analysis (silicone 550 column) indicated that this residue contained ~25% of the desired bromo olefin VIII. A sample of VIII was obtained by preparative gas chromatography (silicone 550 column) and the sample so obtained was identical in infrared and nuclear magnetic resonance spectra with a sample of VIII prepared as previously described.[2]

New Butadiene Dimers

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It is known that treatment of butadiene with a Ziegler type catalyst (combination catalyst of organoaluminum compounds and transition metal compounds) has given stereospecific polybutadiene.[1]

During our examination of the effect of various Ziegler catalysts on butadiene, a new reaction was found which produced linear dimers in good yield.

Treatment of butadiene in a hydrocarbon solution with the combined catalyst of trialkyl aluminum and cobalt(II) chloride resulted in a good yield of the butadiene dimer. These results are summarized in Table I.

TABLE I

DIMERIZATION OF BUTADIENE

Catalyst[a]	AlR_3–$CoCl_2$ molar ratio	Solvent	Product yield (%) Dimer	Higher polymer
$Al(C_2H_5)_3$–$CoCl_2$	3.5	Benzene	90	Trace
$Al(C_2H_5)_3$–$CoCl_2$	3.5	Pentane	85	Trace
$Al(C_2H_5)_3$–$CoCl_2$	3.6	Hexane	82	Trace
$Al(C_2H_5)_3$–$CoCl_2$	3.6	Nonane	Trace	Trace
$Al(iso\text{-}C_4H_9)_3$–$CoCl_2$	3.5	Benzene	80	Trace

[a] The aluminum compound that produced the dimer was limited to trialkyl aluminum.

In comparing alkyl groups, ethyl had a higher rate of reaction than isobutyl. The dimers were not formed when nickel or iron was used as the transition metal in place of cobalt.

The product, a colorless liquid of b.p. 117–118°, slowly polymerized when left standing for a long time. Hydrogenation and bromination indicated that this product was a dimer of butadiene which had the formula C_8H_{12} with three double bonds.

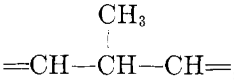
Gas chromatography indicated that this dimer was a mixture of about 85% of A and about 15% of B, both of which were found to have the formula C_8H_{12}. It was assumed that the two components A and B were different, not only in the position of the double bonds but also in the skeleton, because the hydrogenated product was also composed of two components, the per cents of which were the same as the mixture dimers.

The basic skeletons of A and B were established by the fact that the hydrogenated product of A was identified as 3-methylheptane (III), and B as octane (IV).

The position of the double bonds in A and B was indicated by ultraviolet, infrared, and nuclear magnetic resonance spectra.

These spectra showed that only two of the three double bonds were conjugated, since A and B, respectively, had ultraviolet absorption at 226 and 225 mμ.

Infrared spectra of A and B showed the presence of a terminal double bond (900, 1000 cm.$^{-1}$), a conjugated double bond (1605, 1636, 1650 cm.$^{-1}$), and a methyl group (1372 cm.$^{-1}$). Further, strong absorptions at 900 and 915 cm.$^{-1}$ (CH_2 out-of-plane deformation) in A showed the presence of two terminal double bonds, one of which was conjugated.

The n.m.r. spectrum showed that compound A had a secondary methyl group from the presence of a symmetrical doublet at τ = 8.88 p.p.m. and also had the following partial structure,  $=CH-\overset{\overset{CH_3}{|}}{C}H-CH=$, because of the presence of six lines at τ = 7.12 p.p.m.

Further proof for the formula (III) was obtained by the fact that the n.m.r. spectrum showed that the hydrogenated product of A had three methyl groups.

The n.m.r. spectrum of B confirmed the presence of one methyl and methylene group, both of which were not coupled since there was a symmetrical doublet at τ = 8.38 p.p.m. and a symmetrical triplet at τ = 7.19 p.p.m.

Among the possible structures for A and B, only I and II could be proposed for dimers A and B, respectively, since the structures completely satisfied all the observations. (See Scheme I.)

It is evident that dimers like I and II are produced by 1,2-addition and 1,4-addition of butadiene monomers, respectively.

It is well-known that in the case of butadiene polymerization by Ziegler catalysts, fine differences of combined components have a great effect on the structure of the product.

Experimental

Materials.—1,3-Butadiene monomer was dried over sodium hydroxide and activated alumina. Triethylaluminum and triisobutylaluminum (Ethyl Corp., U. S. A.) were vacuum distilled. Cobalt(II) chloride (Wako Pure Chemical Industries, Ltd., Japan) was dried over thionyl chloride. All the solvents were purified or dried from commercial products by conventional procedures.

Dimerization of Butadiene by Triethylaluminum–Cobalt(II) Chloride.—Experiments were carried out in 500-ml. autoclave equipped with an inlet tube and thermometer. Additions of solvents and catalyst were performed in a dry nitrogen atmosphere. The autoclave was first purged with nitrogen, then evacuated. Liquid butadiene (200 ml.) was added to the autoclave which had been charged with 60 ml. of a benzene solution containing 3.6 ml. of triethylaluminum and 1 g. of cobalt(II) chloride. The autoclave was heated at 60° and stirred for 2 hr. After addition of 100 ml. of methanol, the reaction mixture was washed with dilute sulfuric acid and then filtered. The filtrate, dried over calcium chloride and distilled, yielded 40 g. of dimer, b.p. 117–118° (760 mm.). Chromatographic analysis showed the composition of the distillate to be 83% I and 11% II.

Dimer I had b.p. 117–118° (760 mm.), $n^{20}D$ 1.4670, d^{18}_4 0.7724.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.78; H, 11.20.

(For the mixture of I and II: *Anal.* Found: C, 88.54; H, 11.29.)

Isolation of I and II.—Dimers I and II were isolated by gas-liquid chromatography by using a 4-m. Apiezon-M column. The conditions were column temperature, 110°; column pressure,

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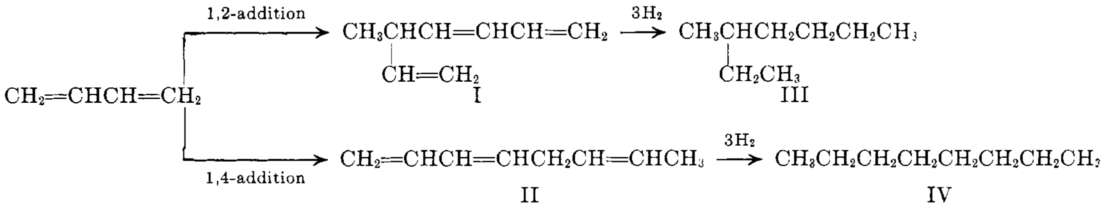
(1) G. Natta, *Makromol. Chem.*, **16**, 213 (1955); G. Natta and P. Corradini, *J. Polymer. Sci.*, **20**, 251 (1956); G. Natta, *Rubber Plastics Age*, **38**, 493 (1959); N. G. Gaylord, T.-K. Kwei, and H. F. Mark, *J. Polymer. Sci.*, **42**, 417 (1960).

SCHEME I



$$CH_2{=}CHCH{=}CH_2 \xrightarrow{\text{1,2-addition}} \underset{\displaystyle CH{=}CH_2}{CH_3CH}CH{=}CHCH{=}CH_2\ (\text{I}) \xrightarrow{3H_2} \underset{\displaystyle CH_2CH_3}{CH_3CH}CH_2CH_2CH_2CH_3\ (\text{III})$$

$$CH_2{=}CHCH{=}CH_2 \xrightarrow{\text{1,4-addition}} CH_2{=}CHCH{=}CHCH_2CH{=}CHCH_3\ (\text{II}) \xrightarrow{3H_2} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3\ (\text{IV})$$

10 p.s.i.; carrier gas, helium; and flash evaporator temperature, 200°. The first and second chromatographic peaks corresponded to I and II. The amount of II isolated was so small that analytical data, refractive index, and specific gravity of II could not be obtained; only spectroscopic data was obtained.

Hydrogenation of I and a Mixture of I and II.—Hydrogenation at atmospheric pressure of I (2.16 g.) using 100 mg. of platinum black resulted in absorption at 1520 ml. (3 equivalents) of hydrogen. After filtration, saturated hydrocarbon III (2.1 g.) was obtained. The infrared spectrum of this hydrocarbon (III) was identical with that of 3-methylheptane. Similarly on hydrogenation, a mixture of I and II absorbed 3 equiv. of hydrogen, and resulted in a mixture of 3-methylheptane (83%) and *n*-octane (11%). Octane was determined by gas chromatography.

Anal. Calcd. for C_8H_{18}: C, 84.22; H, 15.78. Found: C, 84.15; H, 15.80 (hydrogenated product III).

Anal. Found: C, 84.10; H, 15.75 (hydrogenated product of I and II).

Bromination of a Mixture of I and II.—On bromination, a mixture (10.1 g.) of I and II absorbed 3 equiv. of bromine in carbon tetrachloride (50 ml.). After filtration and evaporation, a white solid (50 g.) was obtained. It was purified by recrystallization from chloroform. The analytical sample melted at 129–130°.

Anal. Calcd. for $C_8H_{12}Br_6$: C, 16.35; H, 2.06; Br, 81.59. Found: C, 16.50; H, 2.20; Br, 81.26.

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4-Cholesten-3-one Ethylene Ketal

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In a study designed to extend our work of comparing the behavior of the cholesteryl and pseudo-cholesteryl systems,[1] the reaction of ethylene glycol and 5-cholesten-7-one (I) was undertaken to resolve the question of whether the pseudocholesteryl system (as I) would exhibit the unusual rearrangement of the double bond reported[2] from the preparation of the ethylene ketal III from 4-cholesten-3-one (II).

5-Cholesten-7-one (I) provided a ketal (IV), the optical rotation of which, in contrast to many other cholestane derivatives, was ambiguous[3] with respect to its use in the prediction of structure (see Table I).

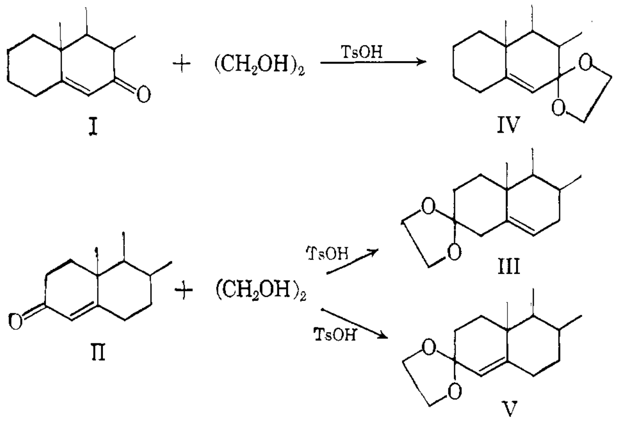
TABLE I

CHOLESTANE DERIVATIVES

Functional group	Hydroxyl position	Reported $[\alpha]_D$	Calculated, $\frac{[\alpha]_D\ \alpha + [\alpha]_D\ \beta}{2}$	Reported $[\alpha]_D$ ethylene ketal
None	3α	+23[a]	+23.5	+21.6[b]
	3β	+24[a]		
5α,6α-Oxido	3α	−44[c,d]	−44.5	−33[f]
	3β	−43[e]		
5β,6β-Oxido	3α	−0.6[c]	+6	+9[f]
	3β	+12[e]		
Δ^4	3α	+121[g]	+83	+75[o]
	3β	+45[h]		
Δ^5	3α	−47[i]	−43.5	−28[k]
	3β	−40[j]		
Δ^4	7α	+45[l]	+67	
	7β	+90[m]		−2.4[o]
Δ^5	7α	−112[n]	−56	
	7β	±0[n]		

[a] L. F. Fieser and W. Huang, *J. Am. Chem. Soc.*, **75**, 4837 (1953). [b] H. Dauben, Jr., B. Löken, and H. Ringold, *ibid.*, **76**, 1360 (1954). [c] P. Plattner, A. Fürst, F. Koller, and H. Kuhn, *Helv. Chim. Acta*, **37**, 258 (1954). [d] A. Fudge, C. Shoppee, and G. Summers, *J. Chem. Soc.*, 958 (1954). [e] R. Baxter and F. Spring, *ibid.*, 613 (1943). [f] See ref. 8. [g] H. McKennis, Jr. and G. Gaffney, *J. Biol. Chem.*, **175**, 217 (1948). [h] P. Plattner, H. Heusser, and A. Kulkarni, *Helv. Chim. Acta*, **32**, 265 (1949). [i] P. Plattner and W. Lang, *ibid.*, **27**, 1872 (1944). [j] L. F. Fieser, *J. Am. Chem. Soc.*, **75**, 5421 (1953). [k] See ref. 2a. [l] G. Kent and E. Wallis, *J. Org. Chem.*, **24**, 1235 (1959). [m] See ref. 1b. [n] A. Nickon and J. Bagli, *J. Am. Chem. Soc.*, **83**, 1498 (1961). [o] Details in this paper.

In order to compare the infrared spectrum of this possible α,β-unsaturated ethylene ketal with that of a known β,γ-unsaturated ethylene ketal, the pro-



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[1] Q. R. Petersen, *J. Am. Chem. Soc.*, **82**, 3677 (1960); Q. R. Petersen and C. T. Chen, *ibid.*, **77**, 2557 (1955); Q. R. Petersen, *Proc. Indiana Acad. Sci.*, **68**, 118 (1959).

[2] (a) E. Fernholtz, U. S. Patent 2,378,918 (1945); *Chem. Abstr.*, **39**, 5052^3 (1945); (b) H. Koster and H. Inhoffen, German Patent 892,450 (1953); *Chem. Abstr.*, **52**, P18,534*g*, (1958); (c) C. Grob, W. Jundt, and H. Wicki, *Helv. Chim. Acta*, **32**, 2427 (1949); (d) R. Antonucci, S. Bernstein, R. Littell, K. Sax, and J. Williams, *J. Org. Chem.*, **17**, 1341 (1952); (e) H. Koster and H. Inhoffen, U. S. Patent 2,302,636 (1942); *Chem. Abstr.*, **37**, 2388^6 (1943).

[3] For another example of anomalous rotational contribution by the 7-oxygen function, see R. Cremlyn, R. Rees, and C. Shoppee, *J. Chem. Soc.*, 3790 (1954). Compound IV is tentatively assigned the Δ^5-structure on the basis of its resemblance (in its mode of formation and in its instability toward hydrolysis) to the unrearranged ketals in the cholesteryl system.