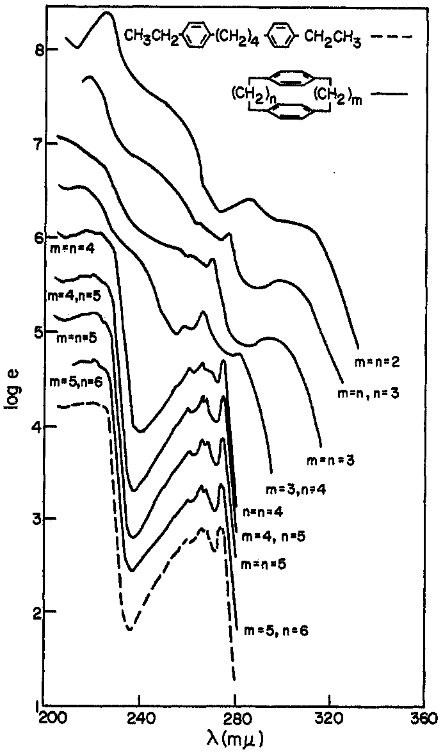

Figure 3.—Absorption spectra of paracyclophanes (each successive curve has been displaced upward by 0.5 log units, omitting the open-chair compounds).

and ϵ_{max} (~1000) very similar to that of [4,4]paracyclophane (λ_{max} 2630; ϵ_{max} 1300). The percyclophane-4 spectra, however, shows only the very broad absorption with no fine structure due to the steric strain and rigidity of the molecule.

Several attempts were made to synthesize similar trimers of commercially available[7] 1,6 cyclotridicadiyne and 1,8-cyclotetradecadiyne, but no tractable products could be isolated. We are presently investigating the chemical properties of this unusual molecule.

Experimental Section

Synthesis of Cyclododecadiyne.—In a 2-l., three-neck flask was placed 1 l. of liquid ammonia. To this was added 1.25 g of $Fe(NO_3)_3 \cdot 9H_2O$. The contents of the flask were blanketed with nitrogen at all times; 4.10 g (0.59 mol) of lithium wire was added in small chunks slowly to the flask. All of the lithium wire had dissolved within 15 min after addition was complete. Over a period of 10 min, 63 g (0.59 mol) of octadiyne-1,7 was added. The reaction mixture was stirred for 1.5 hr.

Into a second 2-l. flask was placed 125 ml of dry, distilled dioxane containing 102.5 g (0.59 mol) of $Br(CH_2)_4Cl$ (K and K Laboratories). The liquid ammonia solution from the first flask was pumped with nitrogen pressure through a filter stick into the second flask. This reaction mixture was allowed to warm with stirring overnight until all of the ammonia was evaporated. Upon evaporation of the ammonia, 500 ml of *n*-heptane was added, then 500 ml of water, and the phases were shaken and separated. The aqueous layer was extracted twice more with 200-ml portions of *n*-heptane. The combined *n*-heptane solutions were washed twice with 300-ml portions of 5% HCl solution and then dried over anhydrous Na_2SO_4. Removal of the *n*-heptane gave 100.2 g of crude product which upon distillation yielded 56 g (50%) of 1-chlorododecadiyne-5,11 (II): major infrared bands 3300, 2920, 2860, 2110, 1430, and 600–650 cm^{-1}; nmr triplet centered at δ 3.58 and complex multiplets centered at δ 2.13 and 1.60 with relative areas 2:7:8.

In a 60-ml glass ampoule was placed 5.0 g of II along with 7.60 g of NaI dissolved in 30 ml of dry acetone. The ampoule was sealed and heated at 80° for 17 hr. The ampoule was opened, and the NaCl was filtered off and washed with ether. Upon dilution of the acetone solution with ether the excess NaI precipitated and was filtered off. Removal of the solvent yielded 6.9 g (94%) of 1-iodododecadiyne-5,11 (III): major infrared bands 3300, 2920, 2860, 2110, 1430, and broad absorption centered around 500 cm^{-1}; nmr triplet centered at δ 3.20 and complex multiplets centered at δ 2.15 and 1.60 with relative areas of 2:7:8.

Into a 2-l., three-neck flask with air stirrer, cold trap, and inert gas head was placed 1 l. of liquid ammonia. $Fe(NO_3)_3 \cdot 9H_2O$ (0.1 g) and then 0.13 g (0.019 g-atom) of Li wire cut into small pieces were added. When the Li had dissolved, 4.28 g (0.015 mol) of III dissolved in 250 ml of dry ether was added dropwise over a period of 4.5 hr. Upon completion of the addition, the ammonia was allowed to evaporate. The product was worked up exactly as described for compound II and this work-up yielded 1.64 g of light yellow oil. This crude product contained residual compound II and III as well as cyclododecadiyne-1,7 (I). The crude product was chromatographed on Woelm neutral alumina, eluting with a gradient of hexane and benzene. Yield of purified cyclododecadiyne was 0.87 g (0.054 mol, 36%). The product crystallized upon refrigeration into large, colorless needles: mp 20 ± 2°;[2] major infrared bands 2900, 2820, 1430, 1330, 755 cm^{-1} (w); nmr showed broad multiplets centered at δ 2.10 and 1.70 with relative areas of 1:1.

Anal. Calcd: C, 90.0; H, 10.0. Found: C, 89.7; H, 10.1.

Percyclophane. Catalysis by Dimesitylcobalt.—Mesitylmagnesium bromide solution in THF was prepared and standardized by standard techniques. High-purity Mg (99.99%) was used in the preparation. Into a 25-ml, three-neck flask, with nitrogen purge, was placed 0.65 g (5.0 mmol) of anhydrous $CoCl_2$, then 58.5 ml (15.0 mmol) of a 0.0256 *M* solution of mesitylmagnesium bromide. The flask temperature was kept at −20° and the solution was stirred for 10 hr. In a second 200-ml flask was placed 1.60 g (10.0 mmol) of cyclododecadiyne dissolved in 50 ml of dry THF. To this was added 2.0 ml of the mesitylmagnesium bromide–$CoCl_2$ solution. The reaction mixture was allowed to stir at −30 to −40° for 2 hr, then allowed to warm to room temperature. The resulting solution was diluted with ether, and this ether phase was washed with water and 5% HCl solution, and then dried over anhydrous K_2CO_3. Removal of the solvent left 2.25 g of a greenish solid. This crude material was placed in a vacuum sublimation apparatus and heated at 150° (0.1 mm). A white, crystalline material, 1.1 g (70%), sublimed: mp 235°, mass spectral analysis showed parent ion of $C_{36}H_{48}$ (mol wt 480.78); major infrared bands 3000, 1450, 730 cm^{-1} (vw); nmr broad resonance centered at δ 2.90, 2.30, and 1.70 with relative areas of 1:1:2.

Anal. Calcd for $C_{36}H_{48}$: C, 90.0; H, 10.0. Found: C, 89.5; H, 9.6.

Registry No.—I, 4641-85-4; II, 39253-36-6; III, 39253-37-7; lithium amide, 7782-89-0; 1-bromo-4-chlorobutane, 6940-78-9; 1,7-octadiyne, 871-84-1; percyclophane-4, 39253-39-9.

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[7] Farchan Research Laboratories, Willouby, Ohio.

Methylation and Chlorination of Internal Olefins with Trimethylaluminum and Hydrogen Chloride

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In the course of our investigations on the fundamentals of cationic polymerizations initiated by alkylaluminum compounds, we are using small molecule model reactions to elucidate aspects of the polymerization mechanism. Since trialkylaluminums or dialkylaluminum halides (*e.g.*, Me_3Al, Et_3Al, Et_2AlCl) in conjunction with suitable cationogens (*e.g.*, HX or *t*-BuX) are most efficient initiator systems for the synthesis of high molecular weight polymers at relatively high temperatures,[1] we have been interested in exploring the chemis-

TABLE I

REACTION OF CYCLOHEXENE AND 1-METHYLCYCLOHEXENE WITH TRIMETHYLALUMINUM AND HYDROGEN CHLORIDE IN ETHYL CHLORIDE AT −50°

Reactants and their sequence of mixing	Products (%)
Cyclohexene + HCl	No reaction
Cyclohexene + Me$_3$Al + HCl	Chlorocyclohexane (14), cyclohexene (80)
Cyclohexene + HCl + Me$_3$Al	Chlorocyclohexane (72), cyclohexene (24)
Cyclohexene + HCl + Me$_3$Al[a]	Chlorocyclohexane (50), methylcyclohexane (10), cyclohexene (10), plus unidentified higher boiling products
1-Methylcyclohexene + Me$_3$Al + HCl	1,1-Dimethylcyclohexane (28) 1-methylcyclohexene (36), plus unidentified higher boiling products
1-Methylcyclohexene + HCl + Me$_3$Al	1,1-Dimethylcyclohexane (92)

[a] In CH$_2$Cl$_2$ at 23° for 48 hr.

try of these species in depth. The facile, clean synthesis of quarternary carbon containing hydrocarbons from tertiary chlorides and trialkylaluminum compound has already been reported[2] (eq 1). These studies have now

$$t\text{-RCl} + \text{R}_3'\text{Al} \longrightarrow t\text{-RR}' + \text{R}_2'\text{AlCl} \quad (1)$$

been extended to the "methanation" (addition of the elements of CH$_3$H across a double bond) of (nonpolymerizable) olefins, *e.g.*, cyclohexene, by the use of Me$_3$Al and HCl. The results of these studies are of interest, as they provide deeper insight into the mechanism of cationic polymerizations.

Results

Cyclohexene and 1-methylcyclohexene have been treated with trimethylaluminum and hydrogen chloride in ethyl chloride at −50°. The mixing sequence of the reactants and the results are shown in Table I.

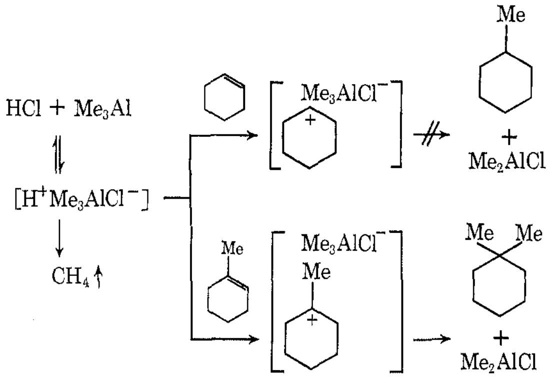
Discussion

We have reported that the reaction of *tert*-butyl halide with trimethylaluminum gives rapidly and quantitatively neopentane.[2] The reaction was proposed to go through a *tert*-butyl cation–trimethylaluminum chloride counterion pair (eq 2). Thus the neo-

$$t\text{-BuCl} + \text{Me}_3\text{Al} \rightleftharpoons [t\text{-Bu}^+\text{Me}_3\text{AlCl}^-] \longrightarrow t\text{-BuMe} + \text{Me}_2\text{AlCl} \quad (2)$$

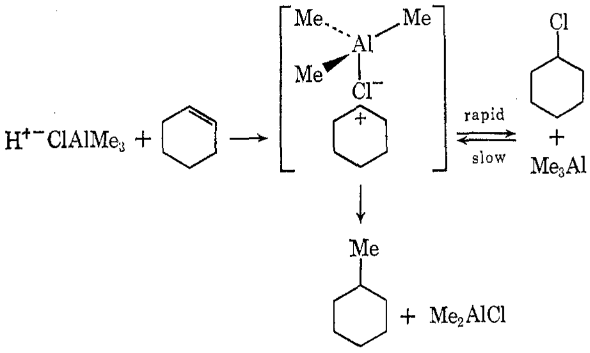
pentane is formed by a transfer of methyl group from the counterion to the *tert*-butyl cation.

Alkylations of benzylic and tertiary chlorides have been reported to proceed with great ease.[2] Thus it was not surprising to find (lines 5 and 6 in Table I) the formation of 1,1-dimethylcyclohexane from 1-methylcyclohexene and Me$_3$Al/HCl or HCl/Me$_3$Al. In contrast, it was quite unexpected that methylcyclohexane did not form from cyclohexene under the same conditions (lines 2 and 3 in Table I) (eq 3).



(3)

Instead, the reaction between cyclohexene and Me$_3$Al–HCl or HCl–Me$_3$Al gave rise to chlorocyclohexane (lines 2 and 3 in Table I). Methylcyclohexane starts to appear only after long reaction periods at higher temperatures. These findings can be explained by assuming first a protonation of cyclohexene by H$^+$ $^-$ClAlMe$_3$ followed by rapid collapse of the ion pair to the chlorinated product (eq 4). The fact that the first isolable product is the chloro and not the methyl derivative could be due to the asymmetrical charge distribution in the trimethylaluminum chloride counteranion. We visualize a virtually instantaneous collapse of the cyclohexyl ion pair to the chlorinated product before the counteranion has had a chance to rotate and to direct a methyl substituent toward the electrophilic center. The first-formed kinetically controlled product (chlorocyclohexane) is subsequently slowly methylated to yield the thermodynamically stable methylcyclohexane.



(4)

With 1-methylcyclohexane the overall reaction is much simpler, since initial protonation gives a stable tertiary cation which, on account of its longer lifetime and/or "looser" nature, rapidly leads to the thermodynamically more stable 1,1-dimethylcyclohexane. Evidently in this system the counterion has the time to rotate before final methylation of the electrophilic center. The possibility that in this reaction 1-chloro-1-methylcyclohexane may be involved as a nonisolable intermediate cannot also be ruled out.

With 1-methylcyclohexene the observation could also be explained by assuming a rapid formation of the tertiary chloro derivative, which rapidly decomposes to the thermodynamically more stable dimethylcyclohexane. This process would not require an asymmetrical charge distribution in the counteranion but only that the chloride is a better leaving group for the tri-

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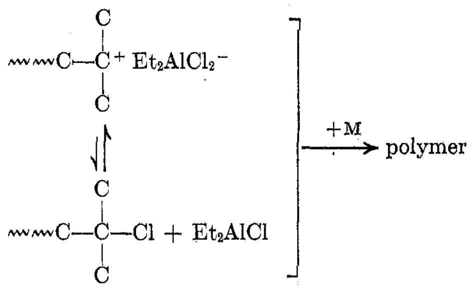
[1] J. P. Kennedy in "Polymer Chemistry of Synthetic Elastomers," J. P. Kennedy and E. Tornquist Ed., Interscience, New York, N. Y., 1968, Part 1, Chapter 5A, p 291.

[2] J. P. Kennedy, *J. Org. Chem.*, **35**, 532 (1970).

methylaluminum chloride anion. (We thank one of the referees for pointing this out.)

In the reaction of cyclohexene with Me$_3$Al and HCl, the order of addition of the reagents influences the extent of conversion (lines 2 and 3, Table I). We propose that, when Me$_3$Al is added to an olefin such as cyclohexene, a Lewis acid–olefin complex is formed, which lowers the reactivity of the Lewis acid and the olefin toward HCl. However, when the Lewis acid is added last, the possibility of complex formation is minimized, resulting in a higher yield of chlorocyclohexane. Complex formation between olefins and alkylaluminum compounds may be a general phenomenon.[3] We have also found that the rate of cationic polymerization of isobutylene initiated by the trimethylaluminum-*tert*-butyl bromide initiator system can be considerably accelerated by adding the alkylaluminum last.[4] Complex formation between olefins and Lewis acids such as SnCl$_4$, BF$_3$, AlBr$_3$, etc., has been demonstrated.[5]

Experiments described in this paper (*i.e.*, lines 2 and 3 in Table I) suggest the formation of chlorinated intermediates in similar other reactions as well. A consequence of these results is the possibility that cationic polymerizations may also involve covalent halides. The direct insertion of monomer into the covalent C–Cl bond, however, is considered to be much less likely.[6] The relative concentration of the conventional ion pairs and the covalent chlorides in the equilibrium (eq 5) is determined by the structure of the monomer (or the stability of the propagating cation) and the particular Lewis acid used. For example, the polymerization of isobutylene by t-Bu$^+$Et$_2$AlCl$_2^-$ (derived from t-BuCl and Et$_2$AlCl) might involve predominantly conventional ion pairs (eq 5). Termination would occur when the counterion is in a favorable orientation to alkylate the positive center.



(5)

Experimental Section

All the experiments and manipulations were performed in a stainless steel enclosure under N$_2$ atmosphere (<50 ppm moisture level).[7] Trimethylaluminum (Texas Alkyl, Inc.) was used as received. Cyclohexene (Aldrich Chemical Co.) and 1-methylcyclohexene (Columbia Organic Chemicals Co.) were dried over molecular sieves and distilled before use. Authentic samples of chlorocyclohexane, methylcyclohexane, and 1,1-dimethylcyclohexane for glpc comparison were obtained commercially. Gas chromatography was done on an HP 5750 instrument equipped with FID on a 6 ft × 0.125 in. silicone gum rubber UC-W-98 column using He (35 ml/min) as the carrier gas. All unknown peaks were identified by peak superposition using authentic materials for comparison. All reactions were generally run for 30 min; however, the reactions were virtually complete in *ca.* 10 min. A representative experiment is described. A three-neck flask equipped with a mechanical stirrer, glass-jacketed addition funnel, and a thermometer was cooled to $-50°$. Cyclohexene, 5.1 ml (50 mmol), dissolved in 25 ml of EtCl ($\sim$1.5 M) was placed in the flask followed by 1.5 ml (50 mmol) of liquid hydrogen chloride dissolved in 25 ml of EtCl. Trimethylaluminum, 4.8 ml (50 mmol), was dissolved in 25 ml of EtCl and was added dropwise through the precooled addition funnel. Upon addition of the first few drops of trimethylaluminum the temperature of the pot rose by $\sim$10°. After addition was complete, the reaction was quenched by the dropwise addition of 5 ml of prechilled methanol. The aluminum alkoxide was coagulated by the addition of a saturated aqueous solution of sodium potassium tartrate. The organic product was extracted into pentane, washed, dried, and analyzed by glpc. *N*-Nonane was used as an internal standard. The products arising from the reaction of cyclohexyl cation with cyclohexene (1-cyclohexylcyclohexene) and from the skeletal rearrangement of the cyclohexyl cation (1-methylcyclopentene, 1,1-dimethylcyclopentane) were shown to be absent.

Registry No.—Cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; trimethylaluminum, 75-24-1; hydrogen chloride, 7647-01-0.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research,

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[3] J. P. Kennedy and A. W. Langer, *Advan. Polym. Sci.*, **3**, 508 (1964); E. I. Tinyakova, T. G. Shuravleva, T. N. Kurengina, N. S. Kirikova, and B. A. Dolgoplosk, *Dokl. Akad. Nauk SSSR*, **144**, 592 (1962); J. P. Kennedy and G. E. Milliman, *Advan. Chem. Ser.*, **91**, 287 (1969).

[4] P. D. Trivedi, unpublished observations, Akron, Ohio, 1972.

[5] J. M. Clayton and A. M. Eastham, *Can. J. Chem.*, **39**, 138 (1961); R. W. Taft, E. L. Purlee, P. Reisz, and C. A. DeFazio, *J. Amer. Chem. Soc.*, **77**, 1584 (1955); T. G. Bonner, J. M. Clayton, and G. Williams, *J. Chem. Soc.*, 1705 (1958).

[6] A. Gandini and P. H. Plesch, *J. Polym. Sci.*, part *B-3*, 1127 (1965); P. H. Plesch, *Polym. Prepr.*, **7**, 492 (1966).

[7] J. P. Kennedy and R. M. Thomas, *Advan. Chem. Ser.*, **34**, 111 (1962).

Base-Catalyzed Reaction of β-Amino Alcohols with Ethyl Trihaloacetates

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The reaction of β-hydroxyalkylamines with ethyl trihaloacetates has been investigated in some detail only by Lesher and Surrey,[1] who obtained 2-oxazolidinones[2] by treatment of *N*-benzylethanolamines with ethyl trichloroacetate (ETC). According to the same authors, N-unsubstituted β-amino alcohols failed to afford any 2-oxazolidinones.

We have investigated the reaction of DL-phenylpropanolamine (**1**) and L-ephedrine (**5**) with ETC and ethyl trifluoroacetate (ETF) and the influence of a basic catalyst on the course of this reaction.

Treatment of **1** with ETC and ETF afforded the corresponding aminolysis products **2** and **3**, respectively. Addition of catalytic amounts of methanolic sodium methoxide increased the conversion rate of **1** into **3**, while added base resulted in the formation of the N-unsubstituted 2-oxazolidinone **4**, as the only product of the reaction with the trichloro ester.

Reaction of **5** with ETF afforded the trifluoroacetamide **6** in the absence of catalyst, while an almost complete conversion into 2-oxazolidinone **7** was obtained

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[1] G. Y. Lesher and A. R. Surrey, *J. Amer. Chem. Soc.*, **77**, 636 (1955).

[2] For a comprehensive review on 2-oxazolidinones, see M. E. Dyen and D. Swern, *Chem. Rev.*, **67**, 197 (1967).