methoxybenzylformamidomalonate, m.p. 102–106°. In addition 1.9 g. of methyl formamidomalonate was recovered. Crystallization from methanol and benzene raised the melting point to 120–120.5°.

Anal. Calcd. for $C_{14}H_{17}NO_6$: N, 4.84. Found: N, 4.72.

Ten g. of methyl formamidomalonate and 5.5 g. of benzyl chloride gave 13 g. (75%) of crude product, m.p. 148–150°. Crystallization from aqueous methanol raised the melting point of the methyl benzylformamidomalonate to 153–154°.

Anal. Calcd. for $C_{13}H_{15}NO_5$: N, 5.29. Found: N, 5.16.

Alkylation of ethyl formamidomalonate with n-butyl bromide. Ten g. of ethyl formamidomalonate, 3.4 g. of sodium ethoxide and 9 g. of *n*-butyl bromide were heated for 8 hr. in absolute ethanol. One crystallization from aqueous ethanol gave 7.9 g. (62%) of ethyl *n*-butylformamidomalonate, m.p. 79–81°. Further recrystallization raised the melting point to 81.0–81.8°. This compound has also been prepared in this laboratory by hydrogenation of ethyl allylcarbinylformamidomalonate.[13] Previously conflicting melting points of 101°[20] and 77–80°[21] have been reported.

Anal. Calcd. for $C_{12}H_{21}NO_6$: N, 5.21. Found: N, 5.51, 5.44.

Alkylation of methyl acetamidomalonate with n-butyl bromide. One g. of methyl acetamidomalonate and 1 g. of *n*-butyl bromide were placed in 5 ml. of absolute methanol to which 0.5 g. of sodium had been added. The mixture was heated under a reflux condenser for 4 hr. and was allowed to stand overnight. Five ml. of water was added, and then a chloroform extraction gave 280 mg. of long cylindrical needles, m.p. 96–98°. The analytical sample of methyl *n*-butylacetamidomalonate was prepared by dissolving the product in benzene and diluting with petroleum ether. The melting point was 99–100° and the analysis was performed by Galbraith Laboratories.

Anal. Calcd. for $C_{11}H_{19}NO_5$: C, 53.86; H, 7.81. Found: C, 53.67; H, 7.65.

Hydrolysis with hydrobromic acid. The malonates were refluxed with constant boiling hydrobromic acid and the vapors were passed through a tower of sodium hydroxide pellets and then into a 4% alcoholic solution of silver nitrate. The rate of hydrolysis was followed by observing the appearance of silver bromide. When the hydrolysis was completed, there was no further precipitate of silver bromide.

It took from 3 to 4 hr. to hydrolyze ethyl *n*-butylacetamidomalonate, ethyl *n*-octylacetamidomalonate, and ethyl *n*-butylformamidomalonate. Complete hydrolysis for the methyl formamidomalonate intermediates took place in an hour for all the compounds studied.

Two hundred mg. of *p*-methoxybenzylformamidomalonate was refluxed with 50 ml. of constant boiling hydrobromic acid. Complete hydrolysis took place in 1 hr. but was continued for an additional 0.5 hr. The hydrobromic acid was removed *in vacuo* and the residue purified on an ion exchange column containing the Duolite resin A2. One hundred ten mg. of *dl*-tyrosine was obtained, yield 98%, m.p. 295–298° dec.; reported m.p. 290–295° dec.[22]

Identification of the tyrosine was obtained by making the *N*-benzoyl-*dl*-tyrosine, m.p. 196–198°; reported 195–197°.[22]

One g. of methyl carboethoxmethylformamidomalonate was refluxed with 50 ml. of constant boiling hydrobromic acid. Hydrolysis was complete in an hour but was continued for another 0.5 hr., yield 80%, m.p. 300–303° dec.; reported, above 300°.[7] Identification of the *dl*-aspartic acid was obtained by a spot test developed by Inukai, Tsurumi, and Sakai.[23]

Four hundred seventy mg. of methyl *n*-butylformamidomalonate was refluxed with 50 ml. of constant boiling hydrobromic acid, hydrolysis was complete in 1 hr. The hydrobromic acid was removed *in vacuo* and the residue purified on an ion exchange column containing the Duolite resin A2, yield 85%, m.p. 274–276°.

Identification of the norleucine was obtained by preparing the *N*-formylnorleucine, m.p. 109–111°, reported 113–115°.[24]

The hydrolysis of methyl benzylformamidomalonate was complete in an hour. The yield was practically quantitative and the product melted at 269–272° with decomposition, reported 271–273°;[25] 257° dec.[16]

Identification of the phenylalanine was obtained by preparing the *N*-benzoyl-*dl*-phenylalanine, m.p. 187–188°; reported 187–188°.[26]

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[20] J. Capkova-Jirku, J. V. Kostir and M. Vondracek, *Chem. Listy*, **44**, 114 (1950); *Chem. Abstr.*, **45**, 7962 (1951).

[21] British Patent **621,706**. (*Chem. Abstr.*, **44**, 2017 (1950).

[22] E. Fischer, *Ber.*, **32**, 3638 (1899).

[23] F. Inukai, M. Tsurumi and S. Sakai, 49, 111, *Bull., Inst. Phys. Chem. Research* (*Tokyo*), 22, 919 (1943). [*Chem. Abstr.*, **41**, 5916 (1947)].

[24] D. Marko, *Ann.*, **362**, 333 (1908).

[25] S. P. L. Sorensen, *Chem. Zentral.*, **74**, 11, 33 (1903).

[26] E. Fischer and A. Mouneyrat, *Ber.*, **33**, 2383 (1900).

[CONTRIBUTION FROM THE INSTITUTE OF GENERAL CHEMISTRY, UNIVERSITY OF PISA]

Synthesis of (+)(S)-3-Methyl-1-pentene

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(+)(S)-3-Methyl-1-pentene (*i.e.*, L-3-methyl-1-pentene) having an optical purity of at least 86% has been prepared in five steps starting from (−)(S)-2-methyl-1-butanol with an over-all yield of 18% and a maximum per cent of racemization of 12.6%. The optical purity of the (+)(S)-3-methyl-1-pentene was calculated by regenerating the (+)(S)-3-methyl-1-pentanol by addition of the olefin to diisobutylaluminum monohydride and by oxidation followed by hydrolysis of the trialkylaluminum thus obtained.

The preparation and the determination of optical purity of aliphatic olefins do not seem to have been investigated extensively. No data have been found in the literature (up to 1957) on the simplest optically active α-olefin, 3-methyl-1-pentene. For the mixture of 4-methyl-hexenes prepared by dehydration of the optically active 4-methyl-2-hexanol over alumina, α_D^{26} (l = 1) +13.7° is reported.[1] For 5-methyl-1-heptene, two very different values (+6.84°[2] and +10.2°[3]) have been reported for the

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[1] G. S. Gordon III and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **71**, 2355 (1949).

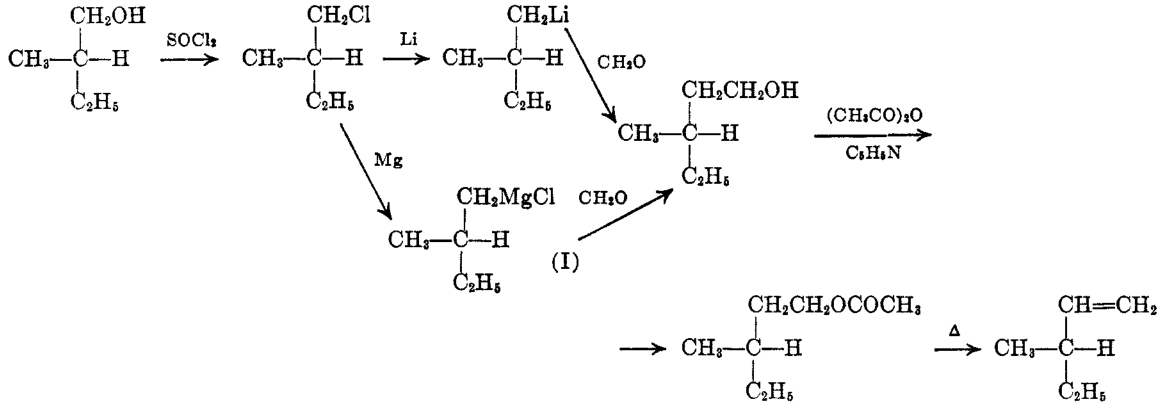
[2] R. L. Burwell, Jr., and G. S. Gordon III, *J. Am. Chem. Soc.*, **70**, 3129 (1948).

specific rotation. Because we needed an optically active α-olefin having a known optical purity for a systematic investigation of some aspects of the chemical reactivity of α-olefins, we have investigated the preparation of the (+)(S)-3-methyl-1-pentene[4] (*i.e.*, L-3-methyl-1-pentene).

The racemic 3-methyl-1-pentene has been prepared by Boord and Schmitt[5] in five steps starting from 2-bromobutane and acetaldehyde. We have preferred to start from (−)(S)-2-methyl-1-butanol which is more readily available[6] than the optically active *sec*-butyl alcohol whose preparation requires the tedious resolution of the racemic 2-butanol. Starting from (−)(S)-2-methyl-1-butanol of known optical purity the 3-methyl-1-pentene was obtained through the following steps (Scheme 1):

In Table II some data on the physical properties of 3-methyl-1-pentanol have been collected.

Conflicting data are reported in the literature for the refractive index and density of the 3-methyl-1-pentanol. Because our data on the density were higher than the data reported by Hovorka *et al.*,[8] we purified the alcohol through its acetate. The purified alcohol had n_D^{25} in close agreement with the data of Hovorka; however, the density, although lower than that of the unpurified alcohol, was still definitely higher than that reported by Hovorka. The density found for a sample of racemic 3-methyl-1-pentanol prepared starting with racemic *sec*-butyl alcohol according to the method proposed by Huston and Agett,[9] was in agreement with that found by us for the optically active alcohol (Table II).



(1)

Preparation and purification of (+)(S)-3-methyl-1-pentanol. From the (−)(S)-2-methyl-1-butanol, the (+)(S)-1-chloro-2-methyl-butane was prepared by the method of McKenzie and Clough.[7]

To obtain the 3-methyl-1-pentanol, two different methods were tested: the first through the (+)-(S)-2-methyl-butyllithium and the other through the (+)(S)-2-methylbutylmagnesium chloride. As is shown in Table I, relatively low yields were obtained in the preparation of the organolithium compound but good yields were achieved in its reaction with formaldehyde. On the other hand, carrying out the synthesis through the Grignard compound resulted in high yields in the preparation of the organomagnesium compound but in lower yields in the reaction between it and formaldehyde.

The per cent of racemization observed in the preparation of 3-methyl-1-pentanol (Table III) was calculated by comparing the optical purity of the starting (−)(S)-2-methyl-1-butanol with the optical purity of the (+)(S)-3-methyl-1-pentanol, assuming for the specific optical activity of the optically pure alcohols the values given by Marckwald and McKenzie[10] and Hardin.[11,12] Racemization occurs to a small extent (1–3%) in the preparation of 1-chloro-2-methyl-butane as well as in the prepara-

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(3) S. F. Velick and J. English, Jr., *J. Biol. Chem.*, **160**, 476 (1948).

(4) We have adopted the nomenclature proposed by Cahn, Ingold, and Prelog [*Experientia*, 12, 81 (1956)], and although it is not required by the nomenclature adopted, we have added (+) and (−) before the prefixes (S) and (R) to indicate the sign of the rotation according with Beilstein's *Handbuch der Organischen Chemie*, Band I, Drittes Erganzunswerk, Springer-Verlag, Berlin (1958).

(5) C. G. Schmitt and C. E. Boord, *J. Am. Chem. Soc.*, **54**, 751 (1932).

(6) F. C. Whitmore and H. J. Olewine, *J. Am. Chem. Soc.*, **60**, 2569 (1938).

(7) A. McKenzie and G. W. Clough, *J. Chem. Soc.*, **103**, 698 (1913).

(8) F. Hovorka, H. P. Lankelma, and I. Schneider, *J. Am. Chem. Soc.*, **62**, 1096 (1940).

(9) R. C. Huston and A. H. Agett, *J. Org. Chem.*, **6**, 123 (1941).

(10) W. Marckwald and A. McKenzie, *Ber.*, **34**, 495 (1901).

(11) D. Hardin, *J. Chim. Phys.*, **6**, 587 (1908).

(12) For the specific rotation of the optically (+)(S)-3-methyl-1-pentanol we have chosen the value of +8.77° found by Hardin for the product obtained from Roman Camomile oil, which is in fair agreement with the maximum value calculated by Levene and Marker [*J. Biol. Chem.*, 91, 77 (1931)]. We have not considered the maximum value calculated by Mosher and La Combe from the fraction having the highest optical activity obtained by rectification of a mixture of 26% of 4-methyl-1-pentanol with 74% of (+)(S)-3-methyl-1-pentanol; in fact on the basis of our experimental results, we think that a separation between 3-methyl-1-pentanol and 4-methyl-1-pentanol takes place during the rectification and must be considered in the calculations made by Mosher and La Combe, *J. Am. Chem. Soc.*, **72**, 4991 (1950).

TABLE I

YIELDS IN THE PREPARATION OF (+)(S)-3-METHYL-1-PENTENE FROM (−)(S)-2-METHYL-1-BUTANOL

	Yield, %
$CH_3CH_2\underset{CH_3}{\underset{\mid}{C}}HCH_2OH$[a] $\longrightarrow CH_3CH_2\underset{CH_3}{\underset{\mid}{C}}HCH_2Cl$	80
$CH_3CH_2\underset{CH_3}{\underset{\mid}{C}}HCH_2Cl \xrightarrow{Mg} CH_3CH_2\underset{CH_3}{\underset{\mid}{C}}HCH_2MgCl$	90[b]
$CH_3CH_2\underset{CH_3}{\underset{\mid}{C}}HCH_2MgCl \xrightarrow{CH_2O} CH_3CH_2\underset{CH_3}{\underset{\mid}{C}}HCH_2CH_2OH$	40[c]
$CH_3CH_2\underset{CH_3}{\underset{\mid}{C}}HCH_2Cl \xrightarrow{Li} CH_3CH_2\underset{CH_3}{\underset{\mid}{C}}HCH_2Li$	56[d]
$CH_3CH_2\underset{CH_3}{\underset{\mid}{C}}HCH_2Li \xrightarrow{CH_2O} CH_3CH_2\underset{CH_3}{\underset{\mid}{C}}HCH_2CH_2OH$	60[e]
$CH_3CH_2\underset{CH_3}{\underset{\mid}{C}}HCH_2CH_2OH \longrightarrow CH_3CH_2\underset{CH_3}{\underset{\mid}{C}}HCH_2CH_2OCOCH_3$	90–95
$CH_3CH_2\underset{CH_3}{\underset{\mid}{C}}HCH_2CH_2OCOCH_3 \xrightarrow{\Delta} CH_3CH_2\underset{CH_3}{\underset{\mid}{C}}HCH{=}CH_2$	70

[a] The (−)(S)-2-methyl-1-butanol had an optical purity of 97.4%, calculated on the basis of the pure (−)(S)-2-methyl-1-butanol $[\alpha]_D^{20}$ −5.9°.[10] [b] Calculated following the procedure of Gilman, Wilkinson, Fishel and Meyers, (*J. Am. Chem. Soc.*, **45**, 150 (1923). [c] Calculated on the rectified 3-methyl-1-pentanol. [d] Calculated following the procedure of Ziegler (*Ann.*, **473**, 21 (1923)). [e] Calculated on the distilled 3-methyl-1-pentanol.

TABLE II

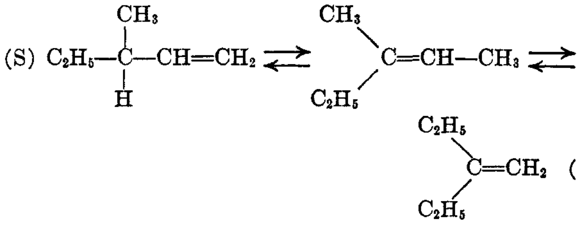
PHYSICAL PROPERTIES OF 3-METHYL-1-PENTANOL

	Literature	Rectified (+)(S)-3-Methyl-1-pentanol	Purified[a] (+)(S)-3-Methyl-1-pentanol	Racemic 3-Methyl-1-pentanol	Purified[a] Racemic 3-Methyl-1-pentanol
Boiling point, °C.	152.44[8] 151–152[9] 151.2–152[12]	99–100 (100 mm.) 152–152.5	65 (18 mm.)	64 (18 mm.) 152.5	64 (19 mm.)
n_D^{25}	1.4178[b] 1.4169[8]	1.4172	1.4170	1.4180	1.4172
n_D^{20}	1.4182 1.4195[12]	1.4192	1.4191	1.4196	1.4192
d_4^{25}	0.8156[b] 0.8187[8]	0.8227	0.8218	0.8230	0.8217
$d_4^{19.5}$		0.8263	0.8260		

[a] Purification through the acetate. [b] P. A. Levene and A. Rothen, *J. Biol. Chem.*, **116**, 217 (1936).

tion of the organometallic compound. Since racemization up to 8–10% is reported by Whitmore[13] in the preparation of the Grignard compound (I), we must conclude that practically no racemization occurs in the reaction between the Grignard compound and formaldehyde.

Preparation of (+)(S)-3-methyl-1-pentene. Many methods have been proposed for preparing the α-olefins from the corresponding alcohols without the formation of other isomeric olefins. In our case a highly specific dehydration method was needed as any double bond shift in the (+)(S)-3-methyl-1-pentene would cause a racemization (Scheme 2):



(2)

Since we needed relatively large quantities of the optically active olefins for our investigations, we chose for the olefin preparation the pyrolysis of the

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(13) F. C. Whitmore and J. H. Olewine, *J. Am. Chem. Soc.*, **60**, 2570 (1938).

TABLE III

RACEMIZATION IN THE PREPARATION OF (+)(S)-3-METHYL-1-PENTANOL FROM (−)(S)-2-METHYL-1-BUTANOL, $[\alpha]^{16}_D$ −5.75°, OPTICAL PURITY,[a] 97.4%

	$[\alpha]^t_D$	t, °C.	Optical Purity,[b] %	Racemization, %
(+)(S)-3-methyl-1-pentanol[c]	+7.89°	19	90[d]	7.6
(+)(S)-3-methyl-1-pentanol[e]	+8.24°	19.5	94	3.5
(+)(S)-3-methyl-1-pentanol[e]	+8.16°	19	93	4.5

[a] Calculated taking for the pure (−)(S)-2-methyl-1-butanol $[\alpha]^{20}_D$ −5.9°.[10] [b] Calculated taking for the pure (+)(S)-3-methyl-1-pentanol $[\alpha]^{20}_D$ +8.77°.[11] [c] Obtained through the lithium compound. [d] Calculated on unredistilled (+)(S)-3-methyl-1-pentanol. [e] Obtained through the Grignard reagent.

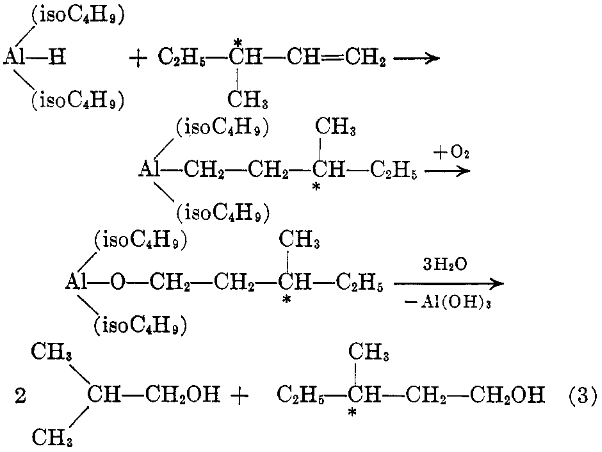
(+)(S)-3-methyl-1-pentyl acetate[14] which involves only two steps starting from (+)(S)-3-methyl-1-pentanol rather than the pyrolysis of the quaternary ammonium bases[15] or of the amine oxides[16] which involves many more reaction steps starting from the same alcohol.

(+)(S)-3-Methyl-1-pentyl acetate was prepared by cautiously heating the alcohol with an excess of acetic anhydride in the presence of pyridine. The acetate was pyrolized. The best yield of (+)(S)-3-methyl-1-pentene was obtained by pyrolizing the acetate of a slow nitrogen stream at 500° (Table I).

Better conversions could have been achieved in the acetate preparation, but we preferred to carry out the reaction under very mild conditions in order to avoid possible racemization.

The yield obtained in the pyrolysis is in the range reported in the literature for the other olefins; the formation of lower boiling highly refractive compounds (probably pentadienes) could not be completely avoided and two fractionations were necessary in order to obtain a product having physical constants in agreement with the literature data. Since we started from 2-methyl-1-butanol containing not more than 3% of 3-methyl-1-butanol, the 3-methyl-1-pentene obtained was actually a mixture of the 3-methyl-1-pentene with small quantities of 4-methyl-1-pentene (probably not more than 3% if no enrichment of the products deriving from 3-methyl-1-butanol took place during the preparation steps). The two isomeric olefins have very close physical properties and therefore the physical properties of the mixture agree very well with the data reported for 3-methyl-1-pentene.[17,18]

The eventual racemization occurring in the preparation of the (+)(S)-3-methyl-1-pentyl acetate was calculated by saponifying the acetate and determining the optical activity of recovered 3-methyl-1-pentanol. The racemization in the pyrolysis of the (+)(S)-3-methyl-1-pentyl acetate was estimated by regenerating the (+)(S)-3-methyl-1-pentanol from (+)(S)-3-methyl-1-pentene. The alcohol was obtained by reacting the olefin with diisobutylaluminum monohydride,[19] oxidizing the trialkylaluminum thus obtained with oxygen, and hydrolyzing the resultant aluminum alcoholate with water (Scheme 3).



The racemization data reported in Table IV are the upper limits for the racemization occurring in the pyrolysis of the (+)(S)-3-methyl-1-pentyl acetate since they include the eventual racemization occurring in the regeneration of the 3-methyl-1-pentanol.

Conclusions. The probable isomeric composition of the 3-methyl-1-pentene obtained is: 91.7% of (+)(S)-3-methyl-1-pentene, 5.7% of (−)(R)-3-methyl-1-pentene, and 2.6% of 4-methyl-1-pentene deriving from 3-methyl-1-butanol present in the starting product. The specific rotation found for the mixture, $[\alpha]^{17}_D$ +32.86°, is remarkably

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[14] J. P. Wibaut and A. J. van Pelt, *Rec. trav. chim.*, **57**, 1055 (1938); A. J. van Pelt and J. P. Wibaut, *Rec. trav. chim.*, **60**, 55 (1941); J. P. Wibaut, A. J. van Pelt, Jr., A. Dias Santilhano, and W. Beuskens, *Rec. trav. chim.*, **61**, 265 (1942); J. P. W. Houtman, J. van Steenis, and P. M. Heertjes, *Rec. trav. chim.*, **65**, 781 (1946); W. J. Bailey and C. King, *J. Am. Chem. Soc.*, **77**, 75 (1955); W. J. Bailey, J. J. Hewitt, and C. King, *J. Am. Chem. Soc.*, **77**, 357 (1955).

[15] W. Hanhart and C. K. Ingold, *J. Chem. Soc.*, 997 (1927); C. K. Ingold and C. C. Norrey Vass, *J. Chem. Soc.*, 3125 (1928); M. J. Schlatter, *J. Am. Chem. Soc.*, **63**, 1733 (1941); P. G. Stevens and H. J. Richmond, *J. Am. Chem. Soc.*, **63**, 3132 (1941).

[16] A. C. Cope, T. T. Foster, and P. H. Towle, *J. Am. Chem. Soc.*, **71**, 3929 (1949); A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953); paper presented before 124th Meeting American Chemical Society, Chicago, Ill., September 1953, p. 11F of Abstracts; D. J. Cram, *J. Am. Chem. Soc.*, **76**, 5740 (1954).

[17] C. E. Boord, A. L. Henne, G. W. Greenlee, W. L. Perilstein, and J. M. Derfer, *Ind. Eng. Chem.*, **41**, 609 (1949).

[18] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. H. Poulson, and G. C. Pimenkel, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburgh, 1953, p. 55.

[19] K. Ziegler and H. G. Gellert, *Angew. Chem.*, **64**, 323 (1952); K. Ziegler, *Angew. Chem.*, **68**, 721 (1956).

TABLE IV

RACEMIZATION IN THE PREPARATION OF 3-METHYL-1-PENTENE FROM 3-METHYL-1-PENTANOL

	Starting Materials		Recovered (+)(S)-3-methyl-1-pentanol		Racemization, %
	$[\alpha]^t_D$	t, °C,	$[\alpha]^t_D$	t, °C.	
(+)(S)-3-methyl-1-pentanol → (+)(S)-3-methyl-1-pentyl acetate	+8.24°	18	+8.17°	20	0.85
(+)(S)-3-methyl-1-pentyl acetate → (+)(S)-3-methyl-1-pentene	+8.30°	18	+7.54°	19	7.70

higher than the values found in the literature for other aliphatic olefins. The relatively high specific rotation can be attributed both to the particular structure of the 3-methyl-1-pentene and to the low optical purity of some of the optically active α-olefins reported in the literature.

EXPERIMENTAL

(−)(S)-2-Methyl-1-butanol was obtained by rectification of fusel oil[6]: samples having b.p. 128–129°, n^{20}_D 1.4108, d^{18}_4 0.8216 (lit.[6] n^{20}_D 1.4109, d^{20}_4 0.8189), $[\alpha]^{16}_D$ −5.75° (97.4% optical purity) were used.

(+)(S)-1-Chloro-2-methylbutane was prepared[7] in 80% yield by treatment of the (−)(S)-2-methyl-1-butanol with thionyl chloride. The halogenated hydrocarbon obtained had b.p. 99–100°, n^{20}_D 1.4125–1.4127, d^{20}_4 0.8857 (lit.[13] n^{20}_D 1.4125, d^{20}_4 0.8852), $[\alpha]^{20}_D$ 1.60–1.64° (94–96% optical purity).

(+)(S)-3-Methyl-1-pentanol. A) *Through the organolithium compound.* (+)(S)-1-Chloro-2-methylbutane (72.4 g., 0.68 mole, $[\alpha]^{20}_D$ 1.63°, n^{20}_D 1.4127) was added to 14.1 g. (2.04 mole) of metallic lithium[20] suspended in 200 ml. of low-boiling petroleum ether (b.p. 40°, olefin-free) at 35–40° under a dry nitrogen atmosphere. The suspension was vigorously stirred for 2 hr. Acidimetric titration indicated a 60% yield of the lithium derivative. Formaldehyde gas (obtained from dry paraformaldehyde[21]) was swept into the organolithium compound solution which had been separated from the unreacted lithium. The complex thus obtained was hydrolyzed by water and extracted with ether. The ether extracts were separated, dried, and distilled from a Claisen flask at reduced pressure. The weight of (+)(S)-3-methyl-1-pentanol (b.p. 60–67° (23 mm.), n^{25}_D 1.4165) was 23.3 g. (33.6% yield based on the (+)(S)-1-chloro-2-methylbutane). In a repeated experiment the same yield was obtained; 23 g. of product having b.p. 60–67° (23 mm.) afforded on redistillation, 16 g. of (+)(S)-3-methyl-1-pentanol, b.p. 65–68° (20 mm.) n^{25}_D 1.4180, $[\alpha]^{19}_D$ +7.89° (90% optical purity).

(B) *Through the Grignard reagent.* An ethereal Grignard solution was prepared from 106.5 g. (1.0 mole) (+)(S)-1-chloro-2-methylbutane, $[\alpha]^{20}_D$ +1.64°, n^{20}_D 1.4126, and 24.3 g. (1.0 mole) magnesium in 1000 ml. of anhydrous ether under a dry nitrogen atmosphere. Titration indicated a 90% yield of the 2-methylbutylmagnesium chloride. The formaldehyde, from depolymerization of dry paraformaldehyde, was carried into the Grignard reagent by a slow current of dry nitrogen.[22] The complex was hydrolyzed by water and extracted with ether; the ether extracts were separated, dried, distilled, and finally rectified at reduced pressure. The weight of redistilled (+)(S)-3-methyl-1-pentanol, b.p. 99–100° (100 mm.), n^{25}_D 1.4172, $[\alpha]^{19.5}_D$ +8.24° (94% optical purity) was 36.7 g. (36% yield based on the (+)(S)-1-chloro-2-methylbutane).

% OH (determined by phthalation method[23]): 16.41. % OH (calculated for $C_6H_{14}O$) 16.66.

(+)(S)-3-Methyl-1-pentyl acetate. (+)(S)-3-Methyl-1-pentanol (46 g., 0.45 mole, $[\alpha]^{19.5}_D$ +8.24°, n^{25}_D 1.4172) was added to 35.6 g. (0.45 mole) of freshly distilled pyridine and 138 g. (1.35 moles) of redistilled acetic anhydride (b.p. 140°, n^{20}_D 1.3903). The mixture was refluxed very gently for 4 hr. and then cooled overnight; it was then worked up by neutralizing with sodium bicarbonate, washing with water until the ester layer was neutral to litmus, and finally drying with anhydrous sodium sulfate. Rectification at 102 mm. pressure afforded (+)(S)-3-methyl-1-pentyl acetate in 65–70% conversion (90–95% yield), b.p. 103–103.5° (102 mm.), n^{25}_D 1.4081 (lit.[24] n^{25}_D 1.4079), d^{19}_4 0.8790, $[\alpha]^{19}_D$ +8.30° (93.15% optical purity).

% Ester (determined by saponification[25]): 99.

(+)(S)-3-Methyl-1-pentene (by pyrolysis of (+)(S)-3-methyl-1-pentyl acetate). The apparatus used for the pyrolysis was similar to that described by Bailey *et al.*[14] (+)(S)-3-Methyl-1-pentyl acetate (100 g., 0.694 mole, $[\alpha]^{19}_D$ +8.30° n^{25}_D 1.4081) was pyrolyzed in a quartz tube at 500–510° with dropping rate of about 1.5–1.6 ml. per min. A slow stream (5.6 ml. per min.) of dried nitrogen was introduced through the top of the tube during the pyrolysis. Fractionation of the pyrolyzate (43.8 g.) yielded several fractions of crude olefin. The crude olefin was rectified and 37.0 g. of (+)(S)-3-methyl-1-pentene, b.p. 54–54.3° (765 mm.), n^{20}_D 1.3840–1.3842, $[\alpha]^{17}_D$ +32.86° (lit.[18] n^{20}_D 1.3842), d^{17}_4 0.6703 was obtained (70% yield). Ten g. of unpyrolyzed (+)(S)-3-methyl-1-pentyl acetate was recovered.

Regeneration of (+)(S)-3-methyl-1-pentanol from (+)(S)-3-methyl-1-pentene. Triisobutylaluminum[26] (45.8 g.) in 8.1 g. heptane was heated at 140–160° for 5 hr. A slow evolution of isobutylene took place, and from the isobutylene evolved, a conversion of 68% to diisobutyl monohydride was calculated. To the mixture of diisobutyl monohydride and triisobutylaluminum thus obtained, 4.7 g. (0.056 mole) of (+)(S)-3-methyl-1-pentene (n^{20}_D 1.3841, $[\alpha]^{17}_D$ +32.86°)

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[20] H. Gilman, W. Langham, and F. W. Moore, *J. Am. Chem. Soc.*, **62**, 2333 (1940); H. Gilman, F. W. Moore, and O. Baine, *J. Am. Chem. Soc.*, **68**, 721 (1941).

[21] The paraformaldehyde had been previously dried for 2 days over phosphorus pentoxide in a vacuum dessicator.

[22] H. Gilman and W. Catlin, *Org. Syntheses*, **Coll. Vol. I**, 188 (1941).

[23] S. Siggia, *Quantitative Organic Analysis via Functional Groups*, 2nd ed., John Wiley and Sons, Inc., New York, 1954, p. 12.

[24] W. G. Young and I. D. Webb, *J. Am. Chem. Soc.*, **73**, 780 (1951).

[25] S. Siggia, *Quantitative Organic Analysis via Functional Groups*, 2nd ed., John Wiley and Sons, Inc., New York, 1954, p. 46.

[26] Generously supplied by Montecatini Co.

was added. The mixture was heated at 80–90° for 2 hr. and the reaction product was cautiously oxidized at 0° by bubbling in oxygen while stirring, until no more oxygen was absorbed. The oxidized product was hydrolyzed with water and the gelatinous mass thus obtained was extracted many times by ether. The ethereal solution, dried over sodium sulfate, was distilled to eliminate the ether and then rectified to eliminate most of the isobutyl alcohol present (resulting from the oxidation of the $\rangle Al\text{-}CH_2\text{-}CH(CH_3)_2$ groups). The residue of the rectification was distilled and a fraction 99–100° (100 mm.), n_D^{20} 1.4170 (0.8713 g.) was separated which was practically pure 3-methyl-1-pentanol containing small quantities of 4-methyl-1-pentanol. This fraction solution has $[\alpha]_D^{25}$ +7.65° in petroleum ether. A solution of the same concentration of the starting 3-methyl-1-pentanol in petroleum ether has $[\alpha]_D^{25}$ +8.35°.

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Reduction of Polymers Using Complex Metal Hydrides

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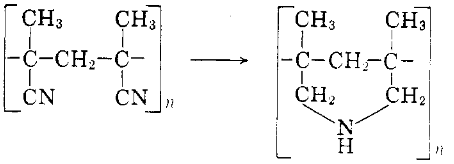
Polymeric nitriles, amides, imides, lactams, and oximes were reduced to the corresponding amines using lithium aluminum hydride. Polymeric hydrazides and hydrazones were reduced to hydrazines by the same procedure. Reduction of polymeric aldehydes and ketones gave alcohols.

Of the large number of publications that have appeared on the use of metal hydrides in reduction, only a few have been concerned with polymers. The reduction of poly(vinyl chloride) and poly(vinyl bromide) to polyethylene by lithium aluminum hydride in a hot (100°) tetrahydrofuran-decalin mixture was reported by Hahn and Muller.[1] Kern and Schulz[2] report the partial reduction of poly(acrolein oxime) by aqueous, alkaline sodium borohydride at 90°. The recent[3–5] publication of several additional papers concerned with the reduction by lithium aluminum hydride of specific polymers leads us to disclose similar, more general work which has been done at these Laboratories on the reduction of polymeric materials by complex metal hydrides. Polymers containing nitrile, amido, imido, oximino, lactam, hydrazide, hydrazone, and keto groups have been successfully reduced.

As with many other reactions of polymers, the proper choice of solvent is a major problem when reductions are carried out using complex metal hydrides. The requirements for the solvent in this case are quite stringent. Besides being a good solvent for both polymer and hydride, the medium must have a relatively high boiling point, as many reactions of polymers are exceedingly slow at ordinary temperatures. At these high temperatures, the solvent must be indefinitely stable to the hydride. Furthermore, because the addition complex formed between hydride and polymer is usually insoluble, the solvent must at least swell the complex so that reaction can go to completion.

N-Methylmorpholine met these requirements. It was also an excellent solvent for most of the reduced polymers, an advantage in that it enabled the use of a strong sodium hydroxide solution to hydrolyze the addition complex. The resulting strongly alkaline inorganic salts are insoluble in the amine, thereby simplifying isolation of the product. Tetrahydrofuran and the dimethyl ether of diethylene glycol (diglyme) were also useful on occasion.

Nitriles. The reduction of the styrene–methacrylonitrile copolymer was typical of the reduction procedures. Infrared analysis of this reduced polymer indicated the complete absence of nitrile groups. A Van Slyke nitrogen analysis indicated that about 70% of the nitrogen present was in the form of primary amino groups, while acetylation showed that the remaining 30% was in the form of secondary amino groups. As the nitrogen percentage was low, it may be assumed that ring closure had taken place, to some extent, with the loss of ammonia, giving a piperidine.



The mechanism of this closure is not known, although the formation of piperidines in the reduction of 1,5-dinitriles is quite common.

Another nitrile reduced was the methacrylonitrile–methyl methacrylate copolymer.

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[1] W. Hahn and W. Muller, *Makromol. Chem.*, 16, 71 (1955).

[2] W. Kern and R. C. Schulz, *Angew. Chem.*, 69, 153 (1957).

[3] B. G. Rånby, Abstracts of Papers, Miami Meeting of American Chemical Society, April, 1957, p. 10-S.

[4] J. Petit and B. Houel, *Compt. rend.*, 246, 1427 (1958). B. Houel, *Compt. rend.*, 246, 2488 (1958).

[5] J. A. Blanchette and J. D. Cotman, *J. Org. Chem.*, 23, 1117 (1958).