_2CO_3$ . Silica and aluminium silicate show very high catalytic activity in the etherification. Titania, alumina and zeolites also show catalytic activity although the yield of BBPE is lower. Other compounds such as MgO, SnO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, NiO, CuO and Cu<sub>2</sub>O show no catalytic activity at all.

The low molecular weight organic silanols such as triphenylsilanol and diphenyldisilanol showed no activity although they were expected to be good catalysts.

Table 4 shows the effect of cuprous and cupric compounds as cocatalysts of silica in the reaction of PCBP with  $Na_2CO_3$ . The ether yield increased considerably with these compounds although they show no catalytic activity towards etherification in the absence of silica.

The activity (as the cocatalyst) of cupric and cuprous compounds is independent of the anionic species. The wide angle X-ray diffraction pattern of the reaction mixture indicates

**Table 4** Effect of cupric and cuprous compounds on the etherification of PCBP with  $Na_2CO_3$ <sup>a</sup>

Cocatalyst	Ether yield (%)
CuCl <sub>2</sub>	86
CuCl	85
CuBr	85
CuBr <sub>2</sub>	84
CuI	72
CuO	74
Cu <sub>2</sub> O	77
CuSO <sub>4</sub> ·5H <sub>2</sub> O	82
Cu(OH) <sub>2</sub>	74
CuS	81
None	30

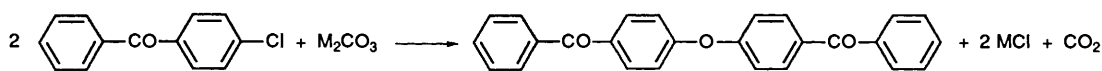
<sup>a</sup> PCBP, 20 g (0.092 mol);  $Na_2CO_3$ , 9.75 g (0.092 mol); silica (Aerosil 300), 1.5 g; diphenyl sulfone (solvent), 20 g; cocatalyst, 0.5 g; 2 h at 300 °C.

that all of the cupric and cuprous compounds listed in Table 4 were largely converted into cuprous oxide and a small amount of metallic copper after the reaction. Other metal compounds such as SnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, NiO and CoO showed no catalytic activity at all.

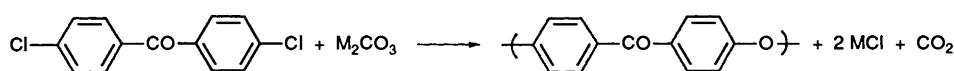
The yield of BBPE in the reaction of PCBP with  $Na_2CO_3$  in the presence of various types of silica (Aerosil, Siloyd and Zeolites) and CuCl<sub>2</sub> as the cocatalyst is shown in Table 5. Aerosil is fumed silica manufactured from SiCl<sub>4</sub>, H<sub>2</sub> and O<sub>2</sub> by a dry process, and consists of a very fine, non-porous particles the surfaces of which are covered with silanol groups. The ether yield increased with the surface area of the Aerosil. Therefore the silanol group on the surface of silica is assumed to be the active site. This idea is supported by the fact that the catalytic activity of methyl-substituted silica is considerably smaller (R-972 and R-812 in Table 3). R-972 and R-812 are obtained by treating Aerosil 200 and Aerosil 300, respectively, with a methylating agent and about 75% of their silanol groups are converted into methyl groups.<sup>5</sup>

Siloyd is a colloidal silica manufactured by a wet process, and is much more porous and larger in particle size. Therefore, the larger surface area consists mostly of internal surface and the relative contribution of external surface area is negligible. Siloyd 244, 800 and 74 have the same surface area as that of Aerosil 300 (300 m<sup>2</sup> g<sup>-1</sup>) and they showed the same ether yield as that of Aerosil 300 (87%). This fact shows that the reaction proceeds in the pores of these Siloyd catalysts (pore size 170–240 Å) as fast as on the external surface. On the other hand, Siloyd 65, the pore size of which is much smaller compared with those of other grades of Siloyd, showed a lower yield (50%) although it has a larger surface area (700 m<sup>2</sup> g<sup>-1</sup>). This indicates that the reaction proceeds more slowly in the pores of Siloyd 65 because of its small pore size.

Zeolite catalysts, ZSM-5, are high-silica zeolites with large surface areas (*ca.* 400 m<sup>2</sup> g<sup>-1</sup>), most of which arises from very fine pores (*ca.* 6 Å). These zeolites showed very low activities, indicating that the reaction does not occur in the fine pores but occurs only on the external surface. The external surface area of ZSM-5 is much smaller in comparison with the total surface area and the ether yield depends on the particle size, as shown in Table 5. Since the ether yield increases with the external surface



Scheme 5

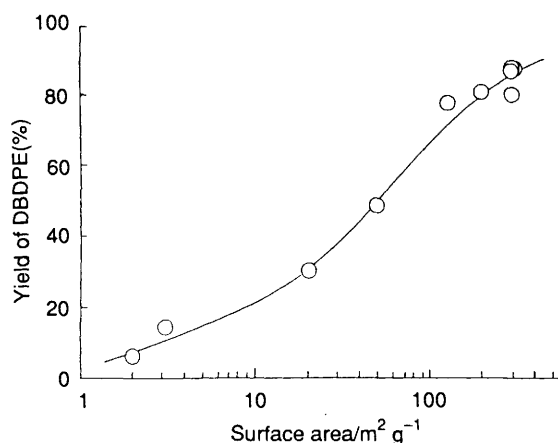


Scheme 6

**Table 5** Catalytic activity of various silicas on the etherification of PCBP with  $\text{Na}_2\text{CO}_3$ <sup>a</sup>

Catalyst		Ether yield (%)	Particle size/ $\mu\text{m}$	Surface area/ $\text{m}^2 \text{g}^{-1}$	External surface area/ $\text{m}^2 \text{g}^{-1}$	Pore size/ $\text{\AA}$	Oil absorption/ $10^{-2} \text{cm}^3 \text{g}^{-1}$	
<i>Silica</i>								
Aerosil <sup>b</sup>	300	$\text{SiO}_2$	87	0.007	300	—	Non-porous	—
	200	$\text{SiO}_2$	81	0.012	200	—	Non-porous	—
	130	$\text{SiO}_2$	78	0.016	130	—	Non-porous	—
	OX	$\text{SiO}_2$	49	0.040	50	—	Non-porous	—
Siloyd <sup>c</sup>	244	$\text{SiO}_2$	87	1.8	300	—	210	310
	800	$\text{SiO}_2$	87	2.7	300	—	240	310
	74	$\text{SiO}_2$	87	3.5	300	—	170	210
	620	$\text{SiO}_2$	80	12.0	300	—	170	180
	65	$\text{SiO}_2$	50	3.5	700	—	25	95
Zeolite ZSM-5	$\text{SiO}_2:\text{Al}_2\text{O}_3 = 27$	30	0.1	400	21	6	—	—
	$\text{SiO}_2:\text{Al}_2\text{O}_3 = 70$	14	1	380	3	6	—	—
	$\text{SiO}_2:\text{Al}_2\text{O}_3 > 150$	6	2	380	2	6	—	—

<sup>a</sup> PCBP, 1 g (4.6 mmol);  $\text{Na}_2\text{CO}_3$ , 0.448 g (4.6 mol);  $\text{SiO}_2$ , 100 mg,  $\text{CuCl}_2$ , 4 mg, diphenyl sulfone (solvent), 1 g; 2 h at 300 °C. <sup>b</sup> Nippon Aerosil. <sup>c</sup> Fuji Davison.



**Fig. 1** BBPE yield vs. effective surface area of silica in the reaction of PCBP with  $\text{Na}_2\text{CO}_3$  in the presence of  $\text{SiO}_2$ - $\text{CuCl}_2$  catalyst: PCBP, 1 g (4.6 mmol);  $\text{Na}_2\text{CO}_3$ , 0.488 g (4.6 mmol);  $\text{SiO}_2$ , 100 mg;  $\text{CuCl}_2$ , 3 mg; diphenyl sulfone (solvent), 1 g; 2 h at 300 °C; see Table 5

area, only the external surface of the zeolite is thought to be effective in this reaction.

Fig. 1 illustrates the relationship between the yield of BBPE and the surface area of Aerosil and Siloyd or the external surface area of zeolites.

In order to clarify the effect of the amount of silica and cuprous oxide on the etherification of PCBP with sodium carbonate, the ether yield at a short reaction time (30 min) was investigated. We studied the relationship between the ether yield and the amount of silica. When sufficient cuprous oxide was present the ether yield increased proportionally with the amount of silica, whereas the yield reached a constant value at 80 mg of silica when the amount of cuprous oxide was small (2 mg). As the silanol concentration of Aerosil 300 on its surface is reported to be about  $1 \text{mmol}^{-1}$ ,<sup>4</sup> the concentration of silanol is roughly twice that of the copper atoms at the point where the ether yield reached a constant value:  $\text{SiOH}$ , 0.08 mmol in 80 mg of Aerosil 300;  $\text{Cu}$ , 0.03 mmol in 2 mg of  $\text{Cu}_2\text{O}$ .

We studied the dependence of the ether yield on the cuprous oxide added. Again the ether yield reached a constant value when the concentration of cuprous oxide was roughly half that of the silanol on the surface. This indicates that cuprous oxide interacts with silanol groups to form a complex, with very high activity, the concentration of which largely determines the rate of etherification. Free cuprous oxide which has no interaction with silanol is assumed to have no catalytic activity.

**Table 6** Etherification of PCBP with various alkali-metal carbonates or hydrogencarbonates in the presence of  $\text{SiO}_2$ - $\text{Cu}_2\text{O}$  catalyst<sup>a</sup>

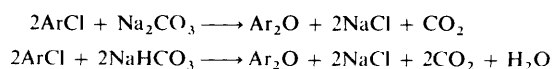
Alkali (hydrogen)carbonate	Particle size/mm	Ether yield (%)
$\text{K}_2\text{CO}_3$	0.5-1	80
$\text{K}_2\text{CO}_3$	<0.2	82
$\text{Na}_2\text{CO}_3$	0.5-1.0	18
$\text{Na}_2\text{CO}_3$	<0.2	77
$\text{Li}_2\text{CO}_3$	<0.2	4
$\text{KHCO}_3$	0.5-1	60
$\text{KHCO}_3$ (9.2 mmol)	0.5-1.0	84
$\text{NaHCO}_3$	0.5-1	57
$\text{NaHCO}_3$ (9.2 mmol)	0.5-1.0	87

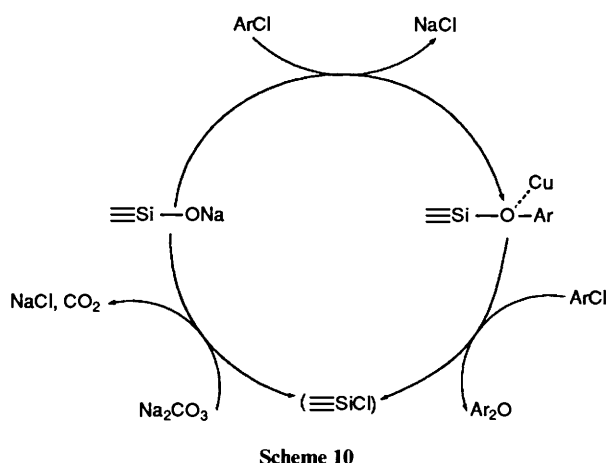
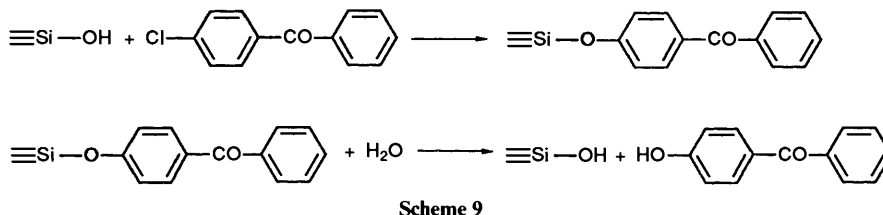
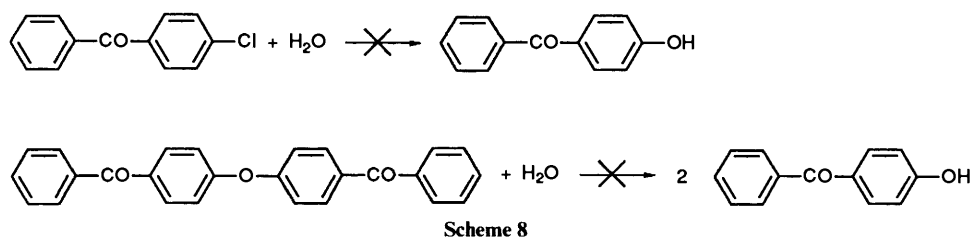
<sup>a</sup> PCBP, 1.0 g (4.6 mmol); carbonate or hydrogencarbonate, 4.6 mmol;  $\text{SiO}_2$  (Siloyd 244), 100 mg;  $\text{Cu}_2\text{O}$ , 10 mg; diphenyl sulfone (solvent), 1.0 g; 1 h at 300 °C.

**Alkali-metal Carbonates.**—Table 6 shows the results of etherification of PCBP with various alkali-metal carbonates and hydrogencarbonates. The ether yield depends on the alkali metal used and is in the order  $\text{K} > \text{Na} > \text{Li}$ .

When sodium carbonate was used, the ether yield was highly dependent on the particle size whereas there was little dependence on the particle size when potassium carbonate or hydrogencarbonate was used. In the case of hydrogencarbonates, they decomposed to finely powdered carbonates on heating, with evolution of water and carbon dioxide. The ether yield from hydrogencarbonate systems is nearly the same as those from finely ground carbonates when twice the molar amount was used.

We studied the dependence of the yield of BBPE on the feed molar ratio of  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$  to PCBP after a prolonged reaction time (6 h). The yield of BBPE increased proportionally with the amount of  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$  added in both cases, but the yield from the  $\text{NaHCO}_3$  system was half that from the  $\text{Na}_2\text{CO}_3$  system at the same feed ratio. The yield was maximised at  $[\text{Na}_2\text{CO}_3]/[\text{PCBP}] = 0.5$  and  $[\text{NaHCO}_3]/[\text{PCBP}] = 1.0$ . This indicates that one mole of  $\text{Na}_2\text{CO}_3$  generates one mole of oxygen atoms to give one mole of BBPE, whereas two moles of  $\text{NaHCO}_3$  are required to produce one mole of BBPE (Scheme 7).

**Scheme 7**



**Table 7** The effect of solvent on the reaction rate of PCBP with  $\text{Na}_2\text{CO}_3$  in the presence of  $\text{SiO}_2\text{-Cu}_2\text{O}^a$

Solvent	Ether yield (%)
Diphenyl sulfone	80
Diphenyl sulfoxide	82
Benzophenone	50
Xanthen-9-one	55
Diphenyl ether <sup>b</sup>	2
Dibenzofuran	3
<i>m</i> -Terphenyl	2
<i>o</i> -Terphenyl	1
$\text{C}_{14}\text{H}_{20}\text{OH}$	2
$\text{C}_{18}\text{H}_{38}$	1
None	43

<sup>a</sup> PCBP, 1 g (4.6 mmol);  $\text{Na}_2\text{CO}_3$ , 0.27 g (2.5 mmol); silica (Siloyd 244), 100 mg;  $\text{Cu}_2\text{O}$ , 10 mg; solvent, 2 g; 2 h at 300 °C. <sup>b</sup> 280 °C.

**Reaction Solvents.**—The ether yields of the reaction of PCBP and  $\text{Na}_2\text{CO}_3$  in the presence of  $\text{SiO}_2$  and  $\text{Cu}_2\text{O}$  in various solvents are listed in Table 7. Polar solvents such as diphenyl sulfone and diphenyl sulfoxide promoted the reaction whereas the addition of a non-polar solvent such as *m*-terphenyl or the alkane  $\text{C}_{18}\text{H}_{38}$  considerably lowered the etherification rate.

**Reaction Mechanism.**—In the liquid chromatogram of the reaction mixture of PCBP with alkali-metal carbonate in the presence of silica, a small amount of *p*-hydroxybenzophenone (PHBP) was observed. The amount of PHBP increased proportionally with the amount of silica added and was independent of the amount of  $\text{Na}_2\text{CO}_3$ , the amount of PCBP, the reaction time, and the ether yield from 5 to 95% as shown in Table 8. Therefore, the idea that PHBP is formed by the

**Table 8** Yield of ether and PHBP in the reaction of PCBP with  $\text{Na}_2\text{CO}_3$

$\text{SiO}_2^b$ (mg)	$\text{Cu}_2\text{O}$ (mg)	$\text{Na}_2\text{CO}_3$ (mmol)	$T/^\circ\text{C}$	$t/\text{h}$	BBPE (%)	PHBP (%)
0	5	2.5	300	1	0.3	0
50	5	2.5	300	1	25	0.4
100	5	2.5	300	1	48	0.8
150	5	2.5	300	1	71	1.3
200	5	2.5	300	1	82	1.6
100	0	2.5	300	1	4	0.7
100	5	2.5	200	1	0.2	0.6
100	5	2.5	250	1	3	0.7
100	5	2.5	300	0.2	5	0.7
100	5	2.5	300	2	75	0.8
100	5	2.5	300	3.5	95	0.8
100	5	1.5	300	1	42	0.8
100	5	4.6	300	1	50	0.8

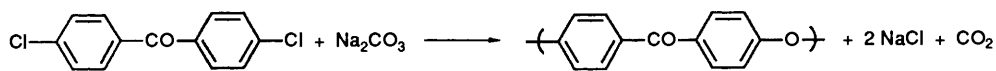
<sup>a</sup> PCBP, 1.0 g (4.6 mmol); phenyl sulfone (solvent), 1.0 g. <sup>b</sup> Aerosil 300.

hydrolysis of PCBP or of BBPE (Scheme 8) should be abandoned.

It is assumed that the silyl ether is formed from the reaction of PCBP and the silanol on the surface of silica, and that this is hydrolysed to hydroxybenzophenone during the liquid chromatography (Scheme 9).

It is considered that the silyl ether is the intermediate of the etherification as illustrated in Scheme 10. When 100 mg of Aerosil 300 is used, 0.04 mmol of PHBP is formed. As the amount of surface silanol in 100 mg of Aerosil 300 is 0.1 mmol,<sup>5</sup> about 40% of the surface silanol is in the form of silyl ether during the reaction.

The rate-determining step of the etherification is presumed to



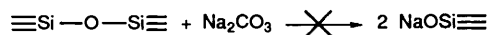
**Table 9** The etherification of PCBP with potassium phosphate or sodium stannate<sup>a</sup>

Alkali-metal salt	Catalyst	Ether yield (%)
K <sub>3</sub> PO <sub>4</sub>	None	10
K <sub>3</sub> PO <sub>4</sub>	SiO <sub>2</sub> <sup>b</sup>	40
K <sub>3</sub> PO <sub>4</sub>	SiO <sub>2</sub> -Cu <sub>2</sub> O <sup>c</sup>	80
Na <sub>2</sub> SnO <sub>3</sub>	None	25
Na <sub>2</sub> SnO <sub>3</sub>	SnO <sub>2</sub> <sup>b</sup>	26

<sup>a</sup> PCBP, 1 g (4.6 mmol); alkali salt, 4.6 mmol; diphenyl sulfone (solvent), 1 g; 1 h at 300 °C. <sup>b</sup> Siloyd 244, 100 mg. <sup>c</sup> Siloyd 244, 100 mg + Cu<sub>2</sub>O, 3 mg.

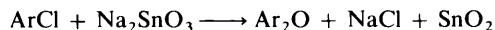
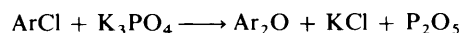
be the reaction between the silyl ether and the aromatic halide, not the formation of the silyl ether, because PHBP is observed under very mild conditions, such as the reaction at 200 °C where the ether yield is very small. As mentioned in the earlier part of this paper, the rate of etherification levels off at a copper concentration of about half that of silanol. This suggests that Cu<sub>2</sub>O activates the silyl ether and promotes the reaction.

As stated earlier, the concentration of PHBP is independent of the reaction time, indicating that the concentration of silanol is also constant. Therefore it is supposed that the cleavage of the Si-O-Si linkage of silica by sodium carbonate does not occur under the present reaction conditions.



**Application to Polyether Synthesis.**—High-molecular-weight aromatic poly(ether ketones) have been synthesized by applying the present etherification reaction to 4,4'-dichlorobenzophenone and alkali-metal carbonate in the presence of a silica-cuprous oxide catalyst system (Scheme 11). The details of this polymerization will be reported elsewhere.<sup>6</sup>

**Etherification by Phosphates or Stannates.**—It was found that alkali-metal phosphates and stannates also serve as oxygen sources in the etherification of PCBP (Table 9). When



potassium phosphate was used, silica and cuprous oxide showed catalytic activity as in the case of alkali-metal carbonates. However, silica showed no catalytic activity towards etherification using sodium stannate. Other compounds such as CaCO<sub>3</sub>, MgCO<sub>3</sub>, K<sub>2</sub>SiO<sub>3</sub> and K<sub>2</sub>SO<sub>3</sub> did not react with PCBP in the presence of SiO<sub>2</sub>-Cu<sub>2</sub>O.

### Conclusions

Aromatic halides activated by nitro, cyano, sulfonyl or carbonyl groups react with alkali-metal carbonates in the presence of silica catalysts to form ethers in high yield. Cuprous and cupric salts further promote the etherification reaction. Silyl ethers formed from the aromatic halides and surface silanol groups on silica are proposed to be intermediates in the etherification.

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