oxocycloheptanecarboxylate.[23] The solution was cooled to −20° and 12.6 g of ethyl vinyl ketone was added dropwise with stirring.[17a] After 1 hr at −20° and 1 hr of warming to room temperature, the mixture no longer gave a ferric chloride test. Accordingly, 5 ml of 3 *N* ethanolic sodium ethoxide was added and after 5 hr at room temperature, the mixture was neutralized with acetic acid and concentrated under reduced pressure. Water was added to the residue and the product was isolated with ether[17b] and distilled. The bulk of the material (18.8 g), bp 102–116° at 0.1 mm, contained mainly the conjugated ketone **16** along with some uncyclized diketo ester. A 10.3-g sample of this mixture was heated at 60° with 11.1 ml of 1.5 *N* ethanolic sodium ethoxide for 6 hr to effect complete aldol cyclization. Work-up, according to the procedure described above, afforded 5.9 g (55%) of the keto ester **16**: bp 110–120° (0.07 mm); $\lambda_{\max}^{\text{film}}$ 5.81 (ester CO), 6.00 (conjd CO), 6.20 (C=C), 8.01, 8.21, 8.42, 8.68, 9.09, 9.23, 9.45, 9.72, 10.06, 10.18, 10.39, 10.72, 11.25, 11.57, and 12.01 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.12 (–OCH$_2$– quartet, $J = 7$ Hz), 1.74 (C-8 CH$_3$), and 1.22 ppm (CH$_2$CH_3 triplet, $J = 7$ Hz). The analytical sample, bp 111–112° (0.07 mm), was secured by redistillation.

Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.7; H, 8.9.

Ethyl 9,9-Ethylenedithio-8-methylbicyclo[5.4.0]undec-7-ene-1-carboxylate (**17**).—The procedure of Fieser was employed.[24] A solution containing 2.50 g of keto ester **16**, 3 ml of 1,2-ethanedithiol, and 3 ml of boron trifluoride etherate in 30 ml of acetic acid was allowed to stand at room temperature for 1 hr.[17a] The mixture was poured into brine and the product was isolated with ether[17b] and distilled, affording 2.98 g (91%) of colorless oily thioketal **17**: bp 150–160° (bath temperature) at 0.04 mm; $\lambda_{\max}^{\text{film}}$ 5.80 (ester CO), 8.00, 8.39, 9.10, 9.19, 9.72, and 10.42 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.01 (–OCH$_2$– quartet, $J = 7$ Hz), 3.42–3.17 (–SCH$_2$-CH$_2$S– multiplet), 1.91 (C-8 CH$_3$), and 1.09 ppm (–CH$_2$CH_3 triplet, $J = 7$ Hz). The analytical sample, bp 155–160° (bath temperature) at 0.04 mm, was secured by redistillation.

Anal. Calcd for $C_{17}H_{26}O_2S_2$: C, 62.53; H, 8.03; S, 19.64. Found: C, 62.4; H, 8.1; S, 19.5.

Ethyl 8-Methylbicyclo[5.4.0]undec-7-ene-1-carboxylate (**18**).—A 2.53-g sample of thioketal **17** in 45 ml of ethanol was stirred with 45 g of W-2 Raney nickel[25] at room temperature for 1 hr and at reflux for 5 hr.[17a] The mixture was cooled, filtered through diatomaceous earth, and the filtrate was distilled, affording 1.36 g (74%) of colorless oily ester **18**: bp 50–60° (bath temperature) at 0.04 mm; $\lambda_{\max}^{\text{film}}$ 5.80 (ester CO), 8.10, 8.20, 8.50, 8.62, 9.10, and 9.65 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.06 (–OCH$_2$– quartet, $J = 7$ Hz), 1.65 (C-8 CH$_3$), and 1.20 ppm (–CH$_2$CH_3 triplet, $J = 7$ Hz). The analytical sample was secured after two successive distillations.

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23. Found: C, 76.4; H, 10.3.

8-Methylbicyclo[5.4.0]undec-7-enylmethanol (**19**). **A.** *Via* **Reduction of Ester 18.**—A mixture containing 704 mg of ester **18** and 228 mg of lithium aluminum hydride in 10 ml of ether was stirred at room temperature for 12 hr. Water (0.46 ml) and 10% aqueous sodium hydroxide (0.37 ml) were added cautiously and, after 2 hr of continued stirring, the mixture was filtered. The ether was removed from the filtrate under reduced pressure affording 532 mg of colorless oil which readily solidified. Recrystallization from hexane gave 418 mg (72%) of crystalline alcohol **19**: mp 62–64°; $\lambda_{\max}^{\text{KBr}}$ 3.08 (OH), 8.23, 8.31, 8.45, 8.51, 8.79, 9.03, 9.14, 9.29, 9.70, 10.00, 10.41, 10.91, 11.48, 11.88, 12.12, 12.79, 13.12, and 14.68 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 3.39 (–CH$_2$O– AB quartet, $\Delta\nu_{AB} = 12.5$ Hz, $J_{AB} = 11$ Hz), 3.11 (OH), and 1.61 ppm (C-8 CH$_3$). The analytical sample, mp 63–65°, was secured after two additional resrystallizations from hexane.

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.4; H, 11.4.

B. *Via* **Reduction of Aldehyde 14.**—A 100-mg sample of aldehyde **14** in 1 ml of ether was stirred with 58 mg of lithium aluminum hydride for 2 hr at room temperature. Water (0.12 ml) and 10% aqueous sodium hydroxide (0.09 ml) were added and after 2 hr of continued stirring the mixture was filtered and the filtrate was concentrated, affording 95 mg of solid. Recrystallization from hexane gave 46 mg (46%) of alcohol **19**, mp 60–62°, undepressed upon admixture of the material obtained in part A. The infrared spectra of the two samples were superimposable.

Registry No.—**2**, 14320-32-2; **5**, 14320-18-4; **6**, 14233-74-0; **7**, 14233-75-1; **8**, 14233-76-2; **9**, 14233-77-3; **11**, 14233-78-4; **12**, 14233-79-5; **13**, 14233-80-8; **14**, 14233-81-9; **16**, 14233-82-0; **17**, 14233-83-1; **18**, 14233-84-2; **19**, 14233-85-3.

Acknowledgment.—We gratefully acknowledge support from the National Science Foundation (GP-4174).

---

[23] Prepared from cycloheptanone and diethyl carbonate.[18]

[24] L. F. Fieser, *J. Am. Chem. Soc.*, **76**, 1945 (1954).

[25] R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 181.

Stereospecific Synthesis of 1,4-Dienes. II[1]

GO HATA AND DAN AOKI

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

Received May 22, 1967

Effects of diene structure in the iron(III) acetylacetonate–triethylaluminum-catalyzed addition of ethylene to substituted 1,3-dienes have been investigated. This reaction gives exclusively *cis* isomers of 1,4-dienes. Methyl and phenyl substituents of the 1,3-dienes control the orientation of addition of ethylene. 1,3-Dienes, of which cisoid conformations are sterically unfavored, do not react with ethylene. Addition of propylene to 1,3-butadiene gives 2-methyl-1-*cis*-4-hexadiene and 1-*cis*-5-heptadiene.

In connection with catalytic behaviors of transition metals, the reaction of 1,3-dienes with ethylene has received considerable attention in recent years.[2–6] In a preliminary communication,[4] the novel synthesis of 1,4-dienes by the reaction of 1,3-dienes with ethylene in the presence of a catalyst consisting of iron(III) acetylacetonate [Fe(AcAc)$_3$] and triethylaluminum has been reported. The present paper is concerned with steric factor and orientation of the reaction by this catalyst. The reaction of substituted 1,3-dienes with ethylene and that of 1,3-butadiene with propylene have been investigated.

Results

Reaction of Substituted 1,3-Dienes with Ethylene.—The catalyst was prepared by mixing iron(III) acetylacetonate and triethylaluminum in 1,3-dienes. When prepared in the absence of the dienes, the catalyst showed only low activity. The reaction was carried out by stirring at 30° under ethylene pressure (40 kg/

---

[1] Presented at the Seventh World Petroleum Congress, Mexico, April 1967.

[2] G. Wilke, *Angew. Chem.*, **75**, 10 (1963).

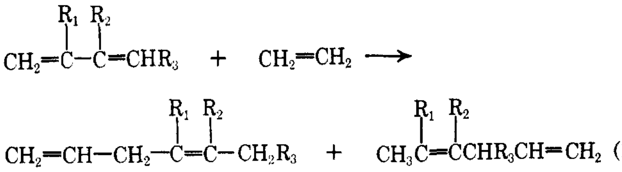
[3] D. Wittenberg, *ibid.*, **75**, 1124 (1963).

[4] G. Hata, *J. Am. Chem. Soc.*, **86**, 3903 (1964).

[5] T. Anderson, E. L. Jenner, and R. V. Lindsey, *ibid.*, **87**, 5638 (1965).

[6] M. Iwamoto and S. Yuguchi, *Bull. Chem. Soc. Japan*, **39**, 2001 (1966); M. Iwamoto and S. Yuguchi, *J. Org. Chem.*, **31**, 4290 (1966).

cm^2). The reaction of unsymmetrical 1,3-dienes with ethylene gave two kinds of 1,4-dienes as shown in



$$CH_2{=}C(R_1){-}C(R_2){=}CHR_3 + CH_2{=}CH_2 \longrightarrow CH_2{=}CH{-}CH_2{-}C(R_1){=}C(R_2){-}CH_2R_3 + CH_3C(R_1){=}C(R_2)CHR_3CH{=}CH_2 \quad (1)$$

eq 1 where R_1, R_2, and R_3 are H, CH_3, or C_6H_5. The results are summarized in Table I.

Table I

Reaction of 1,3-Dienes with Ethylene

1,3-Diene	Conversion, %	Product	Yield,[a] %
Isoprene	77	4-Methyl-1-*cis*-4-hexadiene	69
		5-Methyl-1-4-hexadiene	69
		Conjugated methylhexadienes	9
1,3-Pentadiene	43	3-Methyl-1-*cis*-4-hexadiene	46
		1-*cis*-4-Heptadiene	14
		2,4-Heptadiene	4
2,3-Dimethyl-1,3-butadiene	99	4,5-Dimethyl-1,4-hexadiene	71
		2,3-Dimethyl-2,4-hexadiene	9
2-Methyl-1,3-pentadiene	97	3,5-Dimethyl-1,4-hexadiene	65
		4-Methyl-1-*cis*-4-heptadiene	21
2-Phenyl-1,3-butadiene	80	4-Phenyl-1,4-hexadiene	52

[a] Based on the converted 1,3-dienes.

The most characteristic feature of this reaction is that it affords *cis* isomers of 1,4-dienes selectively. The *cis* configuration of disubstituted double bonds of the 1,4-dienes was confirmed by infrared spectroscopy and gas chromatography. The *cis* configuration of trisubstituted double bonds of the 1,4-dienes was proved by nmr spectroscopy in the following way. Terminal double bonds of 4-methyl-1,4-hexadiene and 4-methyl-1,4-heptadiene were reduced (eq 2) to afford 3-methyl-2-hexene and 4-methyl-3-heptene, respectively.

$$CH_2{=}CHCH_2C(CH_3){=}CH{-}R \xrightarrow[\text{2. } H_2O]{\text{1. } (i\text{-}C_4H_9)_2AlH} CH_3CH_2CH_2{-}C(CH_3){=}CH{-}R \quad (2)$$
$$R = CH_3 \text{ or } CH_3CH_2$$

Chemical shifts of methyl protons of a $-CH_2C(CH_3){=}CHCH_2-$ unit were used to determine the configuration of these olefins. Bates[7] observed that a τ value for methyl protons in a *cis*-$CH_2C(CH_3){=}CHCH_2-$ unit is lower (by about 0.07 ppm) than that of the *trans* unit. Such a difference in chemical shifts was confirmed in a simple olefin, 3-methyl-2-pentene (τ 8.32 for the *cis* isomer and 8.38 for the *trans* isomer). Stereospecific synthesis and assignment of geometrical isomers of 3-methyl-2-pentene have already been established by Cornforth.[8] A mixture of geometrical isomers of 3-methyl-2-hexene was prepared by the Wittig reaction of 2-pentanone with ethylidenetriphenylphosphorane and a mixture of 4-methyl-3-heptenes was prepared in the same way from the ketone and propylidenetriphenylphosphorane. The nmr spectra of the former and the latter mixture showed signals due to methyl protons of the $-CH_2C(CH_3){=}CHCH_2-$ units at τ 8.33 and 8.40 and at 8.37 and 8.45 (Figure 1), respectively. On the other hand, the spectra of 3-methyl-2-hexene and 4-methyl-3-heptene obtained by reduction of the 1,4-dienes prepared in the iron(III) acetylacetonate–triethylaluminum-catalyzed reaction showed signals with the lower τ values alone, which corresponded to the *cis* isomers (Figure 1). Hence it can be concluded that the 1,4-dienes have a *cis* configuration. The infrared spectrum and gas chromatographic retention time of 3-methyl-*trans*-2-hexene were identical with those of the API standard sample of "3-methyl-*cis*-2-hexene."[9]

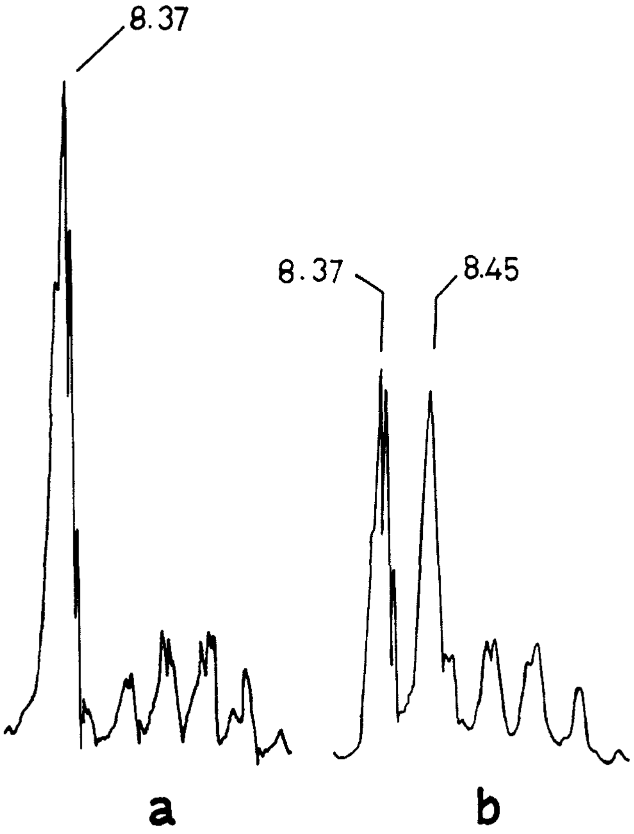


Figure 1.—Nmr spectra of 4-methyl-3-heptene at 100 Mc: (a) *cis* isomer and (b) a mixture of *cis* and *trans* isomer.

Unsymmetrical 1,3-dienes have two nonequivalent sites for addition of ethylene. A temperature effect was observed for the orientation of addition of ethylene to isoprene. The ratio of 5-methyl-1,4-hexadiene to 4-methyl-1,4-hexadiene at an early stage of the reaction approached unity as the reaction temperature was raised. No such an effect was observed in the addition of ethylene to 1,3-pentadiene and 2-methyl-1,3-pentadiene.

The results on the reaction of ethylene with 1,3-pentadiene are shown in Figures 2 and 3. The 1,3-pentadiene used consisted of 78% *trans* isomer and 22% *cis* isomer. It was found that the *trans* isomer of 1,3-pentadiene was consumed approximately 15 times as fast as the *cis* isomer. Since the catalyst also isomerizes 1-*cis*-3-pentadiene to the *trans* isomer, it seems likely that the consumption of the *cis* isomer is due to the isomerization to the *trans* isomer. Figure 3 shows that 2,4-heptadiene was formed through double-bond migration of 1-*cis*-4-heptadiene. No double-bond migration of 3-methyl-1-*cis*-4-heptadiene was observed. A ratio

---

(7) R. B. Bates and D. M. Gales, *J. Am. Chem. Soc.*, **82**, 5749 (1960).

(8) J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, *J. Chem. Soc.*, 112 (1959).

(9) An API standard sample of 3-methyl-*cis*-2-hexene (1074-5S) (American Petroleum Institute Research Project 44, Selected Infrared Spectral Data, Serial No. 2099) actually has *trans* configuration. Based on gas chromatographic data, revision of geometrical assignment of the sample has been recommended: R. A. Hively, *Anal. Chem.*, **35**, 1921 (1963).

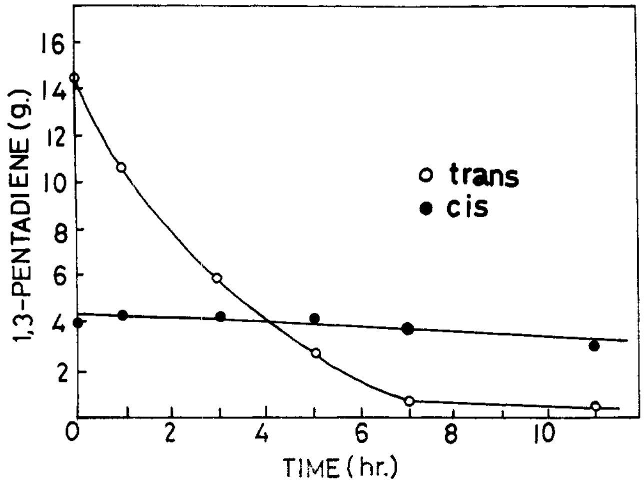


Figure 2.—Difference in reactivity of *cis*- and *trans*-pentadiene (1,3-pentadiene, 0.3 mole; Fe(AcAc)$_3$, 1 mmole; Et$_3$Al, 6 mmoles; ethylene, 40 kg/cm^2 at 30°).

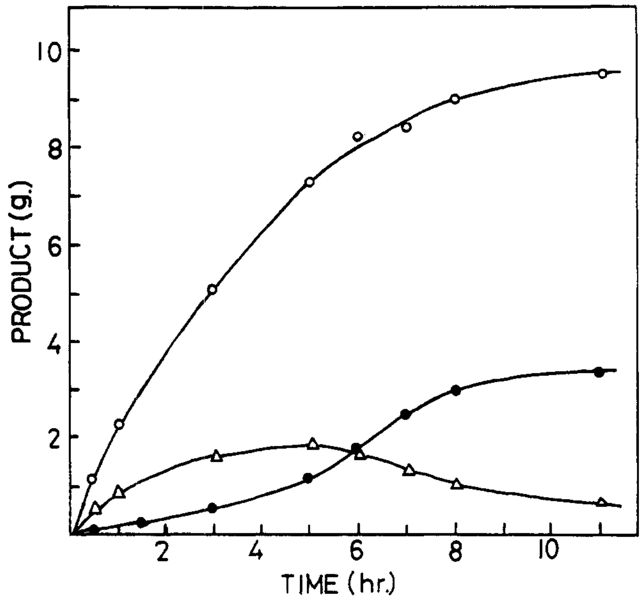


Figure 3.—Reaction of 1,3-pentadiene with ethylene: O, 3-methyl-1-*cis*-4-hexadiene; Δ, 1-*cis*-4-heptadiene; and ●, 2,4-heptadiene.

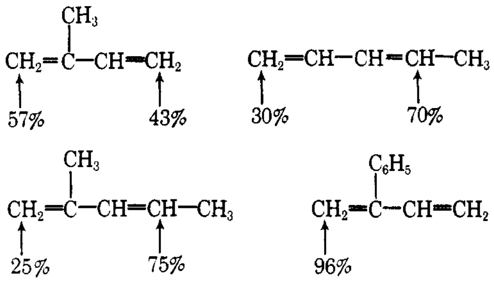
(70:30) of 3-methyl-1-*cis*-4-heptadiene to 1-*cis*-4- and 2,4-heptadiene combined did not change at reaction temperature ranging from 30 to 90°.

Reaction of ethylene with a mixture of methyl-1,3-pentadienes which consisted of the 2-methyl and 4-methyl isomers resulted in the formation of 3,5-dimethyl-1,4-hexadiene and 4-methyl-1-*cis*-4-heptadiene in a ratio of 75:25. Apparently these adducts were derived from 2-methyl-1,3-pentadiene. No adducts of the 4-methyl isomer were found and almost all of the 4-methyl isomer was recovered. There was no double-bond migration of the products.

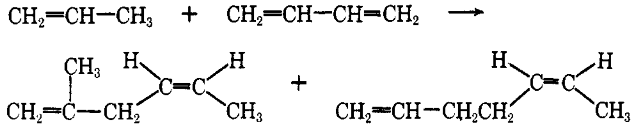
Ethylene added to 2-phenyl-1,3-butadiene to afford 4-phenyl-1,4-hexadiene selectively. In view of the fact that all of the 1,4-dienes obtained from the reactions conducted so far were exclusively *cis* isomers, it is reasonably expected that the 4-phenyl-1,4-hexadiene is a *cis* isomer.

The results on orientation of addition of ethylene to the substituted 1,3-dienes are summarized in Table II. It is apparent that ethylene added predominantly at the terminal carbon atom of the substituted double bond of a 1,3-diene system. For example, ethylene adds at the 4-position carbon of a 1,3-pentadiene molecule rather than at the 1 position. The 4-methyl group of 2-methyl-1,3-pentadiene controls orientation of addition of ethylene more than the 2-methyl group does.

TABLE II
ORIENTATION OF ADDITION OF ETHYLENE TO SUBSTITUTED 1,3-DIENES AT 30°



Reaction of 1,3-Butadiene with Propylene.—Propylene reacted with 1,3-butadiene at 40° to give a 1:1 addition product, though propylene was far less reactive than ethylene. Only 6 moles of addition product was obtained for each mole of iron(III) acetylacetonate. The product was separated, by gas chromatography using a silver nitrate–benzyl cyanide column, into two components, which were identified as 2-methyl-1-*cis*-4-hexadiene and 1-*cis*-5-heptadiene (eq 3). The ratio for these products was 1:1.



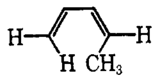
(3)

This reaction was also stereospecific and gave exclusively *cis* isomers.

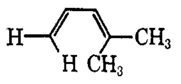
Discussion

The characteristic features of these reactions are as follows: (1) the reaction is stereospecific and gives *cis* isomers of the 1,4-dienes selectively, and (2) the 1,3-dienes unfavorable for taking a cisoid conformation do not react with ethylene.

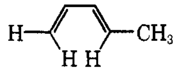
1-*cis*-3-Pentadiene (**1**) and 4-methyl-1,3-pentadiene (**2**) which do not react with ethylene have steric hindrance between 1-H and 4-CH$_3$ in their cisoid conformations. However, 1-*trans*-3-pentadiene (**3**) and 2-methyl-1-*trans*-3-pentadiene (**4**) which easily react with ethylene have no such a serious steric hindrance in



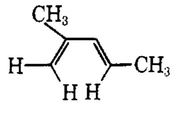
1



2



3



4

their cisoid conformations. These results can be explained reasonably by assuming that the 1,3-dienes co-

Table III

Reaction of Methyl-1,3-pentadienes with Ethylene

		Reaction mixture				
Temp, °C	Time, hr	Recovered methyl-1,3-pentadienes, g	2-Methyl-1-*trans*-3-pentadiene in recovered methyl-1,3-pentadienes, %	3,5-Dimethyl-1,4-hexadiene, g	4-Methyl-1,4-heptadiene, g	Residue, g
30	2	6.4	8	13.2	4.3	0.8
70	1	6.1	7	13.9	4.4	2.0

ordinate with the catalyst species in cisoid conformation. This type of coordination must be responsible for the stereospecific formation of the *cis* isomers of the 1,4-dienes.

The formation of the 1,4-dienes proceeds through transfer of a hydrogen atom of ethylene to the 1,3-dienes. In the reaction of propylene with 1,3-butadiene two types of hydrogen transfer occur. The formation of 2-methyl-1-*cis*-4-hexadiene and 1-*cis*-5-heptadiene can be explained by the transfer of a vinylic hydrogen at the 2 position of propylene and by that of an allylic hydrogen of propylene, respectively. However the mechanism of the hydrogen transfer is not clear.

Experimental Section

Reaction of Isoprene with Ethylene.—A 500-ml stainless autoclave was charged with 200 ml of xylene, 40.8 g of isoprene, and 2 ml of triethylaluminum. After gas within the autoclave was replaced by ethylene, 1.0 g of iron(III) acetylacetonate in 50 ml of xylene was added. The resultant mixture was stirred under ethylene pressure (40 kg/cm^2) at 30° for 1.5 hr. The reaction product was decomposed with methanol and dilute hydrochloric acid. The oily layer was analyzed by gas chromatography using a squalane column. It consisted of unreacted isoprene (9.3 g), methyl-1,4-hexadienes (31.1 g, bp 88–89°), C$_7$-conjugated dienes (4.1 g, bp 108–109°), and a residue (9.6 g). The methyl-1,4-hexadienes were separated by preparative gas chromatography using a silver nitrate–benzyl cyanide column into 4-methyl-1-*cis*-4-hexadiene, bp 88–89°, $n^{20}{\rm D}$ 1.4248, and 5-methyl-1,4-hexadiene, bp 88–89°, $n^{20}{\rm D}$ 1.4256. A mixture of 2.9 g (0.030 mole) of 4-methyl-1,4-hexadiene and 5.6 ml (0.033 mole) of diisobutylaluminum hydride was heated in a sealed tube at 70° for 16 hr and hyrolyzed to give 3-methyl-2-hexene, bp 94°, $n^{20}{\rm D}$ 1.4122. A mixture of geometrical isomers of 3-methyl-2-hexene which was prepared by the reaction of 2-pentanone with ethylidenetriphenylphosphorane was separated by gas chromatography using a squalane column. 5-Methyl-1,4-hexadiene was identified by converting it into 2-methyl-2-hexene. The gas chromatogram (using a squalane column) of C$_7$-conjugated dienes showed two components. The one which eluted first was separated, bp 112°, $n^{20}{\rm D}$ 1.4681, and hydrogenated to give 2-methylhexane.

Reaction of 1,3-Pentadiene with Ethylene.—A 100-ml autoclave was charged with 10 ml of xylene, 20.4 g of 1,3-pentadiene (purity 90%), 6 mmoles of triethylaluminum, 1 mmole of iron(III) acetylacetonate, and 3.40 g of *n*-heptane (an internal standard for gas chromatographic analysis). The mixture was stirred under ethylene pressure (40 kg/cm^2) at 30°. The results are shown in Figures 2 and 3. The nmr spectrum of 2,4-heptadiene showed a triplet at τ 9.07, a doublet at 8.31, a quintet at 7.87, and a multiplet at 4.28.

Reaction of 2,3-Dimethyl-1,3-butadiene with Ethylene.—A 100-ml autoclave was charged with 25 ml of benzene, 3 ml of ethoxydiethylaluminum, 16.4 g of 2,3-dimethyl-1,3-butadiene (purity 91%), and 0.3 g of iron(III) acetylacetonate in 50 ml of benzene. The mixture was heated under ethylene pressure (40 kg/cm^2) at 50° for 80 min. Distillation gave 14.1 g of 4,5-dimethyl-1,4-hexadiene, bp 119–120°, $n^{20}{\rm D}$ 1.4408, and 1.7 g of 2,3-dimethyl-2,4-hexadiene, bp 137–139°, $n^{20}{\rm D}$ 1.4803. A small amount of a residue (1.5 g) remained. The terminal double bond of the nonconjugated diene was reduced by using diisobutylaluminum hydride. Ozonolysis of the resultant product yielded 2-pentanone and acetone, which were identified by conversion into the corresponding 2,4-dinitrophenylhydrazones. The nmr spectrum of the conjugated diene showed signals at τ 8.63 due to methyl protons and a sextet at 5.63 and a doublet at 4.82 due to olefinic protons.

Reaction of Methyl-1,3-pentadienes with Ethylene.—A mixture of 2-methyl- and 4-methyl-1,3-pentadiene (bp 75–75.5°) was prepared by dehydration of 2-methyl-2,4-pentanediol.[10] The gas chromatogram using a silver nitrate–benzyl cyanide column showed the presence of two components (the ratio, 66:34). The infrared spectra of the first eluted major component and the minor one were identical with those of 2-methyl-1,3-pentadiene and 4-methyl-1,3-pentadiene,[11] respectively. Since a 1-*trans*-3-diene is eluted faster than the *cis* isomer on a silver nitrate column,[12] the first eluted component must be 2-methyl-1-*trans*-3-pentadiene. The other component may contain the *cis* isomer. A 100-ml autoclave was charged with 10 ml of xylene, 22 g of the methyl-1,3-pentadienes, 6 mmoles of triethylaluminum, and 1 mmole of iron(III) acetylacetonate in 10 ml of xylene. The mixture was stirred under ethylene pressure (40 kg/cm^2). The results are summarized in Table III. Reduction of terminal double bonds of 3,5-dimethyl-1,4-hexadiene, bp 108°, $n^{20}{\rm D}$ 1.4273, and 4-methyl-1,4-heptadiene, bp 116°, $n^{20}{\rm D}$ 1.4320, by the aforementioned method afforded 2,4-dimethyl-2-hexene, bp 108–109°, and 4-methyl-3-heptene, bp 57–58° (110 mm), respectively. Ozonolysis of these products yielded a mixture of acetone and 2-methylbutyraldehyde, and that of propionaldehyde and 2-pentanone, respectively, which were identified by conversion into the corresponding 2,4-dinitrophenylhydrazones.

Reaction of 2-Phenyl-1,3-butadiene with Ethylene.—A 100-ml autoclave was charged with 10 ml of toluene, 13.0 g of 2-phenyl-1,3-butadiene[13] (purity 92%), 11 mmoles of triethylaluminum, and 1 mmole of iron(III) acetylacetonate in 8 ml of toluene. The mixture was stirred under ethylene (40 kg/cm^2) at 30° for 4.5 hr. The product was distilled to give 6.6 g of 1:1 adducts, bp 90–92° (6 mm). Gas chromatographic analysis showed that 96% of the adducts was 4-phenyl-1,4-hexadiene, $n^{20}{\rm D}$ 1.5430 (the nmr spectrum, doublets at τ 8.30 and 6.81, and multiplets at 4.94, 4.13 and 2.76). Reduction of the terminal double bond of 4-phenyl-1,4-hexadiene afforded 3-phenyl-2-hexene, bp 89° (6 mm), $n^{20}{\rm D}$ 1.5251 (the nmr spectrum, triplets at τ 9.16 and 7.55, a sextet at 8.62, a doublet at 8.30, a quartet at 4.32 and a multiplet at 2.87). Ozonolysis gave acetaldehyde and butyrophenone.

Reaction of 1,3-Butadiene with Propylene.—A 100-ml autoclave was charged with 10 ml of xylene, 2 mmoles of iron(III) acetylacetonate, 0.23 mole of 1,3-butadiene, 12 mmoles of triethylaluminum in 5 ml of xylene, and 30 ml (at 0°) of liquid propylene. The mixture was stirred at 40° for 4 hr. Gas chromatographic analysis showed the formation of 1.2 g of 1:1 adducts. A high boiling residue amounted to 5.6 g. The adducts absorbed 2 moles of hydrogen to give *n*-heptane and 2-methylhexane in equal amount. The adducts were separated into two components by gas chromatography using a silver nitrate–benzyl cyanide column. The infrared spectrum of the first-eluted component showed bands due to $\mathrm{-CR{=}CH_2}$ and *cis*-$\mathrm{CH{=}CH-}$ groups at 885 and 690 cm^{-1}. The infrared spectrum and gas chromatographic retention time of the other component were identical with those of 1-*cis*-5-heptadiene. A mixture of *cis* and *trans* isomer of 1,5-heptadiene was prepared by the reaction of allylmagnesium bromide and crotyl chloride. The *cis* isomer was separated by gas chromatography. Its infrared spectrum showed bands due to $\mathrm{-CH{=}CH_2}$ and *cis*-$\mathrm{CH{=}CH-}$ groups at 910, 990, and 690 cm^{-1}.

---

[10] R. G. R. Bacon and E. H. Farmer, *J. Chem. Soc.*, 1065 (1937); G. B. Bachman and C. G. Goebel, *J. Am. Chem. Soc.*, **64**, 787 (1942).

[11] American Petroleum Institute Research Project 44, Selected Infrared Spectral Data, Serial No. 452 and 453.

[12] B. Smith and R. Ohlson, *Acta Chim. Scand.*, **16**, 351 (1962).

[13] C. C. Price, F. L. Benton, and C. J. Schmidle, *J. Am. Chem. Soc.*, **71**, 2860 (1949).

The nmr spectra of all compounds were recorded on Varian Associates DP-60 or HR-100 nmr spectrometer.

Registry No.—**1**, 1574-41-0; **2**, 926-56-7; **4**, 926-54-5; iron(III) acetylacetonate, 14024-18-1; triethylaluminum, 97-93-8; ethylene, 74-85-1; isoprene, 78-79-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; 2-phenyl-1,3-butadiene, 2288-18-8; 1,3-butadiene, 106-99-0; propylene, 115-07-1; 4-methyl-1-*cis*-4-hexadiene, 761-76-2; 5-methyl-1,4-hexadiene, 763-88-2; 3-methyl-2-hexene, 10574-36-4; 2-methyl-2-hexene, 2738-19-4; 2,4-heptadiene, 14255-14-2; 4,5-dimethyl-1,4-hexadiene, 760-76-9; 2,3-dimethyl-2,4-hexadiene, 5678-98-8; 3,5-dimethyl-1,4-hexadiene, 761-87-5; 4-methyl-1-*cis*-4-heptadiene, 13857-54-0; 2,4-dimethyl-2-hexene, 14255-23-3; 4-methyl-3-heptene, 14255-24-4; 4-phenyl-1,4-hexadiene, 14255-25-5; 3-phenyl-2-hexene, 14255-26-6; 1-*cis*-5-heptadiene, 7736-34-7; 4-methyl-*cis*-3-hexene, 4914-89-0; 4-methyl-*trans*-3-hexene, 3899-36-3.

Some Reactions of 12α-Hydroxymethylabiet-7,8-enoic Acid

D. K. BLACK[1a] AND G. W. HEDRICK

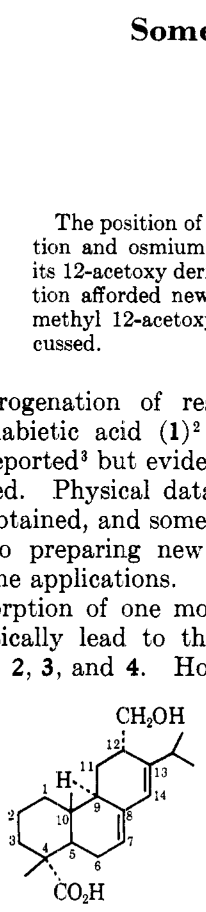
Naval Stores Laboratory,[1b] *Olustee, Florida 32072*

Received May 31, 1967

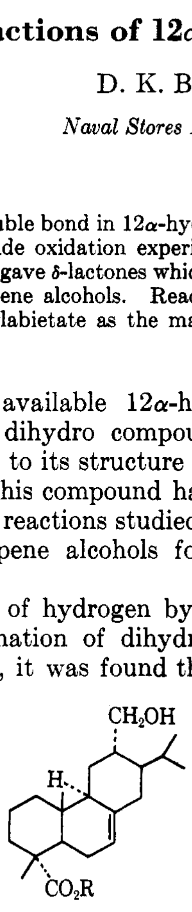
The position of the double bond in 12α-hydroxymethyldihydroabietic acid has been established by hydroboration and osmium tetroxide oxidation experiments. Cyclization of 12-hydroxymethylabiet-7,8-enoic acid and its 12-acetoxy derivative gave δ-lactones which on lithium aluminum hydride reduction and subsequent dehydration afforded new diterpene alcohols. Reaction of the dihydro compound with acetyl hypobromite afforded methyl 12-acetoxymethylabietate as the major product. The mechanistic implications of the latter are discussed.

Hydrogenation of readily available 12α-hydroxymethylabietic acid (**1**)[2] to a dihydro compound has been reported[3] but evidence as to its structure was not obtained. Physical data for this compound have now been obtained, and some of its reactions studied with a view to preparing new diterpene alcohols for polyurethane applications.

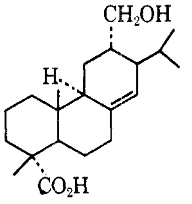
Absorption of one molecule of hydrogen by **1** may theoretically lead to the formation of dihydro compounds **2**, **3**, and **4**. However, it was found that low-pressure hydrogenation followed by repeated recrystallization of the resulting product gave a single pure dihydro compound as the major product. The nuclear magnetic resonance (nmr) spectrum of the dihydro compound (as the methyl ester) suggests it to be 12α-hydroxymethylabiet-7,8-enoic acid (**2a**). The vinyl proton appeared as a broad signal centered at 5.34 ppm, it being rendered diffuse by possible long-range coupling. The vinyl proton signal in the corresponding 12-acetoxy compound **5b** is also found to be a broadened doublet (J = 4.0 cps) centered at 5.33 ppm very similar in shape and position to that found for the H-7 proton signal in methyl 12-acetoxymethylabietate (see later) and in authentic 7,8 compounds.[4,5]



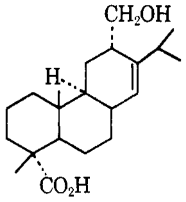
1



2a, R = H
b, R = Me

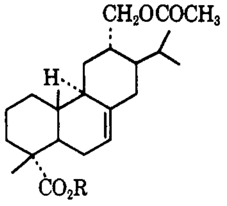


3

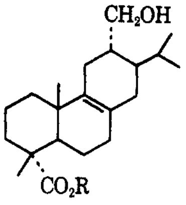


4

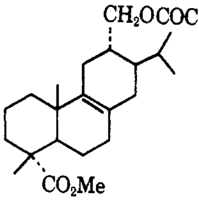
Passage of dry hydrogen chloride gas into a chloroform solution of **2a** at 0° resulted in proton rearrangement[6,7] to give 12α-hydroxymethylabiet-8,9-enoic acid (**6a**). Acetylation and esterification of **6a** gave methyl 12α-acetoxymethylabiet-8,9-enoate (**7**) which showed a deshielded C-10 Me singlet at 1.13 ppm and a broadened signal centered at 1.78 ppm (allylic protons).



5a, R = H
b, R = Me



6a, R = H
b, R = Me



7

Hydroboration of **2b** with lithium aluminum hydride-boron trifluoride followed by alkaline hydrogen peroxide oxidation[8] gave a saturated triol as major product. The nmr spectrum of the corresponding triacetate showed the H-7 proton signal as a broad triplet centered at 4.80 ppm, suggesting it to be axial and vicinal to other axial protons,[9] but no signals in the 2.20–3.40-

---

(1) (a) National Research Council Postdoctoral Resident Research Associate. (b) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) B. A. Parkin and G. W. Hedrick, *J. Org. Chem.*, **30**, 2356 (1965).

(3) B. A. Parkin, H. B. Summers, R. L. Settine, and G. W. Hedrick, *Ind. Eng. Chem., Prod. Res. Develop.*, **5**, 257 (1966).

(4) J. W. Huffman, T. Kamiya, L. H. Wright, J. J. Schmid, and W. Herz, *J. Org. Chem.*, **31**, 4128 (1966).

(5) W. Herz, H. J. Wahlborg, W. D. Lloyd, W. H. Schuller, and G. W. Hedrick, *ibid.*, **30**, 3190 (1965).

(6) *Cf.* L. Velluz, G. Müller, A. Petit, and J. Mathieu, *Bull. Soc. Chim. France*, 401 (1954).

(7) O. E. Edwards and R. Howe, *Can. J. Chem.*, **37**, 760 (1959).

(8) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(9) E. Wenkert, P. W. Jeffs, and J. R. Mahajan, *J. Am. Chem. Soc.*, **86**, 2218 (1964); W. Herz, D. Melchior, R. N. Mirrington, and P. J. S. Pauwels *J. Org. Chem.*, **30**, 1873 (1965).