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STEREOCHEMISTRY OF THE PRIMARY CARBON—X

STEREOCHEMICAL CONFIGURATIONS OF SOME OPTICALLY ACTIVE DEUTERIUM COMPOUNDS*

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Abstract—The *iso*bornyloxymagnesium halide reduction of the appropriate deutero-aldehyde yields benzyl-α-*d* alcohol and 1-butanol-1-*d* having the same configuration and about the same level of optical purity. Arguments are presented that these alcohols are close to optical purity. The relative configurations of each alcohol were established by converting each to 1-phenylbutane-1-*d* using reactions of known or presumed stereochemistry. The rotations and configurations of 18 optically active deuterium compounds are summarized.

WE have previously described the preparation of optically active 1-butanol-1-*d*[1,2] and benzyl-α-*d* alcohol[3] by the partially asymmetric reduction of the corresponding deutero-aldehydes with the Grignard reagent of an optically active secondary alcohol. In this paper we derive the relative and absolute configurations of these alcohols and that of some other optically active deuterium compounds using considerations of stereochemistry based on reaction mechanisms. The alcohols were stereochemically interrelated by converting both to 1-phenylbutane-1-*d*.

Both alcohols have been prepared using the *iso*bornyl system as the reducing agent. The use of this system is especially convenient since it can be prepared readily from camphor which is available as the optically pure dextrorotatory enantiomer. Lithium aluminum hydride reduction yields (—) *iso*borneol contaminated with about 10 per cent of borneol.[4] Vavon and Antonini[5] have shown that *iso*bornyloxymagnesium bromide will reduce phenyloxalic acid to yield mandelic acid of 15 per cent optical purity; borneol was inert to these conditions. Since borneol reacts so much more slowly than *iso*borneol, its presence in the reducing agent is not objectionable.

The reduction of benzaldehyde-*d* with *iso*bornyloxymagnesium bromide gave benzyl-α-*d* alcohol having $[\alpha]_D$ —0·715°.‡ This alcohol is used as an internal standard; in subsequent reactions diluted material was often used but the rotations are readily corrected to correspond to the level of optical purity of the standard benzyl-α-*d* alcohol.

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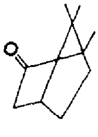
† This paper was taken in part from the Ph.D. Dissertations of J. R. Wolfe, Jr. (1957) and W. D. Schaeffer (1956), University of California.

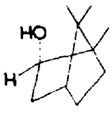
‡ This rotation is about 10 per cent higher than that previously determined,[3] because of the use of benzaldehyde-*d* of higher deuterium content. The deutero-aldehyde was prepared by the Stephen reduction of benzonitrile with stannous chloride and deuterium chloride. Slotta and Kethur[6] have reported that completely anhydrous stannous chloride will not dissolve in ether. The water present in the original preparation explains the isolation of isotopically impure benzaldehyde-*d*.[3] In the present case anhydrous stannous chloride was prepared and some deuterium oxide was added prior to the Stephen reduction. The resulting benzaldehyde-*d* had only a very weak triplet at 3·6 μ indicative of aldehydic hydrogen; the benzyl-α-*d* alcohol prepared from this aldehyde had 0·98 atoms of deuterium per molecule.

[1] A. Streitwieser, Jr., *J. Amer. Chem. Soc.* **75**, 5017 (1953).
[2] A. Streitwieser, Jr. and W. D. Schaeffer, *J. Amer. Chem. Soc.* **78**, 5597 (1956).
[3] A. Streitwieser, Jr. and J. R. Wolfe, Jr., *J. Amer. Chem. Soc.* **79**, 903 (1957).
[4] D. S. Noyce and D. B. Denney, *J. Amer. Chem. Soc.* **72**, 5743 (1950).
[5] G. Vavon and A. Antonini, *C. R. Acad. Sci., Paris* **232**, 1120 (1951).
[6] K. H. Slotta and R. Kethur, *Ber.* **71**, 335 (1938).

The mechanism of reduction by halomagnesium alkoxides has been proposed to involve a quasi six membered ring.[7,8] Hence, our reductions are directly analogous to the elegant work of Doering and Young[9] on the partially asymmetric reductions of ketones with aluminum alkoxides. The absolute configuration of (+) camphor is I.[*] Hence, (—) *iso*borneol which is formed on reduction is II. This configuration can be represented as III in which the small methylene group, S, is at the rear and the large quaternary carbon group, L, is in front. In the reduction of a deutero-aldehyde by a halomagnesium alkoxide from III the cyclic mechanism[7,8] can proceed by each of two transition states. The more stable depicted in IV involves steric interactions between the small group, S, and the large group, R, and between the large group, L, and the small deuterium. The alternative structure involves steric oppositions between the large L group and the large R group and is of higher energy.[9] The deutero-alcohol which results from IV has the configuration in V.



I



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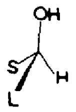

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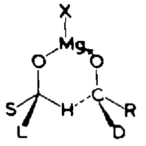
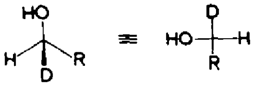
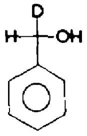


IV



V

Since this reduction with benzaldehyde-*d* yields (—) benzyl-α-*d* alcohol, the (+) alcohol has the configuration VI. It is interesting that (+) α-phenethyl alcohol has the same configuration[15] with a methyl group replacing the deuterium.



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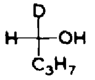

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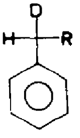

VIII

[*] The stereochemical interrelationships among the terpenes as interpreted by Hückel[10] and their relationship with the sugars by the "quasi-racemate" method of Fredga[11] has been summarized by Birch.[12] Fredga's assignments have been confirmed by the elegant chemical conversions of Freudenberg[13] and of Noyce and Denney.[14]

[7] M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances* p. 160. Prentice-Hall, New York (1954).

[8] H. S. Mosher and E. LaCombe, *J. Amer. Chem. Soc.* **72**, 3994 (1950).

[9] W. E. Doering and R. W. Young, *J. Amer. Chem. Soc.* **72**, 631 (1950); L. M. Jackson, J. A. Mills and J. S. Shannon, *Ibid.* **72**, 4814 (1950). ,

[10] W. Hückel, *J. prakt. Chem.* **157**, 225 (1941).

[11] A. Fredga, *The Svedberg Memorial Volume* p. 261. Almquist and Wiksells Boktryckeri, Upsala (1944); *Acta Chem. Scand.* **1**, 361 (1947).

[12] A. J. Birch, *Ann. Rep. Prog. Chem.* **47**, 192 (1950).

[13] K. Freudenberg, *Angew. Chem.* **65**, 259 (1953).

[14] D. S. Noyce and D. B. Denney, *J. Amer. Chem. Soc.* **76**, 768 (1954).

[15] J. A. Mills and W. Klyne in W. Klyne's *Progress in Stereochemistry* Vol. I, p. 187. Butterworths Scientific Publications, London (1954).

The reduction of undeuterated butyraldehyde with deuterated *iso*borneol yields deuterated butyl alcohol having α_D +0·154 ± 0·104° (l4) and 0·55 deuterium atoms per molecule. Thus the 1-butanol-1-*d* produced in this reduction has $[\alpha]_D$ +0·172 ± 0·004. By the same argument considered above, the (+) alcohol has the configuration in VII. Benzyl-α-*d* alcohol and 1-butanol-1-*d* of the same sign of rotation have the same configuration according to this reasoning. The same conclusion with respect to the absolute configuration of 1-butanol-1-*d* was reported by Levy, Loewus and Vennesland[16] based on application of the same reasoning to the production of (−) 1-butanol-1-*d* by the reduction of butyraldehyde with (+) 2-octanol-2-*d*.[1] This agreement may be taken as additional evidence for the correctness of the relative configurations assigned to *iso*borneol and 2-octanol.

The tosylate prepared from benzyl-α-*d* alcohol having α_D^{25} −0·983 ± 0·004° (*l*4), with tosyl chloride and pyridine was treated with sodioacetoacetic ester in benzene to yield ethyl benzyl-α-*d*-acetoacetate, α_D^{25} −0·263 ± 0·005° (*l*2). The formation of the tosylate ester does not affect the asymmetric center; the subsequent reaction of the tosylate is undoubtedly a direct displacement reaction with complete inversion of configuration;* Hence, the (−) substituted acetoacetic ester is represented by VIII (R = $CH(COOC_2H_5)COCH_3$). Hydrolysis of ethyl benzyl-α-*d*-acetoacetate, α_D^{25} −0·145° ± 0·004° (*l*2), gave 4-phenyl-2-butanone-4-*d*, α_D^{26} −0·158 ± 0·008° (*l*2); Clemmensen reduction gave 1-phenylbutane-1-*d*, α_D^{26} −0·179 ± 0·005° (*l*1·5). Since these reactions take place away from the asymmetric center, the (−) ketone and (−) hydrocarbon are represented by VIII (R = CH_2COCH_3 and $CH_2CH_2CH_3$, respectively). By application of the appropriate corrections the rotation of 1-phenylbutane-1-*d* which corresponds to the standard alcohol is $[\alpha]_D$ −0·78 ± 0·04°.

Thermal decomposition of the chlorosulfite prepared from 1-butanol-1-*d*, α_D^{25}−0·142 ± 0·004° (*l*4), gave 1-chlorobutane-1-*d*, α_D^{25} + 0·147 ± 0·004° (*l*2), with 91 ± 2 per cent inversion of configuration.[17] The stereochemistry of this reaction was established by a comparison of the optical activity of the 1-butyl-1-*d* acetate prepared by esterification of the starting alcohol with that observed by the direct displacement of the butyl chloride with tetramethylammonium acetate in acetone. Hence the configuration of the (+) chloride is IX (R = Cl).

1-Phenylbutane-1-*d* was prepared from the chloride by reaction with excess phenyl lithium in benzene. The reaction of phenyl lithium with *n*-butyl chloride in butyl ether has been shown to yield *n*-butylbenzene in high yield and to follow second order kinetics.[18] Hence this reaction is very probably of the direct displacement type of inversion of configuration.† Because of the solubility of lithium chloride in ethers and the consequent possibility of partial racemization of 1-chlorobutane-1-*d* by the

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* The reaction of benzyl-α-*d* tosylate with alcoholic sodium ethoxide has been demonstrated to go with complete inversion of configuration (J. R. Wolfe, Jr., unpublished results).

† Several analogous cases are known involving the reactions of sodium alkyls with *sec*-alkyl halides.[19–23] The reactions of benzylsodium with *sec*-butyl chloride[22] and of allylsodium with α-phenethyl chloride[23] apparently involve little, if any, racemization. Corresponding reactions of a primary chloride would be expected to involve still less racemization.

[16] H. R. Levy, F. A. Loewus and B. Vennesland, *J. Amer. Chem. Soc.* **79**, 2949 (1957).

[17] A. Streitwieser, Jr. and W. D. Schaeffer, *J. Amer. Chem. Soc.* **79**, 379 (1957).

[18] S. J. Cristol, J. W. Ragsdale and J. S. Meeks, *J. Amer. Chem. Soc.* **73**, 810 (1951).

[19] R. L. Letsinger, *J. Amer. Chem. Soc.* **70**, 406 (1948).

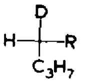
[20] R. L. Letsinger and J. G. Traynham, *J. Amer. Chem. Soc.* **72**, 849 (1950).

[21] S. E. Ulrich, F. H. Gentes, J. F. Lane and E. S. Wallis, *J. Amer. Chem. Soc.* **72**, 5127 (1950).

[22] R. L. Letsinger, L. G. Maury and R. L. Burwell, Jr., *J. Amer. Chem. Soc.* **73**, 2373 (1951).

[23] R. L. Burwell, Jr., A. D. Shields and H. Hart, *J. Amer. Chem. Soc.* **76**, 908 (1954).

chloride ion liberated in the reaction, the displacement with phenyl lithium was carried out in benzene solution, in which lithium chloride is insoluble. There is the possibility that the excess phenyl lithium would cause partial racemization of the product 1-phenylbutane-1-*d* by a metalation reaction. This possibility was eliminated



$$\begin{array}{c} D \\ H - \!\!\!+\!\!\! - R \\ C_3H_7 \end{array}$$

IX

by a comparison of the rotation of 1-phenylbutane-1-*d* isolated after about 80 per cent reaction, α_{D}^{25} $-0{\cdot}142 \pm 0{\cdot}01°$ (*l*1) with that isolated after complete reaction, α_{D}^{25} $-0{\cdot}148 \pm {\cdot}01°$ (*l*1). Hence, the (+) hydrocarbon has the configuration IX ($R = C_6H_5$)—the (−) hydrocarbon is VIII ($R = C_3H_7$). This configuration is identical with that assigned from the benzyl-α-*d* alcohol approach and confirms the relative configurations deduced above for the alcohols.

By comparing the rotations of the 1-phenylbutane-1-*d*'s obtained from the two alcohols and working back in a straight-forward manner, the rotation of 1-butanol-1-*d* of the same optical purity as benzyl-α-*d* alcohol is $[\alpha]_{\mathrm{D}}^{25}$ $0{\cdot}185 \pm 0{\cdot}018°$. The 1-butanol-1-*d* produced by the reduction of butyraldehyde-*d* with 2-octanol had only about one-fourth this rotation; however, that obtained from the *iso*borneol reduction had $0{\cdot}93 \pm 0{\cdot}09$ times this rotation (*vide supra*); i.e., *iso*borneol reduces benzaldehyde and butyraldehyde with about equal stereospecificity although the stereospecificity involves a differential steric effect with a phenyl group on the one and with a *n*-propyl group on the other. In other asymmetric reactions, a phenyl group is usually considered to have a larger effective bulk than a *n*-alkyl group;[24] consequently, we would expect the reduction of benzaldehyde to be rather more stereospecific than the reduction of butyraldehyde. The approximate equality of the stereospecificity strongly suggests that both reductions with *iso*borneol are close to 100 per cent stereospecific; i.e., the rotation of the standard benzyl-α-*d* alcohol (*vide supra*) is rather close to the rotation of optically pure alcohol.

This conclusion about the near optical purity of the alcohols obtained by the *iso*borneol reduction receives further support by the following arguments. In an elegant series of experiments, Loewus, Westheimer and Vennesland[25] demonstrated that ethanol-1-*d* produced by the enzymatic reduction of acetaldehyde-*d* by yeast alcohol dehydrogenase is optically pure. Enough of this alcohol was recently isolated for a determination of the rotation, $[\alpha]_{\mathrm{D}}$ $-0{\cdot}28 \pm 0{\cdot}03°$.[16] It is a reasonable assumption that the molecular rotation of ethanol-1-*d* and butanol-1-*d* be closely comparable.* If they were identical, optically pure butanol-1-*d* would have $[\alpha]_{\mathrm{D}}$ 0·18°. The close correspondence with the observed value is probably fortuitous but demonstrates that our alcohols are probably not far from optical purity.

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[*] In the series of methyl *n*-alkyl carbinols the molecular rotations change smoothly from 10·3° for 2-butanol to 14·5° for 2-tridecanol; the variation from 2-octanol to 2-tridecanol is less than 2°.[26] To the extent that the variations in rotation are due to a comparison of the mass of the alkyl group with the methyl group, substitution of deuterium for methyl should cause the molecular rotations to effectively level off much earlier in the series. *Added in proof:* The analogy may be inappropriate; preliminary experiments suggest that ethanol-1-*d* and butanol-1-*d* of the same configuration have opposite rotations.

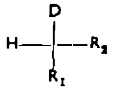
[24] D. J. Cram and F. A. A. Elhafez, *J. Amer. Chem. Soc.* **74**, 5828 (1952).

[25] F. A. Loewus, F. H. Westheimer and B. Vennesland, *J. Amer. Chem. Soc.* **75**, 5018 (1953).

[26] J. H. Pickard and J. Kenyon, *J. Chem. Soc.* **99**, 45 (1911).

A similar argument applies to 1-phenylethane-1-*d* which was originally prepared by Eliel[27] as one of the first compounds known with demonstrated optical activity due to hydrogen-deuterium asymmetry. The optically pure hydrocarbon has a rotation of about $[\alpha]_D$ −0·73 ± 0·06°;* the molecular rotation, $[M]_D$ +0·68 ± ·06° is only slightly higher than the molecular rotation, $[M]_D$ −0·58 ± ·04°, of the 1-phenylbutane-1-*d* obtained from benzyl-α-*d* alcohol and suggests again the near

TABLE 1. ROTATIONS AND CONFIGURATIONS OF OPTICALLY ACTIVE DEUTERIUM COMPOUNDS



R_1	R_2	$[\alpha]_D$[a]	Reference
C_6H_5	OH	+0·715 ± 0·002°	b
C_6H_5	Br	+0·60 ± 0·20°	3
C_6H_5	$OCOCH_3$	+0·172 ± 0·004°	3
C_6H_5	$OCOC_6H_4COOH(o)$	−0·219 ± 0·005°[c]	3
C_6H_5	NH_2	−1·025 ± 0·015°	28
C_6H_5	$CH(COOEt)COCH_3$	−0·39 ± 0·01°	b
C_6H_5	CH_2COCH_3	−0·44 ± 0·03°	b
C_6H_5	OC_2H_5	+0·096 ± 0·003°	28
C_6H_5	$CH_2CH_2CH_3$	−0·78 ± 0·04°	b
C_6H_5	CH_3	−0·73 ± 0·06°	d
$CH_2CH_2CH_3$	OH	+0·185 ± 0·018°	
$CH_2CH_2CH_3$	Cl	+0·39 ± 0·03°	17
$CH_2CH_2CH_3$	$OCOCH_3$	−0·48 ± 0·04°	17, 29
$CH_2CH_2CH_3$	$OSO_2C_6H_4NO_2(p)$	−0·136 ± 0·038°[e]	30
$CH_2CH_2CH_3$	$OSO_2C_6H_4Br(p)$	−0·078 ± 0·016°	29
$CH_2CH_2CH_3$	$OCOC_6H_4COOH(o)$	−0·38 ± 0·05°[e]	29, 31
CH_3	OH	+0·28 ± 0·03°	17
CH_3	CH_2CH_3	−0·56 ± 0·01°	32

[a] Rotations are given for the undiluted liquids (neat) unless stated otherwise; except for 1-phenylethane-1-*d* and ethanol-1-*d*, the rotations refer to compounds of the same relative optical purity. The two exceptions are optically pure compounds.

[b] This paper.

[c] Acetone, c 20.

[d] See text.

[e] Acetone, c 28.

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* Eliel[27] prepared 1-phenylethane-1-*d*, $[\alpha]_D^{25}$ −0·30°, by the reaction of α-phenethyl chloride, $[\alpha]_D^{25}$ −49·2°, with lithium aluminum deuteride. Optically pure α-phenethyl chloride has $[\alpha]_D$ 117 ± 8°;[33] hence, if the reduction is considered to be a direct displacement reaction with complete inversion of configuration, optically pure 1-phenylethane-1-*d* has $[\alpha]_D^{25}$ 0·70 ± ·05°. In a repetition of this experiment in these laboratories, α-phenethyl chloride, $[\alpha]_D^{28}$ +59·9° gave 1-phenylethane-1-*d*, $[\alpha]_D^{26}$ +0·390°, whence for optically pure material the rotation is $[\alpha]_D^{26}$ 0·76 ± ·05° (L. Reif, unpublished results).

[27] E. C. Eliel, *J. Amer. Chem. Soc.* **71**, 3970 (1949).

[28] J. R. Wolfe, Jr., unpublished results.

[29] A. Streitwieser, Jr., *J. Amer. Chem. Soc.* **77**, 1117 (1955).

[30] A. Streitwieser, Jr. and W. D. Schaeffer, *J. Amer. Chem. Soc.* **79**, 6233 (1957).

[31] S. Andreades, unpublished results.

[32] G. K. Helmkamp, C. D. Joel and H. Sharman, *J. Org. Chem.* **21**, 844 (1956).

optical purity of our preparations. It is interesting to note that 1-phenylethane-1-*d* and 1-phenylbutane-1-*d* of the same rotation have the same configuration.

The rotations and configurations of a number of optically active deuterium compounds are summarized in Table 1. The rotations of the compounds derived from the benzyl or butyl systems are given for materials of the same optical purity as the standard benzyl-α-*d* alcohol; by the arguments presented above these rotations all correspond to materials of near optical purity.

EXPERIMENTAL

Benzyl-α-d *alcohol*. The benzaldehyde-*d* used in this preparation was synthesized as before[3] with the following modifications: Anhydrous stannous chloride was prepared by the method of Stephen[33] and was stored over concentrated sulfuric acid under reduced pressure for several days. After the addition of 1·5% by weight of deuterium oxide the material was used for the Stephen reduction of benzonitrile.[8] The deuterium chloride required for this reduction was prepared by the reaction of benzoyl chloride with deuterium oxide. The product benzaldehyde-*d* was isolated and purified as the sodium bisulfite addition compound. In the best of several runs 34% of the addition compound was obtained using 3 moles of benzonitrile, 2·73 moles of deuterium oxide and 3·5 moles of stannous chloride in 1200 ml of dry ether. The reduction to optically active benzyl-α-*d* alcohol was accomplished as previously described.[8] The product had α_{D}^{30} −3·006 ± 0·004° (l4), α_{5463}^{30} −3·669 ± 0·004° (l4), n_{D}^{20} 1·5383 and d_{4}^{25} 1·0509. The density of the alcohol corresponds to a deuterium content of 0·98 deuterium atoms per molecule.[34]

Benzyl-α-d p-*toluenesulfonate*. The method used was essentially that of Edgell and Parts[35] for the synthesis of methyl tosylate. In a dry system 20 g of dry pyridine and 10 ml of benzyl-α-*d* alcohol were cooled to −40°. After the addition of 28·6 g of tosyl chloride, 80 g of dry pyridine was dropped in over a period of 1·5 hr and the mixture was stirred for an additional 1·5 hr while the system was maintained at −40°. The mixture was poured into 2 liters of ice water and extracted with ether. The washed and dried ether solution was cooled to 0° and a large excess of dry pentane or hexane was added to induce crystallization. The filtered crystals were maintained in vacuum at 0° to remove remaining solvent and were stored at dry ice temp until used. The yield was 50–55%.

Ethyl benzyl-α-d-*acetoacetate*: To the sodioacetoacetic ester prepared from 32·6 g of redistilled ethyl acetoacetate and 5 g of powdered sodium in 300 ml of dry benzene, was added at room temp 200 ml of a benzene solution containing the benzyl-α-*d* tosylate prepared from 10 ml of benzyl-α-*d* alcohol having α_{D}^{25} −0·983 ± 0·004°, α_{5463}^{25} −1·216 ± 0·013° (l4). After stirring for 24 hr, the mixture was poured into ice and dilute sulfuric acid. The washed and dried organic phase was distilled yielding 10 g (45% yield) of ethyl benzyl-α-*d*-acetoacetate, b.p. 148–152° (6 mm), having α_{D}^{25} −0·263 ± 0·005° (l2).

4-*Phenyl-2-butanone*-4-d: Ethyl benzyl-α-*d*-acetoacetate, α_{D}^{28} −0·145° ± 0·004° (l2), was stirred with 5% aqueous sodium hydroxide for several hours. After extraction with ether the aqueous solution was acidified with sulfuric acid and was steam distilled. The distillate was extracted with ether. Distillation of the washed and dried ether extract afforded the product ketone, b.p. 115–118° (12–13 mm), α_{D}^{26} −0·158 ± 0·008° (l2).

1-*Phenylbutane*-1-d *from* 4-*phenyl-2-butanone*-4-d: The ketone (3·6 ml) prepared above was refluxed for 10 hr with dilute hydrochloric acid and zinc amalgam prepared from 60 g of mossy zinc and 8 g of mercuric chloride. Additional hydrochloric acid was added at intervals. The cooled reaction mixture was extracted with pentane. Distillation of the dried extract gave 2·3 ml of colorless hydrocarbon, b.p. 106–107° (75 mm), α_{D}^{27} −0·188 ± 0·004° (l1·5). After purification of the product by chromatography on silica gel followed by treatment with acidic potassium permanganate, the redistilled material had α_{D}^{26} −0·179 ± 0·005° (l1·5).

1-*Phenylbutane*-1-d *from* 1-*chlorobutane*-1-d: In an atmosphere of nitrogen 100 ml of a benzene solution ·83 M in phenyllithium and 4·82 g of optically active 1-chlorobutane-1-*d*, α_{D}^{25} +0·147 ± 0·004°

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[33] A. J. Vogel, *Practical Organic Chemistry* p. 193. Longmans, Green, London (1948).

[34] A. McLean and R. Adams, *J. Amer. Chem. Soc.* **58**, 804 (1936).

[35] W. F. Edgell and L. Parts, *J. Amer. Chem. Soc.* **77**, 4899 (1955).

(*12*), was refluxed. Periodically, 1 ml aliquots were withdrawn and titrated to yield the second order rate constants summarized in Table 2. After 24 hr (about 80% reaction) two-thirds of the reaction mixture was poured into dilute hydrochloric acid. The separated organic phase was dried and distilled to yield 1·1 ml of material, b.p. 82–87° (35 mm). The infrared spectrum showed the presence of considerable phenolic material, hence the product was washed with dilute sodium hydroxide and redistilled to yield 0·25 ml of 1-phenylbutane-1-*d*, b.p. 180–185°, α_D^{25} −0·148 ± 0·01° (*l*1).

TABLE 2. KINETICS OF DISPLACEMENT OF 1-CHLOROBUTANE-1-*d* BY PHENYL LITHIUM

Time (sec)	Titer	$k_2 \times 10^5$ (l. mole/sec)
0	0·790	—
2520	0·750	4·4
11900	0·635	2·8
18000	0·610	3·7
61200	0·454	3·4
∞	0·275	—
	Av.	3·6 ± 0·5

The remaining one-third of the reaction mixture was refluxed an additional 24 hr and after cooling was poured into dilute sodium hydroxide. The dried organic phase was distilled to yield 0·3 ml of hydrocarbon, b.p. 78–82° (30 mm), α_D^{25} −0·142 ± 0·01° (*l*1). The infrared spectra of the two samples were identical.