

of diphenic acid by Huntress.¹³ It is important that the diazotization be carried out at 35–37° and that the coupling reaction take place in the presence of a stirrer so designed that the surface as well as the body of the reaction mixture is thoroughly agitated. The yield of acid from the coupling reaction was 85% and after purification with zinc and acetic acid the m. p. (with decomposition) was 295–298°.

Summary

A number of derivatives of diphenyl have been subjected to the conditions for catalytic hydrogenation to the corresponding dicyclohexyls. Reaction ensued with all the compounds except the two which possessed the structure necessary for molecular asymmetry and they resisted hydrogenation even under very drastic conditions.

(13) Huntress, "Organic Syntheses," John Wiley and Sons, New York, 1927, Vol. VII, p. 30.

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The Influence of Branched Chains on Optical Activity. The Configuration of Methyl-tertiary-butylcarbinol

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In a recent paper¹ it was shown that in an homologous series of secondary carbinols, a change of a propyl to an isopropyl group caused a shift of the optical rotation in the opposite direction from that of the propyl carbinol. In the case of methylisopropylcarbinol, the shift was insufficient to change the sign of rotation; but with the other members, ethyl-, propyl- and butylisopropylcarbinols, the shift was accompanied by a reversal of the sign of rotation. It can be seen that if a branched chain (isopropyl group) directly attached to the asymmetric carbon atom causes a shift of the rotation in the opposite direction, a further branching of the chain (tertiary-butyl group) might cause an even greater shift, possibly sufficient to invert the sign of rotation even of the first member of the series.

The correlation of methyl-tertiary-butylcarbinol was therefore undertaken in order to complete the study of the effect of the branched chain on the optical rotation. The only sure method of correlation is by direct chemical means as in the case of methylisopropylcarbinol. The case of methyl-tertiary-butylcarbinol is however a much more difficult one, and up to the present time no direct chemical method has been found.

The only recourse therefore is correlation by means of Freudenberg's Displacement Rule. Freudenberg² has already assigned dextro methyl-tertiary-butylcarbinol as related to the other dextro carbinols. This tentative correlation, however, rests solely upon the rotation of the phthalate,

(1) Stevens, *THIS JOURNAL*, **54**, 3732 (1932).

(2) Freudenberg, "Stereochemie," 1932, p. 696.

and according to Freudenberg³ himself, it cannot be considered as rigorous, for the Displacement Rule does not allow that carbinols be compared with their ethers or esters.⁴ Consequently an attempt has been made here to abide by all the laws of the Displacement Rule.

The correlation of methyl-tertiary-butylcarbinol was accomplished by comparing the rotations of its acetate, benzoate and phthalate and those of methylisopropylcarbinol and methyl-*n*-butylcarbinol, two closely related carbinols.

	CH ₃	Carbinol	Acetate	[M]	Benzoate	Phthalate
A	C ₃ H ₇ - <i>n</i>	+12.1 ⁵	+22.3 ⁵			+95 (CHCl ₃) ⁵
	C ₃ H ₇ - <i>i</i>	+4.3 ⁵	+24.6			+89.3 (CHCl ₃) ⁵
	C ₄ H ₉ - <i>n</i>	+12.0 ⁵	+17.0 ⁵			+117.5 (C ₂ H ₅ OH) ⁵
B	C ₄ H ₉ - <i>n</i>	+12.0 ⁵	+17.0 ⁵			+117.5 (C ₂ H ₅ OH) ⁵
	C ₄ H ₉ - <i>t</i>	+7.8 ⁵	+25.5			+159.7 (CHCl ₃) ⁵
C	C ₃ H ₇ - <i>i</i>	+4.3 ⁵	+24.6		+79.8°	
					+74.3 (CHCl ₃)	+89.3 (CHCl ₃) ⁵
	C ₄ H ₉ - <i>t</i>	+7.8 ⁵	+25.5		+93.4	+159.7 (CHCl ₃) ⁵
					+86.3 (CHCl ₃)	

In the upper set A are compared the acetates and phthalates of three carbinols whose configurations have been determined by direct chemical means. In every case there is a dextro shift proceeding from the acetates to the phthalates. Examining the next two sets, B and C, in which methyl-tertiary-butylcarbinol is compared with methyl-*n*-butylcarbinol and methylisopropylcarbinol, respectively, it is seen that the same relations exist, *e. g.*, a dextro shift from the acetates to the phthalates, and from the acetates through the benzoates to the phthalates. If methyl-tertiary-butylcarbinol had the opposite configuration, then in B and C the shift would be levo, quite out of line with the other carbinols. Therefore according to the Displacement Rule, methyl-tertiary-butyl-, methylisopropyl- and methyl-*n*-butylcarbinols are configurationally related when all have the same sign of rotation.

CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃
HCOH	HCOH	HCOH	HCOH	HCOH	HCOH	HCOH	HCOH
C ₃ H ₇ - <i>n</i>	C ₃ H ₇ - <i>i</i>	C ₄ H ₉ - <i>n</i>	C ₄ H ₉ - <i>t</i>	C ₄ H ₉ - <i>i</i>	C ₆ H ₁₃ - <i>n</i>	C ₆ H ₁₁	C ₆ H ₅
[M] +12.1 ⁵	+4.3 ⁵	+12.0 ⁵	+7.8 ⁵	+21.1 ⁶	+12.7 ⁵	+6.5 ⁷	-52.5 ^{8,9}
						(+7.3) ^{8,9}	

(3) Freudenberg, *Ber.*, **66**, 177 (1933).

(4) This condition rules out the criticism of the Displacement Rule by Levene and Marker [*J. Biol. Chem.*, **97**, 384 (1932)].

(5) Pickard and Kenyon, *J. Chem. Soc.*, **99**, 45 (1911); **101**, 620 (1912); **105**, 830 (1914); **105**, 1115 (1914).

(6) Levene and Marker, *J. Biol. Chem.*, **90**, 669 (1931).

(7) Levene and Marker, *ibid.*, **92**, 379 (1932).

(8) See Freudenberg, "Stereochemie," 1932, p. 696.

(9) These carbinols were correlated by the Displacement Rule, Freudenberg, *Sitzber. Heidelberg Akad. Wiss.*, 1931, 9 Abh.

Above is assembled a series of carbinols showing the effect of the branched chain on optical activity. With the exception of the phenyl group, the isopropyl group causes the greatest depression of the optical activity, the cyclohexyl next and lastly the tertiary-butyl group, while the isobutyl group causes an exaltation.¹⁰ The unexpected fact that the isopropyl group causes a greater shift than the tertiary-butyl group may be due to the presence in the former of a tertiary hydrogen atom. Furthermore, it is not impossible that the depression of the optical rotation in the case of methyl-tertiarybutylcarbinol may be illusory, due to incomplete resolution. A determination of the configuration and maximum rotation of the next higher member of this series, ethyl-tertiary-butylcarbinol, would indicate whether a shift really exists or not. Work in this direction is now in progress.

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Experimental

In this work all rotations are dextro and for the homogeneous state unless otherwise designated.

Dextro Methylisopropylcarbinol Acetate.—8.8 g. of the carbinol was treated with 12.3 g. of acetic anhydride and 15 cc. of dry pyridine. After standing overnight at 25°, the mixture was warmed on the steam-bath for two hours, shaken with ice, ether and dilute sulfuric acid, then with dilute sodium hydroxide, dried over anhydrous potassium carbonate and fractionated through a 61-cm. adiabatic controlled reflux column.

1st fraction b. p. (758 mm.) 124–128.2°	2.7 g.	} 93% yield
2nd fraction b. p. (758 mm.) 128.2–128.9° α_D^{25} 3.64°	6.1 g.	
Residue	3.3 g.	

The second fraction was redistilled.

Dextro Methylisopropylcarbinol Benzoate.—6.0 g. of the carbinol dissolved in 15 cc. of dry pyridine was treated in the cold with 8.6 cc. (10.4 g.) of redistilled benzoyl chloride. The mixture after standing overnight at 25° was worked up as was the acetate, and distilled, b. p. (2 mm.) 80.5–81.0° (bath 105°), yield 9.2 g., α_D^{26} 9.26°. This material was redistilled, b. p. (2 mm.) 83–84° (bath 120°). The benzoate was colorless, almost odorless and contained no halogen by the Beilstein test.

Dextro Methyl-tertiary-butylcarbinol.—The carbinol, b. p. (764 mm.) 118–121°, prepared from tertiary-butylmagnesium chloride and acetaldehyde, was converted into the acid phthalate with phthalic anhydride and pyridine, and then resolved with brucine in acetone solution. Five recrystallizations of the salt were sufficient. The carbinol was recovered in the usual way and fractionated.

Dextro Methyl-tertiary-butylcarbinol Acetate.—9.0 g. of the carbinol was treated with 10.0 g. of acetic anhydride and 15 cc. of dry pyridine exactly as described for methylisopropylcarbinol acetate. The acetate was fractionated.

First fraction (756 mm.) 135–140.5°

Second fraction (756 mm.) 140.5–141.0° α_D^{27} 9.46°

The second fraction was redistilled.

(10) Similar relations hold in the hydrocarbon series, Levene and Marker, *J. Biol. Chem.*, **91**, 405 (1931); **95**, 1 (1932); **100**, 685 (1933).

SUMMARY OF PHYSICAL CONSTANTS AT 25°

	α 589	α 546	α 472	$\frac{472}{589}$ 589	d_4	n_D	B. p. °C.	Mm.
1 Methyl- isopropyl	0.90	1.07	1.45	1.611	0.810
2 Acetate	3.68	4.31	5.91	1.606	.860	1.3932	128.5-129	758
3 Benzoate	9.27 ^a	10.98 ^a	15.28 ^a	1.648	.979	1.4887
Methyl- <i>t</i> -butyl								
4 Carbinol	3.78 ^b	4.50 ^b	6.33 ^b	1.675	.810	120.0	760
5 Acetate	9.63	11.28	15.33	1.592	.856	1.4001	141.0 ¹³	756
6 Benzoate	27.92 ^a	33.03 ^a	46.00 ^a	1.647	.970	1.4882	105-105.5	5

	[M] _D	Max. [M] _D	Max. conv. factor	[α] _D (CHCl ₃)	Max. [M] _D (CHCl ₃)	Formula	Analyses, %			
							Carbon		Hydrogen	
						Calcd.	Found	Calcd.	Found	
1	0.979	4.296 ¹¹	4.39	
2	5.60	24.6	C ₇ H ₁₄ O ₂	64.6	64.5	10.8 10.9	
3	18.18 ^a	79.8	...	8.81 ^a	74.3	C ₁₂ H ₁₆ O ₂	75.0	75.2	8.4 8.2	
4	4.86	7.65 ¹²	1.574	
5	16.21	25.5	C ₈ H ₁₆ O ₂	66.6	66.0	11.2 11.2	
6	59.32	93.4	...	26.61 ^a	86.3	C ₁₃ H ₁₈ O ₂	75.7	75.7	8.8 8.9	

^a At 26°. ^b At 27°.

Dextro Methyl-tertiary-butylcarbinol Benzoate.—The benzoate was prepared as described for methylisopropylcarbinol benzoate, 6.0 g. of the carbinol yielding 8.4 g. of pure benzoate, b. p. (5 mm.) 105.0-106° (bath 138°), α_D^{25} 27.92°. This material was redistilled.

Summary

1. Dextro methyl-tertiary-butylcarbinol is configurationally related, according to the Displacement Rule of Freudenberg, to dextro methyl-*n*-butylcarbinol.

2. The tertiary-butyl group lowers the optical rotation, but not as much as the isopropyl group or the cyclohexyl group.

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(11) Calculated from Pickard and Kenyon's data, *J. Chem. Soc.*, **101**, 637 (1912).

(12) Calculated from data of Pickard and Kenyon, *ibid.*, **105**, 1121 (1914).

(13) Compare Whitmore and Rothrock, *THIS JOURNAL*, **55**, 1106 (1933).