was dried and chromatographed on a cellulose column (500 × 25 mm); elution was carried out with system A, 45 20-ml fractions being collected. Evaporation of fractions 4 and 5 gave 60 mg (4.4%) of needles; purification from ethanol gave X, mp 179–181°, $[\alpha]^{30}_{D}$ +21.5° (*c* 0.5, water) [lit.[14] mp 180–181°, $[\alpha]_D$ +21.8° (water)]; it gave no depression of the melting point when mixed with an authentic sample of *N*-benzoyl-β-D-galactopyranosylamine. Paper chromatography run in system A (and detected with reagent B) gave only one spot, of the same $R_f$ as that of an authentic sample of *N*-benzoyl-β-D-galactopyranosylamine. Solubility of X was 0.536% (w/v) in ethanol at 20°. Fractions 8 and 9 gave 50 mg more of IX, mp 195–196°; recrystallization from ethanol gave mp 203–204°. Fractions 12–19 gave 30 mg (3.4%) of a syrup which, by paper chromatography run in system A and detected with reagent B, gave only one spot, of the same $R_f$ as D-galactose. By treatment of this syrup with *p*-nitrophenylhydrazine a *p*-nitrophenylhydrazone was obtained which, by paper chromatography run in system A, gave only one spot, of the same $R_f$ as an authentic sample of D-galactose *p*-nitrophenylhydrazone.

D-*glycero*-D-*galacto*-**Heptose Oxime (V).**—D-*glycero*-D-*galacto*-Heptose[23] (2.45 g) was added to a solution of 1.233 g of hydroxylamine hydrochloride in 0.7 ml of water to which had been added 0.400 g of sodium dissolved in 10 ml of methanol. The mixture was warmed for 10 min at 60°, and the oxime crystallized spontaneously. After 12 hr at room temperature, the mixture was cooled to 0° and filtered; 2.47 g (91%) of prisms, mp 170°, was obtained. After three recrystallizations from ethanol, V, mp 171–172°, $[\alpha]^{30}_{D}$ + 136.5° → + 101.2° (*c* 0.5, water), was obtained.

*Anal.* Calcd for $C_7H_{15}NO_7$: C, 37.33; H, 6.66; N, 6.22. Found: C, 37.58; H, 6.95; N, 5.82.

**Hexa-*O*-benzoyl-D-*glycero*-D-*galacto*-heptononitrile (VI).**—V (1.84 g) was added to 24 ml of 1:1 solution of benzoyl chloride in pyridine. The reaction was exothermic, and the temperature was kept at 100° by occasional cooling. After 24 hr at room temperature, the mixture was poured into 100 ml of cold water, and the resulting gummy material was washed several times with cold water until it became friable. It was filtered and recrystallized from acetone–ethanol (1:3); there resulted 5.10 g (75%) of rectangular plates, mp 159–160°. Recrystallization from the same solvent gave VI, mp 159–160°, $[\alpha]^{25}_{D}$ +29.4° (*c* 0.9, chloroform) [lit.[9] mp 161–163°, $[\alpha]_D$ +30° (chloroform)].

**Ammonolysis of VI. A. Isolation of 1,1-Bis(benzamido)-1-deoxy-D-mannitol (XI).**—VI (4 g) was dissolved, by shaking, in 100 ml of methanolic ammonia. After 24 hr at room temperature, the solution was evaporated, and the residual syrup was dissolved in 20 ml of boiling ethanol; by cooling and scratching, 600 mg of needles, mp 180°, was obtained. Recrystallization from ethanol gave 480 mg (22%) of XI, mp 227°, $[\alpha]^{32}_{D}$ +4.8° (*c* 1.6, pyridine) [lit. mp 226°,[9] 225–226;[17] $[\alpha]_D$ 3.6°,[9] +2.8°[17]].

**B. Isolation of *N*-Benzoyl-β-D-mannopyranosylamine (XII) and D-Mannose.**—The mother liquor was evaporated, and the resulting solid was dissolved in 5 ml of boiling ethanol; by cooling, 60 mg (4.4%) of XII, mp 246–247°, was obtained. After recrystallization from ethanol, the product melted at 254°, $[\alpha]^{30}_{D}$ +6.1° (*c* 1.4, pyridine) [lit. mp 254°,[9] 253–254°[17]; $[\alpha]_D$ +6.4°[17]]; it gave no depression of the melting point when mixed with an authentic sample of *N*-benzoyl-β-D-mannopyranosylamine. Paper chromatography run in system A (and detected with reagent B) gave only one spot, of the same $R_f$ as that of an authentic sample of *N*-benzoyl-β-D-mannopyranosylamine. Solubility of XII was 0.066% (w/v) in ethanol at 20°.

The mother liquor was evaporated, and the resulting syrup was extracted with four 40-ml portions of boiling ethyl acetate to remove the benzamide and dried; it gave 35 mg (3.5%) of a syrup which, by paper chromatography run with system A (and detected with reagent B) gave only one spot, of the same $R_f$ as D-mannose. By treatment of this syrup with *p*-nitrophenylhydrazine, a *p*-nitrophenylhydrazone was obtained which, by paper chromatography run in system A, gave only one spot, of the same $R_f$ as that of an authentic sample of D-mannose *p*-nitrophenylhydrazone.

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[23] R. M. de Lederkremer and J. O. Deferrari, *J. Org. Chem.*, **27**, 2558 (1962).

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# Reaction of Trialkylaluminums with Halohydrocarbons[1a]

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In the presence of ether, triethylaluminum smoothly effects replacement of benzylic halogens by ethyl groups (alkylation). Thus, benzyl chloride, (1-bromoethyl)benzene, trityl chloride, and benzal chloride yield 65–75% alkylation products. Reduction (up to 20% yield), which usually accompanies alkylation, becomes more important for benzotrichloride, which yielded 26% 3-ethyl-3-phenylpentane and 39% 3-phenylpentane. Primary, secondary, and tertiary haloalkanes show increasing reactivity toward triethylaluminum in the sequence given; the degree of dehydrohalogenation which accompanies alkylation and reduction increases in the same direction. Neopentyl and neophyl chlorides give only rearranged products. Trialkylaluminums and propargyl chloride give in 35–60% yield the corresponding alkylallene. Mechanisms are considered for the various reactions, and the behaviors of trialkylaluminums, alkyl Grignards, and alkyllithiums toward halohydrocarbons are compared.

Alkylaluminums show a formal similarity to such organometallics as alkyl Grignards and alkyllithiums. Speculations[2] that alkylaluminums, too, may react with organic halides as shown in eq 1 (alkylation)

$$\mathrm{Rm} + \mathrm{R'X} \longrightarrow \mathrm{RR'} + \mathrm{mX} \qquad (1)$$

$$\mathrm{m} = \text{a metal atom and one valency}$$

were therefore not unexpected. However, previous studies of the reactions of alkylaluminums with organic halides are fragmentary and inconclusive. In the presence of alkylaluminum halides or alkylaluminum halide–titanium halide mixtures, haloalkanes are variously reported to undergo dehydrohalogenation[2a,3,4] and alkylation.[5] Alkylation of organic halides having special reactivity is less ambiguous. α-Halo ethers[6–8] and allyl chloride[9] are alkylated by alkylaluminums, and 3-halopropylaluminum gives cyclopropane,[10] but, on the other hand, possible alkylation products of 2-chloropropane and triethylaluminum were not de-

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[1] (a) Much of this work was presented at the 20th Southwest Regional Meeting of the American Chemical Society, Shreveport, La., Dec 1964. (b) Polymer Sciences Department, Stanford Research Institute, Menlo Park, Calif.

[2] (a) K. Weyer, Ph.D. Thesis, Technischen Hochschule, Aachen, 1956; (b) H. Hoberg, *Ann.*, **656**, 1 (1962); (c) J. B. Rose, "The Chemistry of Cationic Polymerization," P. H. Plesch, Ed., The Macmillan Co., New York, N. Y., 1963, p 435; (d) D. B. Miller, *Tetrahedron Letters*, 989 (1964).

[3] The observed products may be olefins and an alkane generated by cleavage of the alkyl–aluminum bond by the hydrogen halide.

[4] R. Bacskai, *J. Polymer Sci.*, **A3**, 2491 (1965).

[5] R. T. Sanderson, U. S. Patent 2,404,599 (July 23, 1946).

[6] M. Gaudemar, *Compt. Rend.*, **243**, 1216 (1956).

[7] L. Groizeleau-Miginiac, *Ann. Chim.* (Paris), **6**, 1071 (1961).

[8] K. Weissermel and E. Nölken, *Makromol. Chem.*, **68**, 140 (1963).

[9] D. W. Marshall and W. R. Sorenson, unpublished work.

[10] P. Binger and R. Köster, *Tetrahedron Letters*, 156 (1961).

termined,[11] and, although cyclic ethers are readily polymerized in the presence of triethylaluminum and epichlorohydrin, no reactions of these catalyst components were described.[8]

In the presence of trialkylaluminums, polyhalomethanes undergo halogen–metal exchange which leads to carbenoid reactions.[2d,13,14] Possible carbenoid reactions of such *gem*-polyhalohydrocarbons as 2,2-dichloropropane and benzotrichloride were the initial concern of the present study; subsequently, the reactions of trialkylaluminums with a variety of organic halides were investigated.

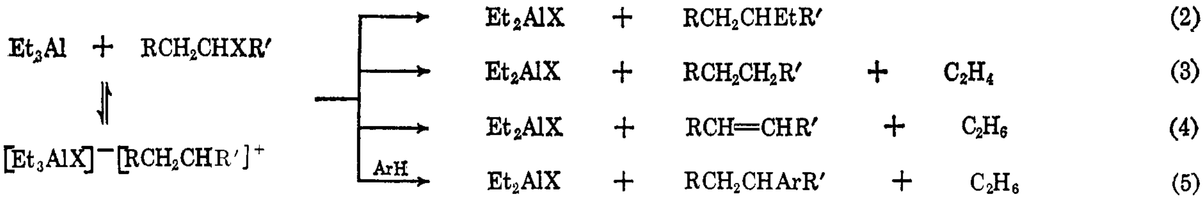
Initial attempts to mix triethylaluminum and benzotrichloride gave nearly violent reactions and complex reaction mixtures. Benzyl chloride reacted nearly as vigorously giving propylbenzene along with much higher boiling material which apparently resulted from a Friedel–Crafts self-alkylation. The finding that addition of the organic halide to excess triethylaluminum in the presence of ethyl ether gave smooth reactions, with negligible formation of Friedel–Crafts products, stimulated a wider study in this area.[15]

The results of the present investigation are summarized in Table I. For benzylic halides, the principal reaction is alkylation, but significant reduction also occurs. Benzal chloride and benzotrichloride undergo both reactions with reduction becoming more important as alkyl groups are added to the benzylic atom.[16] Only rearranged products were observed from the reaction of neophyl chloride [(2-chloro-1,1-dimethylethyl)benzene]; again alkylation predominated, but reduction and dehydrohalogenation were also significant. Free 3-phenylpentane (from benzotrichloride) and isobutylbenzene (from neophyl chloride) were present in the reaction mixtures before hydrolysis. Moreover, ethylene comparable in yield with the isobutylbenzene was formed in the neophyl chloride reaction. Therefore, halogen–metal exchange is not significant in these reactions. Undetected isomerization presumably accompanied the alkylation of (2-chloroethyl)benzene. Only this (haloalkyl)benzene gave no detectable reduction product. Dehydrohalogenation became important for the alkyl halides and was the principal reaction of secondary and tertiary halides. Accompanying the dehydrohalogenation were reduction and alkylation; the latter predominated for 1-haloalkanes. A little isomerization accompanied the alkylation of 1-chlorooctane, and neopentyl chloride gave only rearranged products.

Trialkylaluminums smoothly alkylate propargyl chloride; 1,2-dienes constitute the principal products. That only one of the three alkyl groups can be utilized[17] is in accord with the absence of coupling observed in the preparation of propargylaluminum sesquibromide from aluminum and propargyl bromide.[19]

α-Halo ethers react readily with alkylaluminums,[8] but bis(2-chloroethyl) ether reacted only at elevated temperature. Epichlorohydrin showed an intermediate reactivity.

While other mechanisms are not rigorously excluded, the present results suggest that benzylic and alkyl halides react with alkylaluminums by electrophilic processes, as shown in the following scheme (eq 2–5).[20]



The course of the reaction depends on the nature of the reactants and the reaction conditions. In the presence of aromatic compounds, electrophilic attack may occur at the aromatic ring; *i.e.*, the Friedel–Crafts reaction (eq. 5) may prevail.[22] When the Friedel–Crafts reaction is not favored, electrophilic attack occurs at an alternative electron-rich center, the tetracoordinated aluminum complex. This attack may take a number of paths. Attack on halogen regenerates the starting (or an isomeric) halohydrocarbon. Alkylation occurs by attack at the Al–C bond (eq 2). Transfer of a β-hydrogen from the complex effects reduction (eq 3)[23] and transfer of a proton to the complex results in dehydrohalogenation (eq 4). The intermediate may be a relatively free carbonium ion, an ion pair, or a polar complex. The transient yellow color noted with the benzylic halides indicates that they, like tropenium bromide, have a high degree of ionic character in their reactions. The partial isomerization observed when triethylaluminum alkylates 1-haloalkanes and the rearrangements experienced by the neophyl and neopentyl systems suggest that reactions of alkyl halides

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(11) Reported products (unspecified yield) are ethylene, ethane, propene, propane, and butane.[12]

(12) A. G. Pozamantir and M. L. Genusov, *J. Gen. Chem. USSR*, **32**, 1149 (1962).

(13) J. W. Collette, *J. Org. Chem.*, **28**, 2489 (1963).

(14) The reaction of trialkylaluminums and polyhalomethanes *via* radicals has also been reported: H. Reinheckel, *Tetrahedron Letters*, 1939 (1964).

(15) Diethylaluminum chloride, a product of these reactions, is a more active Friedel–Crafts catalyst than triethylaluminum and is probably the cause of most of the Friedel–Crafts-type reactions. The deactivation of diethylaluminum chloride by its preferential coordination with ether may explain the success of this reaction system.

(16) A possible mixed alkylation and reduction reaction with ethylaluminum sesquichloride has also been reported: H. Reinheckel, *Angew. Chem.*, **76**, 646 (1964).

(17) Although this was established only for the propargyl chloride reaction, the reduced reactivity of the second and third alkyl groups has been observed in numerous reactions of trialkylaluminums.[2a,18]

(18) K. Ziegler, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p 238 ff.

(19) M. Gaudemar, *Ann. Chim.* (Paris), [13] **1**, 161 (1956).

(20) That alkyl halides and trialkylaluminums react *via* cationic intermediates has been suggested previously.[12,21]

(21) G. Natta, I. Pasquon, E. Giachetti, and F. Scalari, U. S. Patent 2,971,950 (Feb 14, 1961).

(22) In the presence of organoaluminum compounds, alkyl halides reportedly yield the "corresponding" alkylbenzenes.[12] We found that at 25° 1-chloropropane and diethylaluminum chloride in benzene give propylbenzene (24%) and isopropylbenzene (32%), but no ethylbenzene. Neither propene nor cyclopropane reacted, even at 80°.

(23) Use of hydride-free triethylaluminum did not lessen the reduction of benzotrichloride, and the presence of added diethylaluminum hydride did not drastically affect the neophyl chloride reaction. Moreover, triethylaluminum is converted to diethylaluminum hydride only at elevated temperature.[24] Therefore, triethylaluminum, not diethylaluminum hydride, is the probable reducing agent.

(24) Reference 18, p 216.

TABLE I

REACTION OF ORGANIC HALIDES WITH TRIETHYLALUMINUM

| Halide | Temp, °C[a] | Ether present | Products | Yield, %[b] | Identification[c] |
|---|---|---|---|---|---|
| $C_7H_7Br$[d] | 0–25 | Yes | 7-Ethylcycloheptatriene | 74 | A, B |
| | | | Cycloheptatriene | 14 | A |
| $Ph_3CCl$ | 0–25 | Yes | 1,1,1-Triphenylpropane | 70 | B, C |
| | | | Triphenylmethane | 18 | A, D |
| $PhCHBrCH_3$ | 0–25 | Yes | 2-Phenylbutane | 67 | B, C |
| | | | Ethylbenzene | 15 | A, B, C |
| $PhCH_2Cl$ | 0–25 | Yes | Propylbenzene | 69 | A, B, C |
| | | | Toluene | 3 | A, C |
| $PhCHCl_2$ | 0–25 | Yes | 3-Phenylpentane | 68 | C |
| | | | Propylbenzene | 18 | A, C |
| $PhCCl_3$ | 0–25 | Yes | 3-Ethyl-3-phenylpentane | 26 | B, C |
| | | | 3-Phenylpentane | 39 | B, C |
| | | | Propylbenzene | 7 | A, B |
| $PhC(CH_3)_2CH_2Cl$ | 0–25 | Yes | 2,2-Dimethyl-1-phenylbutane | 53 | B, C |
| | | | Isobutylbenzene | 27 | B, E |
| | | | 2-Methyl-1-phenylpropene | 9 | B, C |
| $PhCH_2CH_2Cl$ | 50–100 | Yes | Butylbenzene | 89 | A, B |
| $CH_3CCl_2CH_3$ | 0–25 | No | 2-Chloropropene | *e* | B |
| BuEtMeCCl | 0–25 | Yes | 3-Ethyl-3-methylheptane[f] | 21 | B, C |
| $CH_3CHClC_2H_5$[g] | 25–50 | Yes | 3-Methylpentane | 40 | A, C |
| | | | 2-Methylpentane | 8 | A |
| $CH_3CHCl(CH_2)_5CH_3$ | 25–50 | Yes | 3-Methylnonane | 28 | C |
| | | | Linear octenes[h] | 42 | B, C |
| | | | Octane | 9 | A, C |
| $CH_3(CH_2)_7Cl$[i] | 100–150 | Yes | Decane | 49 | A |
| | | | 3-Methylnonane | 2 | A |
| | | | Linear octenes | 5 | A |
| | | | Octane | 23 | A |
| $(CH_3)_3CCH_2Cl$ | 50–100 | Yes | 3,3-Dimethylpentane | 40 | B, C |
| | | | 2-Methyl-2-butene | 17 | A |
| | | | 2-Methyl-1-butene | 1 | A |
| | | | 2-Methylbutane | 17 | A |
| $HC\equiv CCH_2Cl$ | 25–50 | Yes | 1,2-Pentadiene | 50 | B, C, E |
| | | | 1-Pentyne | 2 | A |
| $HC\equiv CCH_2Cl$[j] | 25–50 | No | 1,2-Heptadiene | 59 | B, C, E |
| | | | 1-Heptene | 2 | A |
| $HC\equiv CCH_2Cl$[k] | 25–50 | No | 5-Methyl-1,2-hexadiene | 35 | B, C, E |
| | | | 5-Methyl-1-hexene | 12 | F |
| $C_7H_8Br_2$[l] | 0–25 | Yes | Diethylcycloheptadiene[m,n] | 37 | C |
| $\overline{OCH_2CH}CH_2Cl$ | 25–50 | . . . | 1,2-Epoxypentane | 43 | B, C |
| $(ClCH_2CH_2)_2O$ | 100–150 | . . . | Butyl ether | *e* | A |

[a] Range which gave convenient rate. [b] Determined by vpc analysis. [c] A, vpc comparison with authentic sample; B, structure conforms with nmr spectrum; C, structure conforms with mass spectrum; D, melting point undepressed by authentic sample; E, structure conforms with infrared spectrum; and F, tentative identification. [d] Tropenium bromide. [e] Not determined. [f] Considerable polymer also formed. [g] $C_4$ products, if any, were not analyzed. [h] Shown by nmr analysis to contain *ca.* 75% 2-octene with decreasing amounts of 3- and 4-octene. [i] 1-Bromooctane gave a similar product mixture. [j] Reacted with tributylaluminum. [k] Reacted with triisobutylaluminum [l] Cycloheptatriene dibromide. [m] Detailed structure not determined. [n] Cycloheptatrienes were not detectable.

with alkylaluminums also have appreciable ionic character. That ionic intermediates are not mandatory, however, is indicated by the nonisomerization of much of the alkylated 1-chlorooctane.[25]

While present knowledge of the propargyl chloride reaction does not allow firm conclusions about mechanism, some possibilities can be discounted. Since 1,2-pentadiene is not formed from 1-pentyne at the conditions of the reaction, the latter cannot be an intermediate. The acidic nature of trialkylaluminums makes any nucleophilic mechanism unlikely. A proposed intermediate in the reaction of propargyl halides with Grignard reagents is vinylidenecarbene.[26] That this species is not involved in the reactions of propargyl chloride with trialkylaluminums is indicated by the following results. (a) The free 1,2-dienes are present in the reaction mixtures *before* hydrolysis (nmr analysis). (b) When reacting in cyclohexene or styrene, triethylaluminum and propargyl chloride give the usual yields of 1,2-pentadiene; no cyclopropane derivatives were observed. One possible mechanism is an ionic process similar to the one suggested for benzylic and alkyl halides, with an intermediate which acts as an allenyl cation. Another possibility involves a quasi-

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(25) After this work was nearly completed, it was learned that H. Kaar and G. Schwindlerman [*Izv. Akad. Nauk Eston. SSR, Ser. Tekh. i Fiz.-Mat. Nauk*, **13** (2), 148 (1964); *Chem. Abstr.*, **61**, 10695 (1964)] have described the reaction of triisobutylaluminum with 1-chloroheptane, 1-chlorononane, 2-chloro-2-methylpropane, allyl chloride, benzyl chloride, and trityl chloride. Cationic reaction intermediates were proposed, but it was concluded that the alkylation reaction did not occur.

(26) F. Serratosa, *Tetrahedron Letters*, 895 (1964).

cyclic six-membered transition state which would necessitate the propargyl–allenyl rearrangement.[27]

We can now compare the behavior of alkylaluminums *vis-à-vis* halohydrocarbons with that of the more traditional alkyl Grignards and alkyllithiums. Comparisons can be made of both mechanisms and products. Possible modes of reaction are alkylation, reduction, $\beta$ elimination, metalation ($\alpha$ elimination), halogen–metal exchange, and the Friedel-Crafts reaction.[28] The tendency for halogen–metal exchange decreases from lithium to magnesium to aluminum. Many examples of lithium–halogen exchange are known,[31] but magnesium–halogen exchange is less prevalent.[31d,31e,32] Halogen–metal exchange with trialkylaluminums is reported only for polyhalomethanes.[2d,13,33] Metalation of halohydrocarbons is also effected most readily by alkyllithiums. Examples of this are unambiguous.[31g,34] However, such metalations by alkyl Grignards[26] are questionable, and metalation of halohydrocarbons by alkylaluminums is not known. Alkyllithiums,[35] alkyl Grignards,[32] and alkylaluminums can each cause alkylation, reduction, and $\beta$ elimination, but only alkylaluminums are likely to participate in Friedel–Crafts reactions.

With so many paths available, reactions of halohydrocarbons and organometallics may well be expected to give mixtures of products. The results fulfill all expectations. Since the utility of a reaction is determined by the products, a brief comparison of the products arising from the various reactions is in order. Alkyl Grignards[19] and trialkylaluminums react with propargyl halides to give fair yields of 1,2-dienes which contain little of the isomeric alkynes. The reaction of propargylic halides with alkyllithiums, while somewhat obscure, apparently proceeds at least in part *via* vinylidenecarbenes.[36] Tropenium salts and trityl (triphenyl methyl) halides, with trialkylaluminums or alkyl Grignards,[32,37] give good yields of alkylation products. Again, the reactions with alkyllithiums are less well delineated.[30,34b] Reaction of alkyllithiums,[35] alkyl Grignards,[32] and alkylaluminums with alkyl halides gives mixtures resulting from varying amounts of reduction, dehydrohalogenation, and alkylation; thus, the synthetic applications of these reactions are limited. Alkyllithiums[31a,g] and alkyl Grignards,[29,32] upon reaction with benzylic halides, often yield complex mixtures which contain bibenzyl, stilbene, and related compounds, but relatively little alkylbenzene from the simple alkylation reaction. Triethylaluminum is distinctive by effecting alkylation of benzylic halides (including benzal chloride) in good yield. Reduction, which is the only significant side reaction, becomes serious only with benzotrichloride. Fairly good yields of rearranged alkylation products result from the reactions of triethylaluminum with neopentyl and neophyl chlorides.[38] The cleanest reaction found in this study is the alkylation of (2-chloroethyl)benzene. Among the reactions of halohydrocarbons with alkylaluminums, the preparation of alkylbenzenes by the alkylation of ($\alpha$- and $\beta$-haloalkyl)benzenes is synthetically the most promising.

## Experimental Section

**General.**—Cycloheptatriene dibromide (not isolated) and tropenium bromide were prepared from cycloheptatriene and bromine.[40] 3-Chloro-3-methylheptane,[41] neophyl chloride,[41] propargyl chloride, 2,2-dichloropropane (K & K Laboratories), neopentyl chloride (Matheson Co.), and the other halides (Eastman Kodak Co.) were used as received or after drying over calcium hydride. No significant impurities were detected in halides (*e.g.*, benzotrichloride, propargyl chloride, and 1-chlorooctane) which were analyzed. Triethylaluminum (Ethyl Corp.) which contained about 3 mole % hydride and 2 mole % butyl groups (based on Al–R bonds), triisobutylaluminum, and tributylaluminum (Texas Alkyls Co.) were used as received.

Reactions were conducted in 225-ml beverage bottles which had been cooled under argon, filled with the required solvent, and capped with solvent-resistant rubber septa (Firestone Tire and Rubber Co.) secured by perforated metal caps. Reagents were added with syringes. Alkylaluminums were transferred in a nitrogen-filled glove box; the organic halides were added last.[42] The more slowly reacting systems were monitored by nmr analysis. If no reaction occurred within 1 week at 25°, the mixture was kept for 1 week at 50°. If necessary, the mixture was heated at 100 or 150° to cause reaction. Products identified by nmr, mass, and/or infrared spectroscopy were isolated by distillation or preparative vpc.[43] Illustrative procedures are given below.

**Benzotrichloride and Triethylaluminum.**—The cautious addition at 10–20° of benzotrichloride (4.9 g, 25 mmoles) diluted with 20 ml of hexane to a mixture of triethylaluminum (20.5 ml, 150 mmoles) and ethyl ether (7.8 ml, 75 mmoles) in 50 ml of hexane caused a transient yellow coloration. After 4 days at 25°, the colorless solution was treated with 8 ml of additional ethyl ether and hydrolyzed by addition to 75 ml of cold 10% sodium hydroxide. The low-boiling portion of the organic layer was removed by distillation. Nmr analysis of the less volatile portion indicated the presence of propylbenzene, 3-phenylpentane, and 3-ethyl-3-phenylpentane; the yields (vpc analysis) were 7, 39, and 26%, respectively. Comparative vpc analysis confirmed the identity of propylbenzene. 3-Phenylpentane and 3-ethyl-3-phenylpentane were isolated by preparative vpc; the former was identified by its mass spectrum,[44] the latter by its mass (molecular ion at 176, expected

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[27] That propargylic systems may react *via* a cyclic ($S_Ni'$) mechanism has been suggested by R. J. D. Evans, S. R. Landor and R. T. Smith, *J. Chem. Soc.*, 1506 (1963).

[28] Reactions of alkylmetals and halohydrocarbons *via* free-radical processes have also been reported.[14,29,30]

[29] F. L. Bach, Jr., *Dissertation Abstr.*, **24**, 3039 (1964).

[30] F. S. D'yachkovskii, N. N. Bubnov, and A. E. Shilov, *Dokl. Akad. Nauk SSSR*, **123**, 870 (1958); *Chem. Abstr.*, **55**, 7996 (1961).

[31] For example, see (a) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944); (b) R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 339 (1951); (c) W. T. Miller, Jr., and C. S. Y. Kim, *J. Am. Chem. Soc.*, **81**, 5008 (1959); (d) V. Franzen and L. Fikentscher, *Chem. Ber.*, **95**, 1958 (1962); (e) W. Reeve and L. W. Fine, *J. Am. Chem. Soc.*, **86**, 880 (1964); (f) G. L. Closs and R. A. Moss, *ibid.*, **86**, 4042 (1964); (g) D. F. Hoeg and D. I. Lusk, *ibid.*, **86**, 928 (1964).

[32] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, Chapter 16.

[33] H. Gilman and A. H. Haubein [*J. Am. Chem. Soc.*, **67**, 1033 (1945)] reported an example of possible halogen–aluminum exchange with ethylaluminum sesquiiodide.

[34] (a) G. W. Gibson, *Dissertation Abstr.*, **24**, 2689 (1964); (b) G. L. Closs and L. E. Closs, *Tetrahedron Letters*, **No. 10**, 38 (1960); (c) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960).

[35] J. F. Eastham and G. W. Gibson, *J. Org. Chem.*, **28**, 280 (1963).

[36] H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4990 (1961).

[37] K. Conrow, *ibid.*, **83**, 2343 (1961).

[38] No reactions of these neo halides with alkyllithiums or alkyl Grignards were found, but reaction of either halide with alkylsodiums gives principally cyclopropane derivatives.[39]

[39] (a) F. C. Whitmore and H. D. Zook, *ibid.*, **64**, 1783 (1942); (b) F. C. Whitmore, C. A. Weisgerber, and A. C. Shabica, Jr., *ibid.*, **65**, 1469 (1943).

[40] W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

[41] Kindly furnished by Dr. A. J. Lundeen.

[42] Although alkylaluminums and certain organic halides may react violently, reactions employing excess alkylaluminums have proceeded safely. Nevertheless, caution is required.

[43] Resoflex 728 (polyethylene succinate), polyethylene, Carbowax 20M (polyoxyethylene), and SE 30 (silicone gum rubber) columns were used.

[44] "Catalog of Mass Spectral Data," American Petroleum Institute Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., 1959, Spectrum No. 1185.

cracking pattern) and nmr (expected signals in the proper ratio) spectra. Benzylic hydrogen (nmr signal at *ca.* $\delta$ 2.7) was clearly present in the triethylaluminum–benzotrichloride reaction mixture before hydrolysis. Hydrolysis with deuterium oxide did not lead to detectable (mass analysis) deuteration of the 3-phenylpentane. Use of hydride-free triethylaluminum (distilled from 1-octadecene) did not significantly alter the product composition. When the ether and the alkylaluminum in the reaction mixture were equimolar, the benzylic halide reactions were incomplete.

The neophyl chloride–triethylaluminum reaction was also rapid (but less vigorous than the benzylic halide reactions) at 10°. Isobutyl benzene (doublet nmr signal in the benzylic H region) was present in the reaction mixture before hydrolysis. The gas evolved before hydrolysis contained 30% ethane and 64% ethylene (7.6 and 17% yield, respectively, based on neophyl chloride). Reaction of neophyl chloride with a mixture of 2 molar equiv each of triethylaluminum and diethylaluminum hydride, and 1 equiv of butyl ether gave 2,2-dimethyl-1-phenylbutane and isobutylbenzene in 42 and 36% yield, respectively.

**Propargyl Chloride and Tributylaluminum.**—Addition of propargyl chloride (5.0 g, 68 mmoles) to a solution of tributylaluminum (17 ml, 70 mmoles) in 30 ml of xylene caused no indication of immediate reaction. After 2 days at 25°, the mixture was hydrolyzed by adding cautiously to dilute hydrochloric acid. Distillation of the neutralized organic layer gave 4.4 g of product boiling principally at 96–101°. The product contained 88% 1,2-heptadiene (3.9 g, 40 mmoles, 59%), identified by mass and nmr spectra and by comparison of its infrared spectrum with a published spectrum.[45] At most, a trace of 1-heptyne was present. 1-Heptene (1.5% yield) accompanied the heptadiene.

Triethylaluminum and triisobutylaluminum reacted similarly with propargyl chloride. A larger scale reaction with triethylaluminum gave a pronounced exotherm. Although propargyl chloride and diethylaluminum chloride reacted slowly at 25° to give a dark brown mixture, no 1,2-pentadiene was detectable among the products (these and the following results were obtained with nmr analysis). Propargyl chloride and triethylaluminum in cyclohexene or styrene gave the usual yields of 1,2-pentadiene. Triethylaluminum and diethylaluminum chloride reacted slowly with 1-pentyne; however, no 1,2-pentadiene was formed.

**1-Chlorooctane and Triethylaluminum.**—After 18 days at 100°, a mixture of 1-chlorooctane (5.2 g, 35 mmoles), triethylaluminum (15 ml, 110 mmoles), and ethyl ether (2.7 g, 36 mmoles) in 50 ml of hexane was treated with additional ether (15 ml) and hydrolyzed with 20% sodium hydroxide. The organic hydrolysate was analyzed, and the constituents (1.4% unreacted 1-chlorooctane, decane, 3-methylnonane, octenes, and octane) were identified by vpc. 3-Methylnonane was identified by comparison with the product prepared from 2-chlorooctane.

2-Chlorooctane and 3-chloro-3-methylheptane reacted with triethylaluminum at lower temperatures than did 1-chlorooctane; otherwise, the same procedure was used. The product mixtures obtained from 1- and 2-chlorooctane in the absence of ether were similar to the mixtures obtained with ether.

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[45] J. H. Wotiz, *J. Am. Chem. Soc.*, **73**, 693 (1951). The spectrum was compared with the spectrum of the 103° boiling product in Figure 1.

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# Tropyl as a Migrating Group. I.
# The Acetolysis of 2-Tropyl-2-phenylethyl *p*-Toluenesulfonate

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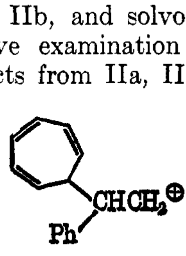
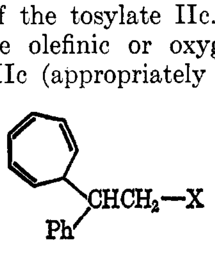
2-Tropyl-2-phenylethyl *p*-toluenesulfonate (IIc) has been prepared from 2-tropyl-2-phenylethanol, obtained in turn by reduction of 2-tropyl-2-phenylacetic acid. The latter acid was prepared by the alkylation of phenylmalonic acid with tropylium bromide in pyridine. Acetolysis of tosylate IIc in refluxing acetic acid yielded a hydrocarbon fraction containing 15% *cis*- and 85% *trans*-1,3-diphenylpropene (III) and an acetate fraction containing seven as yet uncharacterized components. A mechanism is proposed for the ring contraction involved in the transformation IIc → III.

To the best of our knowledge, the 1,3,5-cycloheptatrien-7-yl (tropyl) group has never been observed as a stable migrating entity in cationic 1,2 shifts. Furthermore, recent reviews of the chemistry of cycloheptatriene and its numerous derivatives[3] fail to record experiments specifically designed to examine the possibility that the tropyl group may act as a 1,2 migrant, or—if so—to establish its relative migratory aptitude. Our interest in molecular rearrangements has prompted us to examine this problem, and our preliminary observations are reported herewith.

Our initial efforts have involved attempts to generate the 2-tropyl-2-phenylethyl carbonium ion (I) during dehydration of the alcohol IIa, deamination of the amine IIb, and solvolysis of the tosylate IIc. Degradative examination of the olefinic or oxygenated products from IIa, IIb, or IIc (appropriately labeled with carbon-14 at C-1 or C-2) would then allow evaluation of the relative extents to which phenyl or tropyl had migrated in I prior to its irreversible product-forming step. This simple labeling technique has been successfully utilized to establish relative migra-



I



IIa, X = OH
b, X = $NH_2$
c, X = OTs

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[1] National Science Foundation Science Teaching Faculty Fellow, 1962–1963.

[2] National Science Foundation Science Teaching Faculty Fellow, 1960–1961.

[3] (a) T. Nozoe in "Non-Benzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter VII; (b) A. Heusner, *Angew. Chem.*, **70**, 693 (1958); (c) W. von E. Doering and H. Krauch, *ibid.*, **68**, 661 (1956); (d) P. L. Pauson, *Chem. Rev.*, **55**, 9 (1955); (e) W. Baker and J. F. W. McOmie, *Progr. Org. Chem.*, **3**, 62 (1955); (f) A. W. Johnson, *J. Chem. Soc.*, 1331 (1954); (g) J. W. Cook and J. D. Loudon, *Quart. Rev.* (London), **5**, 99 (1951).