The solid first dissolved, this was followed by the appearance of yellow colored needles. After cooling, the solution deposited a curdy yellow precipitate. The solid was recrystallized from ethyl acetate and melted at 209°; yield 0.12 g.

Anal. Calcd. for $C_{21}H_{21}NO_4$: C, 71.78; H, 6.02; N, 3.99. Found: C, 71.76, 72.15; H, 5.85, 6.14; N, 4.32, 4.24.

Summary

1. Methods have been described for the preparation of 1-cyano-1,4-di-(3′,4′-dimethoxyphenyl)-butanone-2, 1-carbamyl-1,4-di-(3′,4′-dimethoxyphenyl)-butanone-2 and 1,4-di-(3′,4′-dimethoxyphenyl)-butanone-2.

2. Attempts to prepare 1,4-di-(3′,4′-dimethoxyphenyl)-butanone-2 by means of a Friedel–Crafts reaction were unsuccessful.

BROOKLYN, N. Y. RECEIVED AUGUST 17, 1938

[CONTRIBUTION NO. 175 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, AND FROM THE CHEMICAL LABORATORY OF McGILL UNIVERSITY]

The Influence of Branched Chains on Optical Activity. The Configuration of Propyl-*t*-butylcarbinol, with a Note on the Relation between Rotatory Power and Chemical Character

BY PHILIP G. STEVENS, W. EDWARD HIGBEE[1] AND ROBERT T. ARMSTRONG[2]

In a previous paper on this subject[3] the configuration of dextro methyl-*t*-butylcarbinol, as determined by Freudenberg's displacement rule, was found to be the same as dextro methyl-*n*-butylcarbinol. It was therefore apparent from their molecular rotations, +7.8° and +12.0°, respectively, that the *t*-butyl group did not cause as great a shift in the rotation as the isopropyl (+4.7°), or the cyclohexyl (+7.4°) group. This result was unexpected as it was felt that, if branching of the chain were responsible for the observed shift, the completely branched *t*-butyl group would cause a greater shift. Therefore the suggestion was made that the real effect of the singly branched group was due to the presence of a tertiary hydrogen atom. According to the theories advanced by Kuhn and Freudenberg,[6] this hydrogen atom might well bring about a shift in the rotation, since it represents another center of chemical reactivity close to the asymmetric carbon atom.

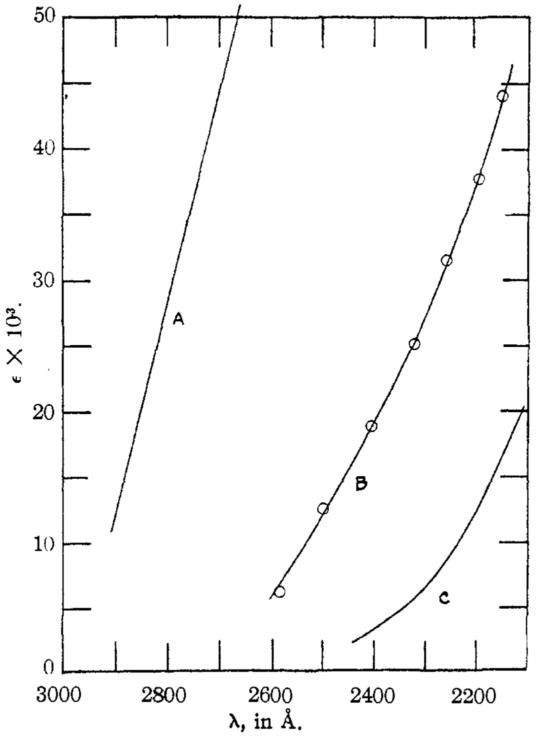

Fig. 1.—A, *n*-Butyl alcohol[4]; B, pinacolyl alcohol; C, ethyl alcohol.[5]

On the other hand, something may be abnormal about the *t*-butyl group. However, methyl-*t*-butylcarbinol shows no anomalous absorption bands in the near ultraviolet, and is similar to other carbinols as shown in Fig. 1. The high transmission of this carbinol as compared with other carbinols with a fewer number of carbon atoms may possibly be attributed to the high purity of the sample used.

Anomalous properties are often found in the lowest member of various series. This has been found to be true for the rotations of the isopropyl series.[7] A determination of the configuration of

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[1] Present address: Dennison Manufacturing Company, Framingham, Massachusetts.

[2] Present address: General Laboratories, U. S. Rubber Products Co., Passaic, New Jersey.

[3] Stevens, THIS JOURNAL, **55**, 4237 (1933).

[4] Bielecki and Henri, *Ber.*, **45**, 2819 (1912).

[5] Harris, *ibid.*, **55**, 1940 (1933).

[6] Kuhn, *Trans. Faraday Soc.*, **26**, 293 (1930); Kuhn, Freudenberg and Wolf, *Ber.*, **63**, 2367 (1930).

[7] Stevens, *ibid.*, **54**, 3732 (1932); Levene and Marker, *J. Biol. Chem.*, **101**, 413 (1933).

the third member of the *t*-butyl series, propyl-*t*-butylcarbinol, has now demonstrated that this is also the case here. This determination shows that levo propyl-*t*-butylcarbinol has the same configuration as dextro methyl-*t*-butylcarbinol on the basis of Freudenberg's displacement rule, for a dextro shift occurs in the rotations on passing from the acetates to the benzoates, and to the phthalates.

TABLE I

	$(M)_D$			
	Carbinol	acetate	Benzoate	Phthalate (CHCl$_3$)
$CH_3CHOHC_4H_9$-*t*	$+7.8$	$+25.5$	$+93.4$ $+86.3$ (CHCl$_3$)	$+159.7$
$C_3H_7CHOHC_4H_9$-*t*	-55.2[8]	-59.3	-19.9 -20.3 (CHCl$_3$)	$+8.4$

The *t*-butyl series belongs therefore to the same class as the isopropyl and cyclohexyl series, as shown in Table II.

TABLE II[9]

	$(M)_D$		
	CH_3	C_2H_5	C_3H_7
$CH_3CH_2CH_2CH_2CHOH$–	$+12.0$	$+9.4$	$+0.95$
$(CH_3)_2CHCHOH$–	$+4.7$	-16.7	-27.1
$C_6H_{11}CHOH$–	$+7.4$	-11.5	-17.0
$(CH_3)_3CCHOH$–	$+7.8$	....	-55.2

The high levo rotation of propyl-*t*-butylcarbinol shows that in cases where anomalies are avoided, the fully branched *t*-butyl group causes a much greater shift in the rotation than either of the other branched groups.[10]

It is therefore obvious that the controlling factor is not the tertiary hydrogen atom of the isopropyl and cyclohexyl groups, but rather the chemical character of the group as a whole. The chemical effect of branched chain groups is well established, as evidenced by the great difference in reactivity between primary, secondary and tertiary alcohols and halides. There is also a chemical effect of these groups when once removed from the hydroxyl group. This is shown by the marked tendency of carbinols containing these groups to undergo rearrangement when dehydrated or converted to halides.[11]

It is significant that only those carbinols which rearrange readily show a large shift in the rotation from the first to the next two higher members of the series. The sign of rotation is actually reversed in the latter two. Cyclohexylcarbinols, which show this large shift, have likewise now been found to rearrange. There seems therefore to be a connection between the chemical effect and rotatory effect of branched groups.

Table III shows the results on the conversion of several active carbinols to halides under standard conditions. The rotations and per cent. of rearrangement may be compared. There appears to be a relationship between the amount of rearrangement caused by each branched chain group, and the degree of rotatory shift, the order being cyclohexyl < isopropyl < *t*-butyl.

TABLE III

	Carbinol α_D	Chloride α_D	Chloride % *t*-Cl	Rearrangement %
$CH_3CHOHC_4H_9$-*n*	$+7.11$	-12.6	1.1	1[12]
$CH_3CHOHC_3H_7$-*i*	$+0.90$	-0.01	92.5	92–93
$CH_3CHOHC_6H_{11}$	$+4.59$	$+.17$	80.6	80–81
$CH_3CHOHC_4H_9$-*t*	$+3.78$	$-.02$	99.4	99–100
$C_3H_7CHOHC_4H_9$-*t*	$+29.82$	$+.72$	94.2	94–95

We are indebted to Professor James F. Norris for the facilities of the Laboratories of the Massachusetts Institute of Technology where the major part of this work was done, and also to the Mallinckrodt Chemical Works for donating so generously the large amounts of strychnine necessary in this work.

Experimental Part

In this work, all rotations are for the homogeneous state unless otherwise stated.

Dextro Propyl-*t*-butylcarbinol.—The carbinol, prepared from *t*-butylmagnesium chloride and *n*-butylaldehyde, was converted into the acid phthalate, and resolved with strychnine in 95% alcohol. After twelve crystallizations, the salt was decomposed, the phthalate examined, $(M)^{24}_D$ (CHCl$_3$) $-7.2°$ (max. $-8.4°$), and converted to the carbinol in the usual way, b. p. (36 mm.) 74.5–75.0°, n^{25}_D 1.4251, d^{25}_4 0.8215, $(M)^{25}_D$ $+47.2°$. The activity of the carbinol obtained from the corresponding unsaturated carbinol by reduction indicates that this value is not the maximum. By calculation the highest observed $(M)_D$ would be $+55.2°$. This is probably close to the maximum, and is tentatively therefore designated as the maximum.

Anal. Calcd. for $C_8H_{18}O$: C, 73.8; H, 13.9. Found: C, 73.9; H, 13.9.

Dextro Propyl-*t*-butylcarbinol Acetate and Benzoate.—These derivatives were prepared as described earlier for

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(8) Probably close to the maximum.

(9) Values from Pickard and Kenyon, *J. Chem. Soc.*, **99**, 45 (1911); **101**, 620 (1912); **105**, 830, 1115 (1914); Levene and Marker, *J. Biol. Chem.*, **97**, 379 (1932); Levene and Harris, *ibid.*, **111**, 723 (1935); Kuhn and Biller, *Z. physik. Chem.*, **B29**, 1 (1935).

(10) On this evidence the *t*-butyl group can be placed tentatively between the isopropyl group and the methyl group in Marker's configurational table]THIS JOURNAL, **58**, 976 (1936)].

(11) Michael and Leupold, *Ann.*, **379**, 271 (1910); Michael and Zeidler, *ibid.*, **385**, 227 (1911); Whitmore and Rothrock, THIS JOURNAL, **54**, 3431 (1932); **55**, 1106 (1933); Whitmore and Johnston, THIS JOURNAL, **60**, 2265 (1938).

(12) This value does not include the amount of rearrangement (presumably very small) resulting in isomeric secondary halides.

SUMMARY OF EXPERIMENTAL DATA[13]

	Carbinol		Carbinol α_D	Time, days	Crude chloride α_D	Crude chloride % tertiary Cl	Crude chloride n^{25}_D
A	CH_3-C_4H_9-*n*	(1)	+ 7.11	1	−12.58	1.1 (2 hr.)	1.4148
		(2)	+ 7.11	19	−11.52	0.8 (2 hr.)	1.4140[a]
B	CH_3-C_3H_7-*i*		+ 0.90	2	− 0.01	92.5 (0.6 hr.)	1.4058[c]
C	CH_3-C_6H_{11}		+ 4.59	7	+ 0.17	80.7 (4 hr.)[d]	...
D	CH_3-C_4H_9-*t*		+ 3.78	2	− 0.02	99.4 (0.5 hr.)	1.4174
E	C_3H_7-*n*-C_4H_9-*t*		+29.82	3	+ 0.72	94.2 (3 hr.)	...

Distilled Chloride

	B. p. °C.	B. p. Mm.	α_D	% tertiary Cl	n^{25}_D	d^{25}_4	Total chlorine, % Calcd.	Total chlorine, % Found
A	122–123	760	..	....	1.4153[b]	..	..	..
B	84.5–86.0[f]	760	..	....	1.4051[c]	..	..	..
C	69.5–70.0	19	+0.09[e]	84.0 (3 hr.)	1.4636	0.9697	24.2	25.0
D	111.0[f]	750	..	....	1.4175	..	..	..
E	56.0–56.3	19	+0.72	94.3 (3 hr.)	1.4320	.8794	23.9	24.6

[a] $n^{21.5}_D$ 1.4156.[14] [b] At 21,5°. [c] At 20°: *t*-amyl chloride before distillation, n^{20}_D 1.4054; *s*-isoamyl chloride, n^{20}_D 1.4095.[15] [d] Total chlorine, calcd. 24.2; found 24.2. [e] Distillation residue, α^{27}_D +0.44°. [f] With slight evolution of hydrogen chloride.

methyl-*t*-butylcarbinol derivatives,[3] the acetate, b. p. (20 mm.) 73.0–73.5°, $(M)^{23}_D$ +50.7° (max. +59.3°), n^{25}_D 1.4133, d^{25}_4 0.8568.

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.7; H, 11.6. Found: C, 69.9; H, 11.8.

The benzoate, b. p. (4 mm.) 117.5–117. 8° $(M)^{23}_D$ +17.0° (max. +19.9°), (max. $CHCl_3$, +20.7°), n^{25}_D 1.4873, d^{25}_4 0.9570.

Anal. Calcd. for $C_{15}H_{22}O_2$: C, 76.9; H, 9.4. Found: C, 77.1; H, 9.5.

Dextro Propenyl-*t*-butylcarbinol.—The highest rotation obtained with this carbinol, previously described,[16] was $(M)^{23}_D$ +23.5°, with a phthalate of $(M)^{23}_D(CHCl_3)$, −16.2°. Another sample, α^{22}_D −0.60°, yielded the saturated carbinol, when reduced with Adams platinum catalyst in alcohol solution, with α^{22}_D −1.41°.

Chloride Formation from Secondary Carbinols.—Seven to eleven cc. of each carbinol was sealed in a tube with 40–60 cc. of concentrated hydrochloric acid saturated with dry hydrogen chloride at −10°. The mixture was then allowed to warm up to 25°, shaking frequently. In all cases, except those of the octanols, the solution was homogeneous. In the latter, the carbinols did not dissolve in the hydrochloric acid, and the carbinol layer at first expanded, and then slowly contracted as the reaction proceeded. When the volume remained constant for a considerable length of time, the reaction was deemed complete. Generally, however, after one to two days, the chlorides had separated completely, and were then washed 2–5 times with concentrated hydrochloric acid, once each with ice water and iced sodium bicarbonate, and dried over anhydrous potassium carbonate. The chlorides were in every case free of olefins as shown by their failure to absorb bromine in either carbon tetrachloride or acetic acid. The chlorides were analyzed by Michael's method[11] for tertiary chlorides. This was carried out by shaking one gram of each with 250 cc. of water[17] until no more acid was evolved. This took about one-half to one hour, except in the cases of the more insoluble octyl chlorides which required three to four hours for hydrolysis to reach a standstill.[18]

Dextro Methyl-*t*-butylcarbinol.—The carbinol, b. p. 120° (760 mm.), α^{27}_D + 3.78°, was redistilled in an all-glass apparatus before determining the absorption spectrum with a Hilger Spekker Photometer and E316 Quartz Spectrograph. The molal extinction coefficient, *e*, was calculated from the formula $e = \frac{1}{cd} \log \frac{I_0}{I}$ where *c* was 7.97, the concentration in moles per liter, and *d* was 2, the length of the cell in centimeters. The sample examined showed continuous absorption as indicated in Fig. 1. After standing for several weeks, the same sample showed an intense absorption band at 2800 Å., due no doubt to partial oxidation to pinacolone.

Summary

1. Dextro methyl-*t*-butylcarbinol is configurationally related, according to the displacement rule of Freudenberg, with levo propyl-*t*-butylcarbinol.

2. The *t*-butyl group, in the third member of that series, causes a greater shift in the rotation than either the isopropyl or cyclohexyl groups.

3. A relation between rotatory power and chemical character has been pointed out, and in a number of cases confirmed.

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RECEIVED MAY 23, 1938

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[13] The rotations were measured at 21–27°.

[14] Compare Zelinski and Przewalski, *Chem. Zentr.*, **79**, II, 1854 (1908).

[15] Whitmore and Johnston, THIS JOURNAL, **55**, 5020 (1933).

[16] Stevens, THIS JOURNAL, **57**, 1112 (1935).

[17] The chloride from *s*-isoamyl alcohol was shaken with only 50 cc. of water.

[18] Compare Woodburn and Whitmore, THIS JOURNAL, **56**, 1394 (1934).