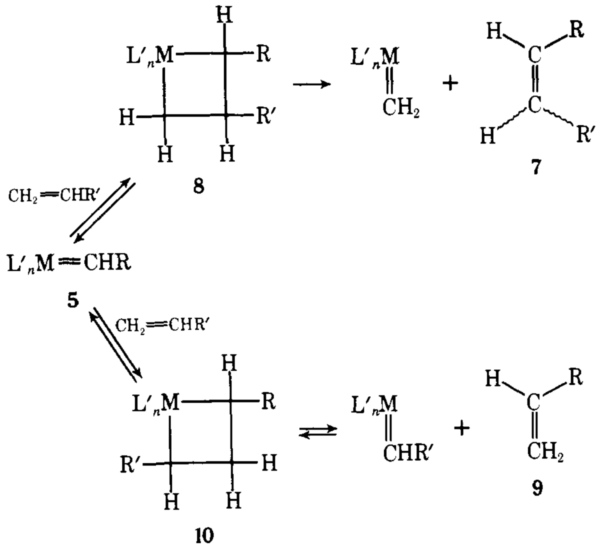
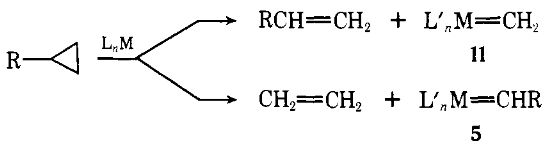


significant concentrations of C-alkyl substituted tungsten-carbene complexes. From our previous work,[12] we knew that ethylcyclopropane (R = C_2H_5) gave 1-butene (73%) and ethylene (11%). We suggested that **11** and **5** were formed as the other fragmentation products in a 6.6:1 ratio. If this hypothesis were correct, we would have in hand a viable method of generating significant concentrations of **5**.



In a typical experiment, 3.5 equiv of ethylcyclopropane and 1 equiv of a terminal olefin in chlorobenzene were treated with 0.005 equiv of the complex generated from phenyltungsten trichloride–aluminum trichloride (1:1) at −20 °C with vigorous stirring in an inert atmosphere. After 30 min, the reaction was quenched by the addition of ethanol. Isolation of the products and identification by GLC, IR, and NMR analyses established that olefins of general type **7** were formed in significant amounts.[13] The results obtained when 1-butene, 1-pentene, and 1-hexene were used as the terminal olefins are shown in Table I. As shown by the data in Table I, the metal-carbene complex, **5**, which was formed in the metalysis of ethylcyclopropane was efficiently captured by the 1-olefin present in solution.[14] If the amount of **5** equaled the amount of ethylene observed, the yields of 3-olefins based on capture of **5** would be 91, 78, and 75% for addition to 1-butene, 1-pentene, and 1-hexene, respectively.[15]

The formation of good yields of 3-olefins in these reactions requires not only the intermediacy of **5** (R = C_2H_5), but also of the highly selective addition of **5** to the 1-olefin to produce **8**. This is inconsistent with terminal olefin degeneracy being determined by either process A or by a sterically controlled mechanism.[16] This study provides additional evidence that the metal-carbene complexes involved in olefin metathesis reactions promoted by phenyltungsten trichloride–aluminum trichloride have resonance structures of general formula **6** as major contributors.[17]

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

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(1) Paper 51 on The Chemistry of Bent Bonds. For the preceding paper in this series see P. G. Gassman and T. H. Johnson, *J. Am. Chem. Soc.*, **98**, 6058 (1976).

(2) For a recent review of olefin metathesis see N. Calderon, E. A. Ofstead, and W. A. Judy, *Angew. Chem., Int. Ed. Engl.*, **15**, 401 (1976).

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(6) C. P. Casey, H. E. Tuenstra, and M. C. Saeman, *J. Am. Chem. Soc.*, **98**, 608 (1976); T. J. Katz and R. Rothchild, *ibid.*, **98**, 2519 (1976).

(7) Distinguishing between process A and a mechanism governed by steric interactions would be difficult, since both explanations would predict the formation of **2** as part of the chain process.

(8) The question of whether there is an initial step, in which the metal–carbene intermediate complexes with the olefin, is not discussed as part of this study. While our results do not require such a complexation step, neither do they rule out such a possibility.

(9) This is not meant to imply that we envisage a purely stepwise addition of the intermediate metal–carbene complex to the terminal olefin. Such polarized additions could involve significant formation of both new bonds in the transition state for the reaction.

(10) In part, this question has been answered by the trapping of intermediates generated in the metathesis of *cis*-2-butene and *cis*-3-hexene by Michael acceptors. P. G. Gassman and T. H. Johnson *J. Am. Chem. Soc.*, **98**, 6055 (1976).

(11) This observation, by itself, points to **6** as the major resonance contributor *if polarization of the intermediate metal–carbene complex is the major factor* in determining the degeneracy of terminal olefin metathesis. If **1** was the major resonance contributor, arguments based purely on patterns of electrophilic additions to olefins would suggest that **1** should add at least as well to an internal olefin, such as *cis*-2-butene, as to a terminal olefin. Unfortunately, steric factors are not easily evaluated relative to this point.

(12) P. G. Gassman and T. H. Johnson, *J. Am. Chem. Soc.*, **98**, 6057 (1976).

(13) In a control experiment, it was demonstrated that the complex derived from phenyltungsten trichloride–aluminum trichloride (1:1) did not produce any metathesis of *cis*-2-pentene in the presence of 1-hexene over a 30-min period.

(14) It is presumed that **11** also reacted with the 1-olefin. However, such an addition would only lead to a degenerate process.

(15) These represent maximum yields based on the premise that all of the ethylene formed was detected. If it was assumed that the yield of ethylene was actually 27% (100% − % of 1-butene), the respective yields would be 37, 32, and 31%. These represent minimum yields.

(16) We caution that, at this time, we have only established this principle for certain tungsten based metal–carbene complexes.

(17) For a well-established example of such polarization in a stable metal–carbene complex see R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 6577 (1975).

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Solid Phase Cosolvents[1]

Sir:

We have recently introduced a technique termed, "triphase catalysis", in which a solid phase catalyst is used to accelerate certain aqueous–organic phase reactions.[2] This method was based on the use of appropriately substituted polystyrene-ion-exchange resins capable of ionic bonding to the water soluble component of the reaction.[3] It occurred to us that if similar triphase catalytic processes could be carried out employing uncharged and neutral polymers, this would constitute a much more general technique worthy of extensive exploitation. Specifically, we reasoned that resins which acted as cosolvents might function as catalysts for aqueous–organic phase reactions by providing (1) a common phase with a high effective concentration of potential reactants and/or (2) an internal resin phase having a microenvironment significantly different from that of the external liquid phases. In this same regard, it also seemed likely that solid phase cosolvents might be useful in accelerating certain types of reactions taking place in a single phase (organic or aqueous phase). Based on these ideas, we have initiated a program aimed at developing insoluble polymers which exhibit *cosolvent-like* properties.

We now wish to report our preliminary results with the preparation of graft copolymer **1** and its use as a solid phase cosolvent in (1) the hydrolysis of 1-bromoadamantane and *tert*-butyl chloride and (2) the displacement by phenoxide ion on 1-bromobutane.

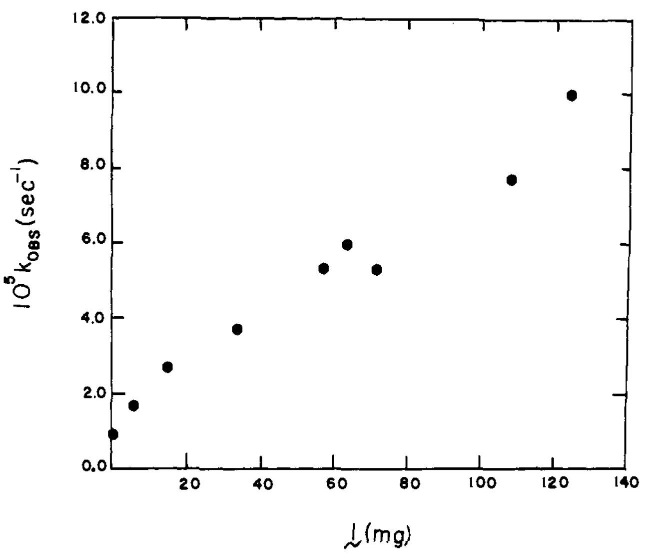
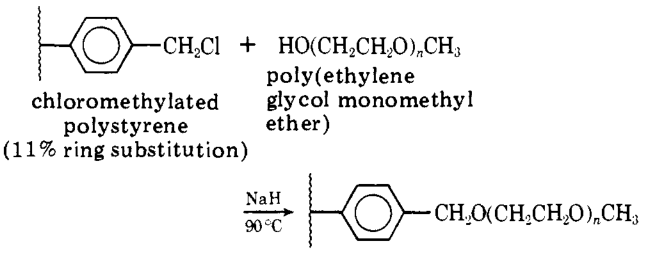


Figure 1. Plot of $10^5 k_{\rm obsd}$ as a function of the amount of catalyst used for the reaction of 0.40 mmol of *tert*-butyl chloride in 2 ml of toluene mixed with 4 ml of water catalyzed by the indicated amount of **1** (mg) at 55 °C.[11]



1, $n_{av} = 13$

Poly(ethylene glycol monomethyl ether) (Polysciences, mol wt 750) was covalently attached to cross-linked polystyrene by reacting its sodium salt with 2% cross-linked chloromethylated polystyrene. In a typical preparation, poly(ethylene glycol monomethyl ether) (20 ml) and sodium hydride (0.48 g, 20.0 mmol) were placed in a dry, degassed 40-ml centrifuge tube equipped with a No-Air stopper and Teflon-coated magnetic stirring bar. After stirring the solution under nitrogen at 50 °C for 2 h, 3.0 g of chloromethylated polystyrene (1.0 mmol chlorine/g of resin (11% ring substitution), 2% divinylbenzene, 200–400 mesh)[4] was added. The tube was then placed in an oil bath maintained at 90 °C and the mixture stirred for an additional 48 h under nitrogen. The resulting resin was collected by filtration, washed successively with 500 ml of 4:1 tetrahydrofuran–water and 500 ml of tetrahydrofuran, extracted (Soxhlet) with tetrahydrofuran for 48 h under nitrogen, and dried under vacuum (10 h, 110 °C (0.05 mm)) to give 4.1 g of colorless polymer **1** (IR (KBr) 1125–1055 cm^{-1} (C- - -O- - -C)). Chlorine analysis indicated complete replacement of chloride ion by the polyether.[5] Elemental analysis further revealed a resin composition in which the average size of the polyether grafted to the polystyrene backbone contained 13 ethyleneoxy units (Anal. Calcd for **1** where $n = 13$: C, 77.46; H, 8.25; O, 14.29. Found: C, 77.29; H, 7.98; O, 14.25).[6]

When resin **1** (100 mg) was suspended at the interface of a heterogeneous mixture of 2 ml of 0.05 M 1-bromoadamantane in toluene and 4 ml of water, and the resulting mixture heated to 110 °C, analysis of the organic phase by GLC revealed the gradual disappearance of the alkyl bromide accompanied by the simultaneous appearance of 1-hydroxyadamantane.[7] The rate of hydrolysis obeyed simple first-order kinetics to 90% completion and gave a half-life of 3.4 h. Rate constants determined from the change in concentration of 1-bromoadamantane agreed to within 5% of those based on appearance of 1-hydroxyadamantane. In the absence of **1**, 1-bromoadamantane had a half-life of 84 h under similar conditions. Resin **1** also proved effective in catalyzing the hydrolysis of *tert*-butyl chloride dissolved in toluene. A plot of the observed first-order rate constant, $k_{\rm obsd}$, measured at 55 °C as a function of the amount of resin used is shown in Figure 1.

We have also found that **1** catalyzes the displacement by phenoxide ion on 1-bromobutane. Thus, when 1-bromobutane (0.066 g, 0.48 mmol) dissolved in 2 ml of toluene was added to 2 ml of 1.0 M of sodium phenoxide in water containing **1** (130 mg) and the mixture was heated to 110 °C for 12 h, *n*-butyl phenyl ether was produced in 60% yield.[7] In the absence of **1**, a similar reaction afforded less than 5% of the corresponding ether.

The origin of the catalysis observed for phenoxide displacement on 1-bromobutane by **1** is not presently clear. Two features of the polymer could be important: (1) the polymer may provide a common phase where a high effective concentration of the reactants is possible; (2) the microenvironment within the resin phase may influence starting material and/or transition state stabilities. Specifically, the phenoxide ion residing within a resin which was largely aprotic might be activated for reaction with 1-bromobutane by destabilization through loss of hydrogen bonding with water.[8,9] Alternatively, the resin phase may stabilize the transition state more than it does the starting material.

Interpretation of the catalytic effect of **1** on the hydrolysis of *tert*-butyl chloride is hampered by the uncertainty of the role which water plays in the reaction. Schleyer has previously pointed out that rate-limiting elimination and nucleophilic solvent participation cannot be rigorously ruled out as significant mechanistic components in the solvolysis of *tert*-butyl chloride.[10] With 1-bromoadamantane, however, the pathway for solvolysis is unambiguous since, for this bridgehead substrate, backside nucleophilic solvent attack and elimination are impossible.[10] The catalysis noted above for the hydrolysis of 1-bromoadamantane with **1** must be a microenvironmental effect where the polymer provides a medium in which ionization can readily occur. The only uncertainty here, is to what extent imbibed water contributes to the resin's ionizing power.

The results presented here demonstrate the feasibility of using an insoluble polymer as a cosolvent. Work in progress is being directed toward (1) the preparation of a series of related resins and the determination of their activity as solid phase cosolvents, (2) defining the microenvironment within the polymer networks, and (3) the development of new synthetic procedures based upon the use of such resin-catalysts.

Acknowledgment. We thank Professor Jerry Smith for helpful discussions.

References and Notes

(1) This work was supported by the National Science Foundation (Grant No. MPS74-23925) and the U.S. Army Research Office (Grant No. DAAG-29-76-G-0330).
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(4) Chloromethylated polystyrene (microporous) was purchased from Bio-Rad Laboratories and was used without further purification.
(5) Chlorine present was determined by a modified Volhard titration using procedures described elsewhere: J. M. Stewart and J. D. Young, "Solid Phase Peptide Synthesis", W. H. Freeman, San Francisco, Calif., 1969, p 55.
(6) Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.
(7) Product mixtures were analyzed by GLC on a Hewlett-Packard Model 5710 A flame ionization instrument (4 ft × 0.125 in. 5% Carbowax 20M on 80–100 mesh Chromasorb P at 110 °C) equipped with a Hewlett-Packard Model 3380A integrator, where yields were determined relative to an internal standard.
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(11) First-order rate constants were determined by following the rate of disappearance of *tert*-butyl chloride from the organic phase. Kinetic experiments were carried out by placing culture tubes containing the appropriate components (after having been shaken vigorously for 2 min) in an oil bath maintained at 55 °C. Reactions were monitored by withdrawing 1-μl samples from the organic phase at no less than 30-min time intervals. Plots made on semilogarithmic paper of the percent of *tert*-butyl chloride remaining as a function of time gave straight lines; slopes were used to calculate first-order rate constants. All data reported here are for nonagitated systems. Within experimental error, stirring reaction mixtures by means of a Teflon-coated magnetic stirring bar caused no significant change in observed rates.

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Organic Chemistry on the Solid Phase. Site-Site Interactions on Functionalized Polystyrene

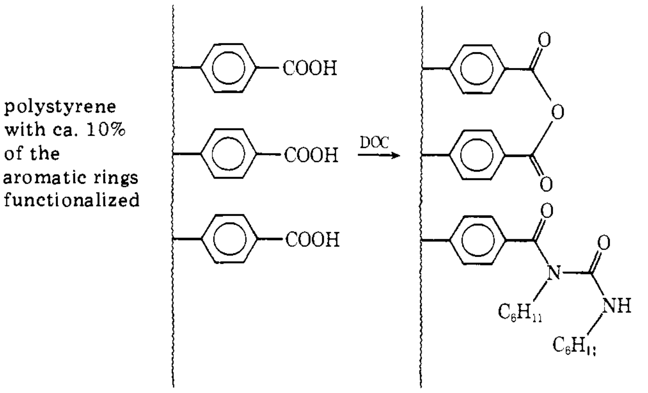
Sir:

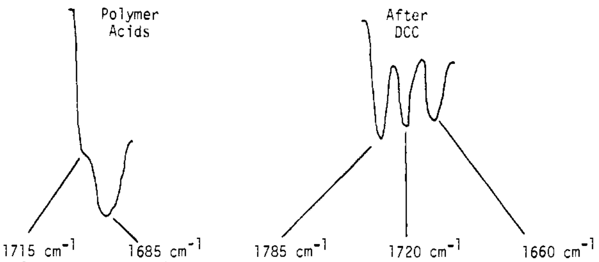
The ability to insulate molecules from one another by attaching them to an inert, rigid matrix could provide a valuable alternative to the high-dilution principle for the supression of undesirable bimolecular reactions in such areas of chemistry as large ring synthesis and the study of highly reactive species. It has often been assumed[1] that the 2% divinylbenzene-styrene copolymer (2% DVB-polystyrene) commonly employed for solid-phase synthesis provides such "matrix isolation"; however, Rapoport and co-workers have demonstrated[2,3] most convincingly that it does not. We have examined the suggestion that more highly cross-linked polymers should provide a more rigid matrix and thereby more effective isolation of functionalized sites.[3] Our findings reveal *significant site-site interaction on functionalized polystyrene, even at high levels of cross-linking.*[4]

As a probe for site-site interaction, a series of polystyrene-bound carboxylic acids was prepared, treated with dicyclohexylcarbodiimide (DCC), and then examined for the presence of anhydride.[5] The extent of anhydride formation in these experiments represents a *lower-limit* of site-site interaction, since the *O*-acylisourea intermediate formed on addition of a carboxylic acid to DCC rearranges to the stable *N*-acylurea unless intercepted by another carboxylic acid[6] (Scheme I).

Polystyrene-bound carboxylic acids (ca. 1 mequiv/g)[7] were prepared by sequential bromination[9] ($Br_2/Tl(OAc)_3/CH_2Cl_2$), lithiation[9] (*n*-BuLi/THF), and carboxylation (CO_2 gas) of commercially available polystyrene beads.[10] This method proved successful for the functionalization of a macroreticular 20% DVB-polystyrene (SM2)[10] and the "swellable" 1, 2, and 4% DVB-polystyrenes (SX1, SX2, and SX4, respectively)[10] but failed[11] with "swellable" 8 and 12% DVB-polystyrenes (SX8 and SX12).[10] The infrared spectra of these carboxylated polymers show carbonyl stretching bands for both free and associated carboxylic acids,[8] the latter band appearing more intense in all cases (Figure 1).

Scheme I





	1715 cm^{-1} free COOH	1685 cm^{-1} associated COOH	1785 cm^{-1} anhydride	1720 cm^{-1} anhydride + free COOH	1660 cm^{-1} N-acylurea
SX1	0.7	1.0	1.0	0.9	0.9
SX2	0.7	1.0	1.0	0.9	0.8
SX4	0.7	1.0	1.0	3.7	3.7
SM2	0.8	1.0	1.0	1.5	1.6

Figure 1. Relative intensities of infrared absorption bands (KBr) for various carboxylated polystyrenes (see text for description) both before and after treatment with DCC. The spectra pictured above the table are for SX2.

Each of the carboxylated polymers was stirred in methylene chloride with excess DCC for 50 h at room temperature.[12] Infrared spectra taken after filtration, washing, and drying are summarized in Figure 1. In all cases, the associated-COOH band (1685 cm^{-1}) disappears, and new bands for anhydride (1785 cm^{-1}) and the *N*-acylurea (1660 cm^{-1}) appear. The second anhydride carbonyl band (ca. 1720 cm^{-1}) unfortunately coincides with that of any remaining free COOH (1715 cm^{-1}). The relative intensities of the band in this region, however, suggest the presence of residual free COOH, which is completely inaccessible to DCC, on the more highly cross-linked polymers (SX4 and SM2).

According to Rapoport et al.[2] the majority of functionalized sites on 2% DVB-polystyrene (SX2, ca. 1 mequiv/g) can interact. Our data show that the extent of site-site interaction on more highly cross-linked polystyrene, although somewhat reduced, still remains significant. Even in the best case we have found (SX4),[10] the number of available, truly insulated sites (<1 mequiv/g) probably falls too far below the practical limit for most applications of organic chemistry on the solid phase.[13]

Note Added in Proof. Resin-bound benzyne (0.23 mmol/g on SX2 and 0.09 mmol/g on SM2) does not "dimerize" but is destroyed by an unknown pathway with a half-life of *ca.* 1 min.[15] This result is in complete agreement with our observation that site-site interaction is time dependent.[12]

Acknowledgments. We wish to thank the National Science Foundation, Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the UCLA Research Committee for financial support of this work.

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