tively. The first peak was shown to be vinylferrocene by enrichment of the mixture with an authentic sample of vinylferrocene. Apparently this impurity resulted from contamination of chloroamine 11 with amine 5. The method of formation and the analytical data identify the main chromatographic component to be 2-chlorovinylferrocene. For melting point and analytical and spectral data, see Table II.

Registry No.—Butyllithium, 109-72-8; **1**, 1271-86-9; **6**, 12441-23-5; **7**, 12441-25-7; **8**, 12441-17-7; **9**, 12441-18-8; **10**, 12441-16-6; **11**, 12441-13-3; **12**, 12441-12-2; **15**, 12441-24-6; **16**, 12441-20-2; **17**, 12441-21-3; **18**, 12441-19-9; **20**, 12441-22-4; **21**, 12441-15-5; **22**, 12441-14-4; **23**, 12441-11-1.

The Reaction of Triisobutylaluminum with 1,5-Cyclooctadiene[1]

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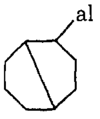
Hydrolysis of the reaction product derived from triisobutylaluminum and 1,5-cyclooctadiene gave rise to *cis*- and *trans*-1-ethyl-2-methylcyclopentane as well as some cyclooctene, but no cyclooctane. Treatment of the reaction product with ethylene in the presence of nickel acetylacetonate afforded 1-methylene-2-vinylcyclopentane.

The unexpected results obtained from the investigation of the triisobutylaluminum–butadiene reaction[3] prompted us to study reactions of other diolefins with triisobutylaluminum (TIBA). 1,5-Cyclooctadiene (**1**) looked like an especially interesting case, because its two double bonds would not necessarily be expected to behave as independent units in this type of reaction.

Isobutylene was not displaced efficiently until a reaction temperature of about 145° was reached. After hydrolysis of the reaction product, a saturated C_8H_{16} hydrocarbon boiling at about 120–125° was obtained in 60% yield based on TIBA. Gas chromatography showed the presence of two peaks. The major component of this cut was proven to be *cis*-1-ethyl-2-methylcyclopentane (**2**) by comparison with a National Bureau of Standards sample. Although a similar reference sample of *trans*-1-ethyl-2-methylcyclopentane (**3**) is not available, there is little doubt that the other component is the trans isomer; besides, hydrogenation of 1-methylene-2-vinylcyclopentane gave the same two 1-ethyl-2-methylcyclopentanes, one of which was the cis isomer and the other one was identical with the trans isomer in question. Furthermore, the infrared spectrum of **3** was identical with the spectrum of *trans*-1-ethyl-2-methylcyclopentane published by Natalis.[4] No cyclooctane was observed and only a small amount of cyclooctene was obtained.

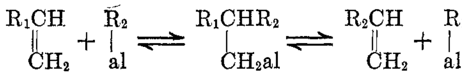
Formation of the ethylmethylcyclopentanes was unexpected. The unusual step is the breakage of a carbon–carbon single bond at some stage. Initial formation of aluminobicyclo[3.3.0]octane (**4**) appeared at first sight a likely possibility (al = $^1/_3$Al).



4

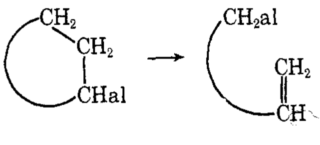
The reversibility of the following reaction, where R_1 and R_2 are alkyl, has been proven (Scheme I).[5] However, this type of reaction with an aluminocycloalkane has never been reported (Scheme II). Therefore, it would have been interesting to subject bicyclo[3.3.0]oct-2-ene to the reaction with TIBA. Since this material was not available, the structurally related tricyclo[5.2.1.0^{2,6}]dec-3-ene was treated with TIBA at 150–190°. However, the desired ring opening did not occur; tricyclo[5.2.1.0^{2,6}]decane was the only product we could detect after hydrolysis of the reaction product. We also attempted unsuccessfully the conversion of cyclooctene with an excess of TIBA at 150–190° into 1,8-dialuminooctane; cyclooctane was the only product formed after hydrolysis. Hence, it is unlikely that aluminobicyclooctane (**4**) is involved in the formation of **2** and **3**.

SCHEME I



$$\underset{\mathrm{CH_2}}{\overset{\mathrm{R_1CH}}{\|}} + \underset{\mathrm{al}}{\overset{\mathrm{R_2}}{|}} \rightleftharpoons \underset{\mathrm{CH_2al}}{\overset{\mathrm{R_1CHR_2}}{|}} \rightleftharpoons \underset{\mathrm{CH_2}}{\overset{\mathrm{R_2CH}}{\|}} + \underset{\mathrm{al}}{\overset{\mathrm{R_1}}{|}}$$

SCHEME II



Although we do not have experimental support for a satisfactory explanation of the observed results, Scheme III may be looked upon as an alternative interesting speculation. The critical step in Scheme III involves, of course, the intermediacy of 3-alumino-1,7-octadiene. The pyrolysis of cyclooctene to 1,7-octadiene can be accomplished in high efficiencies at 500°.[6] This reaction depends on the rupture of a carbon–hydrogen bond in the 5 position of cyclooctene.[7,8] The con-

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[1] A part of this work has been described by E. Marcus and D. L. MacPeek, U. S. Patent 3,388,180 (June 11, 1968).

[2] Author to whom correspondence should be directed.

[3] E. Marcus, D. L. MacPeek, and S. W. Tinsley, *J. Org. Chem.*, **34**, 1931 (1969).

[4] P. Natalis, *Bull. Soc. Chim. Belg.*, **72**, 178 (1963); *Chem. Abstr.*, **59**, 7346 (1963).

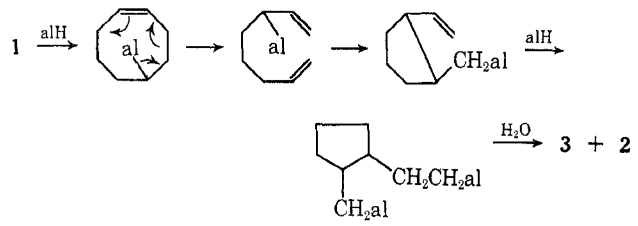
[5] K. Ziegler, K. Nagel, and W. Pfohl, *Justus Liebigs Ann. Chem.*, **629**, 210 (1960).

[6] S. W. Tinsley and E. A. Rick, U. S. Patent 3,388,182 (June 11, 1968).

[7] G. S. Denning, Jr., *Diss. Abstr.*, **21**, 1731 (1961).

[8] A. T. Blomquist and G. S. Denning, Jr., 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961, Abstract 29-O

SCHEME III

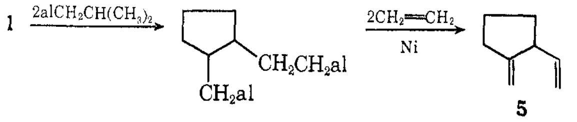


alH = >AlH in R_2AlH

version of 5-aluminocyclooctene to 3-alumino-1,7-octadiene would necessitate breaking of the much weaker carbon–aluminum bond at a considerably lower temperature; this, in our opinion, is a reasonable possibility. Further transformation of 3-alumino-1,7-octadiene to a cyclopentane derivative is straightforward. 1-Alumino-5-hexenes are known to cyclize rapidly to (aluminomethyl)cyclopentanes.[3,9,10] The fact that 3-alumino-1,7-octadiene is an allylic aluminum derivative should enhance the reactivity of this intermediate even further.[3]

When the TIBA–1,5-cyclooctadiene reaction product was treated with ethylene in a bomb in the presence of nickel acetylacetonate as catalyst and benzene as solvent, the C_8 fraction contained as major product the expected 1-methylene-2-vinylcyclopentane (**5**). The overall reaction can be described by Scheme IV.

SCHEME IV



The infrared absorption spectrum showed intense bands at 10.1, 11.0, and 11.35 μ, which confirmed the presence of both a vinyl and a vinylidene group. According to mass spectroscopy it was a C_8H_{12} hydrocarbon. Catalytic reduction over platinum oxide produced both of the 1-ethyl-2-methylcyclopentane isomers.

It is of interest to note that the TIBA–1,5-cyclooctadiene reaction product was soluble in the excess of cyclooctadienes as well as in benzene, which indicates that the polymer was cross-linked only slightly or not at all.

It should also be mentioned that **2** and **3** have been obtained before by catalytic conversion of cyclooctane in the presence of hydrogen;[11,12] the precursor for the ethylmethylcyclopentanes seems to be bicyclo[3.3.0]octane. However, it is difficult to see any close relationship between this reaction and the reaction discussed in the present article.

Experimental Section

The gas chromatograph used for analyzing the composition of a certain fraction was the Barber–Coleman capillary gas chromatograph IDS Model 20, with a 200-ft UCON 50 HB 2000 column and a strontium-90 detector.

The gas chromatograph used for isolating a component from a certain fraction was the Beckman GC-2 analytical gas chromatograph with a packed column containing a UCON-P substrate on firebrick. The amount of material injected varied from 0.03 to 0.05 ml. The desired component was collected by condensation of the effluent from the exit port. Usually the amount collected was sufficient for an infrared or a mass spectral determination. However, in a few cases where the material contained too little of the desired component, collections had to be repeated until a sufficient amount was available.

The yields reported are based on calculations derived from the gas chromatographic spectra. Since the assumption was made that "area %" equals "weight %," yields given are only approximate. Most probably this assumption is fairly valid for similar hydrocarbons.

1,5-Cyclooctadiene–TIBA Reaction Product and Its Hydrolysis.—TIBA (132 g, 0.67 mol) was added with stirring during a period of 190 min to **1** (216 g, 2.0 mol), while the temperature was maintained between 122 and 149°. Heating with stirring was continued for another 50 min at 145°. During the reaction time isobutylene (106 g, 95%) was collected in a Dry Ice trap. Cyclooctadiene (52 g, 24%) was recovered by distillation under reduced pressure at 55°. The reaction product was hydrolyzed with ethanol and then with dilute hydrochloric acid. The organic layer was separated; the aqueous layer was extracted with petroleum ether, bp 35–37°. The combined organic layers were washed with water, dilute sodium hydroxide solution, again with water, dried over calcium chloride, decanted, and distilled through a 15-in. column to give the following fractions: 24 g from 110 to 122°, 57 g from 122 to 125°, 28 g from 62° (50 mm) to 45° (10 mm), 24 g from 65° (0.75 mm) to 92° (1 mm), and 5 g of residue. The first two fractions contained mostly the two ethylmethylcyclopentanes, some cyclooctene, and cyclooctadiene. The third fraction contained mainly cyclooctene and cyclooctadiene. The last fraction is believed to contain C_{16} hydrocarbons. The first three fractions were analyzed by gas chromatography and found to contain four main peaks. The compound of the first peak is believed to be **3**. The second peak is caused by **2**. The third peak represents cyclooctene, and the fourth peak is caused by **1**. The yields on TIBA given in Table I have been obtained assuming that 2 equiv of TIBA are required for the formation of ethylmethylcyclopentane after hydrolysis.

TABLE I

Compd	Yield, g	Yield, %, based on **1**	Yield, %, based on TIBA
trans-1-Ethyl-2-methylcyclopentane	26.5	12	24
cis-1-Ethyl-2-methylcyclopentane	41.3	18	37
Cyclooctene	16.4	7.5	7.5
Cyclooctadienes recovered[a]	69.5	32	
C_{16} hydrocarbons	24	11	

[a] Was shown to be a mixture of 1,3-, 1,4-, and 1,5-cyclooctadiene.

The products represented by peaks I and II were isolated by gas chromatography. Peak II was identified as the cis isomer by comparing its infrared and mass spectra with those of an authentic National Bureau of Standards sample. The reported[4] boiling points for **2** and **3** are 128.4 and 121.35°, respectively.

1-Methylene-2-vinylcyclopentane.—TIBA (264 g, 1.34 mol) was added to **1** (432 g, 4.0 mol) under conditions similar to those described in the previous experiment to give 475 g of a reaction product. After removal of the excess of **1**, which contained now significant amounts of the 1,3 and 1,4 isomers, by distillation under vacuum, there was left 339 g of a colorless polymer. Of this polymer 320 g, which is equivalent to 1.25 mol of initial TIBA, was used for the following run.

A mixture of the TIBA–cyclooctadiene polymer (320 g), benzene (500 ml), and nickel acetylacetonate (0.15 g) was charged to a 3-l. stainless-steel bomb. After the addition of ethylene (351 g, 12.5 mol), the bomb was heated with rocking to 74° within 15 min to give a pressure of 1080 psi. Heating with rocking was continued between 69 and 74° for 17 hr. The pressure had dropped to 680 psi at 70°. The bomb was vented and its

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(9) K. Ziegler, *Angew. Chem.*, **68**, 721 (1956).

(10) G. Hata and A. Miyake, *J. Org. Chem.*, **28**, 3237 (1963).

(11) A. Kazanskiĭ, E. A. Shokova, S. I. Khromov, V. I. Aleksanyan, and Kh. E. Sterin, *Dokl. Akad. Nauk SSSR*, **133**, 1090 (1960); *Chem. Abstr.*, **54**, 24442 (1960).

(12) S. I. Khromov, E. A. Shokova, Kh. E. Sterin, and B. A. Kazanskiĭ, *Dokl. Akad. Nauk SSSR*, **136**, 1112 (1961); *Chem. Abstr.*, **55**, 17534 (1961).

content was transferred under nitrogen to a distillation flask. The product was not soluble in benzene. The benzene and other low-boiling material were removed by distillation without rectification by lowering the pressure gradually to 10 mm at 40°. Most of the benzene was separated by distillation through a 36-in. column. The residue was distilled through a 20-in. spiral wire column to give 28 g, bp 121° at atmospheric pressure to 110° at 200 mm. Gas chromatography showed that it contained about 70% of one material and several other products in small amounts. A fraction boiling between 122 and 124°, which was about 85% pure according to gas chromatography, was analyzed, $n^{30}{}_D$ 1.4572, $d^{20}{}_{20}$ 0.814 (lit.[13] bp 118°, $n^{27}{}_D$ 1.4557).

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18; mol wt, 108. Found: C, 88.55; H, 11.39; mol wt (largest parent peak by mass spectroscopy), 108.

The product was purified further by gas chromatography. Its infrared absorption spectrum showed bands at 6.06, 6.10, 10.12, 11.0, and 11.35 μ indicating the presence of both a vinyl and a vinylidene group. All of the positions of the absorption peaks were identical with the positions reported for **5**.[14]

Reduction of 1-Methylene-2-vinylcyclopentane.—1-Methylene-2-vinylcyclopentane (2 ml), which was about 85% pure, was hydrogenated over platinum oxide in a Parr hydrogenator at 40 psi and room temperature. After 1 hr the pressure had decreased to 37.5 psi. Gas chromatography showed the presence of two major peaks: 35% of peak I and 54% of peak II. A comparison with the two 1-ethyl-2-methylcyclopentanes obtained by hydrolysis of the TIBA–cyclooctadiene reaction product showed that peak I and peak II had the same retention times as **3** and **2**, respectively. Further support was obtained from the infrared and mass spectra of the products which had been purified by gas chromatography.

Hydrogenation of **5** over prereduced platinum oxide in acetic acid has been reported to give 66% of **2** and 34% of **3**.[13]

Registry No.—TIBA, 100-99-2; **1**, 111-78-4.

Acknowledgment.—The authors wish to express thanks to Messrs. H. R. Harless and C. M. Lovell of Union Carbide Corporation for interpretations of spectral data.

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[13] W. D. Huntsman and R. P. Hall, *J. Org. Chem.*, **27**, 1988 (1962).

[14] R. P. Hall, M.S. Thesis, Ohio University, Athens, Ohio, 1961, p 10.

Hydrogenolysis of Cyclopropanes

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Several cyclopropane derivatives bearing unsaturated functional groups directly on the three-membered ring, including ketones, acids, and esters, were prepared and subjected to hydrogenolysis at room temperature and atmospheric pressure over a palladium-on-carbon catalyst. Exclusive C_1–C_2 bond cleavage was observed for all cyclopropyl methyl ketones studied. Predominant C_1–C_2 bond cleavage (>70%) was observed for the cyclopropanecarboxylic acids and cyclopropanecarboxylic acid esters. For cyclopropanes bearing phenyl groups as the only unsaturated substituent, exclusive cleavage adjacent to the phenyl-substituted carbon atom was observed. This preference for C_1–C_2 bond cleavage may be due to polarization effects of the unsaturated substituents and/or binding of the unsaturated functional groups to the catalyst surface.

Although the cyclopropyl system is one that has been extensively studied, relatively few investigations have been carried out involving the ability of cyclopropanes to undergo hydrogenolysis.[2] In the previous studies only a small percentage of the work has dealt with the hydrogenolysis of cyclopropane rings adjacent to unsaturated groups. In addition, comparisons of the effect of structure on reactivity are often difficult to make because different catalysts as well as various reaction temperatures and pressures have been used. Cyclopropyl methyl ketone has been hydrogenated using copper–chromium, Raney nickel, zinc, zinc–copper, and copper catalysts. Various products result depending upon the catalyst employed.[2a] Several alkenylcyclopropanes have been hydrogenated,[2] but the only systematic study of the effect of structure upon the nature of the hydrogenation products has dealt with the differences observed in the behavior of 2-cyclopropyl-1- and -2-alkenes.[3] The only report of the effect of phenyl substituents was concerned with the relative reactivities of phenylcyclopropane and the various diphenylcyclopropanes.[4]

In an attempt to elucidate the effect of adjacent unsaturated groups on the direction of ring opening of the three-membered ring, several such cyclopropanes were prepared and hydrogenated at room temperature and atmospheric pressure in the presence of palladium on carbon. In all the cases studied hydrogenolysis of the cyclopropane ring could result in various products determined by the direction of bond cleavage. The results of these hydrogenolyses and their implications are discussed.

Results and Discussion

The results of the present study into the mode of ring opening of unsaturated cyclopropane derivatives upon hydrogenation at room temperature and atmospheric pressure over 10% palladium-on-carbon catalyst are presented in Table I.

Upon hydrogenation all the cyclopropanes bearing an adjacent carbonyl group preferentially undergo ring opening at the C_1–C_2[5] bond of the three-membered ring. In the case of the cyclopropyl methyl ketones hydrogenolysis occurs exclusively at the C_1–C_2 bond of the cyclopropane ring, while with the esters and acids a minimum of 70% of the ring-opened products results from rupture of the C_1–C_2 bond of the three-membered ring. The results of the hydrogenolyses of the cyclopropylcarbinols (**19**–**21**), acetates (**22**–**24**), *trans*-1,2-diphenylcyclopropane (**25**), and 1,1-dimethyl-2-phenylcyclopropane (**26**) indicate that, in those compounds in which a benzene ring is the only unsaturated moiety in conjugation with the three-membered ring, exclusive

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[1] This work is taken in part from the M.S. Thesis of A. L. S.

[2] For reviews see (a) M. Yu. Lukina, *Russ. Chem. Rev.*, **31**, 419 (1962); (b) J. Newham, *Chem. Rev.*, **63**, 123 (1963).

[3] V. A. Slabey and P. H. Wise, *J. Amer. Chem. Soc.*, **74**, 3887 (1952).

[4] B. A. Kazanskiĭ, M. Yu. Lukina, and I. L. Safonova, *Dokl. Akad. Nauk SSSR*, **130**, 322 (1960); *Chem. Abstr.*, **54**, 10953 (1960).

[5] See Table I for numbering system.