[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Studies in Stereochemistry. XXIII. The Preparation and Complete Resolution of the 1,2-Diphenyl-2-methyl-1-butanol System[1]

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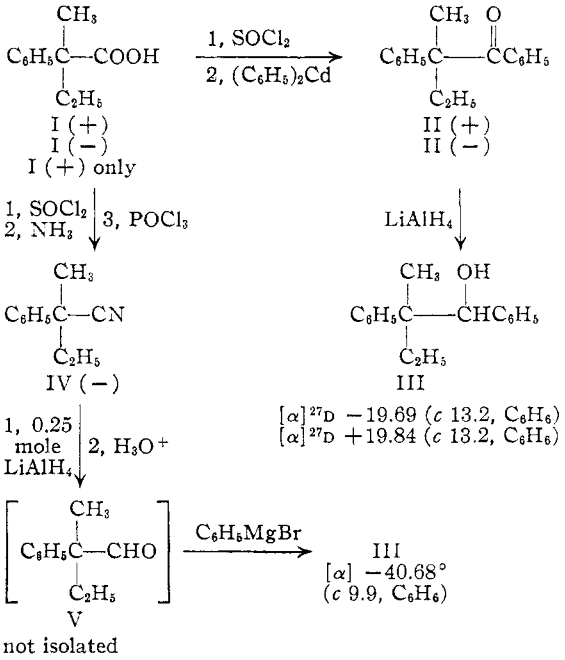
The four stereoisomers of 1,2-diphenyl-2-methyl-1-butanol (III) have been prepared in an optically pure state, and their relative configurations have been assigned on the basis of their modes of preparation. The configuration of the quaternary carbon of this system has been related to that of (+)-glyceraldehyde, thus allowing the absolute configurations of these as well as a number of other substances to be assigned.

Previous investigations of the Wagner–Meerwein rearrangement in this series dealt principally with the mechanism of phenyl migration,[2] one example of hydrogen[3] and one of methyl and ethyl migration[4] having been studied. Although a number of observations of stereospecific methylene rearrangements in bicyclic systems have been made,[5] no *stereospecific* alkyl rearrangements have been found to occur in either the Wagner–Meerwein or pinacol rearrangements. The 1,2-diphenyl-2-methyl-1-butanol system (III) possesses structural characteristics which *it is hoped* will permit the stereochemistry of methyl and ethyl migration to be examined. This paper reports the preparation, resolution and determination of stereochemical structure of the four isomers of III, and a later communication will report the results of solvolysis of certain derivatives of these substances.

Preparation of the Stereoisomers of 1,2-Diphenyl-2-methyl-1-butanol (III).—The preparation of these isomers utilized two synthetic routes, the steps of which are formulated. In each case, virtually optically pure 2-methyl-2-phenylbutanoic acid[6] was the starting material, both enantiomers being employed in the synthesis through ketone II and only one in the route involving aldehyde V. This aldehyde (2-methyl-2-phenylbutanal) was prepared in poor yield (32%) from nitrile IV by reduction with lithium aluminum hydride,[7] a number of other approaches giving poor results. Thus the Rosenmund reduction of the acid chloride,[8a] the Raney nickel reduction of the thiol ester,[8b] the chromic acid[8c] and *t*-butyl chromate oxidation[8d] of the primary alcohol, the lithium aluminum hydride reduction of the N-methyl-N-phenyl amide[8e] and the sodium trimethoxyborohydride reduction of the acid chloride[8f] all failed to yield aldehyde V in significant amounts. The desired alcohol[9] (III) was obtained both by the reduction of ketone II and by the action of phenylmagnesium bromide on aldehyde V, a different mixture of diastereomers being obtained from each of these two reactions.



The diastereomeric mixture of optically pure alcohols III from ketone II was converted to the acid phthalate derivative, the potassium salt of the *erythro*-isomer[9] in each case crystallizing, leaving the *threo*-isomer[9] in solution. The salt of the *erythro*-isomer was purified as such and hydrolyzed to give directly optically pure *erythro*-III. The *threo*-salt was hydrolyzed to alcohol and was purified through the *p*-nitrobenzoate derivative, hydrolysis of which gave optically pure *threo*-III. Table I reports the physical properties and analyses of the above substances.

Configurations of the Stereoisomers of 1,2-Diphenyl-2-methyl-1-butanol (III) and Other Compounds.—Two problems are involved in the assignment of configuration to the isomers of 1,2-diphenyl-2-methyl-1-butanol (III), the first being the establishment of the configuration of one asymmetric carbon atom relative to that of a substance whose *absolute configuration* is known, the second being the elucidation of the relative con-

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(1) This work was sponsored by the Office of Ordnance Research, U. S. Army.

(2) (a) D. J. Cram, THIS JOURNAL, **71**, 3863, 3875 (1949); (b) **74**, 2129, 2159 (1952); (c) **75**, 332 (1953); (d) F. A. Abd Elhafez and D. J. Cram, *ibid.*, **75**, 339 (1953); (e) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **75**, 3189 (1953); (f) **76**, 28 (1954).

(3) D. J. Cram, *ibid.*, **74**, 2137 (1952).

(4) D. J. Cram and J. D. Knight, *ibid.*, **74**, 5839 (1952).

(5) (a) S. Winstein and D. Trifan, *ibid.*, **74**, 1147, 1154 (1952); (b) J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., not yet published.

(6) D. J. Cram and J. D. Knight, *ibid.*, **74**, 5835 (1952).

(7) L. Friedman, Meeting American Chemical Society, Atlantic City, N. J., September, 1949, **116**, 5 M of Abstracts.

(8) (a) E. B. Hershberg and J. Cason, *Org. Syntheses*, **21**, 84 (1941); (b) A. V. McIntosh, Jr., A. M. Searcy, E. M. Meinzer and R. H. Levin, THIS JOURNAL, **71**, 3317 (1949); (c) F. L. Weisenborn and D. Burn, *ibid.*, **75**, 259 (1953); (d) R. V. Oppenauer and H. Oberrauch, *Annales de la Asociacion Quimica Argentina*, **37**, 246 (1949); (e) F. Weygand and D. Tietjen, *Ber.*, **84**, 625 (1951); (f) H. C. Brown and E. J. Mead, THIS JOURNAL, **75**, 6263 (1953).

(9) These configurational assignments will be justified in the next section.

TABLE I

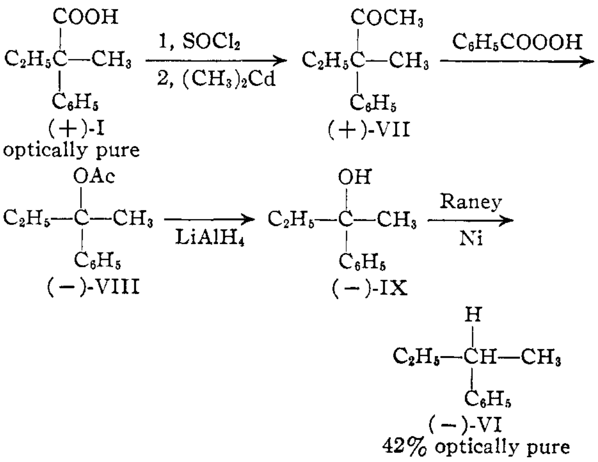
PHYSICAL PROPERTIES AND ANALYSES OF COMPOUNDS INVOLVED IN SYNTHESIS OF ISOMERIC 1,2-DIPHENYL-2-METHYL-1-BUTANOLS

Compound	M.p. or b.p. (mm.), °C.	n^{25}D	[α]D	T, °C.	c in C_6H_6	Mol. form.	Carbon, %		Hydrogen, %	
							Calcd.	Found	Calcd.	Found
2-Methyl-2-phenylbutanoic acid (I)										
Racemic	56.2–58.9	....	.....	..	...	$C_{11}H_{14}O_2$	...	...	..	..
(+)[a]	86.2–87	....	+29.3°	24	4.6	$C_{11}H_{14}O_2$	...	...	..	..
(−)[a]	85.2–87.6	....	−29.2	25	4.8	$C_{11}H_{14}O_2$	...	...	..	..
1,2-Diphenyl-2-methyl-1-butanone (II)										
Racemic	132 (1)	1.5700	.....	..	....	$C_{17}H_{18}O$	85.66	85.64	7.61	7.66
(+)	147 (2.5)	1.5695	+63.7[b]	25	Neat[b]	$C_{17}H_{18}O$	85.66	85.51	7.61	7.69
(−)	144–145 (2.5)	1.5697	−63.7[b]	25	Neat[b]	$C_{17}H_{18}O$	85.66	85.59	7.61	7.43
2-Methyl-2-phenylbutanoic nitrile (IV)										
Racemic	89–89.2 (4)	1.5036	.....	..	...	$C_{11}H_{13}N$	83.02	83.22	8.18	8.29
(−)	119 (16)	1.5033	−7.27	25	Neat[c]	$C_{11}H_{13}N$	83.02	83.16	8.18	8.19
1,2-Diphenyl-2-methyl-1-butanol (III)										
(−)-*erythro*	....	1.5698	−1.82	24	10.1	$C_{17}H_{20}O$	84.95	84.70	8.39	8.29
(+)-*erythro*	....	1.5698	+1.87	25	10.1	$C_{17}H_{20}O$	84.95	84.69	8.39	8.29
(−)-*threo*	....	1.5692	−59.30	25	10.4	$C_{17}H_{20}O$	84.95	84.97	8.39	8.17
(+)-*threo*	....	1.5694	+59.40	25	10.4	$C_{17}H_{20}O$	84.95	84.69	8.39	8.24
p-Nitrobenzoates of III										
(−)-*erythro*	84–85.5	....	+96.0	24	4.5	$C_{24}H_{23}NO_4$	73.99	74.01	5.95	5.82
(+)-*erythro*	84–85.5	....	−96.9	24	4.5	$C_{24}H_{23}NO_4$	73.99	74.29	5.95	5.99
(−)-*threo*	114–115	....	−145	25	4.7	$C_{24}H_{23}NO_4$	73.99	74.04	5.95	5.73
(+)-*threo*	114–115	....	+146	25	4.7	$C_{24}H_{23}NO_4$	73.99	74.28	5.95	6.03

[a] Previously reported physical constants (ref. 6) are m.p. 86–87° (both enantiomers), $[\alpha]^{23}$D + 30.2° (*c* 4.5, C_6H_6) and $[\alpha]^{23}$D −30.0° (*c* 4.8, C_6H_6). [b] $d^{25}{}_4$ 1.068. [c] $d^{25}{}_4$ 0.9599.

figurations of all asymmetric carbons of all the isomers. The first of these problems was attacked as follows.

The configuration of 2-phenylbutane (VI) has been related[10] to that of (+)-glyceraldehyde, which in turn has been related to (−)-tartaric acid,[11] whose enantiomer is the only substance whose *absolute configuration* has been determined directly.[12] Since the active isomers of 2-methyl-2-phenylbutanoic acid (I) were converted without configurational modification to the isomers of 1,2-diphenyl-2-methyl-1-butanol (III), the configuration of the quaternary carbon of II would be related to (+)-tartaric acid if the configuration of the acid I could be related to that of 2-phenylbutane (VI). This link in the chain of relationships was closed by converting optically pure (+)-I to (+)-3-methyl-3-phenyl-2-pentanone (VII) without configurational modification, which was subjected to the Baeyer–Villiger rearrangement to give 2-acetoxy-2-phenylbutane (VIII).[13] This reaction has been demonstrated to occur with retention of configuration in other systems.[14] This ester was converted to 2-phenyl-2-butanol (IX) by reduction with lithium aluminum hydride, the reaction proceeding without modification of configuration.[3] This alcohol was hydrogenolyzed with Raney nickel to give 42% optically pure (−)-2-phenylbutane. The stereochemistry of this last reaction has been demonstrated to occur with predominating retention of configuration in other systems.[15] The formulations summarize the above interconversions.



$$C_2H_5C(CH_3)(COOH)C_6H_5 \xrightarrow[2,\ (CH_3)_2Cd]{1,\ SOCl_2} C_2H_5C(CH_3)(COCH_3)C_6H_5 \xrightarrow{C_6H_5COOOH} C_2H_5—C(CH_3)(OAc)C_6H_5 \xrightarrow{LiAlH_4} C_2H_5—C(CH_3)(OH)C_6H_5 \xrightarrow[Ni]{Raney} C_2H_5—CH(CH_3)C_6H_5$$

(+)-I optically pure; (+)-VII; (−)-VIII; (−)-IX; (−)-VI 42% optically pure

Although in this particular sequence the intermediate tertiary acetate VIII and alcohol IX were not isolated as such, the relationships between the signs of rotation and configuration of the compounds were demonstrated in separate experiments. Thus, optically pure (+)-2-hydroxy-2-phenylbutane (IX)[16] was converted in 70% yield to (+)-2-phenylbutane (64% optically pure) with Raney nickel. Previously,[3] (−)-IX had been acetylated to give (−)-VIII, which in turn had been reduced (lithium aluminum hydride) back to

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(10) D. J. Cram, THIS JOURNAL, **74**, 2149 (1952).

(11) A. Wohl and Fr. Momber, *Ber.*, **50**, 455 (1917).

(12) J. M. Bijvoet, A. F. Peerdeman and A. J. vanBommel, *Nature*, **168**, 271 (1951).

(13) Although methyl migration was looked for, none was detected (see Experimental).

(14) (a) R. B. Turner, THIS JOURNAL, **72**, 878 (1950); (b) K. Mislow and J. Brenner, *ibid.*, **75**, 2318 (1953).

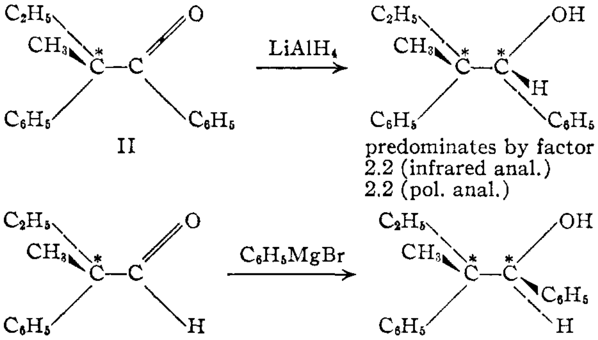
(15) W. A. Bonner, J. A. Zderic and G. A. Casaletto, *ibid.*, **74**, 5086 (1952).

(16) H. H. Zeiss, *ibid.*, **73**, 2391 (1951).

(−)-IX without any configurational changes. The configuration of 2-methyl-2-phenyl-1-butanol (X) was also determined by reducing (+)-I with lithium aluminum hydride to give (+)-X.

The above reactions allow the configuration of the quaternary asymmetric carbon atom of the isomers of 1,2-diphenyl-2-methyl-1-butanol (III) to be assigned. The remaining task is to relate the configuration of this to the other asymmetric carbon of III (assignment of diastereomeric relationships). Provisional assignments of configuration can be made based on the application of the "Rule of Steric Control of Asymmetric Induction"[17] to the partition of products between diastereomers in the two syntheses of III. The two requisites for application of the rule are met in these syntheses. The relative bulks of the substituents attached to the asymmetric carbon atom of the starting materials (ketone and aldehyde) unambiguously fall in the order $C_6H_5 > C_2H_5 > CH_3$; and one diastereomeric alcohol (III) definitely predominates in the synthesis from the aldehyde and the other in the synthesis from the ketone. The last point was clearly established by submitting the mixtures of diastereomers obtained by each synthetic route to both infrared and polarimetric analyses, the results being summarized in the formulation (see Experimental for details)

isomers of III



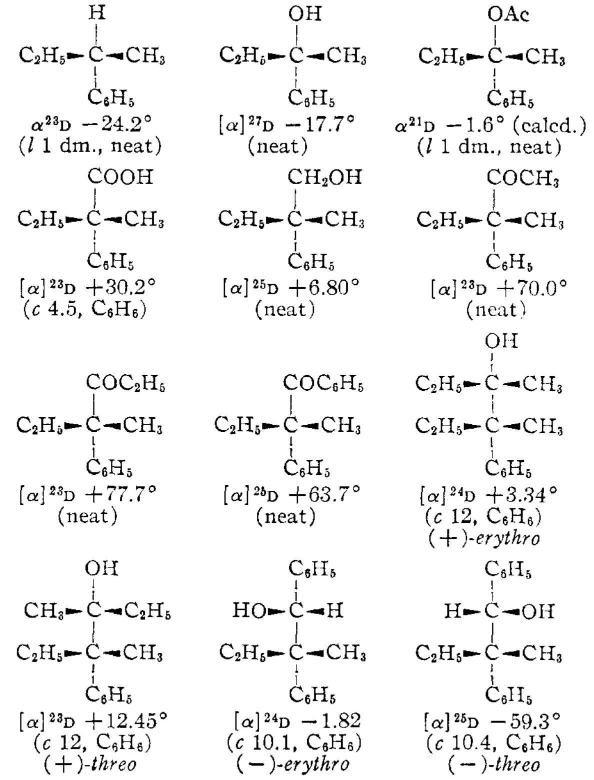
II

predominates by factor
2.2 (infrared anal.)
2.2 (pol. anal.)

predominates by factor
1.9 (infrared anal.)
2.1 (pol. anal.)

Although the naming of configurations of these stereoisomers is trivial, for reference purposes the diastereomer allowing simultaneous eclipsing of a phenyl and phenyl, a methyl and hydrogen, and an ethyl and hydroxyl will be designated as the *erythro*-isomer and the other as the *threo*-isomer. The grossly arbitrary assignment of the terms D- or L- to the enantiomers of each racemate series is not necessary since the simple coupling of the sign of rotation with the terms *threo* or *erythro* and with a three-dimensional formula will suffice until a general and systematic scheme of nomenclature has been adopted by the appropriate agencies.[18]

The configurational assignments that this work allows to be made are set forth in the formulations[19]



$\alpha^{23}D$ −24.2° (l 1 dm., neat)

$[\alpha]^{27}D$ −17.7° (neat)

$\alpha^{21}D$ −1.6° (calcd.) (l 1 dm., neat)

$[\alpha]^{23}D$ +30.2° (c 4.5, C_6H_6)

$[\alpha]^{25}D$ +6.80° (neat)

$[\alpha]^{23}D$ +70.0° (neat)

$[\alpha]^{23}D$ +77.7° (neat)

$[\alpha]^{25}D$ +63.7° (neat)

$[\alpha]^{24}D$ +3.34° (c 12, C_6H_6) (+)-*erythro*

$[\alpha]^{23}D$ +12.45° (c 12, C_6H_6) (+)-*threo*

$[\alpha]^{24}D$ −1.82 (c 10.1, C_6H_6) (−)-*erythro*

$[\alpha]^{25}D$ −59.3° (c 10.4, C_6H_6) (−)-*threo*

Experimental

Distillations unless otherwise specified were performed with a 2.5-foot column of the Podbielniak type. All melting points are uncorrected. Carefully fractionated pentane was used for chromatography.

Racemic 2-Methyl-2-phenylbutanoic Acid (I).—This acid was prepared by the methyl alkylation of 2-phenylbutanoic nitrile followed by hydrolysis of the 2-methyl-2-phenylbutanoic nitrile to acid I. The procedure is as follows. A mixture of 2-phenylbutanamide (200 g.) and 458 g. of phosphorus oxychloride was allowed to reflux on a steam-bath for 2.5 hours. After the reaction mixture had been cooled to 0°, it was vigorously stirred into 4 l. of ice. The resulting mixture was stirred until the organic layer rose to the surface. The oil was extracted with ether, and the organic layer was washed with water, then dried and evaporated. The residual oil was distilled (Claisen) to give 168 g. (95% yield) of 2-phenylbutanoic nitrile, b.p. 122–124° (16 mm.), $n^{25}D$ 1.5070, reported $n^{25}D$ 1.5075.[20]

Dry sodamide (77.5 g. of sodium and 1600 ml. of ammonia) was mixed with 2 l. of anhydrous ether, held at reflux for one hour, and the ether distilled until no ammonia could be detected in the vapor. Sufficient dry ether was added to restore the solution to its original volume. To the mixture was then added (45 minutes), with stirring and cooling, a solution of 484 g. of 2-phenylbutanoic nitrile and 600 ml. of ether. The mixture was held at reflux for ten hours with stirring. Methyl iodide (530 g.) in 1 l. of anhydrous ether was added rapidly with external cooling. The solution was refluxed for one hour and allowed to stand at 25° for ten hours. The mixture was again held at reflux for one hour, cooled, and the flask was washed cautiously with absolute ethanol until the excess sodamide was consumed. A minimum amount of water was added to dissolve the precipitated salt, the layers were separated, the organic layer was

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[17] (a) D. J. Cram and F. A. Abd Elhafez, THIS JOURNAL, **74**, 5828 (1952); (b) ref. 6; (c) D. J. Cram, F. A. Abd Elhafez and H. Weingarten, THIS JOURNAL, **75**, 2293 (1953); (d) D. J. Cram and F. D. Greene, *ibid*, **75**, 6005 (1953); (e) D. J. Cram, F. A. Abd Elhafez and H. LeRoy Nyquist, *ibid.*, **76**, 22 (1954).

[18] Two general schemes for configurational nomenclature have been suggested: R. S. Cahn and C. K. Ingold [*J. Chem. Soc.*, 612 (1951)] and G. E. McCasland [Pamphlet entitled "A New General System for Naming of Stereoisomers," available from *Chemical Abstracts*, Ohio State University, Columbus 10, Ohio].

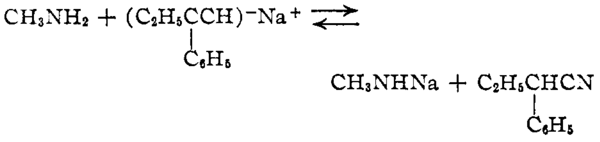
[19] This investigation allows the complete assignment of configuration to be made to the four stereoisomers of 3,4-dimethyl-4-phenyl-3-hexanol (ref. 6), as well as to the intermediate ketones, amides and nitriles.

[20] S. M. McElvain and C. L. Stevens, THIS JOURNAL, **69**, 2663 (1947).

washed (water, sodium bisulfite and sodium carbonate solution), dried and evaporated. A small amount of the residual oil was distilled to give a sample n^{25}D 1.5026. From the indices of refraction of the starting 2-phenylbutanoic nitrile (n^{25}D 1.5070) and the desired 2-methyl-2-phenylbutanoic nitrile (n^{25}D 1.5036, prepared later), the mixture was estimated to contain about 30% of unalkylated nitrile. This material was preferentially consumed with the calculated amount of alkali, making use of the greater rate of hydrolysis of the less hindered nitrile. Accordingly, the crude nitrile mixture was held at reflux with 80 g. of potassium hydroxide and 1 l. of 95% ethanol for 24 hours. The resulting mixture was poured into 3 volumes of water, and the solution was extracted with ether. The organic phase was washed with water, dried, evaporated and the residual oil was held at reflux in a solution of 320 g. of potassium hydroxide and 2.5 l. of diethylene glycol (24 hours). The solution was cooled, mixed with three volumes of water, and the resulting mixture was extracted with ether. The aqueous phase was acidified with cold concentrated hydrochloric acid, and the acid that separated was extracted with ether. The ether layer was washed with water, dried, evaporated, and the residual oil was distilled to give 520 g. of a yellow oil, b.p. 142–144° (3.5 mm.). This material was crystallized from 600 ml. of pentane at 0° to give 505 g. of 2-methyl-2-phenylbutanoic acid (I), m.p. 56.2–58.9° (reported 56–57°),[6] yield 85%.

The use of excess sodamide in the above reaction sequence should be avoided because of the probable intervention of the following reactions. Alteration of the 1:1 mole ratio of starting nitrile and sodamide resulted in drastic reduction of yield of the desired alkylated product.

$$CH_3I + NaNH_2 \longrightarrow CH_3NH_2 + NaI$$



$$CH_3NH_2 + (C_2H_5\underset{\substack{|\\C_6H_5}}{C}CH)^-Na^+ \rightleftarrows CH_3NHNa + C_2H_5\underset{\substack{|\\C_6H_5}}{C}HCN$$

$$CH_3NHNa + CH_3I \longrightarrow (CH_3)_2NH + NaI, \text{ etc.}$$

Alkylation of 2-phenylpropionitrile with ethyl bromide and lithium diethyl amide according to the procedure of Cason, *et al.*,[21] gave similar results.

1,2-Diphenyl-2-methyl-1-butanone (II).—A mixture of 25 g. of racemic 2-methyl-2-phenylbutanoic acid and 33.5 g. of thionyl chloride was allowed to stand for 10 hours at 25° and was then heated at 100° for 10 minutes, the excess thionyl chloride being evaporated under vacuum. Two successive 25-ml. portions of anhydrous benzene were added and evaporated under vacuum. The residue was distilled to give 26.4 g. (95% yield) of the acid chloride as a colorless liquid, b.p. 122–124° (16 mm.) (Claisen).

Diphenylcadmium was prepared in the usual way[22] from 3.92 g. of magnesium, 25.6 g. of bromobenzene, 15.9 g. of anhydrous cadmium chloride and 150 ml. of ether. The ether was distilled until the rate slowed and 75 ml. of pure dry benzene was added. The distillation was then resumed until 25 ml. of additional material had been collected, an additional 150 ml. of dry benzene was added, and the solution was heated to reflux. To the hot solution was then added, as rapidly as possible, a solution of 26.4 g. of the above acid chloride in 75 ml. of pure dry benzene. The reaction mixture was held at reflux for 45 minutes and worked up in the usual manner[22] to give 14.3 g. (79% yield) of colorless oil (ketone II), b.p. 132° (1 mm.).

The oxime of this ketone was prepared in the usual way to give a colorless derivative, m.p. 148.2–148.6° (four crystallizations from ethanol–water).

Anal. Calcd. for $C_{17}H_{19}NO$: C, 80.59; H, 7.56. Found: C, 80.56; H, 7.74.

The active (−)-1,2-diphenyl-2-methyl-1-butanone ((−)-II) was prepared in 74% over-all yield from 15 g. of starting (−)-2-methyl-2-phenylbutanoic acid, $[\alpha]^{25}$D −29.2° (benzene, *c* 4.8), m.p. 85.2–87.6°, the above procedure being employed. Similarly, from 15 g. of (+)-2-methyl-2-phenylbutanoic acid, $[\alpha]^{25}$D +29.3° (benzene, *c* 4.6) was obtained a 75% yield of (+)-1,2-diphenyl-2-methyl-1-butanone ((+)-II). The analyses and physical properties of these ketones are reported in Table I.

1,2-Diphenyl-2-methyl-1-butanol (III).—The mixture of racemates of III was prepared as follows. To a stirred mixture of 1.56 g. of lithium aluminum hydride and 100 ml. of ether was added dropwise 11.85 g. of racemic 1,2-diphenyl-2-methyl-1-butanone (II) in 75 ml. of anhydrous ether (10 minutes). The resulting mixture was stirred for an additional three hours, and the excess reagent was decomposed with ethyl acetate. The mixture was then stirred with ice-cold 5% hydrochloric acid solution, the organic layer was washed with water, with sodium carbonate solution and again with water. The ether solution was dried, evaporated, and the residual oil was distilled to give 9.60 g. (80% yield) of alcohol III, b.p. 164–165° (4.5 mm.), n^{25}D 1.5719.

Anal. Calcd. for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.70; H, 8.59.

Similarly, from 11.0 g. (−)-1,2-diphenyl-2-methyl-1-butanone, $[\alpha]^{25}$D −63.7° (neat), was obtained 9.65 g. of a mixture of optically pure diastereomeric 1,2-diphenyl-2-methyl-1-butanols (III), b.p. 167° (3 mm.), n^{25}D 1.5703, $[\alpha]^{27}$D +19.84° (C_6H_6, *c* 13.2).

From 11.0 g. of (+)-1,2-diphenyl-2-methyl-1-butanone, $[\alpha]^{25}$D +64.7° (neat), was obtained 10.0 g. of the other mixture of optically pure diastereomers of III, b.p. 170° (4 mm.), n^{25}D 1.5704, $[\alpha]^{27}$D −19.69° (C_6H_6, *c* 13.2).

The analyses of these mixtures are reported in a later section.

2-Methyl-2-phenylbutanoic Nitrile (IV).—From 10.1 g. of 2-methyl-2-phenylbutanamide[6] (m.p. 70–75°) was prepared (procedure similar to that reported above for the preparation of 2-phenylbutanoic nitrile) 7.76 g. (87% yield) of nitrile IV. Similarly, from 9.28 g. of optically pure (+)-2-methyl-2-phenylbutanamide, m.p. 72.4–73.4°, $[\alpha]^{25}$D +18.81° (C_6H_6, *c* 4.1), was obtained 7.39 g. (89% yield) of (−)-2-methyl-2-phenylbutanoic nitrile. Analyses and physical constants are reported in Table I.

1,2-Diphenyl-2-methyl-1-butanol (III) ***via*** **2-Methyl-2-phenylbutanal (V).**—A mixture of racemates of III was prepared as follows. A mixture of 13 g. of lithium aluminum hydride and 500 ml. of dry ether was held at reflux for 40 hours, and the resulting mixture was allowed to cool and settle. After about 12 hours the supernatant solution was decanted to a large graduated cylinder and the settling procedure was repeated. The normality of the solution was determined by adding an aliquot of this solution to water and measuring the volume of hydrogen liberated.

To a stirred solution of 9 g. of racemic 2-methyl-2-phenylbutanoic nitrile and 50 ml. of dry ether held at 0° was added dropwise (one hour) 85 ml. of 0.156 *M* lithium aluminum hydride solution in ether. The reaction mixture became cloudy but no precipitate was observed. The mixture was stirred for an additional 30 minutes at 0°, the ice-bath was removed, and 10 ml. of ice-water was added dropwise to the mixture (slight hydrogen evolution was observed). A mixture of 20 ml. of concentrated hydrochloric acid and 30 g. of ice was then stirred into the mixture. The organic layer was washed with water, sodium bicarbonate solution, again with water, and was dried and the ether was evaporated through a short column. To remove traces of water, the residual oil was mixed with 20 ml. of pure dry benzene which was evaporated at 50° under vacuum.

A few drops of the oil (crude 2-methyl-2-phenylbutanal or V) was converted in the usual manner to the 2,4-dinitrophenylhydrazone, which after two crystallizations from ethanol–water gave orange needles, m.p. 122.8–124.2°.

Anal. Calcd. for $C_{17}H_{18}N_4O_4$: C, 59.64; H, 5.26. Found: C, 59.51; H, 5.00.

Similarly, a semicarbazone was prepared, m.p. 158–159° (soft white needles from absolute ethanol), reported[23] m.p. 158–159°.

The residual oil (V) was dissolved in 20 ml. of anhydrous ether and added (two minutes) to a Grignard reagent prepared in 60 ml. of dry ether from 10.2 g. of bromobenzene and 1.56 g. of magnesium. The reaction mixture was heated to reflux for 45 minutes, cooled and 30 g. of ice-water was added, followed by a mixture of 20 ml. of concentrated hydrochloric acid and 20 g. of ice. The organic layer was

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[21] J. Cason, G. Sumrell and R. S. Mitchell, *J. Org. Chem.*, **15**, 850 (1950).

[22] J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 325.

[23] Yves Deaux, *Compt. rend.*, **206**, 1017 (1938).

washed with water, dried and evaporated, and the residual oil was distilled. The fraction, b.p. 160–162° (3 mm.), 4.9 g., n^{25}D 1.5669, was adsorbed on 150 g. of activated basic alumina from a pentane solution. The column was thoroughly washed with pentane and then stripped with ether. The ether solution was evaporated and the residual oil was Claisen-distilled to give 4.14 g. (26% yield) of the desired 1,2-diphenyl-2-methyl-1-butanol (III) as a viscous colorless liquid, n^{25}D 1.5690.

The aqueous acidic phase from the reduction of the nitrile was made basic with 6 *N* potassium hydroxide solution, and the oil that separated was extracted into ether. The ether layer was washed with water, dried, evaporated, and the 1.05 g. of residue was adsorbed on 30 g. of activated basic alumina. The column was washed with pentane, 50-ml. fractions of column eluate being collected. The second fraction (containing the bulk of the solute) was evaporated to an oil which was Claisen-distilled at 16 mm. (bath temperature of 135°) to give 0.85 g. of 2-methyl-2-phenylbutylamine, n^{25}D 1.5208.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.90; H 10.52,. Found: C, 81.00; H, 10.44.

A benzenesulfonamide derivative was prepared in the usual way, m.p. 83.5–84.6° (two crystallizations from absolute ethanol to give white rhombohedra).

Anal. Calcd. for $C_{19}H_{21}NO_2S$: C, 67.00; H, 6.92. Found: C, 66.90; H, 7.23.

Variation of the reaction temperature of the nitrile reduction resulted in poorer yields of the desired aldehyde V.

Utilizing the above procedures, 6.70 g. of (–)-2-methyl-2-phenylbutanoic nitrile, $[\alpha]^{25}$D –7.27° (neat), was converted to impure aldehyde V, which in turn was converted to 1.4 g. (14% over-all yield) of a mixture of optically pure diastereomers of 1,2-diphenyl-2-methyl-1-butanol (III), n^{25}D 1.5694, $[\alpha]^{25}$D –40.68° (C_6H_6, *c* 9.9). No 2-methyl-2-phenylbutylamine was obtained in this experiment.

Other Attempts to Prepare 2-Methyl-2-phenylbutanal (V).—Sodium trimethoxyborohydride reduction[8f] of 2-methyl-2-phenylbutanoyl chloride gave primarily 2-methyl-2-phenylbutyl 2-methyl-2-phenylbutanoate derived from the reaction of starting acid chloride with 2-methyl-2-phenyl-1-butanol formed from complete reduction of the starting material. This ester was a colorless, viscous oil, distilled at a bath temperature of 187° (2 mm.), n^{25}D 1.5287.

Anal. Calcd. for $C_{22}H_{28}O_2$: C, 81.50; H, 8.64. Found: C, 81.47; H, 8.54.

The small amount of aldehyde formed in this reaction formed a constant boiling mixture with the starting acid chloride.

An attempt to prepare V by the inverse addition of one equivalent of lithium aluminum hydride to N-methyl-N-phenyl-2-methyl-2-phenylbutanamide[8e] gave a mixture of 2-methyl-2-phenyl-1-butanol and starting material. The disubstituted amide was prepared in 70% yield by the reaction of 2-methyl-2-phenylbutanoyl chloride with N-methylaniline (mole ratio, 2.5/1) in anhydrous benzene. This amide proved to be a colorless oil, b.p. 166–170° (4 mm.), n^{25}D 1.5621.

Anal. Calcd. for $C_{18}H_{21}NO$: C, 80.89; H, 7.86. Found: C, 80.90; H, 7.76.

The primary alcohol, 2-methyl-2-phenyl-1-butanol, was prepared in the usual way by lithium aluminum hydride reduction of racemic 2-methyl-2-phenylbutanoic acid (I). The product was obtained in 62% yield, b.p. 131–133.5° (16 mm.), n^{25}D 1.5212.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.48; H, 9.75. Found: C, 80.57; H, 9.48.

An attempt to oxidize this alcohol with di-*t*-butyl chromate[8d] to aldehyde V failed to yield significant amounts of the desired product.

Another attempt was made to obtain aldehyde V by the Raney nickel desulfurization[8b] of ethyl 2-methyl-2-phenylthiolbutanoate, with negative results. The starting ester was prepared by an adaptation of the procedure of Levin, *et al.*,[24] to the synthesis at hand. The thiol ester was obtained in 74% yield as a colorless liquid, b.p. 122–126° (4 mm .), n^{25}D 1. 5359.

Anal. Calcd. for $C_{13}H_{18}OS$: C, 70.27; H, 8.10. Found: C, 70.27; H, 8.34.

Separation of Mixtures of Diastereomers of 1,2-Diphenyl-2-methyl-1-butanol (III) into their Two Components.—The mixture of diastereomeric alcohols III, $[\alpha]^{27}$D +19.18° (C_6H_6, *c* 13.2), obtained by the lithium aluminum hydride reduction of optically pure (–)-1,2-diphenyl-2-methyl-1-butanone (II), was converted to the acid phthalate derivative as follows: A mixture of 14.4 g. of III, 9.75 g. of phthalic anhydride and 6 ml. of reagent grade pyridine was heated at 130° for 24 hours. The slightly cooled reaction mixture was shaken with a mixture of 300 g. of ice, 10 ml. of concentrated hydrochloric acid and 200 ml. of ether. The ether layer was washed with water, dried and evaporated to an oil. This oil was dissolved in 50 ml. of absolute ethanol and titrated to phenolphthalein with 1.5 *N* aqueous potassium hydroxide solution. The potassium salt of the acid phthalate of the (+)-*erythro* isomer crystallized immediately. The mixture after standing for two hours was filtered, and the salt was washed with water, and dried to give 16 g. of material. This salt was twice recrystallized from absolute ethanol to give 12.3 g. of pure potassium salt, $[\alpha]^{26}$D –3.03° (CH_3OH, *c* 1.99).

This material was mixed with 2.42 g. of potassium hydroxide, 30 ml. of ethylene glycol and heated at reflux for 18 hours. The solution was cooled, added to three volumes of water, and the oil that separated was extracted into pure pentane. The organic layer was washed with water, dried and evaporated, and the residual oil was adsorbed on a column of 230 g. of activated basic alumina made up in pure pentane. The column was thoroughly washed with pentane, and the desired alcohol was eluted with methanol. The methanol was evaporated to give a residual oil which was taken up in pure pentane. This solution was washed with water, dried, evaporated, and the residual oil was distilled to give 4.74 g. (33% yield) of optically pure (+)-*erythro*-III. This material was converted to the *p*-nitrobenzoate derivative by the usual procedure[17a] to give a 90% yield of yellow needles (ethyl acetate–pentane) of (–)-*p*-nitrobenzoate. Hydrolysis of this material by the usual procedure gave back (+)-*erythro*-III with unchanged properties. See Table I for analyses and physical constants.

The original filtrate from the crystallization of the potassium salt of the acid phthalate (see above) was evaporated, and the residual oil was dissolved in a solution of 1.9 g. of potassium hydroxide and 200 ml. of water. This solution was held at reflux for 18 hours, cooled, and the oil was extracted with pure pentane. The organic layer was washed with water, dried, evaporated, and the residual oil was distilled, wt. 4.35 g. of impure (+)-*threo*-III, $[\alpha]^{27}$D +50.9° (C_6H_6, *c* 10). This alcohol was converted to the *p*-nitrobenzoate derivative in the usual way[17a] to give after three crystallizations from absolute ethanol 4.9 g. of pure (+)-*threo*-*p*-nitrobenzoate (21% yield over-all). Hydrolysis of this ester by the usual procedure gave an 89% yield of pure (+)-*threo*-III (see Table I for analyses and physical constants).

By similar procedures the mixture of diastereomeric alcohols III, $[\alpha]^{27}$D –19.69° (C_6H_6, *c* 13.2), obtained by lithium aluminum hydride reduction of optically pure (+)-1,2-diphenyl-2-methyl-1-butanone (II) was separated into the (–)-*threo* and (–)-*erythro* components. From 19.4 g. of the mixture of alcohols was obtained 2.73 g. of (–)-*threo*-III and 6.03 g. of (–)-*erythro*-III. Table I records the analyses and physical properties of the compounds involved.

Procedures for separating the diastereomers utilizing the solubility properties of the brucine salt of the acid phthalate of (+)-*erythro*-III and the strychnine salt of the acid phthalate of (–)-*erythro*-III were also developed, but were found to be much less satisfactory.

Analyses of the Diastereomeric Mixtures of 1,2-Diphenyl-2-methyl-1-butanol (III).—Both polarimetric and infrared analyses of the mixtures of diastereomers obtained from the aldehyde and the ketone syntheses were carried out. In the former analysis a plot of rotation *vs.* percentage composition of (+)-*threo*-III and (+)-*erythro*-III was virtually linear. For example, a synthetic mixture of 47% (+)-*threo*-III and 53% (+)-*erythro*-III (both optically pure) gave $[\alpha]^{25}$D +29.7° (C_6H_6, *c* 11). If one assumes that the rotation is a linear function of composition, the composition of this mixture would be estimated as 48% (+)-*threo* and 52% (+)-*erythro*-III. The unknown mixture of diastereomers (III) obtained by lithium aluminum hydride reduction of (–)-III (ketone) gave $[\alpha]^{25}$D +19.84 (C_6H_6, *c* 10) from which the composition was estimated to be 31% (+)-*threo* and 69%

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[24] R. H. Levin, A. V. McIntosh, Jr., G. B. Spero, D. E. Raymond and E. M. Meinzer, THIS JOURNAL, **70**, 511 (1948).

(+)-*erythro* material. Likewise, the unknown mixture of diastereomers (III) obtained from (+)-II was estimated to possess the composition 31% (−)-*threo* and 69% (−)-*erythro* alcohol. The unknown mixture of diastereomers (III) obtained by the action of phenylmagnesium bromide on aldehyde V gave $[\alpha]^{25}\mathrm{D}$ −40.68° (C_6H_6, *c* 10), from which the composition was estimated to be 68% (−)-*threo* and 32% (−)-*erythro* alcohol.

The infrared analysis of these same mixtures was carried out with a Beckman I.R. 2T spectrophotometer (sodium chloride prism), pure liquid films of alcohol (0.03 mm. thick) in a rock-salt cell being employed. The analyses were carried out at the most advantageous wave lengths, the optical densities of the pure components and a synthetic mixture as well as the three unknown mixtures being recorded in Table II. Deviations from Beer's law appear to be only very slight. The estimated composition of the unknown mixtures are also recorded in Table II, the values being obtained by solving two independent sets of simultaneous equations in two unknowns.

TABLE II

INFRARED ANALYSES OF MIXTURES OF *threo-* AND *erythro*-1,2-DIPHENYL-2-METHYL-1-BUTANOL (III)

λ, μ Compound slit width, mm.	Optical densities 9.88 0.765	 10.84 1.04	 11.06 1.09	 11.24 1.14
(+)-*threo*-III	0.895	0.341	0.270	0.127
(+)-*erythro*-III	.625	.249	.190	.197
51.4% (+)-*threo*-III and 48.6% (+)-*erythro*-III	.762	.298	.231	.162
(+)-III unknown from (−)-ketone	.710	.276	.209	.176
(−)-III unknown from (+)-ketone	.711	.276	.207	.172
(−)-III unknown from aldehyde	.802	.315	.241	.152

	Estimated composition, % *threo*	 *erythro*	 Total
51.4% (+)-*threo*-III + 48.6% (+)-*erythro*-III	50	49	99
(+)-III unknown from (−)-ketone	31	70	101
(−)-III unknown from (+)-ketone	33	68	101
(−)-III unknown from aldehyde	66	36	102

(+)-2-Methyl-2-phenyl-1-butanol (X).—A solution of 1.0 g. of 2-methyl-2-phenylbutanoic acid (I), $[\alpha]^{25.5}\mathrm{D}$ +28.9° (C_6H_6, *c* 5), was reduced in the usual way with 0.32 g. of lithium aluminum hydride. The reaction mixture was stirred for 12 hours at room temperature, the product being isolated in the usual manner. The crude alcohol was dissolved in 30 ml. of pure pentane and adsorbed on a column of 30 g. of basic activated alumina made up in pure pentane. The column was washed with 300 ml. of pentane and the alcohol was eluted with two 100-ml. portions of an ether-pentane mixture (1:1). The solvent was evaporated through a short column, and the residual oil was distilled at 16 mm. (bath temperature, 136°) to give 0.89 g. (97% yield) of 2-methyl-2-phenyl-1-butanol, $n^{25}\mathrm{D}$ 1.5213, $d^{24.8}_4$ 0.9916, $[\alpha]^{24.8}\mathrm{D}$ +6.80° (neat).

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.16; H, 9.97.

(+)-3-Methyl-3-phenyl-2-pentanol (XI).—A solution of 0.90 g. of optically pure 3-methyl-3-phenyl-2-pentanone,[6] $[\alpha]^{25.2}\mathrm{D}$ +69.1° (neat), $n^{25}\mathrm{D}$ 1.5080, in ether was reduced the usual way with lithium aluminum hydride (0.292 g.), the product being isolated as in the above preparation of (+)-2-methyl-2-phenyl-1-butanol. Distillation of the chromatographed product gave 0.78 g. (86% yield) of the desired 3-methyl-3-phenyl-2-pentanol (bath temperature 140°, 16 mm.), $n^{25}\mathrm{D}$ 1.5189, $d^{24.8}_4$ 0.9866, $[\alpha]^{24.8}\mathrm{D}$ +9.10° (neat).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.70; H, 10.39.

Hydrogenolysis of (+)-2-Phenyl-2-butanol (IX).—This procedure is an adaptation of that of Bonner, *et al.*,[15] as applied to other systems.

A mixture of 1.40 g. of optically pure 2-phenyl-2-butanol,[16] $[\alpha^{27}]\mathrm{D}$ +17.36° (*l* 1 dm., neat), 50 ml. of absolute ethanol and 10.5 g. of W-1 Raney nickel[25] was held at reflux for 90 minutes. The warm solution was filtered (gravity), and the catalyst was washed with hot ethanol. The combined filtrates were diluted with three volumes of water and extracted with pure pentane. The pentane layer was washed with water, dried and the solvent was distilled through a short column. The residual oil was dissolved in 30 ml. of pure pentane and passed through a column of 50 g. of basic activated alumina made up in pure pentane. The column was washed with 300 ml. of pure pentane, and the column eluate was evaporated through a short column. The residual oil was twice distilled (Claisen) at 16 mm. (bath temperature, 115°) to give 0.87 g. (70% yield) of 2-phenylbutane, $n^{25}\mathrm{D}$ 1.4877, $[\alpha]^{27}\mathrm{D}$ +15.48° (*l* 1 dm., neat), 64% optically pure.[10]

Perbenzoic Acid Rearrangement of (+)-3-Methyl-3-phenyl-2-pentanone (VII).—This general reaction procedure was adapted from that of Friess.[26] A chloroform solution of perbenzoic acid was prepared and standardized according to the method described by Braun.[27] A solution of 12.52 g. of optically pure 3-methyl-3-phenyl-2-pentanone [$[\alpha]^{25}\mathrm{D}$ +69.1° (neat), $n^{25}\mathrm{D}$ 1.5080, prepared from optically pure (+)-2-methyl-2-phenylbutanoic acid by reaction of the corresponding acid chloride with dimethylcadmium reagent[28] (78% yield)] and 30 ml. of pure chloroform was added to 332 ml. of 0.226 *M* perbenzoic acid in chloroform. The resulting solution was allowed to stand in the dark at room temperature for 14 days. Titration of the unreacted perbenzoic acid indicated that 60% had been consumed. The reaction mixture was diluted with two volumes of ether and washed with sodium carbonate solution, with water, with potassium iodide in water, with sodium hydrosulfite solution, with sodium carbonate solution and finally with water. The organic layer was dried, and the solvent was evaporated. The residual oil was dissolved in 75 ml. of anhydrous ether, and the resulting solution was added to 4.1 g. of lithium aluminum hydride suspended in 250 ml. of ether. After the mixture had been stirred for six hours at room temperature, decomposition was performed according to the procedure of Zeiss.[16] The organic layer was washed twice with water and dried. The solvent was evaporated through a short column, and the residual oil was dissolved in 50 ml. of pure pentane. This solution was adsorbed on a column of 300 g. of basic activated alumina. The column was washed with 600 ml. of pure pentane (nothing was eluted), and the adsorbed material was eluted with 800 ml. of pure ether. The ether eluate was evaporated through a short column, and the residual oil was dissolved in 50 ml. of absolute ethanol. This solution was mixed with 50 g. of W-1 Raney nickel and 200 ml. of absolute ethanol, and the resulting mixture was held at reflux for 90 minutes. The warm mixture was filtered, and the filtrate was shaken with pure pentane and water. The organic layer was washed with water, dried and evaporated through a short column. The residual oil was dissolved in 30 ml. of pure pentane and adsorbed on a column of 320 g. of activated basic alumina made up in pure pentane. The column was washed with 800 ml. of pure pentane, and the column eluate was evaporated through a short column. The residual oil was twice distilled (Claisen) to give 0.95 g. (10% over-all yield) of 2-phenylbutane, $n^{25}\mathrm{D}$ 1.4877, $\alpha^{29}\mathrm{D}$ −10.12° (neat, *l* 1 dm.). This material is 42% optically pure, based on $\alpha^{23}\mathrm{D}$ +24.2° (neat, *l* 1 dm.)[10] for optically pure material.

The chromatographic column was then washed with ether (1 l.) and these eluates were evaporated through a short column. The residual oil was distilled at 16 mm. (bath temperature 145°) to give 7.84 g. of alcohol, $n^{25}\mathrm{D}$ 1.5183, $\alpha^{24.7}\mathrm{D}$ +10.5° (neat, *l* 1 dm.), probably mainly 3-methyl-3-phenyl-2-pentanol. Further treatment of 1.0 g. of this alcohol fraction with 7.5 g. of W-1 Raney nickel (reflux in 35 ml. of absolute ethanol for 27 hours) gave only a trace of hydrocarbon, most of the alcohol being recovered, $n^{25}\mathrm{D}$

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[25] L. W. Covert and H. Adkins, THIS JOURNAL, **54**, 4116 (1932).

[26] S. L. Friess, *ibid.*, **71**, 14 (1949).

[27] G. Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 431.

[28] J. Cason, THIS JOURNAL, **68**, 2078 (1946).

1.5187, $\alpha^{25}D$ +12.4° (neat, l 1 dm.). Comparison of the infrared spectrum of this alcohol with authentic samples of IX, X and XI indicated that neither the tertiary (IX) nor the primary (X) alcohols were present in detectable amounts.

When 0.4 g. of XI, $n^{25}D$ 1.5189, $\alpha^{25}D$ +9.10° (neat), was treated with 4.0 g. of W-1 Raney nickel (reflux in 20 ml. of absolute ethanol for 21 hours) there was obtained 0.32 g. of alcohol, $\alpha^{24}D$ +11.6° (neat, l 1 dm.), $n^{25}D$ 1.5186, no hydrocarbon being detected. The following explanation is offered to correlate the rotational changes observed. Lithium aluminum hydride reduction of (+)-VII would be expected to give rise to a diastereomeric mixture of 3-methyl-3-phenyl-2-pentanols in which the *erythro* isomer predominated.[17a] By analogy with the previous systems in this series of studies, the *erythro* isomer would be expected to have a lower optical rotation than the *threo* isomer (one exception to this generalization was recently encountered[17e]). Treatment with W-1 Raney nickel has afforded at least partial equilibration to a mixture of alcohols having a greater proportion of *threo* diastereomer and, consequently, a higher optical rotation.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY BRANCH, CHEMISTRY DIVISION, RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION]

Reactions of Nitrate Esters. II. Reactions with Hydrazine[1,2]

BY RAYMOND T. MERROW AND ROBERT W. VAN DOLAH

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It has been found that, with sufficiently high concentrations, simple nitrate esters react with hydrazine at ordinary temperatures in the absence of catalysts. Primary aliphatic nitrates undergo reduction and substitution, yielding nitrogen, nitrous oxide, ammonia, hydrazoic acid, nitrite ion, nitrate ion, alkylated hydrazines, alcohol and traces of aldehyde. High hydrazine concentrations favor the reduction process. A mechanism is proposed for the reduction, based on other known reactions of nitrate esters and on postulated mechanisms for other oxidations of hydrazine. Benzyl nitrate reacts primarily by the substitution process, although a small amount of reduction also occurs with high concentrations of hydrazine. Some α-hydrogen elimination apparently occurs, forming benzaldehyde and nitrous acid. *t*-Butyl nitrate undergoes β-elimination almost exclusively, giving isobutylene and nitrate ion. Small amounts of substitution products are also obtained, but no nitrogen or nitrogen oxides are formed.

Hydrazines have long been known as strong reducing agents toward most inorganic and some organic oxidizers, including nitro compounds and nitrite esters, but only a very limited amount of information has been published regarding their reactions with nitrate esters. The reaction of phenylhydrazine with ethyl nitrate at elevated temperatures, giving nitrogen, aniline and ammonium nitrate, was reported in 1896.[3] From the same reactants at ordinary temperatures in the presence of sodium ethoxide, Bamberger and Billeter[4] obtained nitrite ion, nitrogen, benzene, biphenyl, phenyl azide, azobenzene, aniline, nitrobenzene, acetic acid and derivatives of acetaldehyde. More recently the reduction of hexyl nitrate with hydrazine itself at room temperature, in the presence of a platinum or palladium catalyst, has been reported[5]; the products were nitrogen, nitrous oxide, and the parent alcohol. This latter reaction was said not to occur in the absence of the catalyst under the experimental conditions employed.

It has been found in this Laboratory that simple nitrate esters react with hydrazine at ordinary temperatures and without catalysts, but that the reactions are extremely slow unless high concentrations of the reactants are used.[6] With primary aliphatic nitrates, substitution[7] and reduction processes occur simultaneously, resulting in the formation of nitrate ion and alkylated hydrazines, and of nitrite ion, nitrogen, nitrous oxide, ammonia, hydrazoic acid, the parent alcohol and traces of aldehyde. The reduction process predominates when the nitrate ester reacts with excess hydrazine in the absence of added solvents; in aqueous alcoholic solution, the substitution process becomes increasingly important as the concentrations of reactants decrease. Ethyl, *n*-butyl and isoamyl nitrates all show this behavior.

The amount of gas produced was found to depend on the amount of excess hydrazine present, even in the absence of solvents. This variation is shown in Fig. 1. The maximum amount of gas obtained was 1.35 moles per mole of ethyl nitrate; this required at least a tenfold molar excess of hydrazine. In a typical experiment with 12 moles of hydrazine per mole of ethyl nitrate, the concentrations of nitrous oxide and ammonia were 7.0 and 8.7 mole per cent., respectively. The remainder of the gas, except for a trace of hydrazoic acid, was shown to be nitrogen by analysis in the mass spectrometer. Qualitative tests indicated the presence of azide ion in the solution. Nitrite ion formed rapidly and then disappeared as the reaction progressed, as shown in Fig. 2. Only 9% of the nitrate was found as nitrate ion. A small amount of ethanol was isolated and characterized; in similar experiments with *n*-butyl nitrate, the more easily isolable alcohol was obtained in yields in excess of 50%. A trace of aldehyde was obtained from one similar run using isoamyl nitrate, but none was found in any ethyl nitrate experiments. Ether-soluble basic oils were found which were presumed to be alkylated hydrazines, although the pure compounds could not be isolated. Attempts to characterize these as salts, particularly as oxalates, led to sharply melting ma-

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[1] Previous paper in series: R. T. Merrow, S. J. Cristol and R. W Van Dolah, THIS JOURNAL, **75**, 4259 (1953).

[2] Presented in part before the 123rd National Meeting of the American Chemical Society, Los Angeles, Calif., March, 1953.

[3] R. Walther, *J. prakt. Chem.*, **53**, 433 (1896).

[4] E. Bamberger and O. Billeter, *Helv. Chim. Acta*, **14**, 219 (1931).

[5] L. P. Kuhn, THIS JOURNAL, **73**, 1510 (1951).

[6] It has been observed, qualitatively, that the rate of gas evolution is more rapid from β-chloroethyl nitrate, 1,3-dichloro-2-propyl nitrate, glyceryl trinitrate and diethylene glycol dinitrate than from unsubstituted aliphatic nitrates under the same conditions.

[7] The term "substitution" is used in this paper to denote a displacement reaction at the carbon atom bearing the nitrate group.