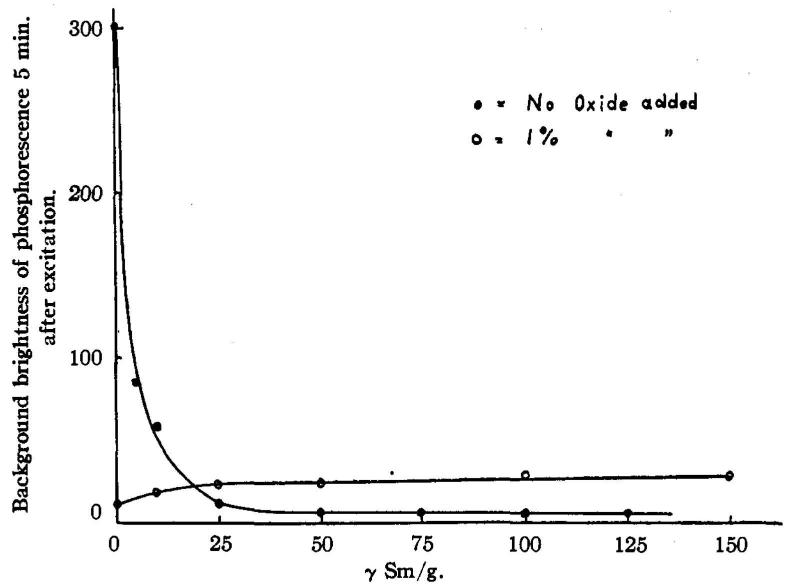

Fig. 14.—The phosphorescence of 100 SrS(0.001Eu, XSm) with and without the addition of oxide.

The phosphorescence was measured at one minute intervals after the phosphor had been fully excited. The data given represent the brightness at five minutes. From these results it would appear that the number of electrons which remain in the excited state is decreased by the addition of europium beyond 10 γ.

Samples of composition $100SrS(0.001Eu)12SrCl_2,xSrO$ where x varied from 0 to 2 were prepared and the phosphorescence measured as described above. The results, given in Fig. 13, show that the phosphorescence is lowered by a factor of one-third upon the addition of 0.5% strontium oxide and becomes practically zero at 1%.

The effect of the addition of samarium upon the phosphorescence of the europium phosphors $100SrS(xSm,0.001Eu)12SrCl_2$ and $100SrS(xSm,0.001Eu)12SrCl_2 \cdot 1SrO$ is shown in Fig. 14.

Unfortunately we have no theoretical interpretation of the peculiar influence of oxide upon the luminescent characteristics of the strontium sulfide phosphors. The measurement of brightness under infrared stimulation is obviously rather superficial. More fundamental information should be forthcoming from the measurement of light sum, quantum efficiency, photoconductivity, etc. Some preliminary investigations of these have been made.

The facts presented here, however, show clearly that impurities other than heavy metals may have profound effects on the behavior of these phosphors and that great care must be exercised in the preparation of samples.

Acknowledgments.—The authors wish to thank R. T. Ellickson and W. L. Parker for the construction of apparatus used in measuring the brightness of the phosphors.

Summary

A method is described by which reproducible measurements of the brightness of infrared sensitive phosphors can be made. The strontium sulfide–samarium, europium phosphor fluxed with lithium fluoride and with strontium chloride was shown to be affected by the addition of small quantities of strontium oxide. The presence of lithium fluoride or of calcium ions increases the tolerance of the phosphor toward oxide.

The dependence of the brightness of the phosphor upon the concentrations of samarium and europium, using strontium chloride as flux, was determined. It was shown that, at activator concentrations from 0 to 15 (γ) parts per million, the brightest phosphors are obtained with about equal concentrations of the two activators. At higher activator concentrations an excess of europium seems to be best. The brightest phosphors contain between 22 and 55 γ of europium and 17 and 42 γ of samarium per gram of strontium sulfide.

BROOKLYN, N. Y. RECEIVED JUNE 24, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Preparation of Optically Active Hydrocarbons by the Wurtz Reaction

BY R. L. LETSINGER

Of the attempts to prepare optically active hydrocarbons by the Wurtz reaction with secondary halides,[1,2] the only successful cases which have been reported are (a) the preparation of (+)2,3-diphenylbutane by the reaction of sodium with (−)1-chloro-1-phenylethane[3] and (b) the preparation of (−)3-methylnonane by the condensation of ethylsodium with (−)2-bromoöctane.[2] Even in these cases the yields were so low and the products so extensively racemized that the reactions are of little synthetic interest.

In the present paper it is shown that benzylsodium condenses with optically active 2-bromoöctane and 2-bromobutane to give good yields of the corresponding hydrocarbons and, furthermore, that in the reaction with 2-bromobutane a major portion of the optical activity is retained and an inversion of configuration probably occurs.

Hydrocarbon Preparation.—Data on the hydrocarbon syntheses are presented in Tables I and II. For comparative purposes, the reaction

---

[1] Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 386.

[2] Brink, Lane and Wallis, THIS JOURNAL, 65, 943 (1943).

[3] Ott, *Ber.*, 61, 2124 (1928).

TABLE I

REAGENTS FOR CONDENSATION OF ORGANOSODIUM COMPOUNDS WITH 2-BROMOALKANES[a]

Reaction	Sodium. g. atom	Alkyl, chloride, m.	Toluene, m.	Sodium reagent	Secondary bromide,		
						m.	$[\alpha]^{25}D$
1	0.50	0.25[b]	1.0	$C_6H_5CH_2Na$	2-BrC$_4$H$_9$[d]	0.037	0
2	.25	.125[b]	0.5	$C_6H_5CH_2Na$	2-BrC$_4$H$_9$	.035	+6.84
3	.25	.10[c]	1.0	$C_6H_5CH_2Na$	2-BrC$_8$H$_{17}$	.049	+28.8
4	.25	.10[c]	1.0	$C_6H_5CH_2Na$	2-BrC$_8$H$_{17}$	.050	−32.5
5	.50	.25[b]	...	C_4H_9Na	2-BrC$_8$H$_{17}$[e]	.050	0
6	.50	.25[b]	...	C_4H_9Na	2-BrC$_8$H$_{17}$	.050	−32.5

[a] Petroleum ether (b. p. 30–60°) was used as solvent. The quantities were: 70 cc. in Reaction 2 which was carried out in a 250-cc. flask, and 200 cc. in the other reactions which were carried out in a 500-cc. flask. [b] *n*-Butyl chloride. [c] *n*-Amyl chloride. [d] Eastman Kodak Co. *s*-butyl bromide was used. [e] The *d,l*-2-bromoöctane was prepared from *d,l*-2-octanol in the same manner as the optically active 2-bromoöctane.

TABLE II

PRODUCTS FROM CONDENSATIONS OF ORGANOSODIUM COMPOUNDS WITH 2-BROMOALKANES

Reaction	Hydrocarbon	Yield,[a] %	$[\alpha]^{25}D$	d^{25}_4	$n^{25}D$	B. p. °C.	Mm.
1	$C_7H_7CH(CH_3)C_2H_5$	64	....	0.8570	1.4856	86–87	20
2	$C_7H_7CH(CH_3)C_2H_5$	69	−2.25	.8572	1.4856	95	30
3	$C_7H_7CH(CH_3)C_6H_{13}$	80	+4.53	.8552	1.4828	135–136	15
4	$C_7H_7CH(CH_3)C_6H_{13}$	81	−5.20	.8534	1.4823	128–129	10
5	$C_4H_9CH(CH_3)C_6H_{13}$	36	....	.7512	1.4205	96–98	20
6	$C_4H_9CH(CH_3)C_6H_{13}$	35	0.00	.7510	1.4200	98–99	20

[a] Calculated on the basis of the 2-bromoalkane.

of an alkylsodium compound, butylsodium, is also included. The complete racemization observed in the butylsodium reaction and the extensive racemization reported for ethylsodium[2] suggest that a practical preparation of optically active hydrocarbons by this procedure may be limited to the use of organosodium compounds which do not appreciably exceed benzylsodium in activity. This point will be investigated further.

Extent of Racemization.—In order to determine the extent of racemization in the condensation step, it is necessary to know the maximum rotation for both the hydrocarbon formed and the alkyl bromide employed. An estimation of these rotations for optically active 1-phenyl-2-methylbutane and 2-bromobutane follows. The remaining discussion is limited to a consideration of the 1-phenyl-2-methylbutane synthesis since an independent value for the rotation of 1-phenyl-2-methyloctane is not available.

A sample of 1-phenyl-2-methylbutane which was prepared by the reaction of phenylsodium with optically active 2-methyl-1-bromobutane ($[\alpha]^{25}D + 3.84°$) had a rotation $[\alpha]^{25}D + 10.73°$. On the basis of Braun's value[4] for the maximum rotation of 2-methyl-1-bromobutane, the bromide employed in this reaction contained 95% optically active amyl bromide and 5% inactive material. The inactive material may have been either isoamyl bromide or *t*-amyl bromide. In order to estimate the amount of amylbenzene which would form from the impurity, therefore, the reactions of these two bromides with phenylsodium were investigated. Isoamyl bromide gave approximately one and a half times as great a yield of amylbenzene as did the active amyl bromide, whereas *t*-amyl bromide yielded no isolatable coupling product with phenylsodium. Therefore, since the 1-phenyl-2-methylbutane sample may have contained from zero to 7.5% of an inactive isomer (depending upon the relative amounts of isoamyl and *t*-amyl bromide which had been present), the maximum rotation for the pure hydrocarbon should lie between $[\alpha]^{25}D + 10.7°$ and $11.6°$[5,6]

The rotation of optically pure 2-bromobutane is not known. Different methods for preparing the bromide lead to different degrees of racemization.[7] The best case observed in this Laboratory was the conversion of 2-butanol, $[\alpha]^{25}D + 7.25°$, to 2-bromobutane with a rotation $[\alpha]^{25}D - 13.66°$. From this information and the maximum rotation of 2-butanol,[8] it is apparent that the rotation of a pure enantiomorph of 2-bromobutane would be at least $[\alpha]^{25}D$ 26.1°.

The extent of racemization in the reaction of benzylsodium with (+)2-bromobutane, which can be calculated from these rotations (11.6° for the hydrocarbon and 26.1° for the bromide) and the data in Tables I and II, is 26%. Since the values for the maximum rotations are only limiting values, however, the actual racemization is probably considerably less.

---

(4) Braun, *J. Research Natl. Bur. Standards*, **18**, 315 (1937).

(5) These limits correspond to $[M]^{25}D$ +15.8° and 17.1°. Therefore, the approximate value, $[M]^{25}D \doteq 9.5°$, set by Levene and Rothen, *J. Org. Chem.*, **1**, 85 (1936), was too low.

(6) These rotations are based on the assumption that no racemization occurred during the Wurtz step. This assumption is valid since the reaction is not at the asymmetric carbon atom, and Whitmore and Olewine, THIS JOURNAL, **60**, 2570 (1938), reported a series of reactions which involved conversion of optically active amyl alcohol to the Grignard, and back to the alcohol, with less than 10% racemization.

(7) (a) Kenyon, Phillips and Pittman, *J. Chem. Soc.*, 1072 (1935); (b) Levene and Marker, *J. Biol. Chem.*, **91**, 412 (1931); (c) Sprung and Wallis, THIS JOURNAL, **56**, 1717 (1934).

(8) Pickard and Kenyon, *J. Chem. Soc.*, **99**, 45 (1911).

Configuration.—(+)1-Phenyl-2-methylbutane corresponds to (−)2-methyl-1-butanol,[9] and (+)2-bromobutane corresponds to (+)2-butanol.[10] The determination of the configurational change in the benzylsodium condensation, therefore, depends upon a knowledge of the relationship of 2-methyl-1-butanol and 2-butanol. Unfortunately, this relationship has not been unequivocally established; however, a considerable body of evidence[7a,11] indicates that (−)2-methyl-1-butanol corresponds to (+)2-butanol. On this basis, the reaction of benzylsodium with 2-bromobutane (reaction 2) took place with an inversion of configuration.

A survey of related reactions revealed at least six other cases for which it is possible to relate the configuration of the reactant to (+)2-butanol and that of the product to (−)2-methyl-1-butanol. These reactions include the condensations of secondary bromides with methylmagnesium bromide,[12] ethylsodium,[2] and sodium malonic ester[7b,12] and the reactions of (+)*s*-butyl-*p*-toluenesulfonate[7a] with potassium cyanide and phenylmagnesium bromide. It is interesting that all of these reactions, and the benzylsodium condensation, are found to take place in the same stereochemical sense,[13] *i. e.*, either all take place with inversion or none of them do.

It has been demonstrated that a Walden inversion occurs in the reaction of sodium malonic ester with cyclopentene oxide.[14] Since this reaction probably takes place in the same manner as the condensation of sodium malonic ester with a secondary bromide,[14] this fact supports the view that all the reactions previously listed are accompanied by an inversion of configuration.

Experimental

2-Bromobutane.—Eastman Kodak Company white label 2-butanol was partially resolved by means of the brucine salt of the acid phthalate ester.[15] Physical constants for the optically active alcohols were: (−)2-butanol, b.p. 99–100°, $[\alpha]^{25}_{\mathrm{D}}$ − 3.82°, d^{25}_{4} 0.806, n^{25}_{D} 1.3931; (+)2-butanol, b.p. 99–100°, $[\alpha]^{25}_{\mathrm{D}}$ + 7.25°, d^{25}_{4} 0.807, n^{25}_{D} 1.3931.

The bromides were prepared by passing dry hydrogen bromide into solutions made up of equal parts of the alcohol and petroleum ether (b.p. 30–60°) at a temperature of 5–10°. The resulting mixtures were allowed to warm up slowly overnight, refluxed for four hours the following day, and worked up as described by Levene[7b]; yield, 50–59%. The bromide from (−)2-butanol boiled at 89–91°, $[\alpha]^{25}_{\mathrm{D}}$ + 6.84°, d^{25}_{4} 1.256, n^{26}_{D} 1.4330; that from (+)2-butanol boiled at 90–91°, $[\alpha]^{25}_{\mathrm{D}}$ − 13.66°, d^{25}_{4} 1.254.

2-Bromoöctane.—Eastman Kodak Co. 2-octanol was resolved by the method of Ingersoll,[15] and converted to the bromide with phosphorus tribromide according to Hsueh and Marvel[16]; b.p. of (+)2-bromoöctane 76° (15 mm.), $[\alpha]^{25}_{\mathrm{D}}$ + 28.8°, d^{24}_{4} 1.102, n^{25}_{D} 1.4481; b.p. of (−)2-bromoöctane, 84° (22-mm.), $[\alpha]^{25}_{\mathrm{D}}$ − 32.5°, d^{25}_{4} 1.101.

Amyl Bromides.—Optically active 2-methyl-1-butanol, obtained by fractionation of fusel oil, had the following constants:[17] $[\alpha]^{25}_{\mathrm{D}}$ −5.74°, d^{25}_{4} 0.8186, n^{25}_{D} 1.4077. It was converted to the bromide by the same procedure employed for the butyl bromides; b.p. of (+)2-methyl-1-bromobutane 120–120.5°, $[\alpha]^{25}_{\mathrm{D}}$ + 3.84°, d^{25}_{4} 1.214, n^{25}_{D} 1.4412.

Eastman Kodak Co. isoamyl bromide was used after distillation, b.p. 119–120°. *t*-Amyl bromide was prepared from Sharples refined *t*-amyl alcohol and hydrogen bromide at 0°; b.p. 44–45° (90 mm.).

Organosodium Reagents.—The preparation of the organosodium reagents and the condensation reactions were carried out in creased flasks with high speed stirring (5000 r.p.m.) in a nitrogen atmosphere. Petroleum ether (b.p. 30–60°) was used as solvent. Butylsodium, amylsodium[18a] and phenylsodium[18b] were prepared from the corresponding chlorides by the method of Morton and co-workers. Benzylsodium was prepared by the metalation of toluene[19]; amylsodium was used to metalate the toluene in the reaction in which 1-phenyl-2-methyloctane was prepared, and butylsodium was used as metalating agent in the preparation of 1-phenyl-2-methylbutane.

Condensations with 2-Bromoalkanes.—For the hydrocarbon synthesis the 2-bromoalkane, dissolved in an equal volume of petroleum ether (b.p. 30–60°), was added dropwise (fifteen-minute period) to the rapidly stirred suspension of organosodium reagent at a temperature of 20°. The resulting mixture was stirred for another hour, allowed to stand overnight and forced from the flask with nitrogen pressure onto Dry Ice the following morning. After the Dry Ice had disappeared, water was added (cautiously at first); the hydrocarbon layer was then separated by conventional methods and distilled at reduced pressure. Tests for unreacted halide were negative in all cases. Data on the quantities of reagents used in these experiments are given in Table I; data on the products are given in Table II.

Anal. (−)1-phenyl-2-methylbutane (Ex.2). Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.99; H, 10.78. (−)1-phenyl-2-methyloctane (Ex.4). Calcd. for $C_{16}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.01; H, 12.17.

Condensations with 2-Methyl-1-bromobutane.—Two reactions with phenylsodium were carried out. In the first case, (a), the major product was 3,6-dimethyloctane; in the second case, (b), the desired 1-phenyl-2-methylbutane was obtained in moderate yield. In both reactions the amyl bromide was added to the phenylsodium at 0° over a fifteen-minute period. After an hour of stirring at 0° and then another hour at 20–25° the mixture was forced with nitrogen pressure into a centrifuge bottle. Solid matter was separated by centrifugation, then recentrifuged with fresh petroleum ether. The combined hydrocarbon portions were distilled through a 6″ Vigreux column, and the solid phenylsodium was converted to sodium benzoate with Dry Ice. In both cases benzoic acid was isolated, and tests for halogen in the hydrocarbon portion were negative.

---

[9] (+)1-Phenyl-2-methylbutane has the same configuration as (−)2-methyl-1-butanol since there was no possibility for inversion in the reactions of hydrogen bromide with (−)2-methyl-1-butanol and of phenylsodium with (+)2-methyl-1-bromobutane. See also Levene, *J. Biol. Chem.*, **110**, 323 (1935).

[10] Cowdrey, Hughes, Ingold, Mastermann and Scott, *J. Chem. Soc.*, 1268 (1937).

[11] (a) Levene and Rothen, *J. Org. Chem.*, **1**, 76 (1936); (b) Levene and Rothen, *J. Biol. Chem.*, **116**, 209 (1936).

[12] Levene and Marker, *ibid.*, **97**, 563 (1932).

[13] The correlations of configurations can be made from the data of Levene and Rothen (note 11a) on the basis that secondary halides (note 10) and sulfonate esters (note 7a, also Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 160) have the same configuration as the corresponding alcohols of the same sign of rotation.

[14] Grigsby, Hind, Chanley and Westheimer, THIS JOURNAL, **64**, 2606 (1942).

[15] Ingersoll, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 400–404.

[16] Hsueh and Marvel, THIS JOURNAL, **50**, 855 (1928).

[17] For reported values for these constants see Whitmore and Olewine, *ibid.*, **60**, 2569 (1938); Braun, note 4.

[18] (a) Morton, Paterson, Donovan and Little, *ibid.*, **68**, 93 (1946); (b) Morton and Letsinger, *ibid.*, **69**, 172 (1947).

[19] Morton, Little and Strong, *ibid.*, **65**, 1339 (1943).

(a) The reaction was carried out in a 500-cc. flask with 11.5 g. (0.50 m.) sodium, 25.5 cc. (0.25 m.) chlorobenzene and 15.1 g. (0.1 m.) active amyl bromide. Distillation of the hydrocarbon layer gave 3.8 g. material boiling at 65–75° (30 mm.) and only 0.2 g. boiling from 75–90° (30 mm.). Redistillation of the first fraction yielded 3.3 g. hydrocarbon, b.p. 65–70° (28 mm.), $[\alpha]^{25}\text{D}$ + 18.7, $d^{25}{}_4$ 0.731, $n^{25}\text{D}$ 1.4166. Literature values for 3,6-dimethyloctane: $[\alpha]^{27}\text{D}$ + 16.85,[20] $d^{27}{}_4$ 0.7269,[20] $d^{15}{}_4$ 0.7402,[21] $n^{20}\text{D}$ 1.4145.[21]

Only a trace of 1-phenyl-2-methylbutane was obtained from this reaction. The principal product, apparently 3,6-dimethyloctane, was probably produced by a Wurtz reaction of the active amyl bromide with metallic sodium. To reduce the amount of sodium present during the condensation, therefore, excess chlorobenzene was employed in preparing the phenylsodium, and the effectiveness of the agitation was increased by carrying the reaction out in a smaller flask.

(b) A 250-cc. creased flask was employed with 5.75 g. (0.25 mole) of sodium, 15.5 cc. (0.152 mole) of chlorobenzene and 9.8 g. (0.065 mole) of amyl bromide.

The following fractions were obtained from the first distillation.

Fraction	B. p., °C. (30 mm.)	Wt., g.
1	60–75	1.4
2	75–94	0.2
3	94–103	3.8
4	Residue	1.2

Fraction 3 was redistilled twice to give 2.6 g. (27%) of 1-phenyl-2-methylbutane: b.p. 94° (28 mm.), $[\alpha]^{25}\text{D}$ + 10.73°, $d^{25}{}_4$ 0.854, $n^{25}{}_4$ 1.4862; literature values:[22] $d^{25}{}_4$ 0.8584, $d^{25}{}_4$ 0.855; $n^{25}\text{D}$ 1.4873, $n^{25}\text{D}$ 1.4849, etc.

Anal. Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.29, 89.34; H, 11.00, 11.11.

From redistillation of fraction 1, 0.8 g. hydrocarbon (3,6-dimethyloctane) was obtained, b.p. 65–70° (28 mm.), $n^{25}\text{D}$ 1.4171. (Compare values with those listed under experiment (a) for 3,6-dimethyloctane.)

Anal. Calcd. for $C_{10}H_{22}$: C, 84.43; H, 15.57. Found: C, 84.60; H, 15.66.

Condensations with Isoamyl Bromide and *t*-Amyl Bromide.—The procedure and quantities of reagents were the same as employed in the previous reaction (condensation of active amyl bromide and phenylsodium, b).

Distillation of the hydrocarbons from the isoamyl bromide reaction gave the fractions:

Fraction	B. p., °C. (31 mm.)	Wt., g.
1	42–85	0.7
2	85–98	0.2
3	98–107	4.5
4	residue	3.0

Isoamylbenzene (4.1 g. 43%) was obtained by distillation of fraction 3: b.p. 94–96° (28 mm.), $n^{24}\text{D}$ 1.4839, $d^{25}{}_4$ 0.854.

No *t*-amylbenzene was isolated from the reaction of phenylsodium with *t*-amyl bromide. After the removal of petroleum ether from the hydrocarbon layer biphenyl (2.2 g.) crystallized out, and on distillation no hydrocarbon forerun was obtained before the biphenyl started passing over.

Diacetamido Derivatives of 1-Phenyl-2-methylbutane.—These derivatives were prepared by the method of Ipatieff and Schmerling.[23] The derivative of (+)1-phenyl-2-methylbutane (from (+)2-methyl-1-bromobutane) melted at 201–202° (taken with an Anschütz thermometer immersed in the sulfuric acid-bath); that of the less active (−)1-phenyl-2-methylbutane (from (+)2-bromobutane) melted at 198–199°. The mixed m.p. was 198–199°. Ipatieff and Schmerling report 198–199° cor. as the m.p. of the *d,l*-diacetamido derivative of 1-phenyl-2-methylbutane.

Acknowledgment.—The author is very grateful to Professor Robert L. Burwell, who kindly supplied the sample of optically active 2-methyl-1-butanol which was used in this work. The analyses were performed by Margaret M. Ledyard and Patricia Craig. Ruth Peterson assisted in the resolution of 2-butanol.

Summary

(−)1-Phenyl-2-methylbutane and (+)1-phenyl-2-methyloctane were prepared in good yields by the reaction of benzylsodium with (+)2-bromobutane and (+)2-bromoöctane, respectively.

(+)1-Phenyl-2-methylbutane was prepared by the condensation of phenylsodium with (+)2-methyl-1-bromobutane.

The extent of racemization in the reaction of benzylsodium and 2-bromobutane was estimated and the stereochemical relationships were discussed.

EVANSTON, ILLINOIS RECEIVED JUNE 9, 1947

---

[20] Hardin and Sikorsky, *J. chim. phys.*, **6**, 179 (1907).

[21] Dupont, *Compt. rend.*, **156**, 1623 (1913). These values were obtained on the *dl* compound.

[22] Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1946.

[23] Ipatieff and Schmerling, THIS JOURNAL, **60**, 1476 (1938).