mersed in a Dry Ice bath and protected from atmospheric moisture with a calcium chloride drying tube. The reaction mixture was heated at 180–183° for 1 hr., at which time the flask was cooled down. A vacuum pump was attached and further material was distilled into the collection flask at 1–2 mm. until the solvent began to distil. The distillate, analyzed by v.p.c. on a 2-m. polypropylene glycol column (Perkin-Elmer column RX), contained only methanol, norbornadiene, and bis(2-ethoxyethyl) ether. Calculations, utilizing Eastman's formula,[14] gave 0.71 g. (25.3%) of norbornadiene. The norbornadiene generated in this reaction was isolated and identified by comparison of its infrared spectrum with that of an authentic sample.

Acknowledgment.—The authors gratefully acknowledge the support of this research by the National Science Foundation (NSF-G13511), and wish to express their appreciation to Dr. Donald P. Hollis and Varian Associates, Palo Alto, California, for the n.m.r. spectra.

---

(14) R. H. Eastman, *J. Am. Chem. Soc.*, **79**, 4243 (1957).

Reaction of α,ω-Dienes with Diisobutylaluminum Hydride

GO HATA AND AKIHISA MIYAKE

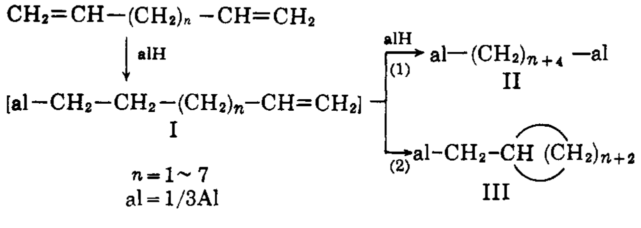
Basic Research Laboratories, Toyo Rayon Company, Ltd., Kamakura, Japan

Received April 22, 1963

It is expected that organoaluminum compounds having two aluminum atoms attached to both ends of the polymethylene chain can be prepared by addition of aluminum hydride to an α,ω-diene. Ziegler[1] reported, however, that 1,5-hexadiene and diisobutylaluminum hydride gave methylenecyclopentane and a cyclopentylmethylaluminum compound, but not the expected 1,6-dialuminohexane derivative. It also was reported that 2,5-dimethyl-1,5-hexadiene easily cyclized to a five-membered ring compound.

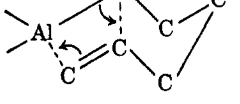
In this type of cyclization, the chain length of the α,ω-diene seems to be a most important factor. In order to clarify the effect of the chain length on the reaction product, we have investigated the reaction between diisobutylaluminum hydride and α,ω-dienes having carbon numbers from five to eleven.

The reaction was carried out by heating a mixture of the α,ω-diene and diisobutylaluminum hydride in a 1:2 molar ratio at 70° for sixteen hours. Two products, II and III, were obtained, but no ω-alkenylaluminum compound (I) was detected (see Table I).



It is clear from the table that the ratio of *n*-alkane to methylcycloalkane varies widely depending on the chain length of the starting diene. The reaction of 1,4-pentadiene resulted in an exclusive formation of 1,5-dialuminopentane derivative and no four-membered ring compound was formed. 1,5-Hexadiene gave predominantly the cyclopentylmethylaluminum derivative (97.6%). On the other hand, 1,6-heptadiene was found to form almost quantitatively the 1,7-dialuminoheptane derivative with a minor amount (0.9%) of the cyclohexylmethylaluminum derivative. The higher dienes gave exclusively the α,ω-dialuminoalkane compounds. Formation of the six-membered ring is very difficult in contrast to the ease of five-membered ring formation.

Reactions 1 and 2 are competitive and reaction 2 would proceed, as shown by formula IV, through the intramolecular addition reaction of the ω-alkenylaluminum compound produced by the addition of one mole of diisobutylaluminum hydride to α,ω-diene.



IV

Under the same reaction conditions, the intermolecular addition reaction of trialkylaluminum to α-olefin was found to be very slow. For example, the reaction of triethylaluminum with 1-hexene (molar ratio 1:1, 70°, 16 hr.) gives an addition compound in only 1% yield. The easy ring closure of 1,5-hexadiene to the five-membered ring compound suggests that the intramolecular addition of the 5-hexenylaluminum derivative is facilitated by the cyclic intermediate in which the carbon–aluminum bond is favorably located to attack the terminal double bond as shown in the preceding formula. On the other hand, difficulty in the six-membered ring formation shows that the steric requirement of the 6-heptenylaluminum derivative is less favorable for this type of attack.

This decisive effect of the chain length of an α,ω-diene on the reaction product indicates that the intramolecular addition reaction of an ω-alkenylaluminum compound is extremely sensitive to steric factor.

The 1,7-dialuminoheptane derivative has considerable stability at a higher temperature. At 125° a small portion of the compound cyclized to the cyclohexylmethylaluminum derivative. This ring closure seems to proceed through the reverse reaction of 1.

Experimental

Diisobutylaluminum Hydride.—The hydride was prepared by the pyrolysis of distilled triisobutylaluminum under a purified nitrogen atmosphere.[2] At the end of the pyrolysis, temperature and pressure were kept at 130° (3 mm.) until evolution of isobutylene ceased.

1,4-Pentadiene.—The previously described apparatus and method[3] were used to give 78% of 1,4-pentadiene from 205 g. (1.1 moles) of 1,5-diacetoxypentane. It was purified by digestion over sodium and repeated distillations through a Widmer column, b.p. 26.0–26.5°,[4] $n^{20}\text{D}$ 1.3889.

1,5-Hexadiene.—The diene was prepared from allyl bromide and magnesium in ethyl ether. Purification was effected by distillation over sodium, followed by preparative gas chromatogra-

---

(1) K. Ziegler, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p. 234.

(2) K. Ziegler, H. G. Gellert, H. Lehmkuhl, W. Pfohl, and K. Zosel, *Ann.*, **629**, 1 (1960).

(3) R. E. Benson and B. C. McKusick, *Org. Syn.*, **38**, 78 (1958).

(4) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **58**, 146 (1936).

TABLE I

REACTION OF α,ω-DIENES WITH DIISOBUTYLALUMINUM HYDRIDE

α,ω-Diene	Mole	$(i\text{-Bu})_2$AlH(mole)	Hydrolyzed products (composition, %)	
			n-Alkane	Methylcycloalkane
1,4-Pentadiene	0.03	0.063	n-Pentane (100)	.....
1,5-Hexadiene	0.02	0.042	n-Hexane (2.4)	Methylcyclopentane (97.6)
1,6-Heptadiene	0.02	0.042	n-Heptane (99.1)	Methylcyclohexane (0.9)
1,7-Octadiene	0.02	0.042	n-Octane (100)	.....
1,8-Nonadiene	0.03	0.063	n-Nonane (100)	.....
1,9-Decadiene	0.03	0.063	n-Decane (100)	.....
1,10-Undecadiene	0.03	0.063	n-Undecane (100)	.....

phy using a Beckman Megachrom instrument equipped with an Apiezon "L" column, $n^{20}\mathrm{D}$ 1.4043.[5]

1,6-Heptadiene.—The procedure used by Marvel and Stille[6] was followed. Reduction of 97.2 g. (0.45 mole) of diethyl pimelate with a solution of 36 g. (0.9 mole) of lithium aluminum hydride in 1400 ml. of ethyl ether yielded 31 g. (53%) of 1,7-heptanediol, b.p. 125–127° (3.5 mm.). The diol (61 g., 0.46 mole) was acetylated with acetyl chloride in ethyl ether, yielding 89 g. (90%) of 1,7-diacetoxyheptane, b.p. 99–100° (0.6 mm.). Using the same apparatus as described for the preparation of 1,4-pentadiene, this acetate was subjected to pyrolysis at 500° with an addition rate of 1 ml./min. to yield 18 g. (45%) of 1,7-heptadiene, b.p. 90–93°. It was purified by distillation over sodium, followed by preparative gas chromatography, $n^{20}\mathrm{D}$ 1.4148.[7]

1,7-Octadiene.—The diene (b.p. 115–121°)[8] was digested over sodium, redistilled and purified by preparative gas chromatography, $n^{20}\mathrm{D}$ 1.4220.

1,8-Nonadiene.—Diethyl azelate was the starting ester for the preparation of 1,9-nonanediol. Pyrolysis of 162 g. (0.66 mole) of 1,9-diacetoxynonane[8] gave 60% of 1,8-nonadiene, b.p. 120–143°. After digestion over sodium and distillation through a Widmer column, it boiled at 142–143°, $n^{20}\mathrm{D}$ 1.4289.[8]

1,9-Decadiene.—Pyrolysis of 87 g. (0.34 mole) of 1,10-diacetoxydecane was carried out at 500° with an addition rate of 2 ml./min., yielding 25 g. (53%) of 1,9-decadiene. The diene was digested over sodium and redistilled through a Widmer column, b.p. 164–165°, $n^{20}\mathrm{D}$ 1.4318.[8]

1,10-Undecadiene.—The previously described method[9] was used to give diene of b.p. 86.5–87.5° (31 mm.), $n^{20}\mathrm{D}$ 1.4354.

Purity of the prepared dienes, determined by vapor phase chromatography on an 8-ft. squalane column, was found to be 99.9% or higher.

Reaction between α,ω-Dienes and Diisobutylaluminum Hydride.—α,ω-Diene and diisobutylaluminum hydride in a 1:2.1 molar ratio were added to a glass tube flushed with nitrogen. After sealing, the glass tube was kept in an oil bath at 70° for 16 hr. The reaction products from 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, and 1,10-undecadiene were viscous at a room temperature. Those from 1,4-pentadiene and 1,5-hexadiene were not viscous. The products from 1,4-pentadiene and 1,6-heptadiene were diluted with 10 ml. of n-hexane. The products from the other dienes were diluted with 10 ml. of n-heptane. The diluted products were decomposed by successive addition of 2.5 ml. of ethanol, 1 ml. of water, and 25 ml. of 6 N hydrochloric acid. The organic layer was washed twice with water and dried over sodium sulfate. The hydrocarbon produced by the hydrolysis was separated by the gas chromatographic technique. n-Pentane, n-hexane, methylcyclopentane, n-heptane, n-octane, n-nonane, n-decane, and n-undecane were identified by comparing their gas chromatographic retention times and infrared spectra with authentic samples. Methylcyclohexane was identified by comparison of its retention time with an authentic sample. The composition of the products was determined from the peak area of gas chromatogram.

Stability of 1,7-Dialumino-heptane Compound.—A mixture of 1.9 g. (0.02 mole) of 1,6-heptadiene and 6.0 g. (0.042 mole) of diisobutylaluminum hydride was at first heated under the same conditions as described previously (16 hr., 70°), and then for an additional 13 hr. at 125°. The reaction mixture was hydrolyzed as in the aforementioned method. The hydrolyzed product consisted of 91.5% of n-heptane and 8.5% of methylcyclohexane. Thus the additional heating at the higher temperature (125°) increased the yield of methylcyclohexane by 7.6%. Methylcyclohexane was separated by gas chromatographic technique and its infrared spectrum was identical with that of an authentic sample.

---

[5] F. Cortese, *J. Am. Chem. Soc.*, **51**, 2266 (1929).

[6] C. S. Marvel and J. K. Stille, *ibid.*, **80**, 1740 (1958).

[7] A. L. Henne and K. W. Greenlee, *ibid.*, **65**, 2020 (1943).

[8] C. S. Marvel and W. E. Garrison, *ibid.*, **81**, 4737 (1959).

[9] J. N. Reformatsky, E. Grischkewitsch-Frochimowsky, and A. Semenzow, *Ber.*, **44**, 1885 (1911).

Ferrocenes. VI. Oxidation in Friedel–Crafts Reactions[1,2]

ROBERT L. SCHAAF AND CARL T. LENK

Research Department, Wyandotte Chemicals Corporation, Wyandotte, Michigan

Received May 20, 1963

During an investigation toward the synthesis of difunctional ferrocenes, a number of attempted Friedel–Crafts reactions under nitrogen resulted in significant oxidation of ferrocene to ferricinium ion.

Although over thirty publications and patents describe Friedel–Crafts reactions on ferrocene with some thirty-five different acyl chlorides, only one was found in which the yield of ferrocene was reported from reduction of the purple aqueous layer obtained upon hydrolysis. In this instance, the reaction of chloroacetyl chloride, aluminum chloride, and ferrocene under conditions chosen for monosubstitution gave 32% ferrocene upon reduction of the aqueous layer.[3] Oxidation can be assumed to be small when hydrolysis produced an aqueous layer that was pale blue[4,5] or when yields of expected products exceeded 90%.[6,7]

Like chloroacetyl chloride, dichloro- and trichloroacetyl chlorides with aluminum chloride were found to oxidize ferrocene significantly; reduction of the purple aqueous layers gave ferrocene in 47 and 48% yields, respectively. Similarly, terephthaloyl, p-nitrobenzoyl, and ethyl oxalyl chlorides gave ferricinium ion in 57, 47, and 64% yields. The high per cent of oxidation with ethyl oxalyl chloride suggests that the failure

---

[1] Presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

[2] This investigation was conducted under Air Force Contract AF 33(616)-7214, monitored by the Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.

[3] K. Schlögl, *Monatsh. Chem.*, **88**, 601 (1957). The organic layer yielded 12% chloroacetylferrocene and 16% unreacted ferrocene.

[4] M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958).

[5] M. D. Rausch and L. E. Coleman, *J. Org. Chem.*, **23**, 107 (1958).

[6] M. D. Rausch, M. Vogel, and H. Rosenberg, *ibid.*, **22**, 903 (1957).

[7] E. L. DeYoung, *ibid.*, **26**, 1312 (1961).