

mixtures of *threo*- and *erythro*-1,2-epoxy-3-alkyl-3-propanols (III). Although these stereoisomeric mixtures of epoxy-alcohols could be fractionated from non-stereoisomeric impurities by vapor phase chromatography (V.P.C.), this technique was not successful in separating the *threo* and *erythro* components from each other. Therefore the mixtures of *threo*- and *erythro*-epoxy alcohols were reduced with a large excess of lithium aluminum hydride (in approximately 60% yields) to the corresponding mixtures of *threo*- and *erythro*-1-alkyl-1,2-propanediols. A satisfactory resolution of the resulting mixtures of *threo*- and *erythro*-diols was achieved through the use of a 10 ft. Uconpolar column.⁵

Independent syntheses of *threo*- and *erythro*-1-isopropyl-1,2-propane-diols (I, R = isopropyl) by *cis*-hydroxylation of the known *cis*- and *trans*-4-methyl-2-pentenenes⁶ served to identify this pair of isomers. Their infrared spectra and V.P.C. retention times were compared with the fractions from hydride reduction of the mixture of epoxides. Authentic *threo*-*t*-butyl-1,2-propanediol also was prepared in the same way from *trans*-4,4-dimethyl-2-pentene. In both cases the *erythro* isomer showed the greater retention time in the vapor phase analysis. The identities of the *erythro*- and *threo*-methyl- and ethylcarbinols (I, R = CH₃, R = C₂H₅) were deduced by analogy with the isopropyl and *t*-butyl cases from their V.P.C. behavior under the same conditions.

Since the yields of epoxide mixtures were less than quantitative, an experiment was carried out to determine the effect, if any, of these losses on the *erythro*-*threo* isomer ratio in the final diols. A sample of the mixture of isomeric oxides (II) from epoxidation of 4-methyl-1-pentene-3-ol (I, R = isopropyl), found by reduction and V.P.C. analysis to be 64% *threo* and 36% *erythro*, was submitted to the action of perphthalic acid under the standard conditions and worked up in the usual manner. A loss of about 25% of the epoxide mixture was observed, presumably from solubility,³ hydrolysis, cleavage⁷ or polymerization; the *erythro*-*threo* ratio in the reduction products was, however, essentially unchanged (62% *threo*, 38% *erythro*). Hence, it is felt that destruction of epoxides at this stage is not stereoselective and that the observed ratios of diols represent those produced during epoxidation.

The epoxides (II) were reduced completely by treatment with lithium aluminum hydrides since no unchanged material could be detected in the infrared or by V.P.C. analysis. The less than quantitative recovery of diols is attributed to the water-soluble nature of these substances. No evidence for 1,3 diols or other side products could be obtained except for faint carbonyl bands in the infrared in some samples. Eliel and Delmonte⁸ found in analogous situations that hydride attack

under our conditions occurs exclusively at the primary carbon.

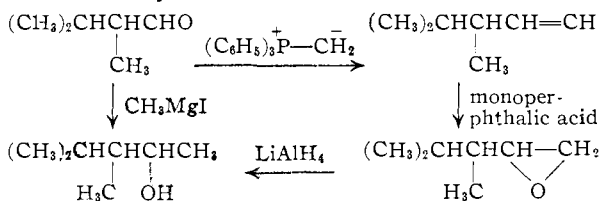
The results of determinations of isomer ratios are shown in Table I.

TABLE I
EPOXIDATION OF ALLYLIC ALCOHOLS (I)

R	Yield of II mixture, ^a %	Yield of III mixture, ^a %	<i>threo</i> -III, %	<i>erythro</i> III, %
CH ₃	41	55	61	39
C ₂ H ₅	54	60	60	40
<i>i</i> -C ₃ H ₇ ^b	56-68	70-84	62-68	32-38
<i>t</i> -C ₄ H ₉	64	60	56	44

^a Based on V.P.C. purified material. ^b Variations observed in several runs using different work-up procedures. Duplicate experiments were reproducible to $\pm 2\%$ in % yield of *threo*- and *erythro*-III.

Since the variations in R had relatively small effect on the *erythro*-*threo* ratio, it seemed of interest to replace the OH group in I by a non-polar group of comparable bulk. To this end 3,4-dimethyl-1-pentene was synthesized as shown from 2,3-dimethylbutanal⁹ by the Wittig¹⁰ procedure. The isomeric 3,4-dimethyl-2-pentanols also were prepared by the action of methylmagnesium bromide on this aldehyde. In a series of reactions, outlined



above, similar to those carried out with the alkylvinylcarbinols, 3,4-dimethyl-1-pentene was epoxidized with monoperphthalic acid, and the stereoisomeric mixture of epoxides so produced was reduced with lithium aluminum hydride to a mixture of *threo*- and *erythro*-3,4-dimethyl-2-pentanols. These alcohols were resolved on a 10-ft. Uconpolar V.P.C. column and found to consist of a mixture of 48% *threo*:52% *erythro* isomer. The 3,4-dimethyl-2-pentanols independently synthesized by the reaction of methylmagnesium iodide with methylisopropylacetaldehyde were produced in a 67%:33% mixture of stereoisomers. The major component was assigned the *erythro* configuration, and the minor component was assigned the *threo* configuration, after Cram's rule.^{10,11}

It should be noted that the epoxidation of 3,4-dimethylpentene-1 resulted in only 23% yield, which may be attributed to the very small scale on which the reaction was run, necessitating fairly dilute concentrations of the reactants. Barring stereospecific side-reactions, which were shown to be absent in the alkylvinylcarbinol epoxidations, the stereochemical results are felt to be independent of yield, since epoxidation reactions have been demonstrated to be kinetically controlled.¹²

It seems worthy of note that although the Grignard addition to 2,3-dimethylbutanal shows con-

(5) This material was obtained from the Wilkens Instrument and Research Co., Walnut Creek, Calif.

(6) From Phillips Petroleum Co.

(7) V. I. Pansevitch-Kolyada, *J. Gen. Chem., U.S.S.R.*, **26**, 1343 (1946).

(8) E. L. Eliel and D. W. Delmonte, *THIS JOURNAL*, **80**, 1744 (1958).

(9) R. A. Barnes and W. M. Budde, *ibid.*, **68**, 2339 (1946).

(10) D. J. Cram and F. A. Abd Elhatez, *THIS JOURNAL*, **74**, 5828 (1952).

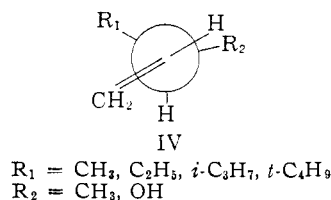
(11) I. Elphimoff-Felkin and H. Felkin, *Bull. soc. chim. France*, 450 (1957).

(12) D. Swern, *Org. Reactions*, **7**, 378 (1953).

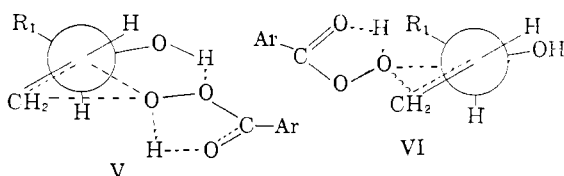
siderable (67:33) stereospecificity, the formally analogous addition of oxygen to 3,4-dimethyl-1-pentene gave nearly a 50:50 mixture. This would support Cram's assignment of a large effective bulk to the carbonyl oxygen in aldehydes in their reaction with Grignard reagents.

The fact that a degree of stereospecificity is observed with the allylic alcohols examined and not with 3,4-dimethyl-1-pentene leads to the speculation that here, as in the cases examined of Henbest and Wilson,⁸ the peracid may be involved with the hydroxyl group in the formation of an intermediate prior to epoxidation.

Assuming, from the postulations of Zimmerman and Chang,¹³ that the preferred conformation of the allylic alcohols is as shown IV, we are led to suggest that the interaction between the peracid



molecule and the hydroxyl group makes the *threo*-producing intermediate, or transition state V, favored with respect to the *erythro*-producing conformation VI



threo-Isomer predominance might be predicted on steric grounds alone, without the intervention of peracid-hydroxyl interaction, since conformation V apparently is less hindered than conformation VI. However it would then be difficult to accommodate the lack of stereospecificity observed in the case of the hydrocarbon IV (R₁ = *i*-C₃H₇, R₂ = CH₃), since the stereochemical interactions in this instance would be very similar to those encountered in the epoxidation of isopropylvinylcarbinol. Therefore we are led to the conclusion that the energy differences between V and VI are due primarily to the availability of the hydroxyl group to the attacking peracid molecule in V, and its non-availability in VI.

Experimental¹⁴

Alkylvinylcarbinols.—The alkylvinylcarbinols described below were made by the reaction of vinylmagnesium bromide¹⁵ or vinylmagnesium chloride¹⁶ with the appropriate aldehyde. Acetaldehyde and propionaldehyde were freshly distilled, isobutyraldehyde was used as supplied, and pivaldehyde was synthesized by the method of Campbell.¹⁷ All of the alkylvinylcarbinols showed a strong band at *ca.* 10.9 μ , and their purity was determined by V.P.C.

(13) H. E. Zimmerman and W. H. Chang, *THIS JOURNAL*, **81**, 3636 (1959).

(14) Percentage purity of liquids was determined by vapor phase chromatography, V.P.C.

(15) H. Normant, *Compt. rend.*, **239**, 1510 (1954).

(16) H. E. Ramsden, *J. Org. Chem.*, **22**, 1602 (1957).

(17) K. N. Campbell, *THIS JOURNAL*, **59**, 1980 (1937).

Both methylvinylcarbinol and ethylvinylcarbinol were found to be contaminated with varying amounts of lower-boiling substances, but these substances did not appear to interfere with the subsequent experiments.

TABLE II

R	ALKYLVINYL-CARBINOLS, RCHOHCH=CH ₂		B.p.		Lit. bp.	
	Yield, %	Purity, %	°C.	Mm.	°C.	Mm.
CH ₃	40	68	90-100	760	93-95	760 ¹⁸
C ₂ H ₅	47	71	100-108	760	74-75	700 ¹⁸
<i>i</i> -C ₃ H ₇	60	90	53-59	45	124-125	760 ¹⁹
<i>t</i> -C ₄ H ₉	55	94	62-65	45	51-52	25 ¹⁹

1,2-Epoxy-3-alkyl-3-propanols.—The alkylvinylcarbinol was added to an ethereal solution of monopero-phthalic acid²⁰ at room temperature. A slight warming of the reaction mixture was noted, but cooling was not required. The stoppered reaction flask was wrapped in aluminum foil and stored at room temperature. The uptake of peracid was followed by iodometric titration of aliquots of the reaction mixture; about 24 to 36 hours was required for complete reaction. Workup was accomplished by filtering off the precipitated phthalic acid and pouring the filtrate into 2 volumes of excess, cold saturated potassium carbonate solution containing some dissolved sodium thiosulfate. The two-phase system was shaken vigorously until the ether layer was neutral to *pH* paper and non-oxidizing to starch-iodide paper. The ether layer was separated and the aqueous layer was extracted with several portions of ether (total volume of ether equal to the original organic layer). The combined ether extracts were dried over sodium sulfate and distilled at atmospheric pressure to remove the ether. The residue was distilled *in vacuo* to yield a stereoisomeric mixture of the 1,2-epoxy-3-alkyl-3-propanols. The products were analyzed by V.P.C. and analytical samples were obtained by this technique. In the following descriptions, the percentage purity of the epoxy-alcohols represents the purity of the stereoisomeric mixtures, relative to other materials present in the vapor phase chromatograms. Concerning these analyses, it was found that a V.P.C. column with a detergent substrate at 98-125° was the only one of several columns which was successful in purifying the epoxy-alcohols. These rather sensitive materials could not be eluted from Ucon-polar or Apiezon columns, and were quite strongly adsorbed and partially rearranged by a silicone column.

Further Experiments on the Epoxidation of Isopropylvinylcarbinol.—The monopero-phthalic acid epoxidation of isopropylvinylcarbinol was repeated exactly as described above, and the reaction mixture was divided into two equal parts. Part one was worked up by the previously described alkaline quench procedure, giving a 68% yield of a stereoisomeric mixture of 1,2-epoxy-3-isopropyl-3-propanols and a still-pot residue of 4.7% (by weight). An aliquot of the aqueous work-up solution was continuously extracted with ether for 3 days to yield 3% of an impure oily residue. A periodic acid titration of an aliquot of the acidified work-up solution showed the presence of 3% of periodic acid-consuming material, based upon the molecular weight of isopropylglycerol, a postulated product of epoxide cleavage.

Part two was worked up after the method of Henbest and Nicholls⁹ by adding solid calcium hydroxide to the reaction mixture and stirring for 24 hours. At that time a negative starch-iodide test and a neutral *pH* paper test were observed. The mixture was filtered and the solids were washed with three 75-ml. portions of dry ether. The combined ether solution was distilled at atmospheric pressure to remove the solvent, and the residue was distilled *in vacuo* to give 63% yield of a stereoisomeric mixture of 1,2-epoxy-3-isopropyl-3-propanols and 10% of a stillpot residue.

A 4-g. portion of the epoxy-alcohol mixture isolated in part one was added to an ether solution containing one equivalent (based upon epoxide) each of monopero-phthalic acid (dissolved) and phthalic acid (undissolved). No consumption of peracid was noted after 36 hours, at which

(18) J. Wieman and J. Gardan, *Bull. soc. chim. France*, 433 (1958).

(19) M. B. Green and W. J. Hickinbottom, *J. Chem. Soc.*, 3268 (1957).

(20) E. E. Royals and L. L. Harrell, Jr., *THIS JOURNAL*, **77**, 3405 (1955).

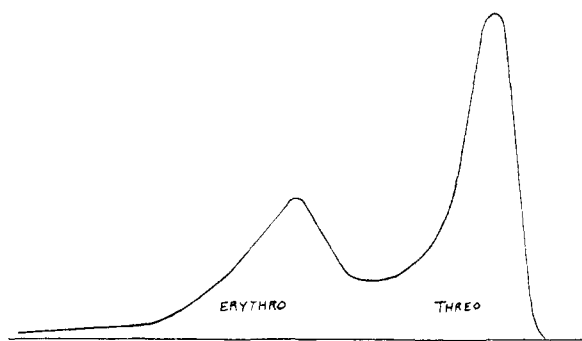
TABLE III
 1,2-EPOXY-3-ALKYL-3-PROPANOLS, RCHOHCH₂CH₂

R	Yield, %	Purity, %	B.p.		<i>n</i> _D ²⁵	Carbon, %		Hydrogen, %	
			°C.	Mm.		Calcd.	Found	Calcd.	Found
CH ₃	41	84	76-80	45	1.4228	54.53	54.33	9.15	9.37
C ₂ H ₅	54	82	80-86	37	1.4327	58.80	58.78	9.87	9.81
<i>i</i> -C ₃ H ₇	56	80	82-90	42	1.4358	62.04	61.88	10.41	10.45
<i>t</i> -C ₄ H ₉	64	90	60-68	11	1.4379	64.58	64.50	10.84	10.91

time the reaction was worked up in the manner described for part one to give a 75% recovery of epoxy-alcohols and 1.5% of a still-pot residue.

Lithium Aluminum Hydride Reduction of the 1,2-Epoxy-3-alkyl-3-propanols.—An ether solution of the 1,2-epoxy-3-alkyl-3-propanol isomer mixture was added dropwise to a well-stirred suspension of lithium aluminum hydride in ether, and the reaction mixture was stirred at room temperature for 24 hours, at which time it was decomposed by addition of excess ethyl acetate, followed by ethanol and water. The decomposed mixture was incompletely neutralized by pouring it into *ca.* 100 ml. of cold saturated ammonium sulfate solution. The ether layer was separated and the aqueous layer was extracted with two 100-ml. portions of ether. The combined ether extract was dried over sodium sulfate and distilled at atmospheric pressure to remove the solvent. The residue was distilled *in vacuo* to yield the stereoisomeric mixture of 1-alkyl-1,2-propanediols. The products were analyzed by V.P.C. and analytical samples were obtained by this method. It should be noted that both the detergent and Ucon-polar columns were satisfactory for the purification of the diols, but only the latter substrate effected resolution of the *threo*- and *erythro*-diols. By use of a 10-ft. Ucon polar column at 155-160°, a satisfactory resolution of these isomers could be achieved.

Even under optimum conditions, however, a complete separation the V.P.C. peaks was not achieved. An extrapolation of the curve of the more rapidly eluted *threo* isomer into that of the *erythro* isomer was carried out based on the observed shape of the curve of the pure, independently synthesized *erythro* form (R = *i*-propyl, *t*-butyl) in order to obtain a quantitative estimate of the composition. Figure 1 shows a typical V.P.C. curve; variations in the extrapolation method had only a minor effect on the isomer ratios.



Time.

Fig. 1.

***threo*-1-Isopropyl-1,2-propanediol.**—A solution of potassium permanganate (80 g., 0.5 mole) in water (1500 ml.) was added slowly to a rapidly stirred, ice-cooled suspension of *trans*-4-methylpentene-2 [42 g., 0.5 mole, Phillips 95% grade] in water (400 ml.) over a 3-hour period. After the reaction stood at room temperature overnight, the precipitated manganese dioxide was filtered off and the filtrate was saturated with potassium carbonate (with cooling). The water was extracted with four 100-ml. portions of ether. The ether was dried over sodium sulfate and distilled off at atmospheric pressure, leaving a residue which was distilled to give *threo*-1-isopropyl-1,2-propanediol, 11 g. (18%), b.p. 86-90° (11 mm.), which solidified in the receiver. Several recrystallizations from hexane gave white needles, m.p. 59-59.7°.

 TABLE IV
 1-ALKYL-1,2-PROPANEDIOLS, RCHCHCH₂OH

R	Yield, %	Purity, %	B.p.		<i>n</i> _D ²⁵	<i>v</i> _{max}	
			°C.	Mm.		<i>threo</i>	<i>erythro</i>
CH ₃ ²¹	55	99	60-62	3	1.4311	61	39
C ₂ H ₅ ²²	60	98	55-57	2	1.4370	60 ^u	40 ^b
<i>i</i> -C ₃ H ₇ ²³	71	95	90-92	11	...	63 ^c	37 ^c
<i>t</i> -C ₄ H ₉	60	56 ^d	44 ^e

^a *n*_D²⁵ 1.4345. ^b *n*_D²⁵ 1.4353. ^c Identical in infrared to synthetic samples below. ^d M.p. 76-77.5°. *Anal.* Calcd. for C₇H₁₆O₂: C, 63.59; H, 12.20. Found: C, 63.76; H 12.11. ^e M.p. 72°. Found: C, 63.48; H, 11.97.

Anal. Calcd. for C₆H₁₄O₂: C, 60.98; H, 11.94. Found: C, 61.41; H, 12.00.

***erythro*-1-Isopropyl-1,2-propanediol.**—In a manner similar to the procedure described for the *threo* compound, potassium permanganate hydroxylation of *cis*-4-methylpentene (Phillips 95% grade) gave *erythro*-1-isopropyl-1,2-propanediol, 13%, b.p. 86-88° (11 mm.), which was recrystallized several times from hexane to give the solid diol, m.p. 49-49.5°.

Anal. Found: C, 61.38; H, 12.07.

***threo*-*t*-Butyl-1,2-propanediol.**—*trans*-4,4-Dimethylpentene-2 was synthesized by the pyrolysis of 3-acetoxy-4,4-dimethylpentane, after the procedure of Cramer and Miller.²⁴ A mixture of olefins was obtained, b.p. 73-76°, which was shown by V.P.C. to contain 78% of the *trans*-olefin (30% yield), *n*_D²⁵ 1.3968, strong *trans*-double bond absorption at 10.3 μ (reported² b.p. 76.6-76.7° (760 mm.), *n*_D²⁵ 1.3983).

trans-4,4-Dimethylpentene-2 (0.386 g., 0.004 mole), dissolved in an equal volume of benzene, was added to osmium tetroxide (0.5 g., 0.002 mole) dissolved in 20 ml. of benzene containing 1 ml. of pyridine. The reaction turned black instantly and was kept in a stoppered, aluminum foil-wrapped flask for 22 hours. It was decomposed by adding water (35 ml.), sodium sulfate (4 g.), sodium bicarbonate (4 g.) and methanol (25 ml.) and stirring the mixture for 5 hours. Then chloroform (150 ml.) was added and the mixture was stirred for 30 min. The chloroform layer was separated and the aqueous layer was extracted with two 100-ml. portions of chloroform. The combined chloroform extract was washed with saturated salt solution and dried over sodium sulfate. The chloroform was evaporated, leaving a residue which was recrystallized from hexane to give *threo*-1-*t*-butyl-1,2-propanediol, white needles, 0.06 g. (23%), m.p. 77.5-78.5°, identical with the previously isolated *threo*-1-*t*-butyl-1,2-propanediol by mixed m.p., infrared spectrum and V.P.C. criteria.

Ethyl Methylisopropylcyanoacetate.—Following the published method for the synthesis of ethyl ethylisopropylcyanoacetate,²⁵ ethyl isopropylcyanoacetate²⁶ (80 g., 0.516 mole) was added to a solution of sodium (12.5 g., 0.543 mole) in absolute ethanol (150 ml.). To the resulting red solution was added 10% excess methyl iodide (87 g., 0.6 mole) at a rate sufficient to control the exothermic reaction (30 min.) The reaction was run in a closed system under a

(21) C. E. Wilson and H. J. Lucas, *THIS JOURNAL*, **58**, 2400 (1936).

(22) H. J. Lucas, M. J. Schlatter and R. C. Jones, *ibid.*, **63**, 22 (1941).

(23) E. D. Bergmann, *J. Appl. Chem.*, **1**, 380 (1951), reported a mixture of these isomers.

(24) P. L. Cramer and V. A. Miller, *THIS JOURNAL*, **62**, 1452 (1940).

(25) E. Fischer, H. Rohde and F. Browns, *Ann.*, **402**, 364 (1914).

(26) E. Fischer and F. Plateau, *Ber.*, **42**, 2983 (1909).

condenser fitted at its top with a balloon to minimize the loss of volatile methyl iodide. After addition was complete, the reaction was refluxed for 15 hours and allowed to stand at room temperature for an additional 24 hours. At this time an aliquot of the reaction mixture tested neutral to β H paper. The mixture was distilled (finally at the water-pump) to remove ethanol. The residue was thinned with water to dissolve the sodium iodide, and extracted several times with a total of 500 ml. of ether. The ether was dried over sodium sulfate and distilled at atmospheric pressure to remove the solvent. The residue was distilled to give ethyl methylisopropylcyanoacetate, 73.2 g., 85% pure (67% yield), b.p. 98–102° (17 mm.), n_D^{20} 1.4222.

Methylisopropylacetonitrile.—Ethyl methylisopropylcyanoacetate (61 g., 85% pure, 0.0306 mole) was added to a solution of 126 ml. of 50% potassium hydroxide (0.92 mole) in methanol (total volume 930 ml. before addition of ester and 995 ml. after addition). After 12 hours at room temperature, titration of an aliquot of the solution showed the hydrolysis was complete. The reaction was worked-up after an additional 12 hours (no change in titer) by adding water (150 ml.) and removing the methanol at the water-pump without heat. The residue was extracted with ether (100 ml.) to remove organic impurities. The water layer was acidified with 50% sulfuric acid and extracted with three 300-ml. portions of ether. The ether was dried over sodium sulfate and removed at the water-pump. Methylisopropylcyanoacetic acid was obtained as a crude oily residue and decarboxylated at 190° for 4 hours, during which time methylisopropylacetonitrile was collected as an impure distillate. The product was taken up in ether, washed with potassium carbonate solution, and dried over sodium sulfate. The ether was removed at atmospheric pressure and the residue was distilled to give methylisopropylacetonitrile, 19.6 g., 92% pure (61% yield), b.p. 55–65° (28 mm.), n_D^{20} 1.3992.

Methylisopropylacetaldehyde.—Lithium aluminum hydride reduction was carried out after the procedure of Smith and Rogier.²⁷ The lithium aluminum hydride solution was standardized by the method of Felkin.²⁸ A solution of lithium aluminum hydride (0.0267 mole) in ether (55 ml.) was added dropwise to a well-stirred solution of methylisopropylacetonitrile (8 g., 92% pure, 0.076 mole) in ether (30 ml.), cooled in a Dry Ice-acetone-bath. After addition was complete (40 min.) the reaction was stirred for 15 min. in the cold and for 30 min. at room temperature. It was decomposed by adding a slight excess of 10% sulfuric acid. The ether layer was separated and the aqueous layer was extracted with two 75-ml. portions of ether. The combined ether extract was dried over sodium sulfate and distilled through a 46 × 0.6 cm. Podbielniak column to remove the ether. The residue was distilled through a 10 × 0.25 cm. Podbielniak column to give methylisopropylacetaldehyde, 2.35 g., 75% pure (23% yield), (contaminated with ca. 25% of the nitrile), b.p. 115–120°; 2,4-dinitrophenylhydrazone, m.p. 118–120° (reported²⁹ b.p. 112–114°; 2,4-dinitrophenylhydrazone, m.p. 119–121°).

Independent Synthesis of *threo*- and *erythro*-3,4-Dimethyl-2-pentanol.—Methylisopropylacetaldehyde (0.28 g., 80% pure, 0.0224 mole) dissolved in 5 ml. of ether was added to a Grignard reagent prepared from methyl iodide (3.6 g., 0.025 mole), magnesium (0.6 g., 0.025 mole) and ether (20 ml.). After being stirred overnight at room temperature, the reaction mixture was incompletely neutralized with cold ammonium sulfate solution and extracted with 100 ml. of ether. The ether was dried over sodium sulfate and distilled at atmospheric pressure to remove the solvent. The residue was distilled in a small Claisen flask to give a stereoisomeric mixture of 3,4-dimethyl-2-pentanol, 0.14 g., 78% pure (42% yield), b.p. 75–80° (49 mm.), containing 67% of one isomer and 33% of a less-rapidly eluted isomer by V.P.C. analysis (105° Ucon polar). The

major component was assigned the *erythro* configuration after Cram's rule. An analytical sample of the *erythro* isomer was obtained by V.P.C.

Anal. Calcd. for C₇H₁₆O: C, 72.35; H, 13.88. Found: C, 72.20; H, 13.95.

3,4-Dimethylpentene-1.—To an ether solution (40 ml.) of redistilled methylisopropylacetaldehyde (1.5 g., 95% pure, 0.0143 mole) was added slowly the Wittig reagent, prepared by the modification of Bergmann and Dusza¹⁰ from triphenylphosphine methyl bromide (7.14 g., 0.02 mole), ether (75 ml.) and butyllithium (12.5 ml. of 1.39 *N* solution, 0.0175 mole). After addition of the aldehyde, more ether was added to the reaction vessel (pressure flask) to facilitate the magnetic stirring of the heavy suspension. After 1 hour at room temperature and 3 hours at 65° (capped pressure flask) the reaction mixture was decomposed by the addition of wet ether. The triphenylphosphine oxide precipitate was filtered off and washed with ether. The combined filtrate and wash ether solution was dried over sodium sulfate and carefully fractionated, first through a 46 × 0.6 cm. Podbielniak column, and then through a 10 × 0.25 cm. Podbielniak column to give 1 g. of a mixture of ether, benzene and 3,4-dimethylpentene-1, b.p. 75–80° (760 mm.), the composition of which was determined by V.P.C. and infrared to be 11.5% ether, 48.9% olefin (35% yield) and 39.7% benzene. An analytical sample of pure olefin, collected by V.P.C., showed n_D^{20} 1.3978, infrared 10.99 μ (strong), (reported³⁰ b.p. 80.8° (760 mm.), n_D^{20} 1.3995, no analysis given).

Anal. Calcd. for C₇H₁₄: C, 85.63; H, 14.37. Found: C, 85.76; H, 14.37.

***threo*- and *erythro*-1,2-Epoxy-3,4-dimethylpentanes via Peroxidation of 3,4-Dimethylpentene-1.**—An ether-benzene-olefin mixture containing 0.372 g. (0.00397 mole) of 3,4-dimethylpentene-1 was dissolved in 6 ml. of ether and added to monoperothalic acid (0.00535 mole) in ether (16 ml.). The reaction mixture was stored at room temperature for 94 hours. Titration of aliquots of the mixture showed the following consumption of peracid: 9.5 hours, 0.22 equiv.; 22.5 hours, 0.39 equiv.; 48.5 hours, 0.59 equiv.; 70 hours, 0.65 equiv.; 94 hours, 0.787 equiv. The reaction was worked-up in the standard manner. The ether extract was dried over sodium sulfate and distilled through a 46 × 0.6 cm. Podbielniak column, leaving a residue which was distilled in a small Claisen flask to give 0.343 g. of a distillate. The composition of this distillate, as determined by infrared and V.P.C. was 32% ether, 45% benzene plus 3,4-dimethylpentene-1 and 23% of a stereoisomeric mixture of 1,2-epoxy-3,4-dimethylpentanes. Based upon unrecovered olefin, the yield of the epoxide mixture was 26%. The infrared spectrum of the V.P.C. peak attributed to 1,2-epoxy-3,4-dimethylpentanes had no band at 10.99 μ , but did show several medium bands in the 10.75–12 μ region. The epoxide mixture was not further characterized, but was used directly in the next experiment.

Lithium Aluminum Hydride Reduction of the Mixture of Stereoisomeric 1,2-Epoxy-3,4-dimethylpentanes.—The 1,2-epoxy-3,4-dimethylpentane mixture obtained above (0.150 g., containing 0.035 g. of stereoisomeric epoxides, 0.000306 mole) was added to a stirred suspension of lithium aluminum hydride (0.2 g., 0.0053 mole) in ether (3 ml.). After being stirred for 24 hours at room temperature, the reaction mixture was decomposed and worked up in the usual manner. The ether extract was dried over sodium sulfate and most of the solvent was removed by distillation through a 10 × 0.25 cm. Podbielniak column, leaving 0.187 g. of residue which was analyzed by V.P.C. without further purification. This residue contained 13% (70% yield) of a mixture of *threo*- and *erythro*-3,4-dimethyl-2-pentanol consisting of 52% *erythro*- and 48% *threo*-alcohols. These compounds were shown to be identical with the authentic alcohols described above, by V.P.C. and infrared comparisons.

(30) A. I. M. Keulemans, *Rec. trav. chim.*, **67**, 298 (1948), partially characterized this olefin.

(27) L. I. Smith and E. R. Rogier, *THIS JOURNAL*, **73**, 4047 (1951).

(28) H. Felkin, *Bull. soc. chim. France*, 347 (1951).

(29) R. A. Barnes and W. M. Budde, *THIS JOURNAL*, **68**, 2339 (1946).