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REACTION OF TRIETHYLALUMINUM AND POLYHALOMETHANES: FORMATION OF CYCLOPROPANE AND CYCLOHEPTATRIENE DERIVATIVES

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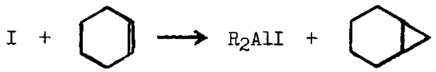
Recently, the reaction of triisobutylaluminum and carbon tetrachloride was shown to yield diisobutylaluminum chloride and isobutyl chloride as major products. Carbenes were proposed as intermediates in the reaction (1,2), but no carbene-trapping experiments were reported. I now report parallel work on the reactions of triethylaluminum with polyhalomethanes; the formation in these reactions of cyclopropane and cycloheptatriene derivatives, however, may or may not involve carbene intermediates.

Reaction of triethylaluminum and diiodomethane in a 2:1 mole ratio in benzene at 25° for seven days gave iodoethane (3) as a major product. If, before hydrolysis, this reaction mixture was heated at 75° for 19 hours, part of the iodoethane disappeared and ethylbenzene became a major product. Ethylene was found in both product mixtures. Reactions analogous to those proposed by Collette can account for the products.

$$\underset{\mathrm{R = Et}}{\mathrm{CH_2I_2} + \mathrm{R_3Al}} \longrightarrow \left\{ \begin{array}{ll} \overset{\mathrm{I}}{\mathrm{R_2AlCH_2I}} \longrightarrow \mathrm{R_2AlI} + \mathrm{C_2H_4} & (1) \\ + & \\ \mathrm{RI} \xrightarrow[\mathrm{C_6H_6}]{\mathrm{R_2AlI}} \mathrm{PhR} & (2) \end{array}\right.$$

The proposed intermediate, I, and its decomposition above -10° (reaction 1) have been described by Hoberg (4). Friedel-Crafts catalysis by alkylaluminum halides (reaction 2) has also been reported (5). Reaction of triethylaluminum and diiodomethane in a 1.5:1 mole ratio in cyclohexene for 3 days at 25° gave, after hydrolysis, unchanged diiodomethane (18%) and norcarane (20%), purified (6) by v.p.c. from a fraction boiling at 85-120° (reaction 3). Norcarane was identified by its n.m.r. spectrum and by comparison of its infrared spectrum with a spectrum (7) of authentic norcarane. Hoberg's study indicates that reaction 3 does not involve carbene, but rather an addition-elimination mechanism (4).



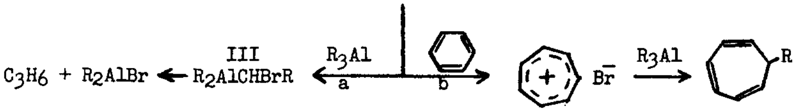
(3)

Although the addition of organometallic bonds to olefins is well precedented, such addition to benzene seems unlikely. Nevertheless, cycloheptatrienes can be generated by the reaction of an alkylaluminum. After 13 days at 25-40°, a benzene solution of triethylaluminum and bromoform (3:1 mole ratio) was hydrolyzed to give ethane, propene (40%; yields based on bromoform), bromoethane (32%), 7-ethylcycloheptatriene (14%), cycloheptatriene (8%), and unchanged bromoform (10%). Cycloheptatriene, purified by distillation and v.p.c., was identified by comparison of its n.m.r. spectrum with a reference spectrum (8). 7-Ethylcycloheptatriene, similarly purified, was identified by comparison of its infrared and n.m.r. spectra with the spectra of authentic 7-ethylcycloheptatriene (9).

Although a mechanistic interpretation of this reaction is complicated by the many possible intermediates, it is most probably an electrophilic species which attacks the benzene ring. One possible electrophile is bromocarbene; another is an α-haloalkylaluminum which can function as an alkylating agent in a Friedel-Crafts type reaction. A proposed intermediate in either mechanism is II. In the carbene mechanism, II generates bromocarbene (reaction 5) which inserts into triethylaluminum to give III (reaction 6a) or into benzene to give tropylium

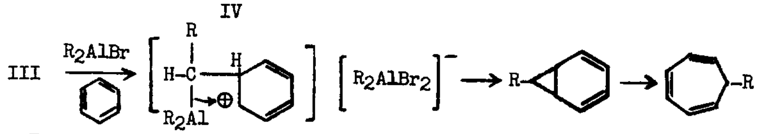
$$R_3Al + CHBr_3 \longrightarrow \overset{\text{II}}{R_2AlCHBr_2} + RBr \qquad (4)$$

$$\text{II} \longrightarrow :CHBr + R_2AlBr \qquad (5)$$



(6)

$$\text{II} + R_3Al \longrightarrow \text{III} + R_2AlBr \qquad (7)$$



(8)

R = Et

bromide (reaction 6b). Decomposition of III gives propene. Reaction of tropylium bromide with triethylaluminum may give 7-ethylcycloheptatriene (10); reduction of II or tropylium bromide by triethylaluminum or the diethylaluminum hydride (11) contained therein can lead to cycloheptatriene. In an alternative mechanism, II gives III by reaction with triethylaluminum (reaction 7) (12). In the presence of diethylaluminum bromide, benzene undergoes electrophilic attack by III, giving IV. Usually a σ-complex rearomatizes by loss of a proton, but IV has an alternative leaving group - a favorably located Et_2Al - which can readily accept the positive charge (reaction 8) (13). If II provides the electrophilic species, the resulting tropylium bromide reacts as before. Again, reduction of II or tropylium bromide leads to cycloheptatriene. Since the carbene mechanism (reactions 4-6) and the non-carbene mechanism (reactions 4,7,8) both lead to the observed products, a selection will be deferred.

Carbon tetrachloride (1), bromoform, and diiodomethane each react with trialkylaluminums to give alkyl halides; thus each serves as a source of positive halogen. Triethylaluminum was found to also react with iodoform, chloroform, carbon tetrabromide, and carbon tetrachloride, giving the corresponding haloethane as one of the major products of each reaction (14). Other products of these and related reactions are under investigation.

REFERENCES

(1) J. W. Collette, J. Org. Chem. 28, 2489 (1963) Additional pertinent references may be found therein.

(2) For recent reviews on carbenes, see E. Chinoporos, Chem. Rev. 63, 235 (1963) and P. Miginiac, Bull. Soc. Chim. France 1962, 2000.

(3) Unless otherwise indicated, products were identified by n.m.r. and/or comparative v.p.c. analyses. N.m.r. spectra were interpreted by Dr. P. W. Flanagan; v.p.c. analyses were under the direction of Messrs. H. T. Ford and J. W. Wimberley.

(4) H. Hoberg, Ann. 656, 1 (1962).

(5) L. Groizeleau, Compt. rend. 244, 1223 (1957).

(6) Separations were performed by Messrs. A. B. Carel and E. E. Smith.

(7) Kindly furnished by Dr. P. G. Gassman, Ohio State University, Columbus, Ohio.

(8) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, NMR Spectra Catalog, Varian Associates, 1962, Spectrum 158.

(9) K. Conrow, J. Am. Chem. Soc. 83, 2343 (1961). An infrared spectrum and a sample of 7-ethylcycloheptatriene were kindly provided by Dr. Conrow.

(10) For analogous reactions, see G. L. Closs and L. E. Closs, Tetrahedron Letters 1960, No. 10, 38, and reference 9.

(11) Commercial triethylaluminum contains 3-4% diethylaluminum hydride. A similar reduction of tropylium bromide by diisobutylaluminum hydride was reported by Z. N. Parnes, M. E. Volpin, and D. N. Kursanov, ibid. 1960, No. 21, 20.

(12) Halogens α to aluminum have enhanced reactivity. H. Hoberg, Ann. 656, 15 (1962). Hoberg has also proposed a coupling reaction of this type (reference 4). Coupling reactions of organoaluminums with α-haloethers are also known. M. Gaudemar, Compt. rend. 243, 1216 (1956); K. Weissermel and E. Nolken, Makromol. Chem. 68, 140 (1963).

(13) A mechanism of this type was proposed for the CuCl catalyzed reaction of diazomethane with benzene. E. Müller and H. Fricke, Ann. 661, 38 (1963).

(14) Although alkylaluminums and polyhalomethanes may react violently under certain conditions, reactions employing excess alkylaluminum have proceeded smoothly.