

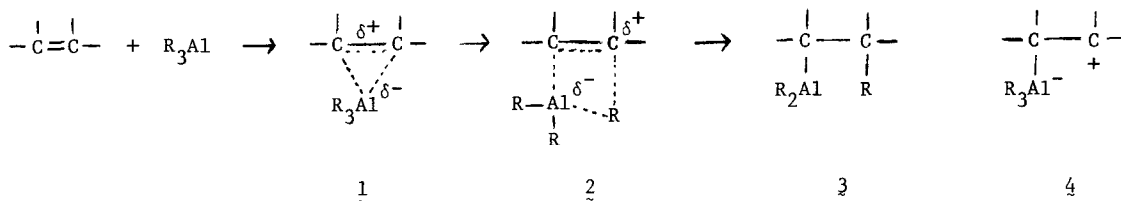
EVIDENCE FOR A CARBONIUM ION REARRANGEMENT IN THE REACTION OF  
 TRIISOBUTYLALUMINUM AND 1,3,3-TRIMETHYLCYCLOPROPENE

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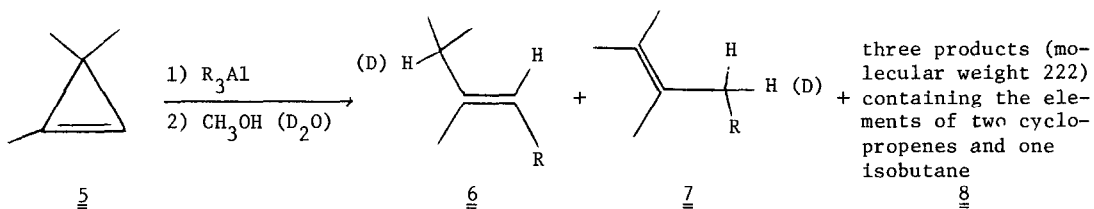
Abstract. Formation of acyclic products in the reaction of triisobutylaluminum and 1,3,3-trimethylcyclopropene can reasonably be ascribed to a carbonium ion rearrangement. This suggestion supports the mechanism for carbalumination of alkenes proposed by Eisch.

Eisch suggested that carbalumination results from electrophilic attack by the aluminum compound to form a  $\pi$  complex (1), which rearranges via an unsymmetrical 4-centered transition state (2) to the addition product (3).<sup>2</sup> Depending on the substrate, the rate-determining step



may be formation of 1 or the rearrangement via 2. Effects of substituents are relatively small, consistent with the development on carbon of only limited cationic character, never approaching that implied by 4. The failure to observe Wagner-Meerwein rearrangements, even with substrates particularly susceptible to rearrangement upon electrophilic attack, has also been attributed to only meager development of positive charge on a carbon.

Addition of 1,3,3-trimethylcyclopropane (5) to a hexane solution of triisobutylaluminum at -70 °C followed by quenching with methanol produces two products containing the elements of one cyclopropene and one isobutane. These were shown by their <sup>1</sup>H NMR spectra to be 6 and 7.<sup>3</sup> When quenching was with D<sub>2</sub>O, 6 and 7 each contained one deuterium in the indicated position. Three



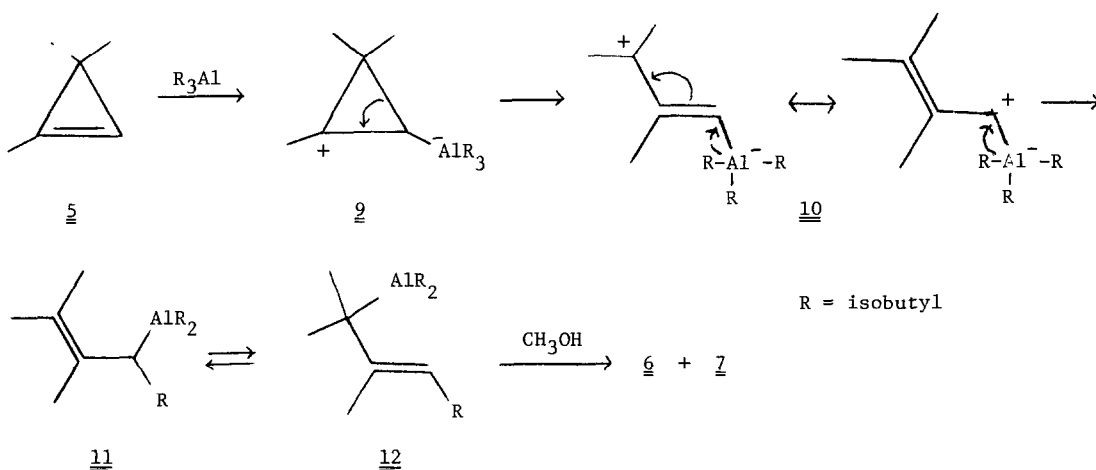
compounds that probably contained the elements of the two cyclopropenes and one isobutane were present, as were compounds having even higher molecular weights. The Table indicates the amounts of the reactant cyclopropene that are accounted for in the products.<sup>4</sup> Formation of the

Table. The percentages of 1,3,3-trimethylcyclopropene molecules in reactions at  $-70^{\circ}\text{C}$  with different amounts of triisobutylaluminum that are incorporated into particular components of the reaction mixtures.

: $\text{R}_3\text{Al}$	<u>6</u>	<u>7</u>	<u>8</u>
0.5 : 1	17.1	11.3	7.0
1.0 : 1	13.6	9.5	9.1
2.0 : 1	9.1	6.4	16.8

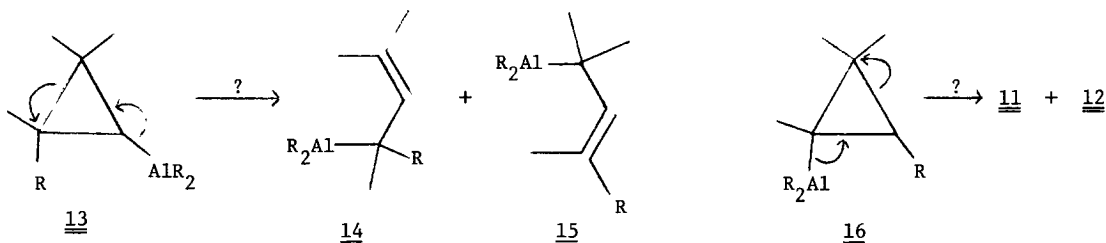
higher molecular weight products by reactions of the organoaluminum precursors of 6 and 7 with additional cyclopropene is consistent with the decreased amounts of 6 and 7 as the cyclopropene to organoaluminum ratio increases.

Formation of 6 and 7 can be rationalized readily by proposing that attack by the organoaluminum compound leads to development of sufficient positive charge at a carbon to make possible the facile electrocyclic ring-opening (9  $\rightarrow$  10) characteristic of cyclopropyl cations.<sup>5</sup>



Migration of an alkyl group from aluminum to the adjoining carbon then can produce 11, which is in equilibrium<sup>6</sup> with its allylic isomer, 12. Quenching the mixture of 11 and 12 will produce 6 and 7. The orientation of attack on the double bond necessary to produce 6 and 7 is that expected for a cationic addition, and the positions of deuterium in 6 and 7 when quenching is with D<sub>2</sub>O are consistent with the intermediacy of 11 and 12. Steps 5 → 9, 9 → 10, and 10 → 11 could be significantly concerted so that the full positive charge shown in 9 and 10 never develops.

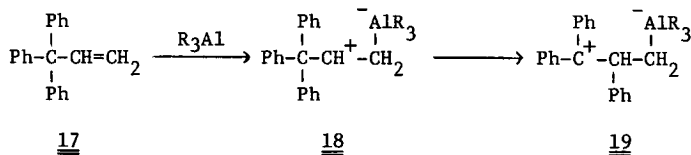
An alternative possibility that a cyclopropylaluminum compound (13 or 16) formed and isomerized to the products seems unlikely.<sup>7</sup> Isomerization of 13 would lead to 14 and 15, whose



hydrolysis would furnish isomers of the observed products. Isomerization of 16 would furnish 11 and 12, but we have found that 16 (R on cyclopropyl ring is ethyl rather than isobutyl)<sup>8</sup> does not isomerize even at room temperature.

Binger and Schäfer isolated a single product from a reaction of 3,3-dimethylcyclopropene and triethylaluminum.<sup>9</sup> This product, containing the elements of two cyclopropenes and one ethane, had a structure that would result from addition to the cyclopropene of an allylic organoaluminum compound corresponding to 6 and 7.<sup>10</sup> They did not observe 1:1 products corresponding to 6 and 7. Moreover, since the double bond carbons of 3,3-dimethylcyclopropene are identical, no evidence about regioselectivity was available to help indicate the mechanism.

Why might carbonium ion rearrangements be more readily initiated by a developing positive charge at carbon in reactions of organoaluminum compounds with cyclopropenes than with other alkenes that have been used as substrates? First, the electrocyclic rearrangement<sup>5</sup> (9 → 10) may be more facile than is a Wagner-Meerwein rearrangement, which requires actual transfer of an organic group from one carbon to another. Second, some Wagner-Meerwein rearrangements have unfavorable features when the electrophile is a neutral organometallic compound. For example, increasing separation of positive and negative charges should make more difficult the migration



of phenyl (18 → 19) that is generally expected in electrophilic additions to 17. Third, some concert of the transfer of R from Al to C with the attack by R<sub>3</sub>Al is probably necessary for

additions to occur. This looks feasible in the reaction of a cyclopropene, but more difficult to achieve if Wagner-Meerwein rearrangement (as in 18 → 19) is shifting the positive charge from  $\beta$ - to a  $\gamma$ -carbon.

Ring-opened products similar to those reported here have been observed in reactions of cyclopropenes with trialkylboranes,<sup>11</sup> but only addition products with intact cyclopropyl rings in reactions with organomagnesium compounds.<sup>12</sup> It will be interesting to see if rearrangements indicative of an electrophilic component to attack can be observed in other reactions of organo-metallic compounds with alkenes.

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#### References and Notes

- (1) Undergraduate research participant.
- (2) See the following and references cited therein: J. J. Eisch and N. E. Burlinson, J. Am. Chem. Soc., 98, 753 (1976); J. J. Eisch, N. E. Burlinson, and M. Boleslawski, J. Organomet. Chem., 111, 137 (1976).
- (3) The configuration of 6 is not known with certainty.
- (4) Yields were determined by GC analysis using undecane as an internal standard. It was assumed that the response of the (flame ionization) detector to different compounds was proportional to their molecular weights.
- (5) For example, see L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, J. Am. Chem. Soc., 95, 6531 (1973), and references cited therein.
- (6) K. L. Henold and J. P. Oliver, Organomet. React., 5, 387 (1975); J. J. Eisch, Adv. Organomet. Chem., 16, 67 (1977).
- (7) Apparently, cyclopropylaluminum compounds are quite stable. For example, see the following and references cited therein: G. Zweifel, G. M. Clark, and C. C. Whitney, J. Am. Chem. Soc., 93, 1305 (1971); D. A. Sanders, P. A. Scherr, and J. P. Oliver, Inorg. Chem., 15, 861 (1976).
- (8) Synthesized from a reaction of 1,1,2-trimethyl-2-lithio-3-ethylcyclopropene and diisobutylaluminum chloride in hexane.
- (9) P. Binger and H. Schäfer, Tetrahedron Lett., 4673 (1975).
- (10) The 2:1 products observed by Binger and Schäfer<sup>9</sup> and by us must result from addition of allyl-Al< to cyclopropenes to form cyclopropylaluminum compounds. The indications that allyl-Al< adds to cyclopropenes without rearrangement suggests that less cationic character develops at a double bond carbon than in additions of R-Al< (R = a saturated alkyl group).
- (11) B. M. Mikhailov, Yu. N. Bubnov, O. A. Nesmeyanova, V. G. Kiselev, T. Yu. Rudashevskaya, and B. A. Kazansky, Tetrahedron Lett., 4627 (1972); Yu. N. Bubnov, O. A. Nesmeyanova, T. Yu. Rudashevskaya, B. M. Mikhailov, and B. A. Kazanskii, J. Gen. Chem. USSR (Engl. Transl.), 43, 125 (1973); Yu. N. Bubnov, B. A. Kazanskii, O. A. Nesmeyanova, T. Yu. Rudashevskaya, and B. M. Mikhailov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 2358 (1977).
- (12) For example, Shell Internationale Research Mattschapp B. V., Neth. Appl. 74 02,879; Chem. Abstr., 83, 27684 (1975); O. A. Nesmeyanova and T. Yu. Rudashevskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1364 (1978), and references cited therein; H. Lehmkuhl and K. Mehler, Justus Liebig's Ann. Chem., 1841 (1978); E. K. Watkins, The Pennsylvania State University, unpublished observations.

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