J. Org. Chem. **1986**, *51*, 929–931 **929**

identified with the previously described sample by comparison of NMR spectra and by a mmp determination.

Crystal Structure of *anti*-9-Acetoxy-*cis*-1,8-bis(2,3-dimethylphenyl)anthracene (14b). A crystal of the acetate **14b** was mounted and data were collected by procedures described in the supplementary material. The crystal belonged to the orthorhombic system and the data collected were consistent only with space groups *Pnma* or $Pna2_1$ (No. 62 or 33).[17] The crystal was centrosymmetric. Assuming the space group *Pnma*, a successful refinement was obtained. From a total of 2195 reflections collected in a complete octant of data, 1415 were accepted as statistically above background. In the data refinement, described in the supplementary material, 178 parameters were varied for the 1415 observations. The full-matrix least-squares refinement converged at $R = 0.0897$ and $R_w = 0.0744$. A perspective view of the acetate **14b** is presented in Figure 1. Lists of the final atomic coordinates and the bond distances and angles are available in the supplementary material as Tables 1 and 2.

Crystal Structure of 9-Acetoxy-*trans*-1,8-bis(2,3-dimethylphenyl)anthracene (14a). A crystal of the acetate **14a** was mounted and data were collected by procedures described in the supplementary material. The crystal belonged to the monoclinic system and the data collected were consistent only with space group $P2_1/c$ (No. 14).[17] From a total of 4249 reflections collected in a complete quadrant of data, 2594 were accepted as statistically above background. In the data refinement, described in the supplementary material, 335 parameters were varied for the 2594 observations. The full-matrix least-squares refinement converged at $R = 0.0789$ and $R_w = 0.0686$. A perspective view of the acetate **14a** is presented in Figure 2. Lists of the final atomic coordinates and the bond distances and angles are available in the supplementary material as Tables 3 and 4.

Supplementary Material Available: Descriptions of the determination of crystal structures for the trans acetate **14a** and the cis acetate **14b**, including tables of atomic coordinates for each compound (10 pages). Ordering information is given on any current masthead page.

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Notes

Polymers as Reagents and Catalysts. 12. Side Chain Bromination of Aromatic Molecules with a Bromine Complex of Poly(styrene-*co*-4-vinylpyridine)

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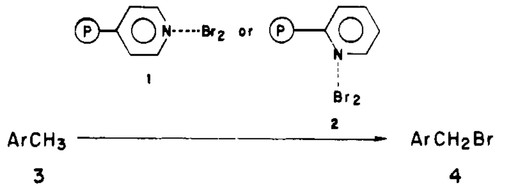
Polymer beads have found a wide range of uses in organic chemistry and can be chemically transformed so that they can act as reagents or catalysts, while the chemical reactivity of the reagent attached to the polymer backbone can also be changed.[1]

Free-radical introduction of halogens into alkanes is one of the most important methods for their functionalization.[2-5]

N-bromosuccinimide is one of the reagents often used for free-radical introduction of bromine into organic molecules, but the mechanism of bromination still seems to be an open question.[6-10]

Table I. The Effect of Reagent, Structure of the Organic Molecule, and Reaction Conditions on Side Chain Bromination



	conversion of 3, %			
	reagent 1		reagent 2	
ArCH$_3$	DBP[a]	hν[b]	DBP[a]	hν[b]
methylbenzene	96	70	87	40.5
1-methylnaphthalene	91	31	78	23.5
2-methylnaphthalene	87	22.5	71.5	23

[a] Conversions were determined by ^{1}H NMR, 20 mL of CCl$_4$, 1 mmol of ArCH$_3$, 1 g of 1 or 2, 4-h reflux, 6 mg of DBP. [b] 10 mL of CCl$_4$, 1 mmol of ArCH$_3$, 1 g of 1 or 2, 3-h irradiation with 125-W HPQ lamp.

Cross-linked polystyrene beads have usually been used for the preparation of reagents and catalysts, while cross-linked poly(vinylpyridine) or cross-linked copolymers of styrene and vinylpyridine have received much less attention, in spite of the fact that pyridine has wide application in organic synthesis by itself or in conjuction with other reagents. It has been demonstrated that a cross-linked copolymer of 4-vinylpyridine with styrene gave various types of complexes with halogens,[11,12] and its bromine complexes have been found to be able to introduce bromine into alkenes stereospecifically.[13] We now report our investigations of the reactivity of the bromine

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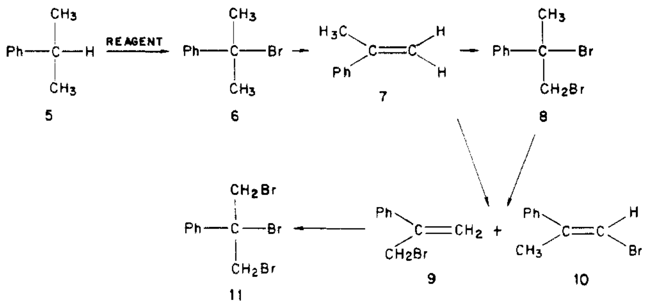
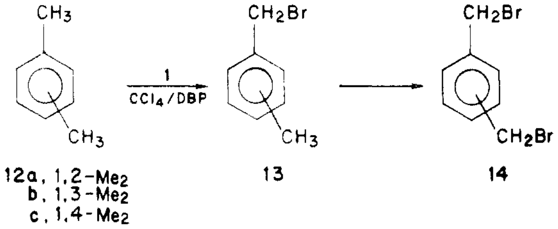
Table II. The Effect of Reagent on the Course of Side Chain Bromination of Isopropylbenzene



reagent	product distribution, % 5	6	7	8	9	10	11	ref
N-bromosuccinimide	10	80		10				14
N-bromopolymaleimide	24				13	15	48	14
1	6	9	18	43	24			
2	45	10	20	11	4			

Table III. The Effect of Reaction Variables on the Side Chain Bromination of Dimethylbenzenes with the Bromine Complex of Poly(styrene-*co*-4-vinylpyridine) in CCl_4 under Reflux



benzene derivatives (mmol)	1, g	reac time, h	product distribution, % 12	13	14
12c:1	1	1	59		41
12b:1	1	1	60		40
12a:1	1	1	26	68	6
12a:1	2	4	10	76	14
12a:1	2	8		65	35
12a:1	3	8		46	54
12a:1	3	17		14	86
12a:1	3	24			100

complex of the cross-linked copolymer of styrene and 4-vinylpyridine with various alkyl-substituted aromatic molecules in order to compare its reactivity with that of *N*-bromosuccinimide.

Results and Discussion

We first searched for appropriate reaction conditions which would lead to the side chain bromination of toluene with the bromine complex of poly(styrene-*co*-4-vinylpyridine) (1) and found that reaction in carbon tetrachloride under reflux and in the presence of dibenzoyl peroxide resulted in benzyl bromide as a sole product, while reaction under photochemical conditions proceeded more slowly. Further, we investigated the effect of the structure of the aromatic molecule and of the complex under both conditions. Results are presented in Table I. Reactions were slower under photochemical conditions, and steric interactions between the polymer reagent and the organic substrate were much more pronounced than in the case of dibenzoyl peroxide initiated reactions. The bromine complex prepared with cross-linked copolymer 2 (styrene–2-vinylpyridine) was also less reactive than bromine complex 1, while bromination with a complex that contained up to four bromine atoms per pyridine ring[13] proved to be a little less reactive. Therefore the reactivity of polymer reagents 1 and 2 was studied under thermal conditions.

Bromination of isopropylbenzene with 1 or 2 in the presence of dibenzoyl peroxide gave four products (Table II) with the product distribution differing markedly from that of both *N*-bromosuccinimide and *N*-bromopolymaleimide. Bromination of isopropylbenzene has been studied by Katchalski and co-workers,[14] and they pointed out the importance of the polymer backbone on the reactivity of the reagent. Differences in the reactivity of reagents 1 and 2 observed in the bromination of toluene were more pronounced in the case of isopropylbenzene because of greater steric interactions with the polymer backbone (conversion of 5 being 94% in the case of 1 and 55% in the case of 2), while in the case of ethyl benzene reaction with 1 led to 1-phenyl-1-bromoethane in high yield.

We further studied bromination of all three dimethyl-substituted benzenes (**12a–c**) with 1 in refluxing carbon tetrachloride and in the presence of dibenzoyl peroxide, and the results are presented in Table III. The ortho isomer of dimethylbenzene (**12a**) was the most reactive, with the monosubstituted product **13a** being the major one, while under the same reaction conditions, the meta (**13b**) and para (**13c**) isomers were converted only to disubstituted products **14b** and **14c**. The effect of the ratio of *o*-xylene (**12a**) to the brominating agent (1) and the reaction time are also presented in Table III, and it is evident that under appropriate reaction conditions, the formation of the dibromide was favored until after a 24-h-reaction,

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Table IV. Side Chain Bromination of Alkyl-Substituted Molecules with 1 under Reflux in CCl_4

substrate	product	substrate (mmol):1 (g)	reac time, h	yield of pure product, %
methylbenzene	(bromomethyl)benzene	3:3	4	78
1-methylnaphthalene	1-(bromomethyl)naphthalene	1:1	4	63
2-methylnaphthalene	2-(bromomethyl)naphthalene	1:1	24	79
ethylbenzene	1-phenyl-1-bromoethane	10:10	4	81
1,2-dimethylbenzene	1,2-bis(bromomethyl)benzene	1:3	24	85
1,3-dimethylbenzene	1,3-bis(bromomethyl)benzene	1:3	24	75
1,4-dimethylbenzene	1,4-bis(bromomethyl)benzene	1:3	24	82
2,6-dimethylpyridine	2,6-bis(bromomethyl)pyridine	1:3	24	66
hexamethylbenzene	1-(bromomethyl)pentamethylbenzene	1:1	4	75

in which the dibromide (**14a**) was formed as the only product.

We further searched for the optimal reaction conditions for converting alkyl-substituted benzene derivatives to mono- or dibromo products. The reaction conditions and the yields of the isolated pure products are presented in Table IV. The structure of the products were determined on the basis of their spectroscopic data and comparison with those of independently synthesized compounds. Many of the products mentioned in Table IV are usually obtained via reactions with two or even more steps, while the yields presented proved to be in almost all cases higher than those reported up to now in the literature.

The preparation of bromo-substituted products with the bromine complex of cross-linked poly(styrene-*co*-4-vinylpyridine) (1) is a manipulatively simple method; after completion of the reaction the polymer beads are filtered off, the solvent is evaporated in vacuo, and the crude products are pure enough for further reactions or can be easily purified by crystallization or distillation. The polymer resins can be easily recovered after the reaction and reused several times.

Experimental Section

IR spectra were recorded using a Perkin-Elmer 727 B spectrometer and ^1H NMR spectra with a Jeol JNM-PS-100 spectrometer, with Me_4Si as internal reference, while mass spectra and high-resolution measurements were taken with a CEC-21-11 spectrometer. GLC analysis was carried out on a Varian Aerograph 1800 instrument and TLC on Merck silica gel F 254. Cross-linked poly(styrene-*co*-4-vinylpyridine) and bromine complexes were prepared according to previously published procedures[11,13] and are commercially available.[15]

Addition and Isolation Procedures. Alkyl-substituted aromatic or heteroaromatic molecules (1–10 mmol) were dissolved in 20–200 mL of CCl_4 and 1–10 g of polymer reagent, 4–40 mg of dibenzoyl peroxide was added, and the reaction mixture was heated under reflux for from 1–24 h. In the case of light-initiated reactions, the reaction mixtures were stirred for 3 h and irradiated with 125-W HPQ lamps. Insoluble polymer was filtered off and the solvent evaporated under reduced pressure, and the reaction mixtures were analyzed by GLC or ^1H NMR. Crude reaction mixtures were purified by distillation or crystallization. The yields of pure products and the reaction conditions are listed in Table IV, while in Tables I–III the effect of the structure of the organic molecule on the course of bromination is presented.

Benzyl Bromide: 79%; bp 199 °C (lit.[16] bp 194–198 °C; yield 59%).

1-(Bromomethyl)naphthalene: crystallization from ethanol (63%); mp 58–60 °C (lit.[16] mp 55–56 °C; yield 57%); NMR δ 4.9 (br s, 2 H, CH_2) 7.5 (m, 7 H).

2-(Bromomethyl)naphthalene: crystallization from ethanol (79%); mp 60–62 °C (lit.[16] mp 54–55 °C; yield 62%); NMR δ 4.38 (br s, 2 H, CH_2), 7.4 (m, 7 H).

1-Phenyl-1-bromoethane: distillation under reduced pressure [T = 107–109 °C, (15 mm Hg); 81%] [lit.[17] bp 92–94 °C (8 mmHg); yield from 1-phenylethanol, yield 74%]; NMR δ 2.18 (d, 3 H, J = 6 Hz, CH_3), 5.64 (q, 1 H CH), δ 8.08 (m, 5 H, Ph).

2,6-Bis(bromomethyl)pyridine: crystallization from petroleum ether (66%); mp 84–87 °C (lit.[18] mp 83–86 °C; yield 20%).

Pentamethylbenzyl bromide: crystallization from petroleum ether (75%); mp 83–85 °C (lit.[19] mp 84–85 °C; yield 94% from methyl ether).

1,2-Bis(bromomethyl)benzene: crystallization from chloroform (85%); mp 92–93 °C (lit.[20] mp 98–99 °C; yield 56%); NMR δ 5.05 (s, 4 H, CH_2), δ 7.98 (m, 4 H, Ph).

1,3-Bis(bromomethyl)benzene: crystallization from chloroform (75%); mp 74–76 °C (lit.[20] mp 70–72 °C; yield 44%); NMR δ 4.85 (s, 4 CH_2) H, 7.92 (m, 4 H Ph).

1,4-Bis(bromomethyl)benzene: crystallization from chloroform (82%); mp 143–145 °C (lit.[20] mp 142–144 °C; yield 50%); NMR δ 4.85 (s, 4 H, CH_2), 8.08 (s, 4 H, Ph).

Regeneration of Resins. Beads were washed with methanol and water, then suspended in 2 N NaOH, stirred for 1 h at 50 °C, washed with water, methanol, and chloroform, and dried at room temperature to constant weight. No loss of polymer activity for the further preparation of complex 1 was found.

Registry No. **3** (Ar = Ph), 108-88-3; **3** (Ar = 1-naphthalene), 90-12-0; **3** (Ar = 2-naphthalene), 91-57-6; **3** (Ar = pentamethylbenzene), 87-85-4; **4** (Ar = Ph), 100-39-0; **4** (Ar = 1-naphthalene), 3163-27-7; **4** (Ar = 1-pentamethylbenzene), 53442-65-2; **4** (Ar = 2-naphthalene), 939-26-4; **5**, 98-82-8; **6**, 3575-19-7; **7**, 98-83-9; **8**, 36043-44-4; **9**, 3360-54-1; **12a**, 95-47-6; **12b**, 108-38-3; **12c**, 106-42-3; **13a**, 89-92-9; **14a**, 91-13-4; **14b**, 626-15-3; **14c**, 623-24-5; Br_2, 7726-95-6; ethyl benzene, 100-41-4; 1-phenyl-1-bromoethane, 585-71-7; 2,6-dimethylpyridine, 108-48-5; 2,6-bis(bromomethyl)pyridine, 7703-74-4.

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(Methoxyethoxy)methyl Group: New Amide and Hydroxyl Protecting Groups of Uridine in Oligonucleotide Synthesis[1]

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Synthesis of oligonucleotides containing uridine has revealed the occurrence of side reactions involving the amide function of the uracil residue during phosphorylating and coupling reactions. Many workers have re-

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(1) This manuscript represents part 34 in a series on oligonucleotide synthesis. For the previous paper this series, see: Imai, K.; Ito, T.; Kondo, S.; Takaku, H. *Nucleosides Nucleotides* **1985**, *4*, 669.