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Synthesis, Catalytic Activity, and Behavior of Phase-Transfer Catalysts Supported on Silica Gel. Strong Influence of Substrate Adsorption on the Polar Polymeric Matrix on the Efficiency of the Immobilized Phosphonium Salts[1]

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Abstract: Phase-transfer (PT) catalysts, namely, phosphonium salts, have been immobilized on silica gel; good organofunctionalization has been obtained ranging from 1.0 to 0.7 mequiv $[PR_4]^+$/g. The synthesis of phosphonium salt functionalized silica gels **1–4**, with different spacer chain lengths between the polymeric matrix and the catalytic center (from 3 to 27 atoms), is reported. Ketone adsorption constants (K_{ads}) on nonfunctionalized and functionalized silica gel, and their comparison with pseudo-first-order rate constants (k_{obsd}) in the aqueous sodium borohydride reduction of ketones under PTC conditions, show that adsorption phenomena are the main factors determining the reaction rate; moreover, C,O-alkylation experiments show that the catalyzed reaction takes place in a very polar environment formed by the functionalized silica gel and the water adsorbed on it. These immobilized catalysts can be reused several times with a little loss of activity, but they are hydrolyzed at high pH values.

Phase-transfer (PT) catalysts, such as the classic onium salts[2,3] or more complex systems, such as crown ethers and cryptands,[3] have been immobilized on insoluble polystyrene matrices with various degrees of cross-linking. Their activity remains reasonably high if the catalytic center is sufficiently far from the polymer backbone (alkyl chain interposed),[4] or if the resin is very porous.[5] This arrangement has certain advantages over the use of free catalyst: the reaction is clean and its products are not contaminated by the catalyst.

However, all the literature reported data seem to show that

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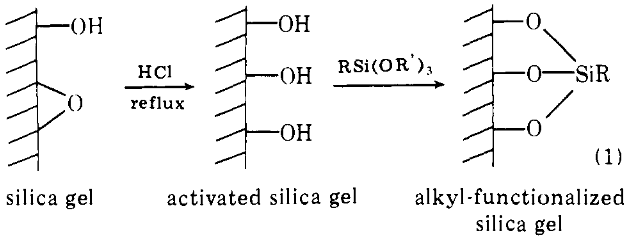
the polymer matrix does not affect the rate or the course of the PT-catalyzed reaction, apart from steric hindrance with respect to the reagents.

It has been established that swelling of the insoluble resin is of great importance in the activity of immobilized onium salts: a conditioning period in the reaction mixture is necessary to reach and maintain optimum activity, and polar solvents must thus be employed to promote widening of the polystyrene matrix pores, to facilitate close contact between the two immiscible phases in the catalytic cavities of the insoluble support.

PT catalysts have also been immobilized on silica polymers (Aerosil-200).[6] Here, however, the low functionalization required the use of massive amounts of catalyst, and the resulting large quantity of solvent probably accounts for the low reaction rates.

Good organofunctionalizations are obtained with silica gel: its surface contains silanol -OH groups mainly responsible for adsorption and -O- strained siloxane atoms[7] that are transformed into -OH by reflux with 35% hydrochloric acid.[8] Silica gel activated in this manner gives good linking reactions with the alkyltrialkoxysilanes to afford the alkyl-functionalized silica gel.[8]

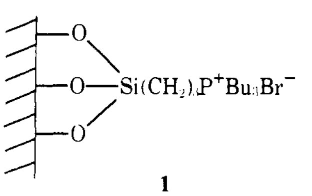
The most likely structure for the chemical linkage is shown in (1). It is also the most stable to hydrolysis. Bridge formation with one or two oxygen atoms between the polymer support and the organosilicic function is also possible, although bridging with one atom occurs less frequently and is of minor importance.[9]



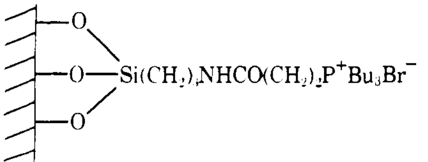
(1)

This paper discusses the catalytic activity and behavior of phosphonium salts supported on silica gel, with chains of different length interposed between the silica polymer and the onium salt. By contrast with the polystyrene matrices, there is in this case clear evidence of the participation of the support. Adsorbing the substrate has a drastic influence on the reaction rate as a function of the polarity of the solvent.

Results



1



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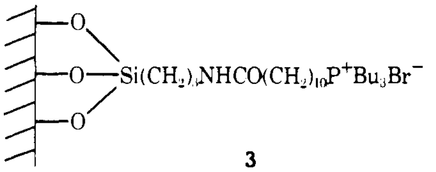

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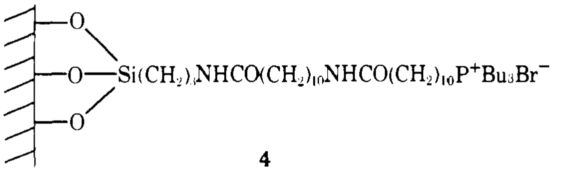
Table I. Pseudo-First-Order Rate Constants ($k_{obsd} \times 10^4$ s^{-1}) for the Reaction of 1-Bromooctane with Potassium Iodide, under Phase-Transfer Conditions,[a] Catalyzed by **1**, **3**, and **5**, at 80 °C

catalyst	no solvent	*n*-heptane	toluene	chlorobenzene
1	7.22	2.86	1.72	1.92
3	2.89	1.19	1.11	1.11
5	21.7	10.0	8.22	9.25

[a] General conditions: 1-bromooctane, 2.0 mmol; KI, 5.0 mmol; H_2O, 0.65 mL; solvent, 1.05 mL (solvent:substrate ratio 3:1 v/v); catalyst, 0.05 molar equiv. Average of at least two runs.



4

$C_{16}H_{33}P^+Bu_3Br^-$

5

Synthesis of 1–4. Phosphonium Salts Immobilized on Silica Gel. The synthetic path, according to Scheme I, envisages initial attachment of a functionalized organosilane on the activated silica gel, followed by transformation of the polymer through several passages to obtain catalysts **1–4**.

Catalyst **1** is therefore prepared by reaction of 3-bromopropyltriethoxysilane with silica, followed by reaction with tri-*n*-butylphosphine for 5 days at 65 °C. In the same way, **2–4** are prepared from the respective ω-bromo functionalized derivatives, which are synthesized via the reaction of the corresponding ω-bromoacyl chlorides with **8** (already known[8]) or with **11**. **10** was converted to **11** with a classic Gabriel synthesis, using a method described for such transformation on Merrifield chloromethylated resins.[10]

The high porosity and therefore considerable surface area of silica gel lead to functionalizations of 0.7–1.3 mequiv $[PR_4]^+$/g for systems **1–4**.

Kinetics of PT-Catalyzed Reaction between Aqueous Potassium Iodide and 1-Bromooctane. By contrast with PT catalysts immobilized on polystyrene matrices,[11] no swelling of the catalyst was noted during the reaction, apart from partial crumbling due to stirring. This, however, did not interfere with its filtration from the reaction mixture and its use in a subsequent reaction.

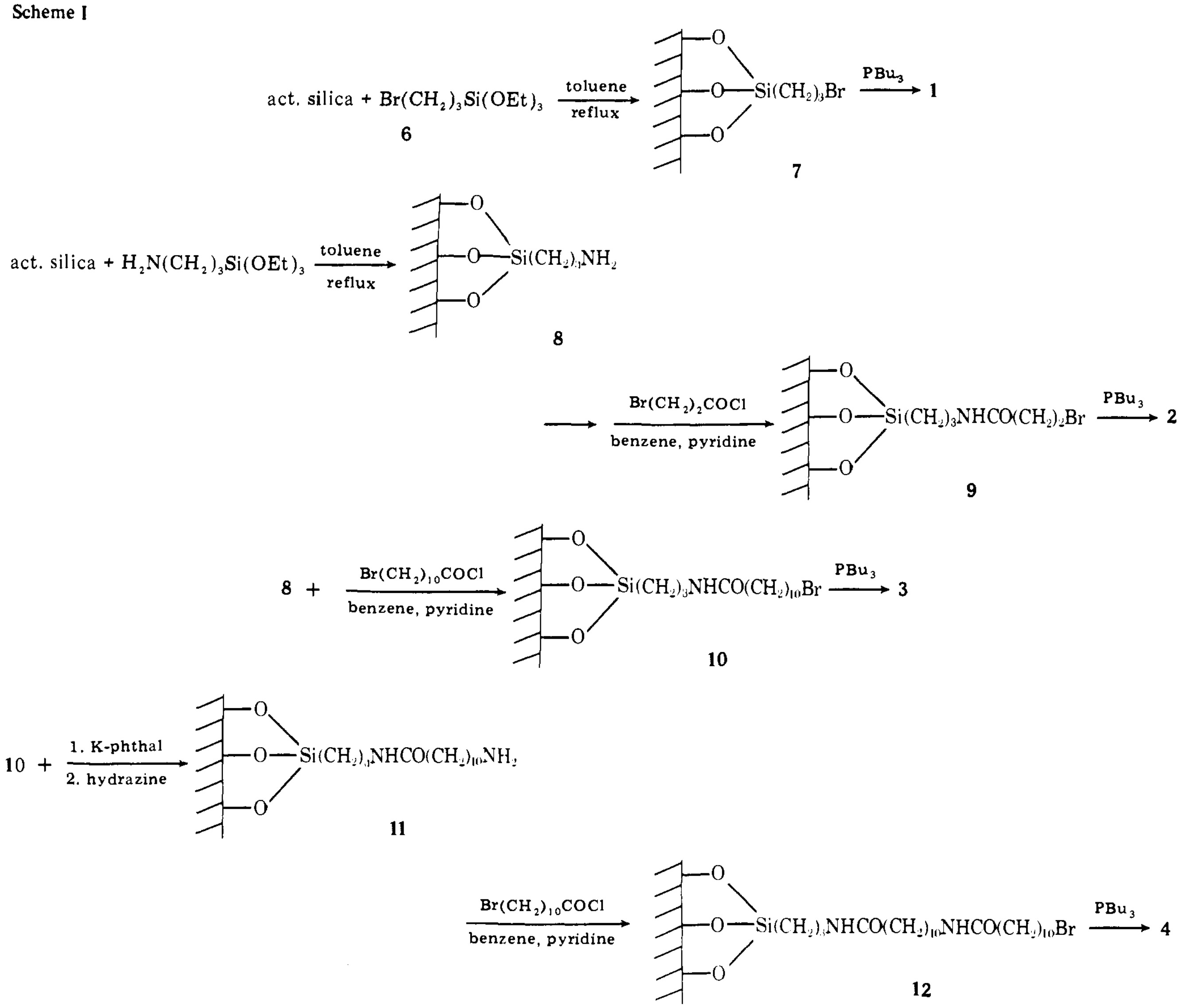
Since there is no swelling, there is no need for a conditioning period of the catalyst in the mixture. The reaction thus begins immediately, as it does with homogeneous catalysts.

If soluble catalyst **5** or polystyrene-immobilized catalysts are used, activity is highly dependent on stirring speed, for identical reaction.[11,12] On the other hand, in the case of **3** with no stirring, the fast bromide–iodide displacement (cf. Experimental Section) shows that exchange between the two immiscible phases on the silica support is very rapid. However, the activity rises as stirring is increased from 0 to 600 rpm; it levels off at 1000 rpm (the value at which all the k_{obsd} values were taken).

Table I compares the activity of **1** and **3** under PT conditions with homogeneous catalyst **5** in the conversion of 1-bromooctane into 1-iodooctane in solvents with different polarity. This reaction always follows pseudo-first-order kinetics and is faster with **5** than with **1** or **3**. **1** is more active than **3** in all the solvents, but particularly in *n*-heptane. This suggests that an important part is played by adsorption of the substrate on the silica gel, which is enhanced by the apolar solvent.

Adsorption Measurements. Ketones were selected for determining adsorption on silica gel in order to investigate the

Scheme I



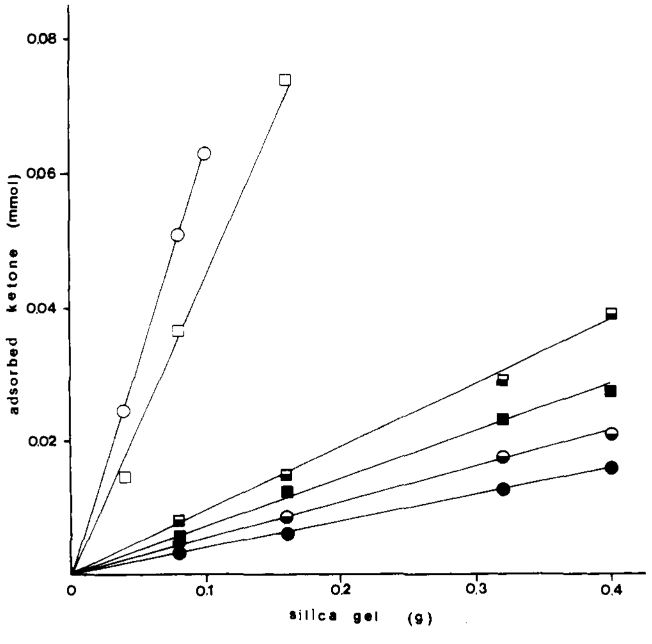


Figure 1. Adsorption coefficients of ketones on the nonfunctionalized silica gel (circles: acetophenone (-○-) in cyclohexane, (-◒-) in chlorobenzene, (-●-) in benzene; squares: 2-octanone (-□-) in cyclohexane, (-⬓-) in chlorobenzene, (-■-) in benzene).

relationship between the K_{ads} and the alcohol reduction rate under PT conditions with aqueous $NaBH_4$.

Adsorption was measured in three different polarity solvents: cyclohexane, benzene, and chlorobenzene at 25 °C. Various quantities of nonfunctionalized silica gel or silica gel functionalized with phosphonium salts were added to an initial solution of 8.0×10^{-3} M ketone (cf. Experimental Section).

Unlike the kinetic experiments (see below), adsorptions were measured at lower concentrations of ketone for more accurate measurement, and in the absence of water to enhance the phenomenon. Water, in fact, competes with ketones and occupies silica gel sites; large amounts of silica must therefore be used if measurements are made in the presence of water.

The concentration of ketone left in solution was analyzed by GLC. The linear relation[13] between the amount of nonfunctionalized silica added and concentration of ketones left in solution was expressed in mmol/g (Figure 1).

The first columns of Table II show the K_{ads} of various ketones obtained in the three solvents with nonfunctionalized silica gel. In Table III K_{ads} (mol/$[PR_4]^+$) for 2-octanone, acetophenone, and dibenzyl ketone in cyclohexane, with functionalized silica gels **1-4**, are reported.

Kinetics of the PT-Catalyzed Reduction of Ketones to Alcohols. The kinetics of the reduction of these ketones to alcohols were then measured. The reactions were conducted in the same

Table II. Adsorption Constants ($K_{ads} \times 10^2$, mmol/g) on Nonfunctionalized Silica Gel of Several Ketones, and Their Pseudo-First-Order Rate Constants ($k_{obsd} \times 10^4$, s^{-1}) in Aqueous Borohydride Reduction, under Phase-Transfer Conditions,[a] Catalyzed by **1–5** (t = 25 °C)[c]

ketone	cyclohexane						benzene						chlorobenzene					
	K_{ads}	k_1	k_2	k_3	k_4	k_5	K_{ads}	k_1	k_2	k_3	k_4	k_5	K_{ads}	k_1	k_2	k_3	k_4	k_5
2-octanone	47.0	7.67	3.50	2.17	3.33	2.17	6.8	3.00	1.28	0.55	1.67	0.53	9.6	5.67	0.87	1.08	1.62	0.70
acetophenone	64.0	46.67	26.67	20.00	23.33	16.50	3.9	7.33	5.50	3.67	4.83	3.33	5.3	8.00	4.33	4.17	7.33	2.33
1,3-diphenyl-2-propanone	62.0	8.00	2.67	1.00	2.00	7.67	3.9	2.50	1.13	0.83	2.00	2.76	5.1	3.00	0.50	0.45	1.63	2.41
cyclododecanone	39.0	0.60				0.35	3.8	0.22				0.10	4.5	0.23				0.07
2,2-dimethyl-3-butanone	42.0	23.33				13.17	*b*	9.33				4.17	*b*	*b*	*b*	*b*	*b*	*b*

[a] General conditions: ketone, 2.0 mmol; $NaBH_4$, 3.0 mmol; H_2O, 2.0 mL; solvent, 1.2 mL; catalyst, 0.05 molar equiv. [b] Not determinable by GLC analysis. K_{ads} and k_{obsd}: average of at least two runs. [c] $k_1 = k_{obsd}$ for the catalyst **1**, $k_2 = k_{obsd}$ for the catalyst **2**, etc.

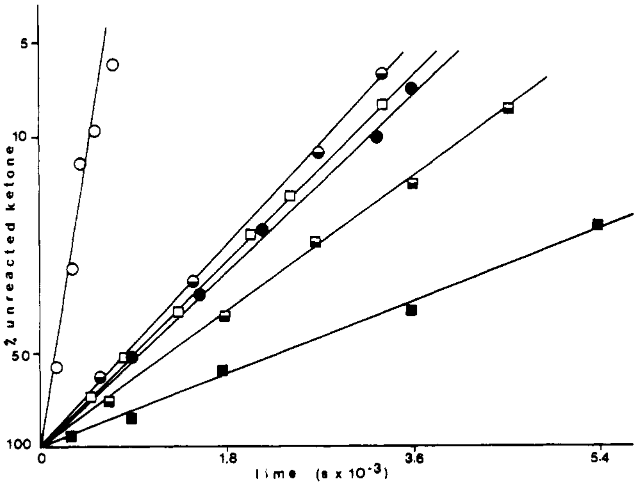


Figure 2. Disappearance of ketones in the sodium borohydride aqueous reduction carried out in solvent with PT-functionalized silica gel. For the reaction conditions, see Table II, footnote *a* (circles: acetophenone (-○-) in cyclohexane, (-◐-) in chlorobenzene, (-●-) in benzene; squares: 2-octanone (-□-) in cyclohexane, (-◧-) in chlorobenzene, (-■-) in benzene).

Table III. Adsorption Constants[a] ($K_{ads} \times 10^2$, mol/[PR_4]$^+$) on Functionalized Silica Gels **1–4** in Cyclohexane, at 25 °C

catalyst	2-octanone	acetophenone	1,3-diphenyl-2-propanone
1	7.4	6.8	4.6
2	2.0	3.2	2.8
3	0.8	1.0	1.8
4	2.0	3.4	3.8

[a] Average of at least two runs.

solvents at 25 °C under PT conditions with 0.05 molar equiv of catalysts **1**, **2**, **3**, **4**, or **5**.

The kinetics are pseudo first order[14] (Figure 2), and k_{obsd} linearly depends, with a slope of 0.95 (r = 0.995; $K_{obsd} \times 10^4$ s^{-1} vs. mol equiv $\times 10^2$ of catalyst **1**), on the amount of catalyst used in the range examined (0.01–0.10 molar equiv with respect to the ketone).

Table II shows the k_{obsd} values for catalysts **1–4** and the homogeneous catalyst hexadecyltributylphosphonium bromide (**5**).

Figure 3 illustrates the trend of the relationship between the reaction rates and the adsorption constants for 2-octanone in cyclohexane, with catalysts **1–4**. The abscissa (obviously arbitrary) represents the number of atoms interposed between the support and the catalyst center. Even K_{ads} and k_{obsd} of acetophenone and dibenzyl ketone show a similar behavior, except for catalyst **4**.

PT-Catalyzed Reaction between Sodium Phenoxide and Benzyl Bromide. C-Alkylation. Benzyl bromide alkylations were carried out on sodium phenoxide under PT conditions.

$$PhOH + PhCH_2Br \xrightarrow[\text{catalyst}]{\text{NaOH, solvent}} PhCH_2OPh + (o,p)\text{-}HOC_6H_4CH_2Ph \quad (2)$$

Table IV shows the results for this reaction in two solvents with different polarity in an aqueous-organic system, using catalysts **1–4**, homogeneous phosphonium salt **5**, and a phosphonium salt immobilized on a polystyrene resin with an alkyl chain interposed between the active center and the polymer matrix:[4] Ⓟ-$C_6H_4CH_2NHCO(CH_2)_{10}P^+Bu_3Br^-$ (**13**).

The reaction catalyzed by phosphonium salts supported on silica is faster with an apolar than with a polar solvent, as in the ketone reduction. In addition, the fairly high percentage

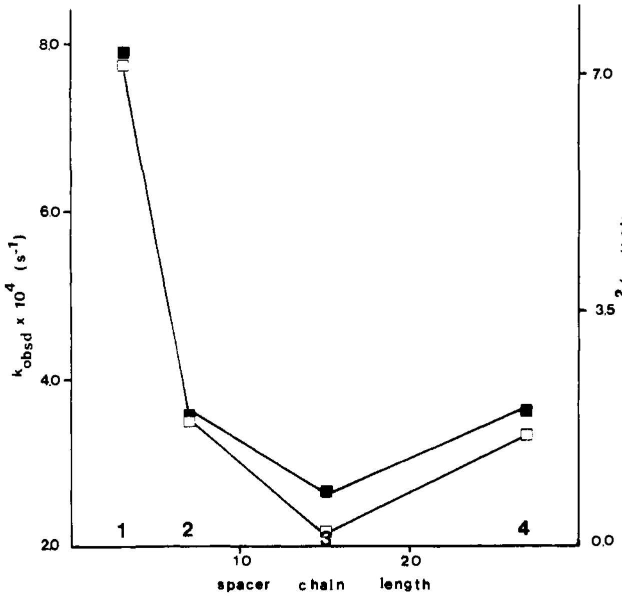


Figure 3. Comparison of pseudo-first-order rate constants (k_{obsd}, open symbols) in the PT-catalyzed sodium borohydride aqueous reduction of 2-octanone in cyclohexane (see Table II, footnote *a*) with the corresponding adsorption constants (K_{ads}, full symbols) in the same solvent.

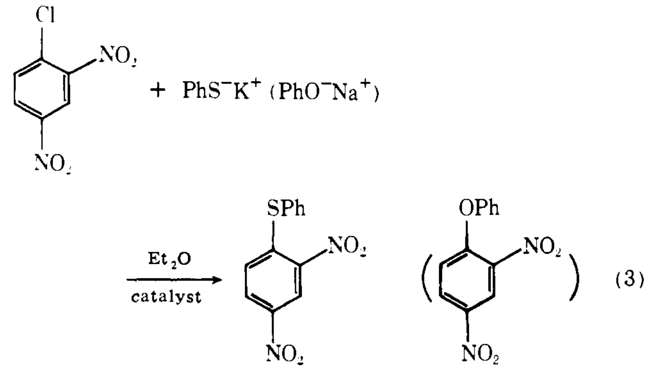
of C-alkylation product present for catalysts **1-4** is virtually constant in both solvents.

PT-Catalyzed Aromatic Nucleophilic Substitution. The solid-liquid PT *N*-alkylphthalimide synthesis with **1** or **3** as catalyst has already been described.[1] The same method can also be used for the synthesis of thioethers: with 0.8 mL of an aqueous solution 3 M in PhSK (2.4 mmol), 1-bromooctane (2.0 mmol), and **1** (0.05 molar equiv), *n*-octyl phenyl sulfide is obtained after 0.5 h (98%). If this reaction is run with 1.05 mL of *n*-pentane, the sulfide is obtained after 1.25 h (97%) (by GLC analysis).

Primary alkyl chlorides can also be prepared from primary alcohols with concentrated HCl at 100 °C; 1-octanol is transformed into 1-chlorooctane (96% conversion after 24 h) in the presence of 0.10 molar equiv of **1** as catalyst (by GLC analysis); if **5** is used, 45 h (94%) is necessary.[15] This reaction is faster with catalyst **1** than with **5**, probably because the high polarity of the substrate increases its concentration on the support.

We have described below a full, hitherto unreported, procedure for a classic aromatic nucleophilic substitution carried out under PT conditions.

When the activated aromatic halide is placed in a two-phase system with a nucleophile source and a PT catalyst, ordinary nucleophilic substitution takes place.



14 **15**

Table IV. C-Alkylation and Conversions[a] for the Reaction of Sodium Phenoxide with Benzyl Bromide, under Phase-Transfer[b] Conditions, in Cyclohexane and Methylene Chloride, at 25 °C

catalyst	cyclohexane C-alk, %	cyclohexane conv, %	methylene chloride C-alk, %	methylene chloride conv, %
1	22.9	74	26.3	37
2	28.5	62	30.0	41
3	28.3	41	21.0	38
4	25.6	63	25.9	36
5	5.2	87	0.0	97[c]
13[d]	10.5	83	3.0	48[c]

[a] Values were determined by ^{1}H NMR spectroscopy in $CDCl_3$ from triple integration of the expanded region (δ 5.0-3.7), and are corrected for di-C-alkylations, but not for traces of O,C-dialkylation; average of two runs. [b] General conditions: $PhCH_2Br$, 20 mmol; PhOH, 3 M, 8.0 mL (24.0 mmol); solvent, 10.0 mL; catalyst, 1.0 mmol (0.05 molar equiv); *t*, 6.0 h. [c] *t*, 3.0 h. [d] Reference 11; unpublished results.

When catalyst **5** is employed, the reaction mixture quickly turns brown, though this does not prejudice the outcome. On the other hand, when catalyst **1** is used, the mixture remains yellow and the product can be obtained in the pure state, without crystallization, after filtration of the catalyst.

An apolar solvent cannot be used because of the low solubility of the substrate.

Discussion

To ensure recovery of PT catalyst immobilized on silica gel, the reaction must take place in a medium that does not favor the hydrolysis of the siloxanic silica bonds. When it is necessary to work in strongly alkaline aqueous solutions (reaction with carbenes generated in situ, production of carbanions, etc.), catalysts **1-4** cannot be salvaged, even though the reaction takes place very quickly, because the silica depolymerizes.

Hydrolysis of siloxanic bonds that bind the organic chain to the gel is also possible. In the reduction of ketones with $NaBH_4$, for example, the activity of catalysts **1** and **3**, when salvaged from a previous reaction, falls by about 30% in the second reaction, but is then constant in the third, fourth, and fifth. This suggests that more than one type of attachment, besides multilayer formation, may take place between the alkyltriethoxysilane and silica gel, and that at least the three-bond form shown in (1) is resistant to hydrolysis in this slightly alkaline environment (pH 9.7).

Adsorption Constant and Pseudo-First-Order Rate Constant. The same type of chemical functionalization is present in catalysts **1-4** and the percentage of surface hydroxyl groups is not high.[16,17] For this reason, the adsorption constants on functionalized silica are lower than those on a nonfunctionalized silica.

The enhanced adsorption of **1** with respect to **2-4** must be attributed to the presence of a polar group, such as onium salt, with a short alkyl chain that does not have a drastic effect on either the polarity of the support or its availability for the substrate. Similar considerations may apply to **2** and **3**: a hydrophobic chain surrounding the matrix decreases its polarity, and hence its adsorption capacity.

In catalyst **4**, on the other hand, there is an obvious increase in K_{ads} that becomes even more evident if the ketone has some phenyl groups. The long alkyl chain in this catalyst acts as a solvent for the ketone and thus takes part in the adsorption processes as well.

For 2-octanone (Figure 3), acetophenone, and dibenzyl ketone K_{ads} and k_{obsd} in cyclohexane parallel one another in the case of catalysts **1-3**: the more ketone adsorbed on the insoluble support, the faster the reduction rate. The catalytic activity pattern of **4**, however, does not fit in with the adsorption of acetophenone and dibenzyl ketone. In this connection, unlike catalysts **1–3**, it may be supposed that an increased local concentration of substrate occurs on the lipophilic film covering the matrix. Furthermore, the reduction probably takes place on the inner, more polar microenvironment, following the model of phenol alkylation; to render the reaction possible ketones should previously diffuse on the support.

In Table II the reaction rates for catalysts **1–4** are always higher in cyclohexane, where all ketones also show higher K_{ads}, and decrease successively in chlorobenzene and in benzene following the same K_{ads} trend. In the comparison between kinetic and adsorption results for different ketones in the same solvent, other factors beside adsorption (steric hindrance, alkyl chain length, conjugation, etc.) must clearly be taken into account to explain the floating trend between k_{obsd} and K_{ads} values.

If soluble catalyst **5** is used, it is not always easy to decide from the literature which solvent is generally the best for PT-catalyzed reactions.

Reduction of ketones with sodium borohydride is generally faster when **1** is used rather than **5**. This result is inconsistent with the prevailing view that the activity of a catalyst decreases when it is supported on polymers. Moreover, it is also known that the reduction reaction will only take place in a solvent capable of forming hydrogen bonds. It proceeds very slowly even in polar aprotic solvents, such as *N,N*-dimethylformamide and diglyme.[18]

The behavior of catalyst **1** in this reaction is comparable with that of ephedrinium salts.[19] These have an -OH group at β in the center and speed up the reaction considerably.

C,O-Alkylation. The reaction between sodium phenate and benzyl bromide is well suited to showing whether the reaction environments consist of (1) organic solvent alone, (2) organic solvent plus silica, or (3) organic solvent, plus silica, plus water. This reaction, in fact, gives quantitative yields of the O-alkylation product in aprotic solvents; even in protic polar solvents, i.e., methanol or ethanol, that do not strongly solvate the anionic phenol oxygen, C-alkylation products are practically absent. Considerable C-alkylation products will be obtained only if the reaction is carried out in 2,2,2-trifluoroethanol or water,[20] and with very polar polystyrene resin as PT catalysts.[21]

Table IV shows that the adsorption of benzyl bromide on the insoluble polymer support is the factor that determines the reaction rate, whereas when catalyst **5** is used the reaction is faster in methylene chloride than cyclohexane. Furthermore, the presence of a considerable percentage of C-alkylation product in all cases suggests that, by contrast with **5** and **13**, where the reaction environment is the organic solvent, reactions catalyzed by phosphonium salts supported on silica gel, in addition to taking place on the substrate adsorbed by the silica, occur in an environment consisting of organic solvent and the water adsorbed on the polar support.[22] Moreover, this mechanism is not dependent on the solvent nor the length of the chain binding the catalysts to the silicic support.

Conclusion

The activity of phase-transfer catalysts immobilized on polystyrene matrices increases if there is a chain between the active center and the matrix.[4] In the case of immobilization on silica gel, however, the length of the hydrophobic chain strictly determines the adsorption capacity of the polar support, which then controls the rate of the reaction.

It is thus correct to speak of three-phase catalysis: two reagents, each derived from a distinct phase, come into close contact on a third phase and react. A similar situation is also observed on nonfunctionalized silica gel, which adsorbs organic compounds by transporting them into the cavities of the polymer matrix where they react with the second reagent, which has also been adsorbed. It may, however, be difficult for the anionic species to migrate up the support. This will depend on the hydrophilic nature of the salt, since both the anion and the cation must be dissociated and solvated by the less polar silica gel.[23] If, however, the gel itself contains positive centers, the local concentration of anions involved in the catalysis will be greater than that of the immobilized onium salt for the same adsorption capacity of the gel.

Furthermore, adsorption of the substrate by the gel is dependent on the solvent: when catalysts supported on silica gel are used, the best solvent will undoubtedly be that which gives the lowest R_f in silica gel TLC. Aliphatic hydrocarbons are always the best solvent for PT reactions catalyzed by phosphonium salts supported on silica gel.

Experimental Section

Nuclear magnetic resonance spectra were recorded on a Hitachi Perkin-Elmer R-24B NMR spectrometer with tetramethylsilane as internal standard.

Kinetic measurements were conducted on a Varian Series 1440 gas chromatograph. The pH values were measured with a Beckman Expandomatic pH meter, the electrodes being checked against a pH 10.0 buffer solution. Thermogravimetric analyses were carried out with a Du Pont 990 thermal analyser.

Material and Solvents. The silica gel used was Merck (Art. No. 7734) Kieselgel 60, 70–230 mesh, pore diameter 60 Å, specific surface area 500 m^2/g, normally used for column chromatography. It was activated, according to Fritz and King,[8] by reflux for 4 h in concentrated hydrochloric acid.

Hexadecyltributylphosphonium bromide (**5**) was prepared according to Starks,[24] mp 54 °C.

3-Bromopropanoyl chloride and 11-bromoundecanoyl chloride were obtained according to the literature (bp, $n^{20}{}_D$, respectively: 56 °C (15 mm), 1.4966; 137 °C (0.4 mm), 1.4806 (lit. bp 69–71 °C (23 mm)[25] and 174–175 °C (10 mm)[26]).

3-Bromopropyltrichlorosilane was prepared according to Mironov,[27] bp 85–86 °C (15 mm) (lit. bp 90 °C (10 mm)).

Potassium phthalimide must be freshly prepared from an alcoholic solution of phthalimide and potassium hydrate.[28]

All the ketones were commercial products, used after purification by standard methods.

Cyclohexane, benzene, chlorobenzene, and *n*-heptane were Analar grade chemical solvents, used without purification in the adsorption and kinetic measurements. All the other compounds were commercial, and were used without purification.

Synthesis of the Catalysts 1–4. 3-Bromopropyltriethoxysilane (6). 3-Bromopropyltrichlorosilane (12.9 g, 50 mmol) in 50 mL of anhydrous benzene was added dropwise over 0.5 h to a cooled and stirred solution of 200 mL of benzene, 45 mL of triethylamine, and 40 mL of absolute ethanol; after filtration of the triethylamine hydrochloride, the solvent was removed and the reaction mixture distilled to afford 12.1 g of **6** (84%), bp 114–115 °C (15 mm), $n^{20}{}_D$ 1.4367. Anal. ($C_9H_{21}BrO_3Si$) C, H. ^1H NMR (δ, CCl_4): CH_3CH_2O, 3.76 (q, 6 H) and 1.18 (t, 9 H); $BrCH_2$ 3.35 (t, 2 H); CH_2 1.90 (m, 2 H); CH_2SiO 0.63 (t, 2 H).

3-Bromopropyl-Functionalized Silica Gel 7. A suspension of 3-bromopropyltriethoxysilane (17.2 g, 60 mmol) and activated silica gel (40.0 g) in 200 mL of toluene was refluxed with stirring; after 1 h, about 50 mL of ethanol-containing toluene was removed by distillation and reflux continued. After 1 h this second procedure was repeated and reflux continued for 0.5 h. The cooled, functionalized silica gel **7** was filtered, washed several times with diethyl ether, and allowed to stand in the air to remove the adsorbed solvent, yield 45.5 g.

The analysis was carried out by transforming the organic bromine into bromide anion by reaction with an excess of pyridine at 100 °C for 2 h. Thus, for 0.30 g of **7** and 4.0 mL of pyridine, after cooling at 0 °C, 6.0 mL of 65% nitric acid and about 10 mL of DMF were added. Volumetrical analysis according to Volhard yielded a titer of 0.87 mequiv Br/g.

3-Aminopropyl-Functionalized Silica Gel 8. The synthesis was carried out according to the procedure described for **7**, starting from 3-aminopropyltriethoxysilane (18.0 g, 81 mmol), 40.0 g of activated silica gel, and 200 mL of toluene; 48.5 g of **8** was obtained.

From the weight increase, a titer of 1.6 mequiv NH_2/g can be calculated. Volumetric acid-base titration (indicator methyl red) did not yield satisfactory results; direct titration with 0.1 N sulfuric acid and indirect titration (by first adding an excess of 0.1 N sulfuric acid and then titrating with 0.1 N sodium hydrate) left a range of uncertainty of 1.40-1.55 mequiv NH_2/g.

3-Bromopropanamidopropyl-Functionalized Silica Gel 9. 3-Bromopropanoyl chloride (17.2 g, 100 mmol) in 50 mL of anhydrous benzene was dropped into a stirred suspension of **8** (31.0 g, ~50 mmol), 20 mL of pyridine, and 50 mL of benzene, by cooling in a water bath. The stirring was continued for 3 h at room temperature and **9** was filtered and carefully washed with ethanol, water, methanol, and then diethyl ether. After evaporation of the solvent, 37.0 g of **9** was obtained, found 1.26 mequiv Br/g (ca. 96%).

11-Bromoundecanamidopropyl-Functionalized Silica Gel 10. Starting from **8** (31.0 g, about 50 mequiv) and 11-bromoundecanoyl chloride (28.4 g, 100 mmol), by using the procedure described for **9**, 43.0 g of **10** was obtained, found 1.10 mequiv Br/g (ca. 96%).

11-Aminoundecanamidopropyl-Functionalized Silica Gel 11. 10 (20.0 g, 18.4 mequiv) was stirred with potassium phthalimide (8.5 g, 46 mmol) in DMF (80 mL) for 4 h at 100 °C. After cooling, the phthalimido-functionalized silica gel was filtered, washed with water and ethanol, and then refluxed for 4 h with a stirred solution of 25 mL of hydrazine hydrate and 50 mL of ethanol. After cooling, **11** was filtered and carefully washed with ethanol, water, methanol, and then diethyl ether, yield 18.7 g. The analysis of **11**, by acid-base titration, as described for **8** shows a titer between 0.9 and 1.0 mequiv NH_2/g (calcd, 1.18 mequiv NH_2/g). Bromine analysis was negative.

11-Bromoundecanamide-11-Undecanamidopropyl-Functionalized Silica Gel 12. Starting from **11** (10.0 g, ~10 mequiv) and 11-bromoundecanoyl chloride (5.4 g, 19 mmol), the procedure described for **9** gave 12.2 g of **12**, found 0.85 mequiv Br/g (ca. 93%).

Synthesis of 1-4. The precursor bromides **7**, **9**, **10** and **12** (10.0 g) in 15 mL of tributylphosphine were carefully degassed under vacuum and left without stirring for 5 days at 65 °C. After cooling, they were recovered with diethyl ether, filtered, and carefully washed several times with diethyl ether and methanol, yields 11.7, 12.5, 11.8, and 11.3 g, respectively, of **1**, **2**, **3**, and **4**. Analysis of ionic bromide was carried out according to Volhard, starting from 0.30 g of immobilized phosphonium salts in 10 mL of ethanol; 10 mL of 0.05 N silver nitrate was added and the suspension was stirred in the dark for 0.5 h at room temperature. The excess silver nitrate was titrated with 0.05 N ammonium thiocyanate.

Found for **1**, 0.71 (96%); **2**, 1.00 (98%); **3**, 0.77 (86%); **4**, 0.66 (91%) mequiv Br/g.

Adsorption Measurements. Silica gel nonfunctionalized (0.04-0.40 g) or 0.10-0.80 g of silica gel functionalized with phosphonium salts was added to 10.0 mL of an 8.0×10^{-3} M solution of the ketone in cyclohexane, benzene, or chlorobenzene. After intermittent stirring for 24 h, no variation was observed and the equilibrium ketone concentration was analyzed by GLC (column filled with FFAP 5% on Varaport) against known concentrations. The measured ketone concentrations must be multiplied by 10 to obtain the millimoles of adsorbed ketone (Figure 1), and divided by nonfunctionalized silica gel grams added (K_{ads}, Table II), or by functionalized silica gel grams/$[PR_4]^+$ to obtain the K_{ads} shown in Table III.

Kinetic Measurements. The kinetics under PTC conditions were run in a 5-mL flask fitted with a small bar magnet; the stirring speed was 1000 ± 50 rpm, and the reaction solutions were prepared by weighing the reagents in the amounts suitable for use at 80 ± 1 °C in the 1-bromooctane-1-iodooctane transformation and at 25 ± 1 °C in the reduction of ketones.

In a typical bromide-iodide procedure, the flask was filled with 1-bromooctane (0.38 g, 2.0 mmol), potassium iodide (0.83 g, 5.0 mmol), water (0.65 mL) and solvent (1.05 mL); then the catalyst was added (0.05 molar equiv corresponding to 0.14, 0.13, and 0.05 g of **1**, **3**, and **5**, respectively). Small samples of reaction mixture were withdrawn at various times by stopping the stirring for a few seconds and analyzed by GLC on a column filled with SE-30 5% on Varaport at 180 °C. The gas chromatograph was calibrated with a standard molecular mixture of 1-bromo- and 1-iodooctane.

A preparative run was also carried out: 9.65 g of 1-bromooctane, 20.7 g of potassium iodide, 16.2 mL of water, and 3.25 g of **3** were stirred at 80 °C for 2.5 h. After cooling, diethyl ether was added, the catalyst was filtered out, and the dried organic phase was distilled under vacuum to give 1-iodooctane: yield 11.0 g (92%); bp 106-107 °C (19 mm) (lit.[29] bp 103-104 °C, 15 mm), n^{20}_D 1.4887 (lit.[30] n^{20}_D 1.4889).

The recovered catalyst was used for three more identical preparative reactions with the same results. Kinetic measurement showed a 15% final loss of activity.

The same preparative run was also carried out without stirring: after 1.25 h 50% of conversion was observed, 98% after 6.0 h (by GLC).

In a typical PTC reduction procedure, the flask was filled with 2.0 mmol of ketone, 2.0 mL of water, 1.2 mL of solvent, and 0.05 molar equiv of catalyst; then sodium borohydride (3.0 mmol, 0.091 g) was added. The samples were analyzed by GLC on a column filled with FFAP 5% on Varaport, against a standard molecular mixture.

A preparative run was also carried out starting from 2-octanone, with **3** as catalyst: 12.0 g of ketone, 60 mL of cyclohexane, 4.55 g of sodium borohydride, 100 mL of water, and 6.50 g of **3** were stirred at 25 °C. After 2 h the catalyst was filtered and washed with diethyl ether. The dried organic phase was distilled to afford 11.6 g of 2-octanol (93%), bp 80-81 °C (17 mm), n^{20}_D 1.4263 (lit.[31] bp 93 °C (26 mm), n^{20}_D 1.4264).

Reaction of Sodium Phenoxide with Benzyl Bromide (C,O-Alkylation). The reaction was carried out in a 50-mL flask fitted with a small bar magnet, at 25 °C. In a typical procedure, the flask was filled with benzyl bromide (3.42 g, 20 mmol), sodium phenoxide (8.0 mL of a 3 M aqueous solution, 24 mmol), 10.0 mL of cyclohexane or methylene chloride, and 0.05 molar equiv of catalyst. Stirring (1000 ± 50 rpm) was maintained for 6 h. Concentrated hydrochloric acid was then added, the catalyst was filtered, and the organic phase, extracted with diethyl ether, was dried. The solvent was removed (0.4 mm) to afford a mixture analyzed by ^1H NMR (δ, $CDCl_3$): $PhCH_2OPh$, 4.95; $PhCH_2Br$, 4.40; $HOC_6H_4CH_2Ph$, $HOC_6H_4(CH_2Ph)_2$, and their O-alkylation products, 4.05-3.80; $PhCH_2OH$, 4.60, was absent.

The reaction with catalyst **1** in cyclohexane was also carried out up to the disappearance of benzyl bromide (about 12 h), and the reaction mixture was purified by column chromatography on silica gel (eluent benzene-light petroleum, 30:70). The products, and those from the reaction carried out in water according to Kornblum,[20] were the same in ^1H NMR, GLC, and melting point.

PT-Catalyzed Aromatic Nucleophilic Substitution. 2,4-Dinitrodiphenyl Sulfide (14). A suspension of 2,4-dinitrochlorobenzene (4.05 g, 20 mmol), potassium thiophenoxide (8.0 mL of a 3 M aqueous solution, 24 mmol), and 0.05 molar equiv of catalyst (**1**, 1.41 g; **5**, 0.051 g) was magnetically stirred for 15 min under nitrogen in a water bath (t = 25 °C); the sulfide precipitated.

If the reaction was catalyzed by **1**, methylene chloride was added, the catalyst was filtered, and the organic phase, washed with 5% aqueous sodium hydroxide and water, was dried. The solvents were removed to yield 5.4 g (97%) of **14**, mp 118-119 °C (lit.[32] 121 °C).

If **5** was used as catalyst, the reaction mixture was brown, but by washing with 5% aqueous sodium hydroxide it became yellow. The solvent was removed and the product crystallized from 20.0 mL of a mixture (1:4) of diethylene dioxide-ethanol to afford 4.8 g of **14** (87%), mp 119 °C.

2,4-Dinitrodiphenyl Ether (15). Using sodium phenoxide (8.0 mL of a 3 M aqueous solution, 24 mmol), according to the procedure described for **14**, the suspension was stirred for 3 h at 25 °C. If the reaction was catalyzed by **1**, diethyl ether was added, the catalyst was filtered, and the organic phase, washed with 5% aqueous sodium hydroxide and water, was dried. The solvent was removed to yield 5.0 g of **15** (96%), mp 70-71 °C (lit.[33] 71 °C).

If **5** was used as catalyst, the reaction mixture was brown but became yellow on washing; the solvent was removed and the product crystallized from 25 mL of ethanol to yield 4.3 g of **15** (83%), mp 71 °C.

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Supplementary Material Available: Figures 4 and 6 and comparisons of pseudo-first-order rate constants (4 pages). Ordering information is given on any current masthead page.

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(17) Thermogravimetric analysis (nitrogen flow rate 90 mL/min, progress rate 10 °C/min) was done on nonfunctionalized silica gel, **7** and **1**, after careful washing with methanol and drying in an oven for 1 h at 150 °C. The nonfunctionalized silica gel still contained 6.0% adsorbed water by weight; this was completely removed at 200 °C. Between 200 and 1000 °C, the surface hydroxyls gradually condensed to release water, leading to an overall decrease of 3.5%. The water released at 200 °C was only 1.7 and 2.1% by weight for **7** and **1**, respectively. Between 200 and 1000 °C, the further loss of 14.6 and 23.0% by weight, respectively, was accompanied by the total loss of organic functionalization.

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(22) The water present in the microenvironment of the supported PT catalysts may be physically adsorbed as well as hydrogen bonded to the oxygen atoms. Zettlemoyer and Hsing (note 9) showed that in the organosilane-treated silica surfaces the reacted silanes formed hydrophobic umbrellas over reacted –OH silanol groups, which are nevertheless available to water molecules. Wettability tests showed that **1** and **8** are fully wettable, and behave in the same way as nonfunctionalized silica gel in water. **2**, **3**, **4**, and **7**, on the other hand, remain in suspension and form clumps. Moreover, 1.0 g of **1**, **2**, **3**, and **4** displayed an increase in weight of 0.8, 1.2, 1.0, and 1.1 g H_2O, respectively, after filtration from their aqueous suspension, equivalent to 1.1, 1.2, 1.3, and 1.6 g H_2O/mmol $[PR_4]^+$.

(23) While slower than catalyst **1**, 0.14 g of nonfunctionalized silica gel in benzene led to the complete reduction of 2-octanone with aqueous sodium borohydride (90% conversion in 3 h) under the conditions set out in Table II, footnote a, but result in only 5% conversion after 6 h in the bromine displacement in *n*-heptane with potassium iodide (Table I, footnote a). These results agree with Regen's findings (S. L. Regen and C. Koteel, *J. Am. Chem. Soc.*, **99**, 3837 (1977): the aqueous $KMnO_4$ is activated by impregnation onto silica gel in the oxidation of alcohols to ketones.

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