7.2, 1.6 Hz, 2 H), 5.45 (tt, $J = 7.2$, 2.4 Hz, 1 H), 7.03–7.46 (m, 5 H); mass spectrum, m/e (relative intensity) 172 (M$^+$, 100), 143 (32), 129 (63), 104 (100), 91 (71), 81 (88); calcd for C$_{13}$H$_{16}$ m/e 172.1251, found m/e 172.1222.

Partial Hydrogenation of 3f in the Presence of Pyridine (Eq 5b). Complex **3f** (0.4 mmol) was dissolved in 10 mL of MeOH containing 0.1 mL of pyridine. The mixture was stirred at ambient temperature under H$_2$ until an uptake of 9 mL of H$_2$ was observed. The usual workup and purification by column chromatography (silica gel, benzene) provided a mixture of **16f** and **17f** (1:1) in 63% yield.

(*E*)-1-(Neophylsulfonyl)-3-hexene (16f): bp 160 °C (0.1 mmHg) (as a mixture of **16f** and **17f**); IR (neat film) 2960 (s), 1605 (w), 1445 (m), 1310 (s), 1285 (m), 1130 (s), 1120 (s), 970 (m), 840 (m), 770 (s), 700 (s) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 0.93 (t, $J = 7$ Hz, 3 H), 1.2 (m, 2 H), 1.62 (s, 6 H), 1.92–2.16 (m, 2 H), 2.22 (d, $J = 3$ Hz, 2 H), 3.10 (s, 2 H), 5.2–5.53 (m, 2 H), 7.4 (m, 5 H); mass spectrum, m/e (relative intensity) 280 (M$^+$, 10), 199 (100), 133 (96), 119 (100). Anal. (mixture of **16f** and **17f**) Calcd for C$_{16}$H$_{24}$SO$_2$: C, 68.63; H, 8.63; O, 11.41. Found: C, 68.65; H, 8.74; O, 11.71.

(*E*)-1-(Neophylsulfonyl)-2-hexene (17f): IR (neat film) 2950 (s), 1600 (w), 1285 (m), 1130 (s), 1120 (s), 970 (m), 840 (m), 765 (m), 700 (s) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 0.91 (t, $J = 7$ Hz, 3 H), 1.25–1.54 (m, 2 H), 1.62 (s, 6 H), 2.06 (m, 2 H), 2.93 (d, $J = 7$ Hz, 2 H), 3.05 (s, 2 H), 5.1–5.6 (m, 2 H), 7.4 (m, 5 H); mass spectrum, m/e (relative intensity) 280 (M$^+$, 1), 199 (92), 133 (100), 119 (67), 91 (100).

Reduction of 3f with NaBH$_4$ (Eq 5c). A methanol solution of NaBH$_4$ (0.56 mmol in 5 mL of MeOH) was added to the solution of complex **3f** (1.7 mmol) in methanol (70 mL) with stirring at 0 °C. The reaction mixture was allowed to stir at 0 °C for an additional 1 h. After evaporation of the methanol, the residue was extracted with ether. The extract was washed with water and dried over Na$_2$SO$_4$. Evaporation of the solvent and column purification (silica gel, benzene as an eluent) gave 1-(neophylsulfonyl)-hexa-1,3-diene: 63% yield; bp 163 °C (0.15 mmHg); IR (neat film) 2970 (s), 1640 (m), 1600 (m), 1310 (s), 1280 (sh), 1130 (s), 1115 (s), 995 (m), 850 (m), 765 (m), 700 (m) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 1.02 (t, $J = 7$ Hz, 3 H), 1.60 (s, 6 H), 2.16 (dq, $J = 6$, 7 Hz, 2 H), 3.24 (s, 2 H), 5.56 (d, $J = 15$ Hz, 1 H), 5.77 (dd, $J = 15$, 10 Hz, 1 H), 6.17 (td, $J = 15$, 6 Hz, 1 H), 6.82 (dd, $J = 15$, 10 Hz, 1 H), 7.4 (m, 5 H); mass spectrum, m/e (relative intensity) 199 (M$^+$ – C$_6$H$_7$, 2), 157 (13), 133 (31), 119 (23), 105 (17), 91 (100). Anal. Calcd for C$_{16}$H$_{22}$SO$_2$: C, 69.02; H, 7.97; O, 11.49. Found: C, 69.22; H, 8.14; O, 11.74.

Acknowledgment. We acknowledge support for this work provided by the ministry of Education, Science and Culture (Grant in Aid for Special Profect Research No. 57118006 and for Scientific Research B No. 58470066).

Registry No. **1a**, 106-99-0; **1b**, 78-79-5; **1c**, 513-81-5; **1d**, 123-35-3; **1e**, 504-60-9; **1f**, 592-48-3; **1g**, 2783-10-0; **1h**, 64255-45-4; **1i**, 4549-74-0; **1j**, 4549-74-0; **1k**, 37580-41-9; **3a**, 87567-02-0; **3c**, 67677-32-1; **3c** *tert*-butylsulfonyl derivative, 87585-74-8; **3e**, 87567-03-1; **3e** *tert*-butylsulfonyl derivative, 87567-04-2; **3f**, 87567-05-3; **3f** *tert*-butylsulfonyl derivative, 87567-06-4; **3g**, 87567-07-5; **3h**, 87567-08-6; **3i**, 87567-09-7; **3j**, 87567-10-0; **3k**, 87567-11-1; **5** ($n = 3$), 28638-58-6; **5** ($n = 4$), 2622-21-1; **5** ($n = 6$), 80304-18-3; **5** ($n = 8$), 72315-25-4; **5** ($n = 10$), 75531-52-1; **5a**, 57065-77-7; **5b**, 473-00-7; **5c**, 87567-27-9; **5d**, 87567-28-0; **5e** (isomer 1), 23155-97-7; **5e** (isomer 2), 87567-29-1; **5f** (isomer 1), 62008-31-5; **5f** (isomer 2), 62008-26-8; **5g** (isomer 1), 87567-30-4; **5g** (isomer 2), 87567-31-5; **6** ($n = 3$), 87585-75-9; **6** ($n = 4$), 87567-12-2; **6** ($n = 6$), 87567-13-3; **6** ($n = 6$) *p*-toluenesulfonyl derivative, 87567-14-4; **6** ($n = 8$), 87567-15-5; **6** ($n = 10$), 87567-16-6; **6a**, 87567-17-7; **6b**, 87567-18-8; **6b** phenylsulfonyl derivative, 87567-19-9; **6c**, 87567-20-2; **6d**, 87585-76-0; **6e**, 87567-21-3; **6f** (isomer 1), 87585-77-1; **6f** (isomer 2), 87567-69-9; **6g**, 87567-70-2; **6g** (isomer 2), 87585-81-7; **8b**, 87567-22-4; **8c**, 87585-78-2; **8d**, 87567-23-5; **8f**, 87567-24-6; **8h**, 87567-25-7; **9**, 87567-26-8; **10**, 77944-33-3; **11**, 77944-34-4; **12a**, 87567-32-6; **12b**, 87567-33-7; **12c**, 67686-38-8; **12d**, 67686-39-9; **12e**, 87567-34-8; **12f**, 77944-25-3; **12g**, 77944-26-4; **12h**, 77944-27-5; **12i**, 77944-28-6; **12j**, 77944-29-7; **12k**, 87567-35-9; **13a**, 87567-36-0; **13k**, 87567-37-1; **14e**, 77944-30-0; **14f**, 77944-31-1; **15j**, 87567-38-2; **16f**, 77944-36-6; **17f**, 77944-35-5; **19** ($n = 3$), 87567-39-3; **19** ($n = 4$), 87567-40-6; **19** ($n = 6$), 87567-41-7; **19** ($n = 6$) *p*-tolylsulfonyl derivative, 87567-42-8; **19** ($n = 8$), 87567-43-9; **19** ($n = 10$), 87567-44-0; **19a**, 87567-45-1; **19b**, 87567-46-2; **19c**, 87567-47-3; **19d**, 87567-48-4; **19e**, 87567-49-5; (*E*)-**19f**, 87567-50-8; (*Z*)-**19f**, 87567-51-9; (*E*)-**19g**, 87567-52-0; (*Z*)-**19g**, 87567-53-1; **20** ($n = 8$), 87567-54-2; **20** ($n = 10$), 87567-55-3; **21** ($n = 6$), 87567-56-4; **21** ($n = 8$), 87567-57-5; **21** ($n = 10$), 87567-58-6; **22**, 87567-59-7; 2-methyl-4-*p*-tolyl-1-butene, 56818-01-0; 2-methyl-4-*p*-tolyl-2-butene, 32094-39-6; 2,3-dimethyl-4-*p*-tolylbutene, 87567-61-1; 2-methoxy-2,3-dimethyl-4-*p*-tolylbutane, 87567-61-1; 1-*p*-tolyl-3-(4-methyl-3-penten-1-yl)-2-butene, 87585-79-3; (2-phenylethylidene)cyclopentane, 87567-62-2; sodium benzenesulfinate, 873-55-2; sodium *p*-toluenesulfinate, 824-79-3; 1-(neophylsulfonyl)-*trans*-pent-3-ene, 87567-63-3; neophyl methyl sulfone, 87567-64-4; *trans*-crotyl chloride, 4894-61-5; 1-(neophylsulfonyl)-(*E*)-3-methylpent-3-ene, 87567-65-5; (*E*)-2-methyl-2-butenyl bromide, 57253-30-2; (*Z*)-2-methyl-2-butenyl bromide, 57253-29-9; (*E*)-2-phenyl-2-butenyl tosylate, 87585-80-6; phenyl ethyl ketone, 93-55-0; ethyl (dimethylphosphono)acetate, 311-46-6; (*E*)-ethyl 3-phenyl-2-butenoate, 1504-72-9; (*Z*)-ethyl 3-phenyl-2-butenoate, 87567-66-6; (*E*)-1-(2-hydroxyethylidene)-2-methylcyclohexane, 87637-55-6; sodium neophylsulfinate, 67686-36-6; *cis*-1-acetoxy-1-vinyl-2-methylcyclohexane, 67902-66-3; *trans*-1-acetoxy-1-vinyl-2-methylcyclohexane, 67902-67-4; 1-(neophylsulfonyl)-hexa-1,3-diene, 87567-67-7; palladium chloride, 7647-10-1; (*E*)-4-(neophylsulfonyl)-2-butene, 87567-68-8.

Polystyrene-Supported Carbodiimide Catalysts

Curtis P. Smith and George H. Temme*

Donald S. Gilmore Laboratories, The Upjohn Company, North Haven, Connecticut 06473

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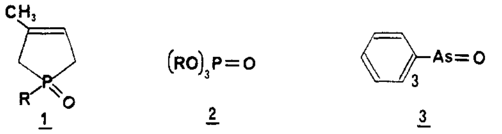
Polystyrene-anchored triphenylarsine oxide 8 has been prepared from brominated polystyrene beads by a lithium-mediated arsenation–hydrogen peroxide oxidation sequence. Compound 8 with only 0.6 mequiv of As/g has been found to be a highly effective, insoluble catalyst for the conversion of aryl isocyanates to diarylcarbodiimides in high yield. Up to 5.6×10^4 turnovers of the catalyst 8 in the carbodiimide-forming reaction have been measured when appropriate measures are taken to prevent its deactivation. Several arylcarbodiimides have been prepared in high yield by using 8.

Carbodiimides are often used in polyurethane technology as a functionality to either lower the melting point of the diisocyanate monomer (as an aid to processing) or to prevent the aging and hydrolysis of the polymeric product.[1] In such applications, the carbodiimide is usually synthesized by the condensation of part of all of the diisocyanate monomer in the presence of catalysts. Compounds such as phospholene oxide 1, trialkyl phosphates 2, or triphenylarsine oxide 3[2] have all been used to catalyze this reaction as shown in eq 1.

$$2RNCO \longrightarrow RN{=}C{=}NR + CO_2$$



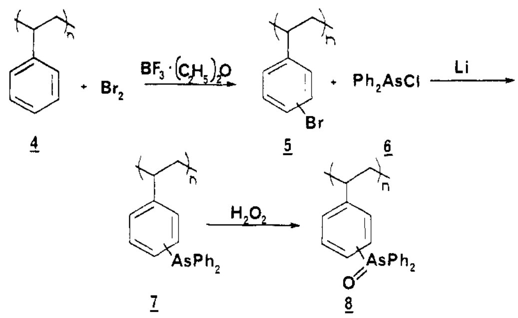
1 2 3 (1)

One problem with this approach is that the catalyst is difficult to remove from the isocyanate–carbodiimide mixture. Subsequent processing conditions can often lead to unwanted further carbodiimide formation. To eliminate this problem, we have undertaken the synthesis of a polystyrene anchored carbodiimide catalyst. A solid supported catalyst can readily be removed from the product by filtration after the desired amount of carbodiimide has been formed. The recovered catalyst can then be recycled in subsequent syntheses. In this paper, we report the synthesis of such a catalyst and some of its synthetic applications.[3]

Results and Discussion

Synthesis of the Catalyst. The polystyrene-anchored triphenylarsine oxide 8 was chosen as the synthetic goal. This polymer was expected to possess catalytic activity similar to triphenylarsine oxide 3, one of the most effective catalysts for carbodiimide formation from isocyanates.[3]

The initial synthetic approach, shown in eq 2, was a modification of a sequence by Relles and Schluenz for the synthesis of polystyrene-anchored triphenylphosphine oxide.[4] Polystyrene beads (cross-linked with 2% divinylbenzene) 4 are brominated in the presence of $BF_3 \cdot Et_2O$ in nitromethane to give 5 containing 5.4 mequiv bromine/g. Resin 5 is treated with lithium wire and excess diphenylarsinous chloride 6 in THF to give a polymer-supported triphenylarsine 7. This product is readily oxidized with dilute hydrogen peroxide to yield 8 containing 2.7 mequiv arsenic/g. This corresponds to functionalization of about 95% of the aromatic rings.



(2)

Infrared analysis of 8 shows a strong band at 881 cm^{-1} characteristic of the As=O stretch found in triphenylarsine oxide (880 cm^{-1}).[5] Another strong unidentified band at 1086 cm^{-1} is present in both 8 and triphenylarsine oxide. These two bands are present in samples of 8 prepared by different methods. The intensity of the bands is proportional to the amount of arsenic found in the polymer.

The catalytic activity of 8 can be readily demonstrated. When *o*-tolyl isocyanate **9** and 0.75% (wt/wt) of 8 are heated in refluxing benzene for 3 h, CO_2 is evolved and a 90% yield of di-*o*-tolylcarbodiimide **10** is obtained. Catalyst 8, recovered by filtration, can be used in several successive reactions giving comparable yields of **10**. The polymeric nature of the catalyst can be demonstrated by heating both filtered and unfiltered portions of a partially completed reaction of **9** to **10**. Reaction of the unfiltered sample proceeds to completion while the composition of the filtered sample does not change on prolonged heating.

Several aspects of the synthesis of 8 were investigated in some detail to provide the most practical route to a catalyst of high activity. The costly diphenylarsinous chloride needed to be replaced by other less expensive reagents in the arsenation of the brominated polystyrene. The degree of loading of the arsine oxide on the polymer 8 that would give the most active carbodiimide catalyst needed to be determined. Lastly, reaction conditions for the bromination step needed to be studied to improve its practicality. Potential catalysts for this step needed to be screened to determine what effect they might have on the activity of 8 for carbodiimide formation.

Alternate Routes to 8. It was found that the polymer-supported triphenylarsine 7 can be obtained by the reaction of 5 with arsenic trichloride, lithium wire, and bromobenzene in THF. This is an exothermic reaction in which all the reagents and polymer 5 are combined in THF under argon and the mixture is allowed to warm to 60 °C. The reaction mixture is maintained at this temperature for 2 h and then worked up. After a hydrogen peroxide treatment 8 can be obtained in 50–65% yield based on the amount of bromine in 5. Catalysts containing 0.2–0.8 mequiv As/g can be obtained by this route, as shown in eq 3.

$$3PhBr + AsCl_3 + 8Li + \underset{5}{Br\text{-}Ⓟⓢ} \longrightarrow \underset{7}{Ph_2As\text{-}Ⓟⓢ} + PhLi + 7LiX \qquad (3)$$

Under these reaction conditions, phenyllithium should be formed and then reacted with the arsenic trichloride to yield 6 as shown in eq 4. Compound 6 can then react with lithium metal forming the diphenylarsine anion **11** which can then be alkylated to 5 to yield 7 (eq 5). An expected side reaction, eq 6, the formation of triphenylarsine[6] (**12**) from 6 and phenyllithium is not a problem in this reaction. Excess lithium readily reacts with **12** to form the desired intermediate **11** and phenyllithium[7] (eq 7).

$$\begin{aligned} 6Li + 3PhBr &\longrightarrow 3PhLi + 3LiBr \\ 2PhLi + AsCl_3 &\longrightarrow \underset{6}{Ph_2AsCl} + 2LiCl \end{aligned} \qquad (4)$$

$$\underset{}{6} + Li \longrightarrow \underset{11}{Ph_2AsLi} + LiCl \xrightarrow{Br\text{-}Ⓟⓢ} \underset{7}{Ph_2As\text{-}Ⓟⓢ} + LiBr \qquad (5)$$

$$PhLi + \underset{6}{Ph_2AsCl} \longrightarrow \underset{12}{Ph_3As} + LiCl \qquad (6)$$

$$Ph_3As + 2Li \longrightarrow \underset{11}{Ph_2AsLi} + PhLi \qquad (7)$$

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Table I. Catalyst Loading vs. Activity

catalyst[a]	As, wt %	As, mequiv/g	substitution	time, min/200 mL CO_2 evolved at 125 °C
8a	2.67	0.35	4%	6.9[b]
8b	4.75	0.60	8%	3.3[b]
8c	6.22	0.86	11%	3.2[b]
8d	20.48	2.73	85%	60.0[c]

[a] Catalysts **8a–c** are prepared by using $AsCl_3$, PhBr, Li, and polymer **5** brominated in the presence of $TiCl_4$. Catalyst **8d** is prepared by using **6** and polymer **5** brominated in the presence of $BF_3 \cdot Et_2O$. [b] These times are obtained by using 50 mg of catalyst/35 g of MDI (neat). [c] This time is obtained by using 250 mg of catalyst/35 g of MDI (neat).

Since the polymer-supported arsine **7** is a separate solid phase, reaction of **7** with the lithium is not possible and so the desired product is formed in good yield. This reaction of triphenylarsine with lithium can in fact be used as an alternate synthesis of polymer-supported triphenylarsine. When brominated polystyrene **5**, triphenylarsine **7**, and lithium wire are heated for several hours in refluxing THF under argon, polymer **8** can be obtained after the usual workup and hydrogen peroxide treatment. Although the yield of **8** is lower by this route (20–25%) and the amount of arsenic incorporated (0.2–0.3 mequiv of As/g) is less than the routes to **8**, the product obtained is an active carbodiimide catalyst.

Optimum Arsenic Loading in 8. The effect of the degree of substitution of arsenic in **8** on its catalytic activity was investigated to optimize the synthetic scheme. A series of polymers (**8a–8d**) containing increasing amounts of arsenic were prepared. The polymers were used to catalyze carbodiimide formation from bis(4-isocyanatophenyl)methane (MDI) in a reaction at 125 °C. The reactions can be followed volumetrically and the times needed for the evolution of 200 mL of CO_2 are compared in Table I. The observed times for the evolution of CO_2 decrease sharply on going from 0.35 to 0.60 mequiv of As/g loading on the catalysts **8a** and **8b**. The higher loading on catalyst **8c** does not decrease the reaction time further and a large increase in the reaction time is observed with catalyst **8d**.

The fact that maximum catalytic activity is achieved with low loading of the arsenic on the polymer allows milder conditions as well as minimal amounts of costly reagents to be used in the synthesis. The extremely low activity of the highly substituted catalyst **8d** is probably due to limited access of the MDI to the interior catalytic sites since **8d** is observed to swell in the MDI much less than the other catalysts. This reduced swelling of **8d** may be due to an increase in crosslinking on the polymer which occurred during the synthesis. When **8a** is synthesized with 4% crosslinked polystyrene, the activity is much lower than the catalyst prepared with 2% crosslinked polystyrene. Alternately, the lower swelling may be due to the formation of aggregates of the highly polar arsine oxide groups within the polymer.

Effect of the Bromination Catalyst on Activity in 8. The bromination of polystyrene was investigated. This was done to determine what effect the choice of catalyst in this step may have on the activity of **8** as a carbodiimide catalyst. A series of brominations with different Lewis acids were carried out. The product **5** from each reaction was converted to **8** by using the $AsCl_3$, phenyl bromide, and lithium reaction followed by hydrogen peroxide treatment. The catalytic activity of each polymer **8** for carbodiimide formation was evaluated by using neat MDI. Table II shows the results of this screening. $AlBr_3$ (prepared in situ), $AlCl_3$, and $FeCl_3$ work well in the bromination step, but the products obtained give samples of **8** with the lowest catalytic activity. The most active arsenic catalyst is prepared from **5** made with thallic acetate and known to be an excellent catalyst for brominations.[8] Other samples of **8** with good activity are prepared from brominated polystyrenes made with titanium tetrachloride and tin tetrachloride. These are mild Lewis acids and are less active in the brominations as judged by the larger amounts of catalyst and reaction times of several hours needed for the observed conversions to **5**. This observed difference in catalytic activities among the resins prepared with different bromination catalysts may be due to the different ortho/para ratio of the products obtained. The catalysts that result in a higher degree of parasubstitution,[9] thallium acetate, titanium tetrachloride, all give precursors to polymer supported arsenic oxides that show good activity in the carbodiimide reactions. Of the better para-directing bromination catalysts, titanium tetrachloride was chosen for use in subsequent reactions on the basis of such factors as cost, toxicity, and ease of handling.

Scope and Limitations of Catalysis of Carbodiimide Formation with 8. With the methodology for the synthesis of **8** established, the parameters affecting the conversion of isocyanates to carbodiimides catalyzed by **8** were investigated. Reactions were conveniently followed by volumetric measurements of the CO_2 liberated during the reaction. Either model isocyanates such as phenyl isocyanate or, more commonly, commercial diisocyanates such as bis(4-isocyanatophenyl)methane (MDI) were used as substrates in this reaction.

The catalyst lifetimes and the rates of reaction of MDI at various ratios of MDI:**8** were studied at 160–200 °C (Figure 1). The temperatures chosen are representative of those used to prepare commercial carbodiimide containing diisocyanates. Reactions were usually followed to 10% conversion based on CO_2 evolved. Initial rate studies were run with 70 mg of catalyst **8** containing 0.63 mequiv As/g in 700 g of MDI at 160 °C. By the use of a weight ratio of 10 000:1 for the ratio of MDI:**8** (a mole ratio of 6.4×10^4:1), a 10% conversion can be obtained in 7.5 min with deactivation of **8** occurring at 15% conversion. This corresponds to 9 500 turnovers of catalyst **8**. By comparison, when triphenylarsine oxide is used as a catalyst under the same conditions, deactivation occurs at 6.5% conversion after 11.5 min. Catalyst **8** is more active and longer lived than free triphenylarsine oxide. Increasing the MDI:**8** ratio to 15 000:1 and 20 000:1 causes the catalyst to deactivate at 7.5% and 6.0% conversion, respectively, or 8 000 turnovers. A series of experiments were then run to determine the cause of the observed catalyst deactivation. Reactions run at 175 and 200 °C show the same deactivation rate as the reaction run at 160 °C. This demonstrated that the deactivation was independent of temperature. The stabilizer that was present in the MDI at 500 ppm levels, 2,6-di-*tert*-butyl-4-methylphenol, was also investigated. This was found to have no effect on the rate of reaction or the deactivation of the catalyst.

The MDI used in all of these experiments contained 10–20 ppm HCl. This HCl results from the phosgenation process used to prepare the isocyanates and would be ex-

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Table II. Effect of Various Bromination Catalysts on the Catalytic Activity of 8

catalyst	mole ratio[a] catalyst:Br$_2$:PS	mequiv of Br/g 5	% convn to 5	mequiv of As/g 8[b]	% convn to 8	catalytic activity,[c] min/mL of CO$_2$ evolved
Tl(OAc)$_3$	1:92:106	0.75	94	0.31	42	8.9/200
FeCl$_3$	1:3.9:46	0.77	100	0.18	23	23/200
Al, Br$_2$	1:13.9:12	0.94	100	0.43	49	30/18
AlCl$_3$	1:3.6:41	0.69	85	0.34	51	30/87
5nCl$_4$	1:1.1:14	0.44	59	0.29	62	9.8/200
TiCl$_4$	1:2:13	0.94	71	0.60	63	14.9/200

[a] The brominations were carried out in refluxing CCl$_4$ in the dark. [b] The reaction used to prepare polymer 8 is that of AsCl$_3$, PhBr, and Li with polymer 5 followed by peroxide treatment. [c] The reaction used to evaluate this catalysis is the conversion of neat MDI to carbodiimide at 125 °C with a catalyst; isocyanate ratio: 17.2 μmol As:0.24 mol MDI. 200 mL of CO$_2$ evolution is equivalent to 7% conversion of the isocyanate to carbodiimide.

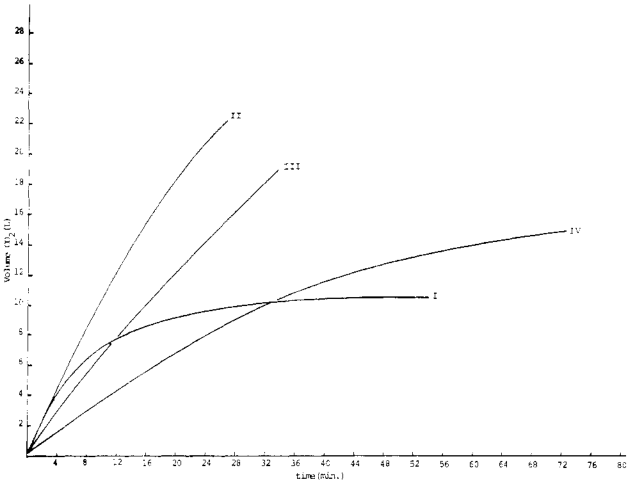

Figure 1. CO$_2$ evolution vs. time in carbodiimide-forming reactions of MDI with catalyst 8 at 160 °C: (I) 10 000:1 ratio of untreated MDI:8; (II) 10 000:1 ratio of MDI:8 with MDI pretreated with 0.1% propylene oxide; (III) 20 000:1 ratio of MDI:8 with MDI pretreated with 0.1% propylene oxide; (IV) 40 000:1 ratio of MDI:8 with MDI pretreated with 0.1% cyclohexene oxide.

pected to react with the basic arsine oxide catalyst. Addition of only 100 ppm HCl (as aniline hydrochloride) to the reaction mixture dramatically accelerates the deactivation of the catalyst. The catalyst loses all activity within 1.6 min of the addition of the acid. Other strong acids, such as sulfuric and trifluoroacetic acids also have a similar effect on the catalyst. Since the presence of acid in the isocyanate has such a severe effect on the catalyst, treatment of the isocyanate to remove the acid would be expected to increase the catalyst lifetime. Strong bases cannot be used due to the potential for catalysis of other isocyanate reactions such as isocyanurate formation. Epoxides have been used to scavenge HCl from isocyanates and so the effect of pretreatment of the MDI with epoxides was studied. Initially, the MDI was treated with 0.1% (wt/wt) propylene oxide prior to heating to 160 °C. This increased the lifetime of 8 to 23 000 turnovers for a reaction using a 10 000:1 weight ratio of MDI:8. Other higher boiling epoxides such as cyclohexane oxide also work well as acid scavengers in the MDI. The effect of these epoxide treatments on catalyst lifetime at various MDI:8 ratios is shown in Figure 1. Curve I is a plot of the CO$_2$ evolution vs. time measured with untreated MDI at a 10 000:1 (MDI:catalyst) weight ratio. Conversion to carbodiimide (10%) is reached at 7.5 min and the catalyst deactivates after 9 600 turnovers. When MDI is pretreated with propylene oxide, 10% conversion is reached at 6.5 min and the catalyst is active after 23 000 turnovers by using the same 10 000:1 ratio (curve II). In a reaction with a 20 000:1 ratio of pretreated MDI:catalyst, 10% conversion is reached in 13.0 min (curve III). Using a 40 000:1 ratio, 10% conversion is reached in 24.5 min and the catalyst is active to more than 56 000 turnovers (curve IV).

The polymer 8 can be conveniently used for preparation of carbodiimides from aromatic isocyanates. For example, phenyl isocyanate and 0.4% by weight 8 were heated for 30 min at 150–190 °C. The solution was filtered and distilled to give diphenylcarbodiimide in 88% yield. Di-*o*-tolylcarbodiimide and di-*p*-tolylcarbodiimide were obtained in 90% yields from the respective isocyanates under similar conditions. The catalyst recovered from reaction of *o*-tolyl isocyanate was reused twice in the reaction giving carbodiimide in 94% yield each time. Other reactions catalyzed by 8 as well as mechanistic aspects of the chemistry involved are currently being investigated.

Experimental Section

The resin used in all preparations is a 2% divinylbenzene, styrene copolymer in the form of 200–400 mesh beads (Eastman Kodak). Prior to use, the resin is washed successively with mixtures of methylene chloride and methanol (volume ratios of 9:1), 3:1, 2:3, and 1:9) and finally with methanol and then dried at 80 °C for at least 4 h.

All solvents are analytical reagent (AR) grade and they are used as received with the exception of THF. THF is dried over 4-Å molecular sieves and stored under N$_2$. Results of reactions using THF dried by this procedure are the same as those using THF that is distilled from sodium benzophenone ketyl prior to use. Diphenylarsinous chloride (Strem), arsenic trichloride (Alfa), and all Lewis acids are used as received. Lithium wire (Alfa) is stored under xylene and wiped dry when used. MDI (Isonate 125, The Upjohn Co.) is stored at 60 °C and decanted from isoluble material when used. Infrared spectra are recorded on either a Perkin Elmer 621 spectrometer or a Beckman 252 MX spectrometer. Elemental analyses are performed by Galbraith Laboratories, Knoxville, TN 37921 or by MicAnal, Tucson, AZ 85717.

Bromination of Polystyrene: Boron Trifluoride Etherate Method. This method is that which is reported by Relles and Schluenz in ref 4. A suspension of brominated polystyrene (3.5 g, 0.0188 mol) in THF (90 mL) is stirred 30 min at 25 °C under N$_2$. A solution of diphenylarsinous chloride (10 g, 0.0378 mol) in THF (30 mL) is added followed by Li wire (0.64 g, 0.093 mol, cut into ca. $^1/_8$ in. lengths under hexane). A very slight exotherm occurs. After about 10 min the whole reaction mixture is an orange-red color. After stirring for 18 h excess Li is removed and the beads are filtered, washed with 2:3, 3:1, and 9:1 CH$_2$CL$_2$:CH$_3$OH and pure CH$_2$Cl$_2$ and dried at 50–60 °C for 2 h.

Bromination of Polystyrene: TiCl$_4$ Method. This method is used for all of the brominations listed in Table II with the catalysts used in the mole ratios listed. A suspension of 25.0 g (0.24 equiv) of the washed resin in 250 mL of carbon tetrachloride, stirred mechanically in a reaction flask and protected from light, is treated with 3.9 mL (0.035 mol) of titanium tetrachloride and a solution of 9.39 g (0.059 mol) of bromine in 10 mL of carbon tetrachloride. The mixture is heated to reflux for 2.5 h and then an additional 2.3 mL (0.021 mol) of titanium tetrachloride is added. After heating 1 h longer, the solution is cooled to room temperature and the reaction mixture is quenched with a small volume (10–20 mL) of methanol and then filtered. The polymer is washed successively with 200-mL portions of methanol/water, methanol, and toluene and then dried at 80 °C overnight to yield

28.09 g of yellow beads. Elemental analysis: 11.71% Br or 1.46 mequiv Br/g resin corresponding to bromination of 17% of the aromatic rings (theory 25%).

Preparation of Polymeric Arsine Oxide 8d: Diphenylarsinous Chloride Method. This method is a modification of that which is used by Relles and Schluenz to prepare polymer supported triphenylphosphine oxide in ref 4. To a suspension of 2% divinylbenzene-crosslinked 200–400 mesh polystyrene beads (47.07 g, 0.45 equiv) in nitromethane (250 mL)) BF_3–etherate (64.5 g, 0.45 mol) is added. The reaction flask is wrapped with aluminum foil (dark reaction) and bromine (144 g, 0.9 mol) is added over 30 min while the temperature is maintained at 25 °C with an ice bath. The mixture is stirred for 18 h and the beads are then filtered. They are washed with 100-mL portions of 9:1, 3:1, 2:3, and 9:1 CH_2Cl_2:CH_3OH and pure CH_2Cl_2, oven dried at 50 °C, and dried then in vacuo at 80 °C and 0.3 mm overnight (to remove all traces of solvent). The yield was 74.4 g. Elemental analysis (calcd (based on repeating unit) Br, 43.7; found Br, 43.0) indicated bromination occurred on 98.4% of the rings.

A suspension of the polymeric arylarsine (5.6 g) in acetone (50 mL) is treated with 30% H_2O_2 (2.8 g, 0.025 mol). After the reaction stirred for 18 h, the water was removed by azeotropic distillation. The beads were then filtered, washed with 3:1, 2:3, 3:1, and 9:1 CH_2Cl_2:CH_3OH and pure CH_2Cl_2, and dried in vacuo overnight at 80 °C and 0.3 mm. The yield was 5.5 g. IR (KBr) 1086, 880 cm^{-1}. Elemental analysis (calcd (based on repeating unit) As, 21.55; found As, 20.48) indicated As on 94.9% of the rings.

Preparation of Polymeric Arsine Oxide 8c: $AsCl_3$ Method. A suspension of 10.00 of g resin (14.6 mequiv Br) in 100 mL of dry THF, stirred mechanically under argon, is treated with 36 cm × 3.2 mm of lithium wire (215 mmol), 2.10 mL (25 mmol) of arsenic trichloride, and 12.00 g (75 mmol) of bromobenzene. An exothermic reaction occurs shortly after the addition and the mixture turns dark red. After 30 min the warm (55–60 °C) reaction mixture is heated to reflux for 1 h and is then stirred at room temperature overnight. The reaction mixture is treated with 15 mL of methanol to quench the excess lithium and the polymer is removed by filtration and washed with water. The wet polymeric arsine 7 is suspended in 100 mL of acetone, and 6.0 g of 30% H_2O_2 (53 mmol) is added to the suspension. After stirring for 1 h the polymer is removed by filtration and washed with successive 200-mL portions of acetone and toluene. The polymer is dried overnight at 80 °C to yield 10.1 g of yellow beads. IR (KBr) 1086, 880 cm^{-1}. Elemental analysis indicated 6.22% As (0.83 mequiv/g) and 0.18% Br (0.02 mequiv/g).

Preparation of 8: Triphenylarsine Method. A suspension of 13.92 g of briminated polystyrene (0.75 mequiv Br/g) in 75 mL of THF stirred mechanically under argon, is treated with 4 cm × 3.2 mm of lithium wire (23 mmol) and 3.18 g (10.4 mmol) of triphenylarsine. The mixture is stirred at 25 °C for 1 h during which time the lithium begins to react and the solution turns red. The solution is heated to reflux for 2 h and then stirred at 25 °C overnight. The polymer is removed by filtration and washed with successive 200-mL portions of mixtures of methylene chloride and methanol in ratios of 2:3, 3:1, and 9:1 and finally with methylene chloride. The wet polymer is suspended in 100 mL of acetone and treated with 6.0 g of 30% hydrogenperoxide, and the mixture is stirred for 1 h. The polymer is filtered, washed with successive 100-mL portions of acetone and toluene, and dried at 80 °C overnight to yield 12.28 g of yellow beads. Elemental analysis indicated 1.40% As (0.19 mequiv As/g) and 0.10% Br(0.01 mequiv Br/g).

Diphenylcarbodiimide. Phenyl isocyanate, 23.5 g (0.197 mol), is heated to 150 °C. Compound 8 0.10 g (0.08 mequiv As) is added and a reaction occurred with vigorous evolution of CO_2. After 30 min the heating is stopped when the solution temperature has risen to 190 °C. The reaction is cooled and diluted with CH_2Cl_2 and filtered. The filtrate is concentrated in vacuo and the residue is distilled to yield 16.82 g (88%) of diphenylcarbodiimide, bp 132 °C (0.5 mmHg).

Di-*p*-tolylcarbodiimide, bp 148 °C (0.5 mmHg), is prepared from *p*-tolyl isocyanate by using the same reaction conditions.

Di-*o*-tolylcarbodiimide. A mixture of 13.3 g (0.1 mol) of *o*-tolyl isoocyanate, 13 mL of benzene, and 0.1 g of 6 is heated at reflux for 3 h and then filtered to remove the catalyst. The filtrate is distilled under reduced pressure to obtain 10 g (90%) of di-*o*-tolylcarbodiimide, bp 135–137 °C (0.3 mmHg).

The polystyrene catalyst recovered from the above reaction is then used as a catalyst in a second reaction of 13.3 g (0.1 mol) of *o*-tolyl isocyanate in 13 mL of benzene. Di-*o*-tolylcarbodiimide 10.4 g (94% yield) is obtained after workup and distillation. A third reaction using the recovered catalyst gives identical results.

Evaluation of Catalytic Activity in 8. A 30 g sample of bis(4-isocyanatophenyl)methane (MDI) is heated to 125 °C in a constant temperature bath for 15 min and then 50 mg of catalyst **8a** is added. The gas evolution is measured with a gas burette and the time needed for the evolution of 200 mL of gas, 6.9 min, is recorded. This is repeated for catalysts **8b** and **8c** by using the same rection conditions. With catalyst **8d**, it is necessary to use 250 mg of catalyst to obtain a measurable amount of gas evolution.

For the evaluation of the catalysts prepared from the various bromination reactions listed in Table I similar conditions are used except that a mole ratio of catalyst:MDI of 17.2 mmol As:0.24 mol MDI is kept constant instead of the weight ratio listed above.

Catalyst Lifetime Studies. A mechanically stirred 2-L flask fitted with a thermometer and a condenser leading to a wet test meter (saturated with CO_2) is charged with 731.1 g (2.92 mol) of MDI and heated to 160 ± 1 °C. A mixture of 0.5 g of unsubstituted polystyrene resin and 36.5 mg of **8b** (a 20 000:1 wt ratio) containing 2.2 mol As is added to the heated isocyanate and the CO_2 evolution measured on the wet test meter. A total of 4.50 L of CO_2 is evolved over a 40.7-min period (4.0 L of CO_2 evolves in the first 16.5 min) at which time the catalyst deactivates. This corresponds to 8 500 turnovers of the catalyst or 6% conversion to carbodiimide.

Lifetime studies with pretreated MDI are carried out in a similar fashion. The MDI, 729.6 g (2.92 mol), is treated with 1.0 mL (14.3 mmol) of propylene oxide and this is heated to 160 ± 1 °C for 1 h. A mixture of 0.5 g of unsubstituted resin and 72.9 mg of catalyst **8b** (a 10 000:1 wt ratio) containing 44 μmol of As is then added to the MDI. The evolution of CO_2 is followed until 22.4 L of CO_2 (STP) has been evolved. This corresponds to 34% conversion based on MDI or 2.3×10^4 turnovers of the catalyst. The reaction is not followed further as the viscosity of the mixture begins to rapidly increase.

Acid Deactivation of Catalyst 8b. The above reaction is repeated with 871.7 g (3.48 mol) of MDI pretreated with 1.2 mL (17.7 mmol) of propylene oxide and 43.6 mg (a 2×10^4:1 wt ratio) of catalyst **8b** containing 26 mmol As at 160 °C. The CO_2 evolution is followed and after 7.6 L of CO_2 evolution (9.0% conversion of 13 000 turnovers of the catalyst) 150 mg (1.2 mmol) of aniline hydrochloride is added. The catalyst deactivates in several minutes with 0.4 L of CO_2 evolution occurring after addition of the acid.

Registry No. $Tl(OAc)_3$, 2570-63-0; $EeCl_3$, 7705-08-0; Al, 7429-90-5; $AlCl_3$, 7446-70-0; $SnCl_4$, 7646-78-8; $TiCl_4$, 7550-45-0; polystyrene (homopolymer), 9003-53-6; diphenylarsinous chloride, 712-48-1; *o*-tolyl isocyanate, 614-68-6; di-*o*-tolylcarbodiimide, 1215-57-2; triphenylarsine, 603-32-7; bis(4-isocyanatophenyl)methane, 101-68-8; phenyl isocyanate, 103-71-9; arsenic trichloride, 7784-34-1; diphenylcarbodiimide, 622-16-2; di-*p*-tolylcarbodiimide, 726-42-1; *p*-tolyl isocyanate, 622-58-2.