Block and Graft Copolymers by Selective Cationic Initiation. I. Selective Alkylation with Trialkylaluminums on the Chlorine of Chlorobrominated Alkanes

Joseph P. Kennedy* and Earl G. Melby

Institute of Polymer Science, The University of Akron, Akron, Ohio 44325

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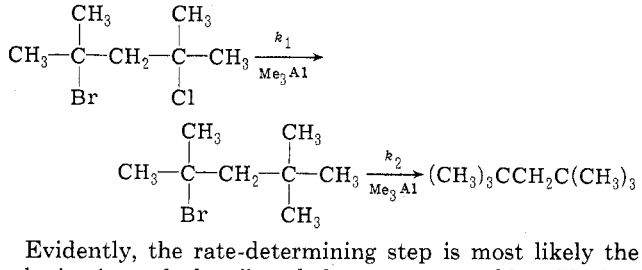
Selective alkylation with trialkylaluminum compounds on the chlorine of tertiary alkyl chloride and bromide mixtures, and chlorobrominated alkanes has been studied. Using trimethylaluminum and mixtures of *tert*-butyl chloride and bromide, methylation selectivity is limited owing to the early methylation of *tert*-butyl bromide by the dimethylaluminum chloride by-product formed in the fast methylation of *tert*-butyl chloride. Similar results have been obtained using mixtures of 2,6-dichloro-2,6-dimethylheptane and 2,6-dibromo-2,6-dimethylheptane. The reaction between 2-bromo-4-chloro-2,4-dimethylpentane and trimethylaluminum gave exclusively 2,2,4,4-tetramethylpentane. This observation was explained in terms of a rate-determining methylation on the chlorine followed by a rapid, strain relief induced methylation on the bromide. Satisfactory alkylation selectivity for subsequent block-copolymer synthesis was achieved with 2-bromo-6-chloro-2,6-dimethylheptane. While selective chlorine removal has been demonstrated with both trimethyl- and triethylaluminum, greatest selectivity was obtained with the latter, i.e., ~50% chlorine substitution before bromine loss.

In the course of our fundamental studies on cationic polymerization of olefins, it was found that the rate of reaction of t-BuX + Me_3Al → t-BuMe + Me_2AlX follows the sequence t-BuCl ≫ t-BuBr > t-BuI.[1,2] This unexpected observation has been exploited for the selective alkylation of tertiary chlorides with trialkylaluminums in the presence of tertiary alkyl bromides and subsequently in a synthetic method for the preparation of block copolymers.[3]

Results and Discussion

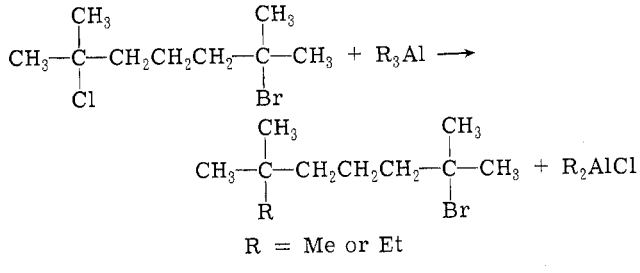
On the basis of the large differences in the rates of methylation of t-BuCl and t-BuBr with Me_3Al,[2] it was theorized that tertiary alkyl chlorides could be selectively methylated in the presence of tertiary alkyl bromides. Thus, we studied the rates of competitive methylation of mixtures of tertiary alkyl halides with Me_3Al in CH_3Cl by NMR spectroscopy. Results of experiments using mixtures of t-BuCl with t-BuBr, and 2,6-dichloro-2,6-dimethylheptane with 2,6-dibromo-2,6-dimethylheptane, are shown in Figure 1. Methylations proceeded quantitatively and faster with the tertiary chlorides than with tertiary bromides to yield the corresponding quaternary carbon compounds. That the tertiary alkyl bromides react faster in the presence of tertiary alkyl chlorides than in their absence[2] is due to the in situ formation of Me_2AlCl, a stronger Lewis acid and a more aggressive methylating agent than Me_3Al.

Subsequently, the alkylation by alkylaluminum compounds of chlorobrominated alkanes (containing tertiary chlorine and bromine in the same molecule) was studied. Interestingly, the reaction of 2-bromo-4-chloro-2,4-dimethylpentane with Me_3Al in CH_3Cl at −60° gave 2,2,4,4-tetramethylpentane and no monomethylated product was observed.



Evidently, the rate-determining step is most likely the substitution of the first halogen, presumably chlorine, while the subsequent (bromine) substitution must occur rapidly. At least two possibilities would account for this observation. The ionization of the chlorine is probably slowed down considerably because of the inductive electron-withdrawing effect of the bromine in β position. Furthermore, once formed, the transitory 2-bromo-2,4,4-trimethylpentane is expected to ionize rapidly owing to the energy gained in relieving internal strain.[4] In addition, the strong Lewis acid, Me_2AlCl, formed in the first methylation step would further accelerate the ionization of the tertiary bromine.

To overcome these unfavorable steric and inductive effects, we have synthesized 2-bromo-6-chloro-2,6-dimethylheptane and studied its rate of alkylation with Me_3Al and Et_3Al. Representative data are shown in Figure 2. In both experiments, chlorine is removed at a faster rate than bromine. Selectivity is greatest with Et_3Al, i.e., ~50% of chlorine substitution occurs before bromine loss. This observation can be explained in terms of relative Lewis acidities as follows.



R = Me or Et

The stronger Lewis acids, R_2AlCl, formed in the first methylation facilitate ionization of the bromine in the monoalkylated product. Increased selectivity obtained with Et_3Al is due to the relatively lower Lewis acidity of Et_2AlCl as compared to Me_2AlCl., i.e., Et_2AlCl is less active in mobilizing the tertiary bromine than Me_2AlCl. Also, the Lewis acidity difference between Et_3Al and Et_2AlCl is smaller than that between Me_3Al and Me_2AlCl.[5] This conclusion is supported by the fact that very little selectivity was observed when 2-bromo-6-chloro-2,6-dimethylheptane was treated with Me_2AlCl and Et_2AlCl, respectively, in CH_3Cl at −80°.

Since either ethylation or hydridation[5] can occur with Et_3Al and Et_2AlCl, three possible final products can arise from 2-bromo-6-chloro-2,6-dimethylheptane. Table I summarizes our results obtained by mass chromatography. Evidently ethylation predominates (~60%) with Et_3Al whereas hydridation prevails (~84%) with Et_2AlCl. Ethylation with

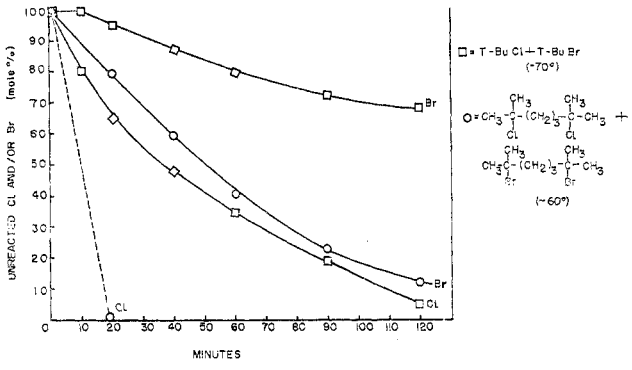


Figure 1. Relative reactivities of tertiary chloride and bromide mixtures with Me_3Al in CH_3Cl (concentrations: tertiary halides 0.1 *M*, Me_3Al 0.4 *M*).

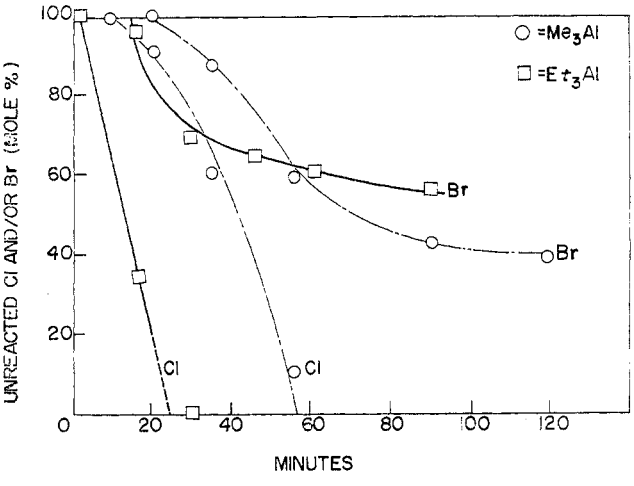
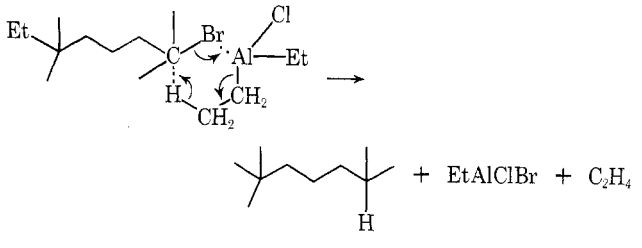


Figure 2. Reaction rate of 2-bromo-6-chloro-2,6-dimethylheptane with Me_3Al at −55° and with Et_3Al at −70° in CH_3Cl solvent.

Et_3Al has been shown to proceed by a conventional SN1 mechanism[2] while hydridation is proposed to proceed by a concerted mechanism.[5]



According to the results in Table I, Et_2AlCl is a much more effective hydridating agent than Et_3Al, the reason(s) for which is not understood.

Table I
Relative Amounts of Products Obtained from the Reaction of 2-Chloro-6-bromo-2,6-dimethylheptane with $AlEt_3$ and $AlEt_2Cl$[a]

	Obtained, %, with Et_3Al	Obtained, %, with Et_2AlCl
$CH_3CH(CH_3)CH_2CH_2CH_2CH(CH_3)CH_3$	6	84
$CH_3CH(CH_3)CH_2CH_2CH_2CEt(CH_3)CH_3$	34	14
$CH_3CEt(CH_3)CH_2CH_2CH_2CEt(CH_3)CH_3$	60	2

[a] Reaction conditions: [$AlEt_3$] or [$AlEt_2Cl$] = 0.4 *M*, [2-chloro-6-bromo-2,6-dimethylheptane] = 0.2 *M*, CH_3Cl solvent, −70°, time 5 min with $AlEt_2Cl$, 180 min with $AlEt_3$.

Since cationic polymerizations proceed rapidly even at low temperatures, bromine loss demonstrated in the later stages of these model reactions is not a serious problem in the synthesis of a polymer containing a tertiary bromine end group. We have demonstrated this[3] by adopting the selective conditions obtained with 2-bromo-6-chloro-2,6-dimethylheptane and Et_3Al to synthesize a block copolymer, poly(styrene-*b*-isobutylene).

Experimental Section

Experiments were performed in a stainless steel enclosure under N_2 atmosphere (<50 ppm moisture). Alkylaluminums (Texas Alkyl Co.) were distilled prior to use. Methyl chloride (Linde) was purified by passing through a column packed with anhydrous molecular sieves, BaO, and Drierite. All tertiary halides were dried over CaH_2 before use. Methallyl chloride (Eastman Kodak Co.) and 6-methyl-5-hepten-2-one (Aldrich Chemical Co.) were used without further purification. NMR analysis was done on Varian A-60 and T-60 instruments. Molecular weights were obtained using a Chromalytics MC-2 mass chromatograph employing SF_6 and CO_2 carrier gases. Gas chromatographic analyses were carried out with an HP-5750 gas chromatograph with a flame ionization detector. Distillations were performed using a Nester-Faust adiabatic spinning band column. All melting and boiling points are uncorrected.

2-Bromo-4-chloro-2,4-dimethylpentane. 2,4-Dimethyl-4-hydroxy-1-pentene was obtained in 70% yield from the reaction of methallyl chloride (2.0 mol) and acetone (2.0 mol) with magnesium (2.3 mol) in ether using a procedure which minimizes Wurtz coupling.[6] This alcohol was purified by distillation, bp 59–61° (20 mm) [lit. bp 126° (760 mm)].[7] To 2,4-dimethyl-4-hydroxy-1-pentene (13.0 g) was added pyridine (9.5 ml) and CH_2Cl_2 (30 ml) followed by dropwise addition of thionyl chloride (9.0 ml) at 0°. After stirring at room temperature for 1 hr, the mixture was twice extracted with 75-ml portions of water. The organic layer was dried with anhydrous $MgSO_4$ and filtered, and the solvent was removed by vacuum. The residual organic material was distilled, resulting in a 35% yield of 4-chloro-2,4-dimethyl-1-pentene: bp 64° (100 mm); NMR (CCl_4) δ 1.60 (s, 6 H, CH_3), 1.65 (s, 3 H, CH_3), 1.78 (s, 2 H, CH_2), 5.05 (d, 2 H, $=CH_2$). HBr was bubbled directly into 4-chloro-2,4-dimethyl-1-pentene at −78° in a two-necked reaction vessel. The product solidified after 1 hr and melted at −30°. HBr addition was continued for an additional 1 hr, resulting in a 100% yield of 2-bromo-4-chloro-2,4-dimethylpentane, which was dried with anhydrous K_2CO_3: NMR (CCl_4) δ 1.82 [s, 6 H, $(CH_3)_2C$], 2.05 [s, 6 H, $(CH_3)_2C$], 2.65 (s, 2 H, CH_2). No further purification was necessary since NMR revealed no detectable impurities.

2-Bromo-6-chloro-2,6-dimethylheptane. Using a published procedure,[8] the reaction of 6-methyl-5-hepten-2-one (0.40 mol) with CH_3MgI (0.40 mol) in ether resulted in an 89% yield of 2,6-dimethyl-6-hydroxy-2-heptene: bp 85° (14 mm) [lit. bp 79° (13 mm)];[8] NMR (CCl_4) δ 1.10 [s, 6 H, $C(CH_3)_2$], 1.95 [m, 4 H, $(CH_2)_2$], 1.60 [d, 6 H, $=C(CH_3)_2$], 2.60 (m, 1 H, OH), 5.10 (t, 1 H, =CH–). Thionyl chloride (0.34 mol) was added dropwise at 0° to a stirred solution of 2,6-dimethyl-6-hydroxy-2-heptene (0.34 mol) in pyridine (0.34 mol) and CH_2Cl_2 (75 ml). The resultant mixture was stirred at room temperature for 1 hr followed by extraction with two portions of water (100 ml). The organic layer was dried over anhydrous $MgSO_4$ and filtered and the solvent was removed by vacuum. The organic residue was distilled, resulting in a 63% yield of 6-chloro-2,6-dimethyl-2-heptene: bp 68° (12 mm) [lit. bp 71–72° (15 mm)];[9] NMR (CCl_4) δ 1.58 [s, 6 H, $(CH_3)_2$], 1.63 [d, 6 H, $=C(CH_3)_2$], 2.00 [m, 4 H, $(CH_2)_2$], 5.00 (t, 1 H, =CH–). HBr was bubbled directly into 6-chloro-2,6-dimethyl-2-heptene (25 g) in CH_2Cl_2 (100 ml) at −78°. After 2 hr, the solution was warmed to room temperature, dried with anhydrous K_2CO_3, and filtered and the solvent was removed by vacuum. The product, 2-bromo-6-chloro-2,6-dimethylheptane, was recrystallized from ethanol: mp 33–34°; NMR (CCl_4) δ 1.58 (s, 6 H, CH_3) 1.90 (s, 6 H, CH_3), 1.90 (s, 6 H, CH_2); ir 2900, 1440, 1360, 1300, 1290, 1230, 1190, 1130, 840, and 730 cm^{-1}.

2,6-Dichloro-2,6-dimethylheptane. 2,6-dimethyl-6-hydroxy-2-heptene (5 g) was treated with 50 ml of concentrated HCl at 0°. The mixture was stirred at 0° for 15 min and extracted with 50 ml of CH_2Cl_2. The organic layer was dried with anhydrous K_2CO_3 and filtered and the solvent was removed by vacuum. After three treatments with concentrated HCl, a 100% conversion to 2,6-dichloro-2,6-dimethylheptane resulted which was recrystallized from etha-

nol: mp 40° (lit. mp 43°);[10] NMR (CCl_4) δ 1.60 (s, 12 H, CH_3), 1.78 (s, 6 H, CH_2).

2,6-Dibromo-2,6-dimethylheptane. 2,6-dimethyl-6-hydroxy-2-heptane (5 g) was cooled to −78° in CH_2Cl_2 (50 ml). HBr was bubbled into the solution for a total of 3.5 hr. The mixture was extracted with water (50 ml) and dried with K_2CO_3 and the solvent was removed. A 100% yield of 2,6-dibromo-2,6-dimethylheptane resulted which was recrystallized from ethanol: mp 34° (lit. mp 34°);[11] NMR (CCl_4) δ 1.90 (s, 12 H, CH_3), 1.90 (s, 6 H, CH_2).

Alkylation Experiments. A solution of the appropriate halide (0.2 *M*) in CH_3Cl was added to an equal volume of the trialkylaluminum (0.4 *M*) in CH_3Cl. Periodically, 5-ml samples were withdrawn and quenched with 1 ml of cold methanol. Saturated aqueous $KNaC_4H_4O_6$ was added to the samples and the organic layer was extracted into CCl_4 and dried with K_2CO_3. The samples were analyzed by GC, mass chromatography, and NMR,. The extent of alkylation was followed by NMR spectroscopy by determining the decrease in intensity of the methyl protons adjacent to the tertiary chlorine and tertiary bromine in the starting materials.

Final Hydrocarbon Products. 2,2,4,4-Tetramethylpentane resulting from the methylation of 2-bromo-4-chloro-2,4-dimethylpentane was identified by NMR and GC by comparison with an authentic sample (Chemical Samples Co.). 2,2,6,6-Tetramethylheptane[12] was identified by NMR and molecular weight: NMR (CCl_4) δ 0.93 (s, 18 H, CH_3), 1.15 (s, 6 H, CH_2). Calcd for $C_{11}H_{24}$: mol wt, 156.3. Found: mol wt, 155. Final products resulting from the reaction of Et_3Al and Et_2AlCl with 2-bromo-6-chloro-2,6-dimethylheptane (Table I) were analyzed by mass chromatography. Calcd for $C_{13}H_{28}$ (3,3,7,7-tetramethylnonane): mol wt, 184.4. Found: mol wt, 183. Calcd for $C_{11}H_{24}$ (2,6,6-trimethyloctane): mol wt, 156.3. Found: mol wt, 154. Calcd for C_9H_{20} (2,6-dimethylheptane[13]): mol wt, 128.29. Found: mol wt, 128. No other products were observed by gas chromatography.

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Registry No.—$AlEt_3$, 97-93-8; $AlEt_2Cl$, 96-10-6; $AlMe_3$, 75-24-1; 2-bromo-4-chloro-2,4-dimethylpentane, 54191-86-5; 2,4-dimethyl-4-hydroxy-1-pentene, 19781-53-4; methallyl chloride, 563-47-3; acetone, 67-64-1; 4-chloro-2,4-dimethyl-1-pentene, 54166-29-9; 2,6-dimethyl-6-hydroxy-2-heptene, 6090-15-9; 6-chloro-2,6-dimethyl-2-heptene, 6076-48-8; 2,6-dichloro-2,6-dimethylheptane, 35951-36-1; 2,6-dibromo-2,6-dimethylheptane, 54166-30-2; 2,2,6,6-tetromethylheptane, 40117-45-1; 3,3,7,7-tetramethylnonane, 54166-31-3; 2,6,6-trimethyloctane, 54166-32-4; 2,6-dimethylheptane, 1072-05-5; 2-chloro-6-bromo-2,6-dimethylheptane, 54166-33-5.

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Diacylium Cations from Tetrahaloterephthalic Acids and Their Electrophilic Reactivity

James O. Knobloch* and Fausto Ramirez

Research and Development Department, Amoco Chemicals Corporation, Naperville, Illinois 60540

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Diacylium bis bisulfate complexes are prepared from the reaction of sulfur trioxide with tetrabromoterephthalic acid, Br_4TA, and tetrachloroterephthalic acid, Cl_4TA. The spectra of the diacylium cations in the ultraviolet, visible, and infrared regions can be determined in SO_3–SO_2 and in SO_3–Freon 113 solvents. The diacylium complexes are excellent reagents for laboratory and industrial syntheses of diacid chlorides, diamides, and diesters of tetrahaloterephthalic acids; these products are obtained from the reactions of the complexes with chlorosulfonic acid, sulfamic acid, and alcohols, respectively. The diacylium complexes react with tetrahaloterephthalic acids to produce homopolymers and heteropolymers with an anhydride backbone. The perhalo polyanhydrides are stable at relatively high temperatures and are quite resistant to hydrolysis.

The extensive research of Olah and his coworkers[1] on stable oxocarbonium ions has demonstrated the possibility of generating diacylium cations from the acid fluorides of dicarboxylic acids. Thus, glutaryl fluoride and higher aliphatic diacid fluorides, as well as terephthaloyl fluoride, form 1:2 complexes with SbF_5 which have been formulated as diacylium bis(hexafluoroantimonate) salts, $SbF_6^{-+}OC(CH_2)_xCO^{+-}SbF_6$, on the basis of ir and NMR spectral data.

Diacylium cations have not, so far, been generated from dicarboxylic acids; however, monoacylium cations have been prepared from monocarboxylic acids by Deno and his coworkers.[2-4] These authors emphasized the potential value of such species in organic syntheses.

This paper describes the formation of diacylium cations from tetrahalogenated terephthalic acids, and from the corresponding terephthaloyl fluorides, $YCOC_6X_4COY$ (X = Br or Cl and Y = OH or F). The preparation of the diacylium cations from the reaction of SO_3 with tetrabromoterephthalic acid, Br_4TA, and with tetrachloroterephthalic acid, Cl_4TA, is economic and useful since the relatively stable dications serve as intermediates for the large-scale syntheses of acid chlorides, amides, nitriles, esters, and polyanhydrides derived from tetrahaloterephthalic acids. This type of dicarboxylic acid is notable for its lack of reactivity, as has been pointed out by several investigators.[5-7] The new perhalopolyanhydrides reported here are stable substances at relatively high temperature and are also quite resistant toward alkaline hydrolysis.

Results and Discussion

Spectrophotometric Detection of Diacylium Cations from the Reaction of Tetrahaloterephthalic Acids with Sulfur Trioxide. The Br_4TA (1) is soluble in a mixture of SO_3 and SO_2 in 85:15 wt % proportion. The resulting red solution has absorption maxima in the infrared, ultraviolet, and visible regions of the spectrum as shown in Table I. These data are consistent with the diacylium bis