The Reaction of Triisobutylaluminum with Butadiene[1]

E. MARCUS, D. L. MACPEEK, AND S. W. TINSLEY

Research and Development Department, Union Carbide Corporation, Chemicals and Plastics, South Charleston, West Virginia

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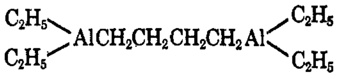
The reaction of triisobutylaluminum with butadiene in an open vessel yielded a polymer which on hydrolysis gave butane and three 1,2,3-trimethylcyclopentane isomers. Treatment of the polymer with ethylene in the presence of nickel acetylacetonate afforded a mixture of 2-methyl-1,3-dimethylenecyclopentane and 1-methyl-2,3-dimethylenecyclopentane.

Considerable work has been devoted in the last decade, especially by Ziegler and his group,[2-4] to the study of the preparation and reactions of trialkylaluminum compounds. However, very little information is available about dialuminoalkanes derived from diolefins and triisobutylaluminum (TIBA).

Ziegler found that 1,5-hexadiene and TIBA did not give any of the desired 1,6-dialuminohexane polymer; the products isolated were (aluminomethyl)cyclopentane and methylenecyclopentane.[5] Gellert and Kempkes tried to prepare triallylaluminum and 1,3-dialuminopropane from allene. In addition to complicated ring closures involving three molecules of allene, some 1,3-dialuminopropane was obtained.[6] Ziegler reported that the reaction of butadiene with aluminum alkyls has not yet been studied in detail in his laboratories.[7] Compound **1** was prepared from diethylaluminum hydride and butadiene.[8] The dialuminobutane polymer of the proposed composition $[Al_2(C_4H_8)_3]_x$ has been obtained from **2** and triethylaluminum.[9] Zakharkin, Savina, and Antipin[10] have found that diethylaluminum hydride reacts with butadiene to give, after hydrolysis, butane, butenes, and unknown C_8H_{16} hydrocarbons. A recent patent[11] claims as an intermediate an organoaluminum reaction product containing a substantial amount of tributenylaluminum obtained from diisobutylaluminum hydride and an excess of butadiene; however, no detailed information is given concerning the structure of the reaction product. Hata and Miyake[12] have investigated the reaction of diisobutylaluminum hydride with α,ω-dienes ranging from pentadiene to undecadiene; their studies with 1,5-hexadiene confirmed earlier work by Ziegler,[5] while the reaction with the other dienes yielded mainly the expected dialuminoalkanes.[13]



$$(C_2H_5)_2AlCH_2CH_2CH_2CH_2Al(C_2H_5)_2$$

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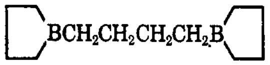

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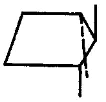
We attempted to prepare dialuminobutane by bubbling butadiene through TIBA at 100–120°. The desired alkylation can be described by eq 1 (al = $\frac{1}{3}$Al).

$$CH_2{=}CHCH{=}CH_2 + 2alCH_2CH(CH_3)_2 \longrightarrow alCH_2CH_2CH_2CH_2al + 2CH_2{=}C(CH_3)_2 \quad (1)$$

The amount of isobutylene displaced together with unchanged butadiene was collected in a cold trap, and the composition was determined by mass spectroscopy. At the end of the reaction the polymeric product was a very viscous liquid at the reaction temperature and a colorless solid glass at room temperature. Hydrolysis of the product gave about 29% butane and 27% saturated hydrocarbons that boiled between 110 and 120°. By far the largest component of this cut was 1,*trans*-2,*cis*-3-trimethylcyclopentane (**3**); some of the 1,*cis*-2,*trans*-3 isomer (**4**) and the 1,*cis*-2,*cis*-3 isomer (**5**) was also present.



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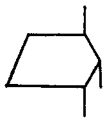

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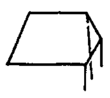

5

The isomers were separated by gas chromatography. Isomers **3** and **5** were identified by comparing their infrared and mass spectra as well as their gas chromatographic retention times with those of National Bureau of Standards samples. The structure of the predominant 1,*trans*-2,*cis*-3 isomer (**3**) was further confirmed by comparing its nuclear magnetic resonance spectrum with that of an authentic sample. Although a National Bureau of Standards sample of **4** was not available, there is little doubt that this isomer was actually obtained; besides, hydrogenation of 2-methyl-1,3-dimethylenecyclopentane (**6**) and 3-methyl-1,2-dimethylenecyclopentane (**7**) gave the same three isomeric trimethylcyclopentanes, one of which was identical with the 1,*cis*-2,*trans*-3 isomer (**4**) in question.

In addition there was found a very small amount of a fourth compound, which according to mass spec-

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(1) Presented in part at the 145th Meeting of the American Chemical Society, New York, N. Y., Sept 1963, Abstracts p 74Q; see also E. Marcus, U. S. Patent 3,356,704 (Dec 5, 1967).

(2) K. Ziegler, *Angew. Chem.*, **72**, 829 (1960).

(3) K. Ziegler, *et al.*, *Ann.*, **629**, 1 (1960).

(4) American Chemical Society Monograph No. 147, Reinhold Publishing Corp., New York, N. Y., 1960. pp 194–269.

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

(6) A. Kempkes, "Über Neue Reaktionen des Allens and über Allylaluminiumverbindungen", Ph.D. Thesis, Technische Hochschule Aachen, 1959.

(7) See ref 4, p 235.

(8) K. Ziegler and H. G. Gellert, U. S. Patent 2,826,598 (March 11, 1952).

(9) E. Stahnecker and H. Friederich, German Patent 1,108,217 (June 6, 1959).

(10) L. I. Zakharkin, L. A. Savina, and L. M. Antipin, *Bull. Acad. Sci. USSR*, 931 (1962).

(11) H. L. Johnson and G. G. Eberhardt, U. S. Patent 3,035,077 (May 15, 1962).

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

(13) Similar work by the authors of the present paper had been carried out independently prior to 1962, but was never published. α,ω-Dienes, ranging from pentadiene to octadiene, were treated with TIBA at about 100° in a molar ratio of 3:2. Our data agreed essentially with those reported in ref 12; however, in the case of 1,6-heptadiene we obtained a larger amount of methylcyclohexane, after hydrolysis of the reaction product. The C_7 fraction contained 38% methylcyclohexane, while under the conditions employed by Hatta and Miyake only 1–8% of this hydrocarbon was formed.

TABLE I

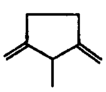
NMR DATA OF METHYLDIMETHYLENECYCLOPENTANE

Hydrogen type	Position, ppm[a]	Relative integrated intensities			Special pattern
		Found	Calcd for pure 1,3-dimethylene isomer	Calcd for 80:20 isomer mixture[b]	
Methyl hydrogens	1.12	2.8	3.0	3.0	Doublet
Singly allylic hydrogens	2.33	3.8	4.0	3.8	Single resonance with fine structure
Doubly allylic hydrogens	2.86	1.0	1.0	0.8	Broad, unresolved resonance
Vinylidene hydrogens	4.79	4.0	4.0	4.0	Single resonance with fine structure
Other methylene hydrogens	1.62	0.4	0.0	0.4	Broad unresolved resonance

[a] Chemical shift from tetramethylsilane. [b] 80% 2-methyl-1,3-dimethylenecyclopentane and 20% 3-methyl-1,2-dimethylenecyclopentane.

troscopy was a C_8H_{14} hydrocarbon. In the infrared spectrum, absorptions were noted at 5.95 (weak) and at 12.45 μ (strong) which are characteristic of trisubstituted ethylenes. This compound has not been further identified.

When the TIBA–butadiene reaction product was treated with ethylene in a bomb at 75° for 7 hr in the presence of nickel acetylacetonate as catalyst and benzene as solvent, the C_8 fraction contained, after hydrolysis, as major products **3**, two dimethylmethylenecyclopentanes and methyldimethylenecyclopentane. However, when the same reaction was carried out for 21 hr and the reaction product worked up without hydrolysis, the butadiene dimer, methyldimethylenecyclopentane, was isolated as the only hydrocarbon in the C_8 range. Vapor phase chromatography indicated the presence of only one major component which the mass spectrum characterized as a C_8H_{12} hydrocarbon. The infrared spectrum showed a strong absorption at 6.06 and 11.35 μ which is characteristic of nonconjugated vinylidene groups; it also showed a weak absorption at 7.3 μ indicative of a methyl group. The infrared absorptions at 6.06 and 11.35 μ were much stronger than those of two dimethylmethylenecyclopentanes isolated in another experiment; the absorption at 7.3 μ was much weaker that that of the dimethylmethylenecyclopentanes. The nuclear magnetic resonance spectrum showed peaks in the approximate 3:4:1:4 intensity ratio for methyl, singly allylic, doubly allylic, and vinylidene hydrogens, respectively (see Table I). These data are in good agreement with the proposed structure **6** for this hydrocarbon.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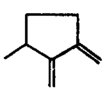
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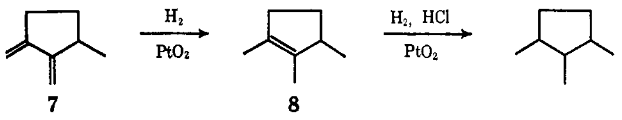
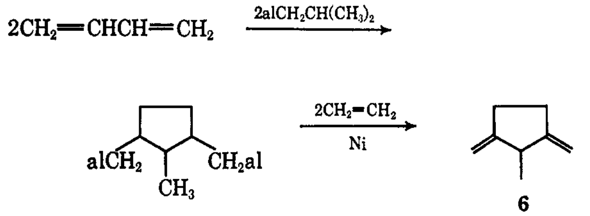
However, the ultraviolet spectrum did show an absorption at 2480 Å (ϵ_{max} 1900), exactly where the known conjugated diene **7**, 3-methyl-1,2-dimethylenecyclopentane, has a molar extinction coefficient of 8500.[14] Careful investigation of the infrared spectrum showed also a shoulder at 6.14 μ, the frequency at which the conjugated dimethylene compound absorbs Hydrogenation of the butadiene dimer over platinum oxide produced not only the three expected trimethylcyclopentanes, but also a small amount of a fourth compound of mass 110 having a weak C=C absorption at 5.95 μ with no evidence of a hydrogen attached to the double bond. Blomquist reported that 3-methyl-1,2-dimethylenecyclopentane (**7**) absorbed only 1 mol of hydrogen, when it was hydrogenated over platinum oxide. However, addition of a few drops of hydrochloric acid to the half-hydrogenated product allowed the uptake of the second mole of hydrogen.[14] Most probably the intermediate 1,2,3-trimethylcyclopentane (**8**) resists hydrogenation under ordinary conditions (Scheme I).

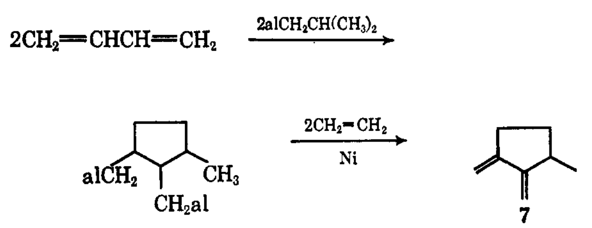
SCHEME I



Hydrogenation of our butadiene dimer produced 52% **5**, 25% **4**, 8% **3**, and 15% of the fourth compound (**8**). Continued hydrogenation after the addition of a few drops of hydrochloric acid eliminated the fourth compound and produced 66% **5**, 26% **4**, and 8% **3**. On the basis of the ultraviolet absorption spectrum and the hydrogenation data it appears that the butadiene dimer is approximately an 80:20 mixture of the 1,3-dimethylene and the 2,3-dimethylene isomers (**6** and **7**), respectively. The over-all reaction leading to methyldimethylenecyclopentane can be described by reactions 2 and 3.



(2)



(3)

It is of interest to note that hydrogenation over platinum oxide results predominantly in the formation

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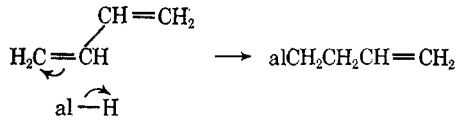
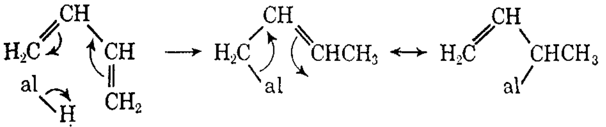
[14] A. T. Blomquist, J. Wolinsky, Y. C. Meinwald, and D. T. Longone, *J. Amer. Chem. Soc.*, **78**, 6057 (1956).

of the 1,*cis*-2,*cis*-3 isomer (**5**), *i.e.*, the thermodynamically least stable isomer. This result is in agreement with data found by investigators[15,16] who studied the hydrogenation of dimethylcyclohexenes and methylenemethylcyclohexanes. On the other hand, hydrolysis of the bis(aluminomethyl) methylcyclopentane polymer gives rise to a predominant amount of the 1,*trans*-2, *cis*-3 isomer (**3**), the thermodynamically most stable isomer. The stereochemical distribution of isomers gives us a clue about the possible mechanism.

It is reasonable to assume that addition of alH to butadiene occurs both in 1,2 and 1,4 fashion (eq 4 and 5, respectively). The 1,4 adduct can then by allylic rearrangement be in equilibrium with the reverse 1,2 adduct.

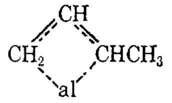


$$H_2C{=}CH{-}CH{=}CH_2 + \text{al}{-}H \longrightarrow \text{al}CH_2CH_2CH{=}CH_2 \qquad (4)$$



(5)

or possibly



alH = >AlH in R_2AlH

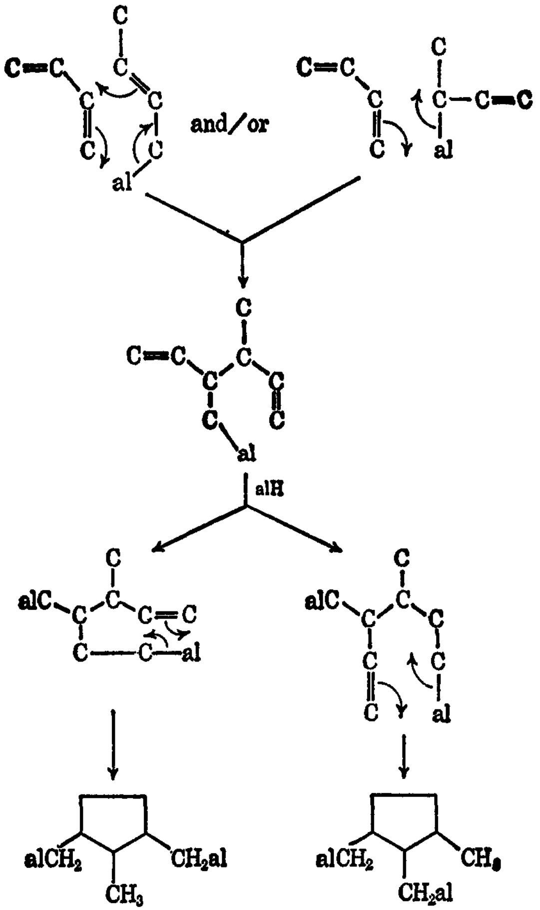
The situation here is probably similar to that of the well-known butenyl Grignard reagent.[17] It is of interest to note that allylmagnesium halides are markedly more reactive in addition reactions than alkylmagnesium halides.[18] It is thought that β,γ unsaturation exerts a weakening influence upon the carbon-metal bond.

The reactive butenylaluminum intermediate can add to another molecule of butadiene and cyclize to give a variety of C_8H_{16} hydrocarbons after hydrolysis. Possible products are 1,2,3-trimethylcyclopentane, 1-ethyl-1-methyl- and 1-ethyl-3-methylcyclopentane, ethylcyclohexane, and 1,2- as well as 1,4-dimethylcyclohexane. 1,2,3-Trimethylcyclopentanes were the only C_8H_{16} hydrocarbons we were able to detect. If any of the other hydrocarbons mentioned are in the reaction product, they must be present in very small amounts. The formation of the trimethylcyclopentanes can be rationalized as in Scheme II.

The predominance of the 1,*trans*-2,*cis*-3 isomer (**3**) is in agreement with Scheme III. During the addition of a second molecule of butadiene such conformations which are of lowest energy will be preferentially assumed; after cyclization the new CH_2al group prefers to be *trans* with respect to the CH_3 group on the neighboring carbon atom.

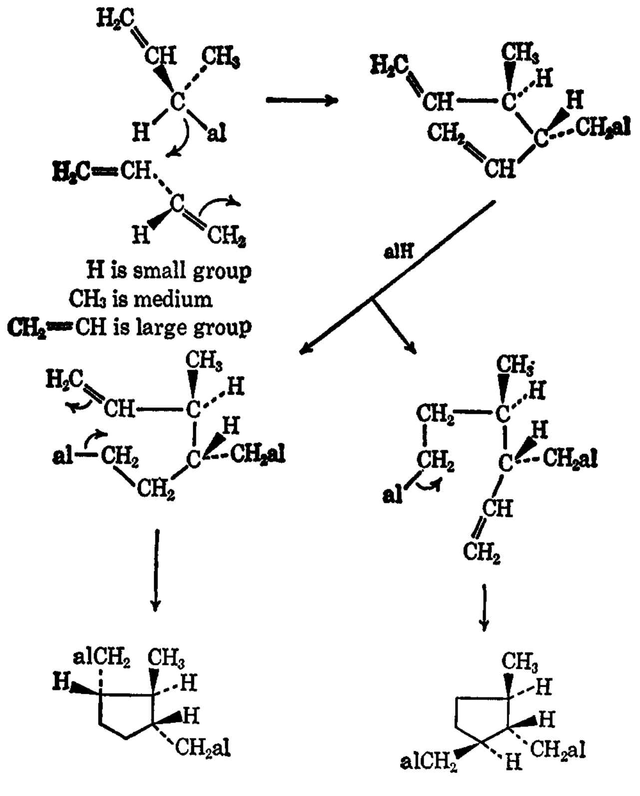
When TIBA and butadiene were heated in a closed vessel, the result was much more complex. In this case the isobutylene, which could not escape, reacted with the butenylaluminum or dialuminobutane to give after hydrolysis significant amounts of 2,2-dimethylhexane

SCHEME II



alH = >AlH in R_2AlH

SCHEME III



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[15] S. Siegel and G. V. Smith, *J. Amer. Chem. Soc.*, **82**, 6082 (1960).

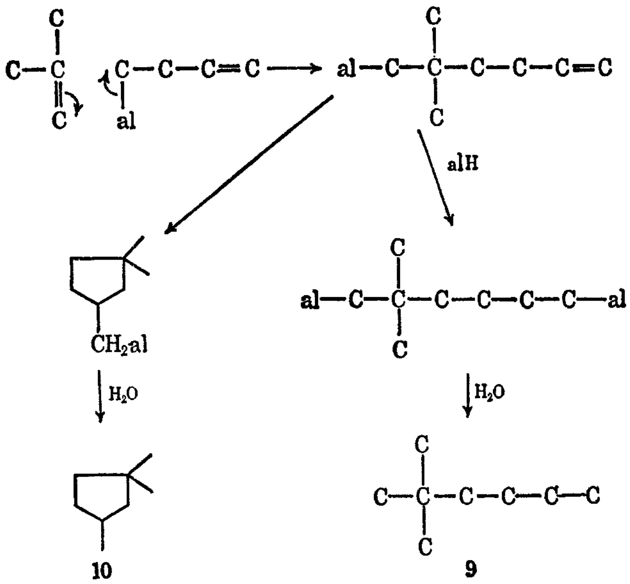
[16] J. F. Sauvage, R. H. Baker, and A. S. Hussey, *ibid.*, **82**, 6090 (1960).

[17] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1954, pp 1154-1158.

[18] H. Gilman and J. Eisch, *J. Amer. Chem. Soc.*, **79**, 2150 (1957).

(**9**) and some 1,1,3-trimethylcyclopentane (**10**) (Scheme IV).

SCHEME IV



Both compounds were again isolated by gas chromatography. **9** was identified by comparing its mass and infrared spectra as well as its gas chromatographic retention time with corresponding properties of a National Bureau of Standards sample. **10** could not be obtained pure even by gas chromatography. However, a comparison of the mass and infrared spectra with an authentic sample showed that compound **10** possessed all of the significant features of 1,1,3-trimethylcyclopentane; besides, the gas chromatographic retention times were identical.

The liberated isobutylene was also able to interact with the bis(aluminomethyl)methylcyclopentanes to produce two dimethylmethylenecyclopentanes whose exact structures were not determined. When the reaction between TIBA and butadiene in the bomb was carried out in the presence of added isobutylene, the amounts of 2,2-dimethylhexane, 1,1,3-trimethylcyclopentane, and the two dimethylmethylenecyclopentanes formed increased still further.

Experimental Section

The nmr spectra were obtained from a Varian A-60 spectrometer with tetramethylsilane as internal standard. The infrared spectra were taken on a Perkin-Elmer Model 21. The ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer. The mass spectra were obtained with a General Electric 60-deg sector magnetic focusing mass spectrometer.

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 long Ucon 50 H.B. 2000 column, a Strontium 90 detector, a column temperature varying from 50 to 200° and an argon pressure of 35 pounds. 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. In the case of complex mixtures, where separation by distillation was not successful or not attempted, 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.

TIBA-Butadiene Reaction Product and Its Hydrolysis.—Butadiene was bubbled through TIBA (160 g, 0.81 mol) with stirring during a period of 28 hr, while the temperature was maintained between 110 and 120°. The unchanged butadiene together with the displaced isobutylene was collected in a Dry Ice trap and analyzed by mass spectroscopy. It was found that 126 g (93%) of isobutylene had been displaced together with about 410 g of unchanged butadiene. The reaction product, which was very viscous at 110° and a colorless glassy solid at room temperature, weighed 125 g. It was hydrolyzed carefully with ethanol (300 g) to give 34 g of low-boiling material which was collected in a Dry Ice trap and analyzed by mass spectroscopy; it contained 20.2 g (29% yield) of butane, 10.3 g (7.4%) of recovered isobutane derived from unchanged TIBA, 2.3 g of isobutylene, 1.0 g of butadiene and traces of butenes. Then the reaction product was hydrolyzed with dilute hydrochloric acid. The upper layer was separated, washed with water, dried over magnesium sulfate and filtered to give 55 g. The major amount (44 g) of the 55 g was distilled through a short column to give the fractions listed in Table II.

TABLE II

Fraction	Wt, g	Bp, °C (mm)	n^{30}_{D}	d^{25}_{25}
1	29	110–120 (1 atm)	1.413	0.757
2	3	120 (atm)–70 (50)	1.426	0.775
3	2	70 (50)–118 (50)	1.443	0.813
4	8	118 (50)–82 (0.3)	1.454	0.833
Residue	4			

Gas chromatography, using a capillary chromatograph at 113°, showed that fractions 1 and 2 contained the four major components given in Table III.

TABLE III

	Peak			
	I	II	III	IV
Retention time, min	$5\frac{1}{8}$	$5\frac{1}{2}$	$5\frac{3}{4}$	$6\frac{1}{2}$
% of fraction 1	82	8	5	5
% of fraction 2	20	20	20	40

Since fraction 1 contained 1,*trans*-2,*cis*-3-trimethylcyclopentane (**3**) as predominant component, this compound could be identified in fraction 1 without difficulty. Gas chromatography afforded an even purer sample. The last three components were separated by gas chromatography from fraction 2. Peak I was found to represent 1,*trans*-2,*cis*-3-trimethylcyclopentane (**3**), peak II 1,*cis*-2,*trans*-3-trimethylcyclopentane (**4**), peak III 1,*cis*-2,*cis*-3-trimethylcyclopentane (**5**), and peak IV the unknown cyclic C_8H_{14} olefin as has already been discussed. Fraction 3 contained mostly $C_{12}H_{22}$ and $C_{12}H_{24}$ hydrocarbons (highest mass units 166 and 168). Fraction 4 contained probably C_{12} and C_{16} hydrocarbons. The yield of 1,2,3-trimethylcyclopentanes was about 27%.

For comparison, the physical constants of the three 1,2,3-trimethylcyclopentanes, which have been reported previously,[19] are given in Table IV.

None of the two dimethylmethylenecyclopentanes, 2,2-dimethylhexane (**9**), and 1,1,3-trimethylcyclopentane (**10**) found in various runs could be obtained pure by distillation.

TABLE IV

	Bp, °C	$n^{20}D$	d^{20}_{4}
1,*trans*-2,*cis*-3	110.2–110.3	1.4140	0.7540
1,*cis*-2,*trans*-3	118–118.2	1.4216	0.7695
1,*cis*-2,*cis*-3	122–122.1	1.4250	0.7766

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(19) A. V. Koperna and B. A. Kazanskii, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 302 (1948); *Chem. Abstr.*, **43**, 155 (1949).

TABLE V

Compound	Bp, °C
2,2-Dimethylhexane	106.8[a]
1,1,3-Trimethylcyclopentane	104–104.2[b]
1,*trans*-2,*cis*-3-Trimethylcyclopentane	110.2–110.3[c]
1,*cis*-2,*trans*-3-Trimethylcyclopentane	118–118.2[c]
1,*cis*-2,*cis*-3-Trimethylcyclopentane	122–122.1[c]
Dimethylmethylenecyclopentane "A"	~117
Dimethylmethylenecyclopentane "B"	~120
Unknown cyclic olefin (C_8H_{14})	>122
2-Methyl-1,3-dimethylenecyclopentane	120–121°

[a] C. B. Willingham, W. J. Taylor, J. M. Pignocco, and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **35**, 219 (1945). [b] H. Pines and J. T. Arrigo, *J. Amer. Chem. Soc.*, **79**, 4958 (1957). [c] See ref 19.

However by repeated distillations we were able to enrich certain fractions with the desired components so that isolation in a fairly pure state by gas chromatography was possible. In Table V are the nine components found in the C_8 fraction in the order of increasing retention times using the Barber–Coleman capillary gas chromatograph with a UCON column. Some of the boiling points are only approximate.

2-Methyl-1,3-dimethylenecyclopentane and 3-Methyl-1,2-dimethylenecyclopentane.—Butadiene was bubbled through TIBA (768 g, 3.87 mol) under conditions similar to those described in the previous experiment to give 612 g of a colorless polymer. Of this polymer 215 g, which is equivalent to 1.36 mol of initial TIBA, was used for the following run.

A mixture of TIBA–butadiene polymer (215 g), benzene (350 g), phenylacetylene (0.3 ml), and nickel acetylacetonate (0.1 g) was charged under nitrogen to a 3-l. stainless steel bomb. After the addition of ethylene (276 g, 9.86 mol) the bomb was heated with rocking to 71° within 35 min to give a pressure of 860 psi. Heating with rocking between 71 and 78° was continued for 21 hr. The pressure had dropped to 420 psi at 75°. The bomb was connected to two Dry Ice traps and vented at room temperature. A 44-g sample of material was collected in cold traps. This material was analyzed by mass spectroscopy and found to contain about 12 g of benzene, 28 g of butenes, and 4 g of butadiene. The contents of the bomb were transferred under nitrogen to a distillation flask. The bomb was rinsed with some benzene, and the distillation was continued. All of the product was now soluble in benzene. The vacuum was gradually reduced to 200 mm at room temperature, and another 82 g was collected in a Dry Ice cold trap that contained 6 g of benzene, 65 g of butenes, and 11 g of butadiene. Finally, the vacuum was reduced to 3 mm at room temperature to give 566 g of distillate, which according to gas chromatography consisted of only two compounds. The major one was benzene, the other one (38 g based on gas chromatographic calculations, 17% yield based on initial TIBA) was methyldimethylenecyclopentane. The 566-g portion was washed with water. Most of the benzene was removed by distillation through a 4-ft long column. Then the distillation was continued on a 20-in. long spiral wire column to give 23 g of methyldimethylenecyclopentane, bp 118–121°. The remainder of the methyldimethylenecyclopentane distilled over with the benzene. The major fraction (12 g) had the following physical properties: bp 120–121°; $n^{20}D$ 1.4621; d^{20}_4 0.8172 [ϵ_{max} (2480 Å) 1900 in methanol].

Anal. Calcd for C_8H_{12}: C, 88.32; H, 11.18; mol wt, 108; MD for pure 1,3-dimethylene compound, 36.02. Found: C, 88.61; H, 11.41; mol wt (largest parent peak), 108; MD, 36.40.

The capillary gas chromatograph showed the presence of only one major peak (several smaller peaks corresponded to a total of 5%), when the sample was sent through a 200-ft long UCON column at 49°. Despite this it is believed that the material contains about 20% of the 2,3-dimethylene compound; this assumption would explain the uv absorption, the slightly high molecular refractivity caused by exaltation, and the shoulder at 6.14 μ in the infrared spectrum. The nuclear magnetic resonance spectrum was in agreement with the 1,3-dimethylene compound as the predominant structure.

After removal of benzene and methyldimethylenecyclopentane there was obtained 119 g (77% yield), bp 65 (3 mm)–78° (1 mm), of fairly pure triethylaluminum. Hydrolysis of this cut produced ethane as almost the only hydrocarbon. The residue (57 g) was not identified.

Reduction of Methyldimethylenecyclopentane.—The starting material is believed to have contained about 80% of the 2-methyl-1,3-dimethylenecyclopentane (**6**) and 20% of the 1-methyl-2,3-dimethylenecyclopentane (**7**).

This methyldimethylenecyclopentane (3 ml) was hydrogenated over platinum oxide in a Parr hydrogenator at 40 psi and room temperature. After 50 min the pressure had decreased to 37.5 psi. The gas chromatographic spectrum showed the presence of four peaks: 8% of peak I, 25% of peak II, 52% of peak III, and 15% of peak IV. The infrared spectrum of the product showed all the significant features of 1,*cis*-2,*cis*-3-trimethylcyclopentane (**5**). Peaks I and III had the same retention times as the authentic 1,*trans*-2,*cis*-3 and 1,*cis*-2,*cis*-3 isomers (**3** and **5**), respectively. The products representing peak II and IV were isolated by gas chromatography and investigated by infrared and mass spectroscopy. The compound representing peak II was identical with the 1,*cis*-2,*trans*-3 isomer (**4**) which was obtained from TIBA and butadiene after hydrolysis. The compound representing peak IV was a C_8H_{14} hydrocarbon (highest mass unit 110). The infrared spectrum showed weak C=C absorption at 5.95 μ, but no absorption indicating the attachment of a hydrogen to the double bond. It is believed to be 1,2,3-trimethylcyclopentene (**8**).

When the hydrogenation was repeated with methyldimethylenecyclopentane (3 ml) dissolved in ethanol (3 ml), the same result was obtained. However, addition of 2 drops of concentrated hydrochloric acid followed by hydrogenation for 50 min converted all of the compound representing peak IV into 1,2,3-trimethylcyclopentane. The reaction product was washed with water, dried over magnesium sulfate and then investigated by gas chromatography again. This time only compounds representing peaks I, II, and III were present in 8, 26, and 66%, respectively.

Registry No.—Triisobutylaluminum, 100-99-2; butadiene, 106-99-0; **3,** 19374-46-0; **4,** 19374-47-1; **5,** 19374-48-2; **6,** 15890-38-7; **7,** 15890-39-8.

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