The next benzene fractions (1500 ml. total) contained 1.89 g. of solid that crystallized from methylene chloride–ethanol, m.p. 204–208°, $[\alpha]^{25}\text{D}$ −95°, λ^{Nujol} 5.75 and 5.80 μ $(O\overset{\displaystyle O}{\overset{\|}{C}}CH_3)$, for VI.

Anal. Calcd. for $C_{60}H_{90}O_4$: C, 82.32; H, 10.36; mol. wt., 875.5. Found: C, 82.56; H, 10.12; mol. wt., 876.

Elution was continued with 10% ether in benzene (1000 ml.) and 2.36 g. of 3β-acetoxy-6-ethoxy-7(8),22-ergostadien-5α-ol was obtained. After crystallization from methylene chloride–ethanol, the sample VII melted at 167–168°. Further crystallization gave an analytical sample, m.p. 174–175°, $[\alpha]^{26}\text{D}$ −95°, λ^{Nujol} 2.91 (–OH), 5.80 and 5.89 μ $(-O\overset{\displaystyle O}{\overset{\|}{C}}-CH_3)$.

Anal. Calcd. for $C_{32}H_{52}O_4$: C, 76.75; H, 10.47. Found: C, 76.90; H, 10.20.

When 750 mg. of the chromatographic fraction of VI was crystallized from ether, 90 mg. of colorless crystalline material (m.p., 225–260°) was obtained. Further crystallization gave an analytical sample, m.p. 259–263°, $[\alpha]^{26}\text{D}$ −49° (0.75%).

The analyses was calculated as 3β-acetoxy-7(8),22-ergostadiene-5α-6β-diol.

Anal. Calcd. for $C_{29}H_{46}O_4$: C, 75.94; H, 10.11. Found: C, 75.94; H, 10.19.

Acetylation of 35 mg. of this C-6 alcohol with acetic anhydride in pyridine yielded 25 mg. of the 3,6-diacetate which, after trituration with methanol, melted at 165–166°, $[\alpha]^{24}\text{D}$ −129°; lit.[8] m.p. 171°, $[\alpha]\text{D}$ −146°.

Oxidation of 3β-Acetoxy-6-ethoxy-7(8),22-ergostadien-5α-ol.—A solution of 200 mg. of the steroid in 40 ml. of acetone was treated dropwise, at room temperature, with Jones chromium trioxide solution until a slight excess was present. The mixture was filtered through Celite, and the volume of the filtrate was reduced to approximately one-half under reduced pressure; it was then poured into ice–water (200 ml.). The precipitate was filtered and washed with water. After crystallization from methylene chloride–ethanol, the 3β-acetoxy-7(8),22-ergostadien-5α-ol-6-one melted at 253–259°, $\lambda_{\text{max}}^{\text{ether}}$ 240 mμ (12,000). Another recrystallization raised the melting point to 261–263°, $[\alpha]^{25}\text{D}$ −1° [lit.[8] m.p. 269°, $[\alpha]\text{D}$ ±0, $\lambda_{\text{max}}^{\text{ethanol}}$ 248 (12,900)].

Hydrolysis of the Dimer VI.—The dimer VI with aqueous potassium hydroxide in methanol dioxane (1:1) yielded a diol, after crystallization from acetone, m.p. 191–193°, λ^{Nujol} 2.9 μ (OH), $[\alpha]^{26}\text{D}$ −258° (pyridine); reported[3] for bisergostatrienol, m.p. 202–203°, $[\alpha]^{16}\text{D}$ −209 (pyridine). A mixture melting point determination showed m.p. 181–190°.

Oxidation of the Dimer VI. **A.**—A solution of 200 mg. of the diol prepared from VI in 20 ml. of pyridine was added to a mixture of anhydrous chromium trioxide (300 mg.) and 10 ml. of pyridine. The mixture was allowed to stand at room temperature for 18 hr. It was poured into ice–water, and sodium bisulfite was added to decompose excess chromium trioxide. Hydrochloric acid was added until the solution was slightly acidic and the precipitate was filtered and washed with water. The yellow solid (132 mg.) was dissolved in a minimum amount of benzene and chromatographed on 6 g. of acid-washed alumina (Merck). Benzene (65 ml.) eluted 56 mg. of 4,6,8(14),22-ergostatetraen-3-one, m.p. 108–113°, $\lambda_{\text{max}}^{\text{ethanol}}$ 350 mμ (24,500), $[\alpha]^{25}\text{D}$ +526°; lit.[7] m.p. 114–115°, $[\alpha]^{35}\text{D}$ +590, $\lambda_{\text{max}}^{\text{ethanol}}$ 348 mμ (26,500).

B.—To 200 mg. of VI in 10 ml. of benzene and 10 ml. of acetone was added 1.8 g. of aluminum *t*-butoxide. After refluxing the mixture for 6 hr. under a nitrogen atmosphere, 10 ml. of a 1:1 mixture of acetone–benzene was added. After 13 hr. of refluxing, an additional 1.0 g. of aluminum *t*-butoxide and 10 ml. of acetone–benzene (1:1) was added. After refluxing for 23 more hr., the solution was cooled and 25 ml. of benzene was added. The mixture was poured into a cold dilute solution of sulfuric acid and Rochelles salt. The benzene layer was separated, and a benzene extract (50 ml.) of the aqueous layer was added. The benzene was washed with two 100-ml. portions of water and with saturated salt solution (50 ml.). It was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure to leave a yellow oil weighing approximately 500 mg. The oil was dissolved in a minimum amount of benzene and filtered through a column of Florisil (4 g.). A benzene wash (25 ml.) yielded 420 mg. of a yellow-brown oil. This oil was then redissolved in benzene and chromatographed on 12 g. of Florisil. Benzene (160 ml.) eluted 332 mg. of a multicomponent oil. Methylene chloride (150 ml.) eluted 70 mg. of 4,6,8(14),22-ergostatetraen-3-one of an estimated 80% purity by its ultraviolet spectrum. The infrared spectrum and thin layer chromatography showed this material to be identical with that prepared *via* the chromium oxide–pyridine oxidation.

Reduction of 3β-Acetoxy-6,22-ergostadiene-5α,8α-diol (X) with Chromous Chloride.—The triol corresponding to X was obtained by the method of Windaus and Linsert[10] and acetylated with pyridine and acetic anhydride to yield X. A solution of 1.51 g. of X in 150 ml. of tetrahydrofuran and 150 ml. of ethanol was treated with 180 ml. of chromous chloride reagent in a manner identical with that employed for the reduction of the epidioxide IV. A colorless solid (1.37 g.) obtained by this procedure was chromatographed on 45 g. of Florisil. The first two benzene fractions (50 ml. each) eluted 451 mg. of ergosteryl acetate. The next three benzene fractions totalling 220 ml. eluted 354 mg. of the dimer diacetate VI. Elution with ether (100 ml.) afforded 515 mg. of the hydroxy acetate VII. The physical and spectral characteristics of the products obtained from this reduction were identical in all respects with the compounds obtained from the reduction of ergosteryl acetate epidioxide.

The Reactions of Nortricyclyl and Dehydronorbornyl Chloride with Sodium

Peter K. Freeman, Daniel E. George,[1]
and V. N. Mallikarjuna Rao

Department of Physical Sciences,
University of Idaho, Moscow, Idaho

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An interest in whether α-elimination would occur in the reaction of nortricyclyl chloride with sodium, since β-elimination is prevented by Bredt's rule, prompted the investigation reported here.

Nortricyclyl chloride (I) reacts with sodium in decane at 85–90° to produce a 19–20% yield of C_7 hydrocarbons, isolated directly from the reaction mixture by vacuum distillation. Vapor phase chromatographic and infrared analysis of this volatile hydrocarbon mixture demonstrated that there were four components present: nortricyclene (II), 71%; norbornene (III), 10%; and two additional C_7H_{10} hydrocarbons, 5.9%, 13.1%. The ultraviolet and infrared spectra indicated that the structures of these two hydrocarbons must be reasonably limited to 3-vinylcyclopentene (IV) and 4-vinylcyclopentene (V). The 13.1% component showed only end absorption in the ultraviolet (ϵ_{210} 250), while the infrared spectrum indicated a vinyl double bond (ν_{max} 905, 992, 1638 cm.$^{-1}$)[2] and a cyclopentene double bond (ν_{max} 1610 cm.$^{-1}$).[3] The spectra of the 5.9% component were very similar (end absorption, ϵ_{210} 1774; ν_{max} 910, 990, 1608, and 1635 cm.$^{-1}$). The n.m.r. spectrum of this minor component exhibits complex multiplet absorption centered at 4.38 (3.0 H), 5.04 (1.8 H), and 6.70 τ (0.9 H) and a complex absorption region, 7.50–8.50 τ (4.0 H), while the major (13.1%) component shows complex multiplet absorption centered at 4.16 and 4.39 (3.1 H), 5.08 (2.0 H), and a complex absorption region 6.93–8.10 τ (4.9 H). In both cases the internal olefinic absorption near 4.38

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(1) National Defense Act Fellow, 1959–1962.

(2) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, Chap. 3.

(3) R. N. Jones and C. Sandorfy, "Technique of Organic Chemistry, Volume IX. Chemical Applications of Spectroscopy," W. West, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 371.

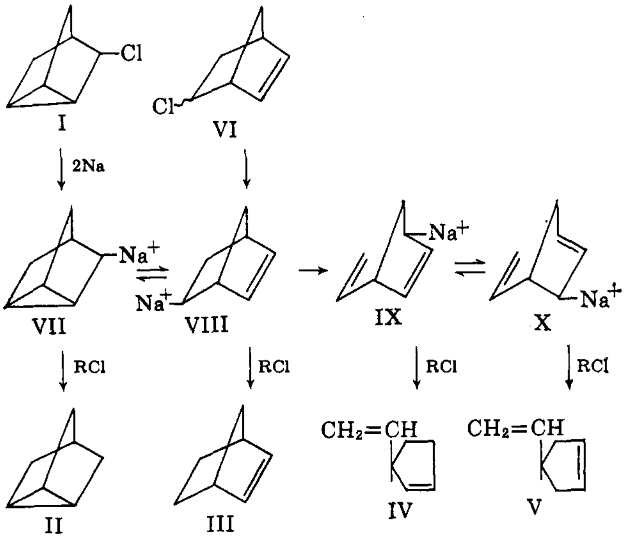
TABLE I

RCl	Reaction temperature,[a] °C.	Yield, %	II, %	III, %	IV, %	V, %	Norbornadiene, %
I	85–90 (133)	19.2	71.0	10.0	5.9	13.1	. . .
VI	85–90 (133)	27.1	64.0	13.0	7.5	13.5	2.0

[a] Temperature of oil bath. The figure in parentheses is maximum temperature reached inside the reaction flask due to the exothermic nature of the reaction.

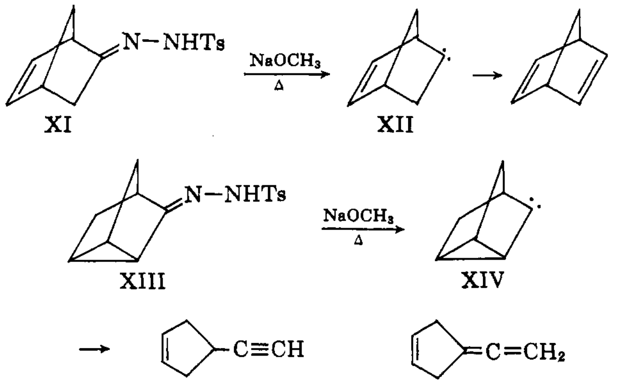
τ and the terminal methylene near 5.04 τ are consistent with 3- and 4-vinylcyclopentene structures.[4]

A choice may be made between the two possibilities, since in the spectrum of the minor (5.9%) component the single proton absorption at 6.70 τ appears at an appropriate position for a C–H alpha to two double bonds. This is supported by the fact that the methylene absorption region extends further upfield in the spectrum of the minor component—a reflection of the fact that one of the methylenes in the minor component is beta to the double bonds, while both methylenes in the major component are alpha.[4a] Thus, the minor component may be assigned structure IV, the major component V. Additional confirmation of the basic skeletal structure was obtained by hydrogenation of a mixture of IV and V. The only product obtained was the known ethylcyclopentane.



When dehydronorbornyl chloride (VI) (50% *endo*, 50% *exo*) was allowed to react with sodium, using the same reaction conditions, a 27% yield of C_7 hydrocarbons was obtained. The composition of this volatile fraction (Table I) was very similar to that obtained from nortricyclyl chloride.

With the exception of the small amount of norbornadiene formed in the dehydronorbornyl chloride reaction, all the C_7 hydrocarbons formed are C_7H_{10} hydrocarbons and would not be expected to arise by way of a bivalent carbon precursor. The two bivalent carbon intermediates anticipated (XII and XIV) have been generated by decomposition of *p*-toluenesulfonylhydrazones XI and XIII. Decomposition of XI with sodium methoxide in bis(2-ethoxyethyl) ether at 180° resulted in a 25% yield of norbornadiene as the only C_7 hydrocarbon. Thus, the small amount of norbornadiene generated in the dehydronorbornyl chloride reaction may arise by either α- or β-elimination. Cristol and Harrington[5] have shown that decomposition of XIII with sodium methoxide in bis(2-methoxyethyl) ether at 160°, also results in a C_7H_8 hydrocarbon fraction: a 19% yield of a mixture of 4-ethynylcyclopentene (69%) and 4-vinylidenecyclopentene (29%). Evidence is presented which suggests that the 4-vinylidenecyclopentene arises as a result of base-catalyzed isomerization of 4-ethynylcyclopentene.



The similarity in skeletal structure of 4-ethynylcyclopentene to 3- and 4-vinylcyclopentene raised the possibility that 4-ethynylcyclopentene may possibly be a precursor of the vinylcyclopentenes. This possibility was tested by repeating the nortricyclyl chloride–sodium reaction and isolating the C_7 hydrocarbon fraction after neutralization of the reaction mixture with methyl alcohol. Small amounts of 4-vinylidenecyclopentene (0.6%) and 4-ethynylcyclopentene (2%) appeared to be present. A second experiment carried out with a mixture of nortricyclyl chloride (1.00 g.) and 4-ethynylcyclopentene (97 mg.), using identical reaction conditions, resulted in a 47% recovery of ethynylcyclopentene. Thus perhaps 4–5% 4-ethynylcyclopentene was originally formed in the nortricyclyl chloride–sodium reaction. However, the difference between the amount presumably generated and the amount isolated would not appear sufficient to explain vinylcyclopentene formation by way of an ethynylcyclopentene intermediate.

Since the C_7 hydrocarbon products are formed in very similar percentage compositions from both nortricyclyl and dehydronorbornyl chloride, it seems reasonable to suggest a common reaction pathway. Nortricyclene and norbornene may be pictured as arising *via* an equilibrium of homoallylic carbanions VII and VIII.[6] The dehydronorbornyl carbanion may rearrange through a shift of the pair of electrons at C-5 to form a double bond (C-5, C-6) and release

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[4] (a) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, pp. 51–62; (b) the olefinic proton absorption regions in both spectra are quite similar to the olefinic proton absorption region of 4-vinylcyclohexene: N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 210.

[5] S. J. Cristol and J. K. Harrington, *J. Org. Chem.*, **28**, 1413 (1963).

[6] A similar homoallylic carbanion rearrangement has been observed by G. Wittig and E. Hahn, *Angew. Chem.*, **72**, 781 (1960).

of the electron pair bonding C-6 and C-1 to form allylic carbanions IX and X, which in turn may then proceed to product hydrocarbons IV and V. The rearrangement of VIII to IX is similar to the mechanism suggested for the cleavage of dehydronorcamphor with sodium amide.[7]

The experimental results presented do not rule out representation of the reactions in terms of mesomeric homoallylic and mesomeric allylic carbanions. Furthermore, a second mechanistic possibility is that the rearrangments occur *via* free radical intermediates, analogous to carbanions VII, VIII, IX, and X, which could be generated by a one electron transfer reaction of alkyl chloride and sodium.

Although it is unlikely that nortricyclene, norbornene, and the vinylcyclopentenes were generated *via* carbene intermediates, neutralization of the carbanions VII, VIII, IX, and X may occur by abstraction of an α-proton from I or VI. Since only trace amounts of C_7H_8 products (norbornadiene, 4-ethynylcyclopentene, and 4-vinylidenecyclopentene) were detected, the electrophilic carbene intermediate produced by α-elimination presumably adds to an alkylsodium to form a C_{14}-carbanion (after proton abstraction, a Wurtz hydrocarbon product[8]) more rapidly than it rearranges.[9]

Experimental[10]

Reaction of Nortricyclyl Chloride with Sodium.—A solution of 10 g. (0.078 mole) of nortricyclyl chloride in 10 ml. of redistilled *n*-decane was added, dropwise, with stirring, to a mixture of 1.80 g. (0.078 g.-atom) of freshly cut sodium pieces and 15 ml. of redistilled *n*-decane. The reaction was carried out at 85–90° (oil bath temperature) and under an atmosphere of nitrogen. After all the chloride had been added, stirring was continued for 1 hr. at 85–90°. An independent measurement using the conditions as described revealed that the temperature inside the reaction flask rose to a maximum of 133° during a 12-min. period from the time the chloride addition was begun, then fell back to the oil bath temperature.

After the stirring period was completed, the reaction mixture was subjected to vacuum distillation; the reaction flask was heated until decane (b.p. 63°, 20 mm.) reached the thermometer in the distillation head. The C_7 products (1.43 g., 19.2%) collected in the Dry Ice trap. Vapor phase chromatographic analysis on a 2-m. DC-200 silicone oil column (Perkin-Elmer column CX) demonstrated that this mixture consisted of 71.0% nortricyclene, 10.0% norbornene, and a 19.0% peak representing both 3- and 4-vinylcyclopentene. Nortricyclene and norbornene were separated and identified by comparison of their infrared spectra with a published spectrum of nortricyclene[11] and with the spectrum of an authentic sample of norbornene. The vinylcyclopentenes were also isolated by v.p.c.

Anal. Calcd. for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 89.15; H, 10.65.

Subsequent v.p.c. on a 1-m. 40% phenylacetonitrile–silver nitrate (saturated at 90°) on firebrick column resolved the two vinylcyclopentene isomers to give 69% (13.1% of the total C_7 hydrocarbons) 4-vinylcyclopentene and 31% (5.9% of total) 3-vinylcyclopentene. A 0.78-g. mixture of the vinylcyclopentenes, isolated by v.p.c. on a 2-m. DC 200 silicone oil column was hydrogenated in ether over a 10% palladium-on-charcoal catalyst. The only product, separated from the solvent by v.p.c. was identified as ethylcyclopentane by comparison of its infrared spectrum with a published spectrum.[12]

The reaction of nortricyclyl chloride with sodium was repeated using one-half quantities, an oil bath temperature of 85–95° and otherwise identical reaction conditions. After the stirring period was completed, the reaction mixture was neutralized with methanol. The organic layer was washed several times with water and dried over anhydrous magnesium sulfate. Vapor phase chromatographic analysis (on a 3-m. DC-200 column) of a 2.46-g. fraction (b.p. 30–61° at 20 mm.) indicated the formation of 431 mg. (12%) of a four-component mixture: 84.8% nortricyclene, 5.2% norbornene, 9.4% 3- and 4-vinylcyclopentene, and 0.6% 4-vinylidenecyclopentene (identified by retention time comparison with an authentic sample). Since it was not possible to resolve 4-ethynylcyclopentene and norbornene simply by v.p.c., infrared analysis was used to detect 4-ethynylcyclopentene. The absorption at 3360 cm.$^{-1}$ indicated that as much as 2% of 4-ethynylcyclopentene was present in the C_7 hydrocarbon fraction.

Reaction of Nortricyclyl Chloride and 4-Ethynylcyclopentene with Sodium.—A solution of nortricyclyl chloride (1.00 g.) and 97 mg. of 4-ethynylcyclopentene in 420 mg. of a hydrocarbon mixture (23.2% of 4-ethynylcyclopentene, 8.2% 4-vinylidenecyclopentene, and 68.6% of pentane) in 2 ml. of *n*-decane was added to 180 mg. of sodium in 2 ml. of *n*-decane with stirring, under nitrogen, using an oil bath temperature of 85–95°. The remaining procedure was identical with the nortricyclyl chloride–sodium reaction in which the C_7 hydrocarbons were isolated after neutralization with methanol. Vapor phase chromatographic and infrared analysis showed that the 720 mg. fraction obtained (b.p. 30–50° at 20 mm.) contained a total of 162 mg. of C_7 hydrocarbons which included 46 mg. of ethynylcyclopentene (a 47% recovery).

Reaction of Dehydronorbornyl Chloride with Sodium.—The procedure for this reaction was identical with that described for nortricyclyl chloride in which the C_7 hydrocarbons were isolated directly from the reaction mixture by vacuum distillation. The dehydronorbornyl chloride used was a 50/50 mixture of the *exo* and *endo* isomers. A 27.1% yield of C_7 hydrocarbons was obtained. Vapor phase chromatographic analysis on a 2-m. DC 200 silicone–oil column and a 1-m. 40% phenylacetonitrile–silver nitrate (saturated at 90°) on firebrick column showed that the C_7-hydrocarbon composition was 64.0% nortricyclene, 13.0% norbornene, 7.5% 3-vinylcyclopentene, 13.5% 4-vinylcyclopentene, and 2.0% norbornadiene. Norbornadiene had the same retention time as the vinylcyclopentenes on the silicone–oil column, but was completely separated on the silver nitrate column.

Dehydronorcamphor *p*-Toluenesulfonylhydrazone.—A solution of 15.0 g. (0.139 mole) of dehydronorcamphor, prepared by the procedure of Cristol and Freeman[7] involving the Oppenauer oxidation of dehydronorborneol, and 25.95 g. (0.139 mole) of *p*-toluenesulfonylhydrazine in 225 ml. of 95% ethanol and 45 ml. of 6 *N* hydrochloric acid was heated at an oil bath temperature of 45–50° for 1 hr. After cooling to room temperature, the crystalline product was filtered and washed with petroleum ether. The filtrate was allowed to cool overnight in the refrigerator and a second crop of crystals was collected. The total yield amounted to 27.40 g. (71.4%) and had m.p. 177–181° dec. Recrystallization from 95% ethanol gave 16.90 g. with m.p. 183–184° dec. An analytical sample had m.p. 185–188° dec.

Anal. Calcd. for $C_{14}H_{16}N_2O_2S$: C, 60.84; H, 5.84. Found: C, 60.78; H, 5.91.

Carbenoid Decomposition of Dehydronorcamphor *p*-Toluenesulfonylhydrazone.—The method of Friedman and Shechter[13] was adapted to the decomposition of this particular hydrazone. In a 500-ml. three-necked flask, fitted with nitrogen inlet tube, mechanical stirrer, and Claisen distillation head, was placed 250 ml. of bis(2-ethoxyethyl) ether, which had been distilled from sodium, and 3.70 g. (0.0685 mole) of solid sodium methoxide, weighed and transferred in a nitrogen atmosphere. To this mixture was added 8.44 g. (0.0305 mole) of dehydronorcamphor *p*-toluenesulfonylhydrazone, and the system was flushed with nitrogen. The reaction mixture was heated with stirring to 180–183°. Distilling material was collected in a flask which was attached to the Claisen head by an adapter. The flask was im-

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[7] S. J. Cristol and P. K. Freeman, *J. Am. Chem. Soc.*, **83**, 4427 (1961).

[8] The Wurtz hydrocarbons were not investigated.

[9] G. L. Closs, *J. Am. Chem. Soc.*, **84**, 809 (1962), has reported that chlorocarbene, generated by addition of methylene chloride to a mixture of *n*-butyllithium and olefin, adds to the olefin to produce only trace quantities of chlorocyclopropane. It seems clear that the low yields are due to the competing addition of the electrophilic carbene to *n*-butyllithium.

[10] Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

[11] K. Alder, H. K. Schafer, H. Esser, H. Krieger, and R. Reubke, *Ann.*, **593**, 23 (1955).

[12] S. F. Sadtler, "Sadtler Standard Spectra, Midget Edition," S. F. Sadtler and Son, Philadelphia, Pa., 1957, Spectrum No. 11829.

[13] L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); **82**, 1002 (1960).

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

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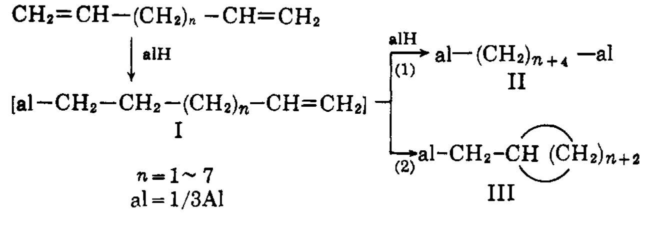
It is expected that organoaluminum compounds having two aluminum atoms attached to both ends of the polymethylene chain can be prepared by addition of aluminum hydride to an α,ω-diene. Ziegler[1] reported, however, that 1,5-hexadiene and diisobutylaluminum hydride gave methylenecyclopentane and a cyclopentylmethylaluminum 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.

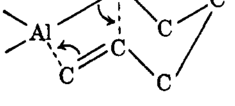
In this type of cyclization, the chain length of the α,ω-diene seems to be a most important factor. In order to clarify the effect of the chain length on the reaction product, we have investigated the reaction between diisobutylaluminum hydride and α,ω-dienes having carbon numbers from five to eleven.

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}_{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-

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(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).