[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Displacement Reactions Involving Optically Active Alkyl Bromides and Organometallic Compounds[1]

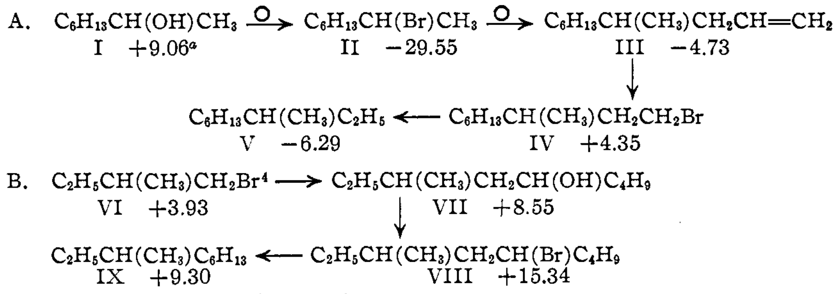
BY ROBERT L. LETSINGER AND JAMES G. TRAYNHAM

Although the displacement reactions which occur with optically active halides and the comparatively weaker bases (such as sodium hydroxide and sodium alkoxide) have been extensively investigated, only a very limited amount of information has been available on the analogous reactions which involve the strong bases of the organometallic compound class. In the cases examined, the yields of coupling products were generally low or unreported and the products were extensively or totally racemized.[2] Where appreciable optical activity was retained, data concerning the extents of racemization and configurational changes were lacking. We undertook an investigation to see if there were displacement reactions which would give good yields of optically active hydrocarbons and for which the extent of racemization and configurational changes could be determined. The reaction of benzylsodium with (−)2-bromobutane was found to be of this type and has been reported.[3] In this paper we describe a similar reaction, the formation of (−)4-methyl-1-decene from allylsodium and (−)2-bromoöctane. For the purpose of comparison, the reactions of benzylmagnesium chloride and allylmagnesium bromide with optically active 2-bromobutane and 2-bromooctane, respectively, were also investigated.

Allylsodium Reaction.—Allylsodium was prepared by the cleavage of diallyl ether in hexane with sodium metal. The reaction with optically active 2-bromoöctane ($[\alpha]^{20}D - 29.55$) proceeded smoothly to give an 83% yield of the decene ($[\alpha]^{20}D - 4.73$).

Racemization and Configuration.—In order to determine the extent of racemization in this reaction, it was necessary to know the optical rotation for the pure enantiomorphs of both 4-methyl-1-decene and 2-bromoöctane.

The former value was calculated from the rotation of two samples of 3-methylnonane, one of which was prepared from the (−)4-methyl-1-decene and the other from (−)2-methyl-1-butanol. A flow sheet for these reactions follows.



$$\begin{tikzcd} \text{A.}\ \underset{\text{I}\ +9.06^a}{C_6H_{13}CH(OH)CH_3} \arrow[r, "O"] & \underset{\text{II}\ -29.55}{C_6H_{13}CH(Br)CH_3} \arrow[r, "O"] & \underset{\text{III}\ -4.73}{C_6H_{13}CH(CH_3)CH_2CH{=}CH_2} \arrow[d] \\ & \underset{\text{V}\ -6.29}{C_6H_{13}CH(CH_3)C_2H_5} & \underset{\text{IV}\ +4.35}{C_6H_{13}CH(CH_3)CH_2CH_2Br} \arrow[l] \end{tikzcd}$$

$$\begin{tikzcd} \text{B.}\ \underset{\text{VI}\ +3.93}{C_2H_5CH(CH_3)CH_2Br^4} \arrow[r] & \underset{\text{VII}\ +8.55}{C_2H_5CH(CH_3)CH_2CH(OH)C_4H_9} \arrow[d] \\ \underset{\text{IX}\ +9.30}{C_2H_5CH(CH_3)C_6H_{13}} & \underset{\text{VIII}\ +15.34}{C_2H_5CH(CH_3)CH_2CH(Br)C_4H_9} \arrow[l] \end{tikzcd}$$

[a] These values are specific rotations.

The (+)4-methyl-1-decene (III) was ozonized to give a mixture of 3-methylnonanoic acid and 3-methylnonanal. These compounds were reduced with lithium aluminum hydride to the corresponding alcohol, which was converted with hydrogen bromide to 1-bromo-3-methylnonane (IV). Finally, reaction of the Grignard of IV with dilute acid yielded 3-methylnonane (IV) with a rotation of $[\alpha]^{25}D$ −6.29. Series B reactions involve the action of the Grignard from (+)2-methyl-1-bromobutane on valeraldehyde, conversion of the alcohol thus formed to the bromide with phosphorus tribromide, and the reduction of this halide with lithium aluminum hydride to 3-methyl nonane ($[\alpha]^{25}D$ +9.30).[5a] Since these reactions do not involve the asymmetric carbon atom, there should be no loss in asymmetry in these transformations.[5b] The specific rotation for optically pure 4-methyl-1-decene calculated from these data is $[\alpha]D$ 7.0.

The highest reported rotation for 2-bromoöctane, $[\alpha]^{25}D$ 34.3[6], represents a lower limit for the rotation of the pure enantiomorph. An upper limit of $[\alpha]D$ 38.1 has been set by Hughes, Ingold and Masterman from data on the hydrolysis of

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[1] Presented at the meeting of the American Chemical Society in San Francisco, March, 1949. This investigation was supported by a grant from the Abbott Fund of Northwestern University.

[2] (a) Brink, Lane and Wallis, THIS JOURNAL, **65**, 943 (1943); (b) Bergmann, *Helv. Chim. Acta*, **20**, 611 (1937); (c) Kenyon, Phillips and Pittman, *J. Chem. Soc.*, 1072 (1935); (d) Levene and Marker, *J. Biol. Chem.*, **97**, 568 (1932).

[3] Letsinger, THIS JOURNAL, **70**, 406 (1948).

[4] The (+)2-methyl-1-bromobutane was kindly supplied to us by Professor Robert L. Burwell and George S. Gordon. It was prepared from (−)2-methyl-1-butanol ($[\alpha]^{25}D$ −5.76°) and phosphorus tribromide. See Burwell and Gordon, *ibid.*, **70**, 3128 (1948).

[5a] The maximum rotation for 3-methylnonane could be slightly higher than 9.30 since the 2-methyl-1-bromobutane used in the synthesis was not quite optically pure (The maximum rotation is $[\alpha]D$ 4.04, Braun, *J. Research Natl. Bur. Standards*, **18**, 315 (1937), as compared to our sample with $[\alpha]^{25}D$ 3.93). Our bromide had been prepared from optically pure 2-methyl-1-butanol and phosphorus tribromide. When it was shaken with an aqueous silver nitrate solution, the rotation rose to $[\alpha]^{25}D$ +4.02. The contaminant therefore was probably *t*-amyl bromide. Levene and Rotben, *J. Org. Chem.*, **1**, 85 (1936), reported the maximum rotation of 3-methylnonane to be $[M]^{25}D$ 12.5 ($[\alpha]^{25}D$ 8.8), but did not give experimental details.

[5b] For the possibility of racemization occurring during ozonolysis, see the last paragraph of the Experimental section.

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

the bromide.[7] On the basis of these limits, optically pure 2-bromoöctane would have yielded 4-methyl-1-decene with a rotation in the range of $[\alpha]_{\mathrm{D}}$ 5.5 to 6.1; so the racemization in the allylsodium condensation must have amounted to at least 13% but not more than 21%.

While no opportunity for an inversion of configuration exists in the transformation of (+)2-methyl-1-bromobutane (or (−)2-methyl-1-butanol) to (+)3-methylnonane, it is well established that an inversion does occur in the preparation of 2-bromoöctane from 2-octanol.[8a] To accord with the signs of rotation (see flow sheet) an inversion of configuration must be assigned to the allylsodium reaction provided (+)2-octanol corresponds in configuration to (−)2-methyl-1-butanol (and therefore (+)2-methyl-1-bromobutane).[8b] Evidence that these alcohols are so related is sufficiently great that the inversion in the reaction of allylsodium with 2-bromoöctane can be considered to be established.[2a,3,9]

Grignard Reactions.—Both the allylsodium and the benzylsodium reactions were heterogeneous. We have carried out coupling reactions with the corresponding magnesium compounds to see if these homogeneous reactions would follow the same course.

Allylmagnesium bromide reacted with 2-bromoöctane $[\alpha]^{25}_{\mathrm{D}}$ +30.03 to give a 78% yield of 4-methyl-1-decene with a rotation $[\alpha]^{25}_{\mathrm{D}}$ +4.79. The extent of racemization and change in configuration in this reaction were identical to those obtained in the allylsodium condensation. Apparently the solubility of the metallic compound and the nature of the metal were of incidental importance, the course of the reaction being determined by the characteristics of the allyl ion. This does not mean, of course, that the metal ion is not involved in the reaction. A possible mechanism for this displacement is that the metal ion of the allylmetallic compound coordinates with the bromine in bromoöctane; then (or perhaps simultaneously) the γ carbon of the allyl group displaces the bromine as bromide ion and the bond between the α-carbon and the metal breaks. Little work has been reported on the coupling of allylmagnesium bromide with secondary halides,[10] and the high yield obtained here suggests that this reagent may prove useful in certain synthesis.

In contrast to these results, benzylmagnesium chloride was found to react very differently from benzylsodium. Whereas the sodium reagent gave a high yield of coupling product with little if any racemization, benzylmagnesium chloride and 2-bromobutane ($[\alpha]^{25}_{\mathrm{D}}$ −16.80) gave only a 17% yield of 1-phenyl-2-methylbutane ($[\alpha]^{25}_{\mathrm{D}}$ +0.64).[11] Approximately 91% of the asymmetry had been lost. We plan to investigate displacements of these types further in the hope of elucidating the factors responsible for the retention or loss of optical activity.

Experimental

(−)4-Methyl-1-Decene by Allylsodium Reaction.—2-Octanol was resolved through the brucine salt of the half phthalate ester[12] and converted to the bromide with phosphorous tribromide.[13] Allylsodium was prepared in 200 cc. of petroleum ether (b. p. 60–70°) from 24.5 g. (0.25 mole) of diallyl ether and 9.2 g. (0.40 g. atom) of sodium sand as previously directed.[14] To the allylsodium suspension (under a nitrogen atmosphere) was added with high speed stirring (5000 r. p. m.) 20.6 g. (0.106 mole) of 2-bromoöctane ($[\alpha]^{20}_{\mathrm{D}}$ − 29.55, d^{20}_{4} 1.101, n^{23}_{D} 1.4500) in an equal volume of petroleum ether. The time of addition was thirty minutes and the temperature was maintained at 0°. After the mixture had stirred for an hour longer, the temperature was permitted to rise to 25°. At this point, stirring was stopped and the pale blue mixture left overnight. The following morning it was carbonated, and the hydrocarbon portion was worked up by conventional procedure. The fraction boiling at 70° (12 mm.) weighed 13.5 g. (83%); $[\alpha]^{20}_{\mathrm{D}}$ −4.73, d^{20}_{4} 0.750, n^{25}_{D} 1.4246. Evidence that the hydrocarbon thus formed is 4-methyl-1-decene has been presented previously.[14]

Anal. (by M. Hines). Calcd. for $C_{11}H_{22}$: C, 85.62; H, 14.38. Found: C, 85.90; H, 14.28.

Another experiment carried out in the same manner with 13.1 g. (0.13 mole) of diallyl ether, 3.5 g. (0.15 g. atom) of sodium and 6.3 g. (0.03 mole) of 2-bromoöctane ($[\alpha]^{25}_{\mathrm{D}}$ − 31.25) yielded 2.5 g. of 4-methyl-1-decene boiling at 71° (12 mm.); $[\alpha]^{20}_{\mathrm{D}}$ − 4.96, d^{20}_{4} 0.750, n^{24}_{D} 1.4242.

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[7] Hughes, Ingold and Masterman, *J. Chem. Soc.*, 1199 (1937).

[8a] Gilman, "Organic Chemistry, An Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 278.

[8b] In tracing through the configurational relationships it must be born in mind that, on the basis of the indicated inversions, (+)-2-octanol and (−)2-methyl-1-butanol (or (+)2-methyl-1-bromobutane) would yield samples of 3-methylnonane with opposite signs of rotation. This relationship exists since, by the nature of the syntheses, the hydroxyl group of 2-octanol becomes the ethyl group of 3-methylnonane (methylethylhexylmethane) whereas the hydroxymethyl group of 2-methyl-1-butanol becomes the hexyl group of methylnonane.

[9] Levene and Rothen, *J. Org. Chem.*, **1**, 76 (1936). This problem is, of course, related to that of the relative configuration of 2-butanol and 2-methyl-1-butanol. Additional evidence that (+)-2-butanol corresponds to (−)2-methyl-1-butanol is obtained from the work of Fredga, *Arkiv Kemi, Mineral. Geol.*, **14B**, No. 27, 1 (1941); *ibid.*, **15B**, No. 23 (1942), (See also A. Fredga, "Thé Svedberg," Almquist and Wirksells, Uppsala, 1945, p. 269) who related from fusion data L (−)malic acid and (−)methylsuccinic acid. Now, (+)2-butanol can be directly related to the L series, and (−)2-methyl-1-butanol can be related to (−)methylsuccinic acid through the work of Brown, Kharasch and Chao, This Journal, **62**, 3435 (1940), and Braun and Jostes, *Ber.*, **59**, 1091 (1926). These correlations were pointed out to us by A. Schnizer.

[10] Shoemaker and Boord, This Journal, **53**, 1505 (1931); Summerbell and Bauer, *ibid.*, **58**, 759 (1936).

[11] Glattfeld and Cameron, *ibid.*, **49**, 1045 (1927), reported a 10% yield of 1-phenyl-2-methylbutane from benzylmagnesium chloride and inactive 2-bromobutane. In neither this case nor in ours has the possibility been excluded that some 1-methyl-1-(2-methylphenyl)-propane might be present. However, our sample readily formed a diacetamido derivative which gave no depression with the derivative of an authentic sample of 1-phenyl-2-methylbutane; so if the rearranged product was present at all, it was probably present in small amounts only.

[12] Ingersoll in "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 400–404. In order to maximize the amount of alcohol resolved by a given quantity of brucine, 0.6 mole of brucine was used for 1.0 mole of the acid phthalate.

[13] Shriner and Young, This Journal, **52**, 3337 (1930). The only deviation from their procedure was that the bromide was taken up in petroleum ether (b. p. 30–60°) rather than ethyl ether and washed with sulfuric acid.

[14] Letsinger and Traynham, *ibid.*, **70**, 3342 (1948).

Ozonolysis.—4-Methyl-1-decene (10.5 g., 0.068 mole, $[\alpha]^{20}_{\mathrm{D}}$ −4.73) in 125 cc. of ethyl acetate was cooled to −25° and treated with a stream of oxygen containing 3% ozone until an exit trap containing a potassium iodide solution indicated that the reaction was complete. To the ozonide was added 10 g. of zinc dust, 30 cc. of acetic acid, and 70 cc. of water along with traces of silver and hydroquinone. The mixture was shaken vigorously for twenty minutes, warmed on a steam-bath to evaporate the ethyl acetate, filtered and extracted with ether. Distillation of the dried ether extract gave 5.1 g. (48%) of aldehyde, b. p. 77–79° (7 mm.); m. p. of the 2,4-dinitrophenylhydrazone derivative, 72–73°. An acid residue (3.0 g., 25.7%) remained in the distilling flask.

(+)3-Methyl-1-bromononane.—The combined aldehyde and acid portions from the ozonolysis were reduced with 6.0 g. lithium aluminum hydride according to the procedure of Nystrom and Brown.[15] The 3-methyl-1-nonanol thus obtained was then placed in a small distilling flask fitted with a condenser and an inlet tube reaching to the bottom of the flask. Hydrogen bromide was passed into the alcohol (heated to 100°) for ninety minutes. Then, after the mixture had stood overnight, the bromide was isolated as directed in "Organic Syntheses"[16]; 7.1 g. product was obtained; b. p. 100° (9 mm.), $[\alpha]^{25}_{\mathrm{D}}$ +4.35, d^{25}_{4} 1.070, n^{23}_{D} 1.4558.

Anal. (by M. Hines). Calcd. for $C_{10}H_{21}Br$: C, 54.29; H, 9.58. Found: C, 54.18; H, 9.08.

(−)3-Methylnonane.—The Grignard of (+) 3-methyl-1-bromononane was prepared in 35 cc. of dry ether by conventional means from the bromide (7.5 g., 0.034 mole) and 1.2 g. (0.049 g. atom) of magnesium. After the addition of the bromide to the magnesium, which required fifteen minutes, the solution was stirred for one hour and then decomposed with 3 N hydrochloric acid. From the organic layer was obtained 1.8 g. of product, b. p. 46–48° (8 mm.); negative Beilstein test for halogen. It was further purified by a washing with concentrated sulfuric acid and redistillation; b. p. 57° (16 mm.), $[\alpha]^{25}_{\mathrm{D}}$ −6.29°, d^{25}_{4} 0.730, n^{24}_{D} 1.4113.

Anal. (by M. Hines). Calcd. for $C_{10}H_{22}$: C, 84.40; H, 15.60. Found: C, 84.43; H, 15.26.

(+)3-Methyl-5-nonanol.—An ether solution of 2-methylbutylmagnesium bromide was prepared in the conventional manner in a 500 cc. three-necked flask from 33.2 g. (0.220 mole) 2-methyl-1-bromobutane[4] ($[\alpha]^{25}_{\mathrm{D}}$ +3.93) and 6.0 g. (0.25 g. atom) of magnesium turnings. After the addition of bromide was complete, the mixture was refluxed for an additional forty-five-minute period. It was then cooled to −15°, and 17.0 g. (0.198 mole) of valeraldehyde (b. p. 99–101°, prepared from butylmagnesium bromide and ethyl orthoformate[17]) in ether was added dropwise while the temperature was maintained at −20 to −10°. After another hour of stirring at −15°, the mixture was permitted to warm to room temperature, stirred thirty minutes, and finally cooled to −30° and decomposed with dilute hydrochloric acid. The combined organic portions were then dried over anhydrous potassium carbonate and distilled; yield 18.3 g., b. p. 97–99° (17 mm.), $[\alpha]^{25}_{\mathrm{D}}$ +8.55, d^{25}_{4} 0.821, $n^{25.5}_{\mathrm{D}}$ 1.4305.

(−)3-Methyl-5-bromononane.—This bromide was prepared from 17.5 g. (0.111 mole) of 3-methyl-5-nonanol and 37.0 g. (0.137 mole) of phosphorus tribromide as described by Shriner and Young.[13] A 79% yield (19.4 g.) of 3-methyl-5-bromononane was obtained; b. p. 83–84° (9 mm.), $[\alpha]^{25}_{\mathrm{D}}$ + 15.34, d^{25}_{4} 1.068, n^{23}_{D} 1.4549.

(+)3-Methylnonane.—3-Methyl-5-bromononane (10.8 g., 0.0490 mole) was reduced with lithium aluminum hydride (2.85 g., 0.0750 mole) in tetrahydrofuran (100 cc.) by the procedure of Johnson, *et al.*[18] The product (4.6 g., b. p. 78–80° (38 mm.)) gave a positive Beilstein test, so it was treated with sodium at 100° for thirty minutes and redistilled; weight 4.3 g., b. p. 80° (39 mm.), n^{23}_{D} 1.4118. This sample was bromide free but appeared to be slightly unsaturated (discolored bromine in carbon tetrachloride). It was therefore dissolved in methyl alcohol and shaken at 23° with a platinum catalyst and hydrogen at thirty-pounds pressure. The hydrocarbon was then recovered, shaken with cold concd. sulfuric acid, water and dilute sodium carbonate solution, and redistilled; weight recovered, 3.2 g., b. p. 80° (39 mm.), $[\alpha]^{25}_{\mathrm{D}}$ + 9.30, d^{25}_{4} 0.730, n^{24}_{D} 1.4110.

Anal. (by M. Hines). Calcd. for $C_{10}H_{22}$: C, 84.40; H, 15.60. Found: C, 84.12; H, 15.46.

(+)4-Methyl-1-decene by Grignard.—Allylmagnesium bromide was prepared from 60.5 g. (0.50 mole) of allyl bromide and 36.5 g. (1.5 g. atom) of magnesium. The Grignard solution was then siphoned from the excess magnesium into a nitrogen-filled flask, and after the addition of 13.5 g. (0.070 mole) 2-bromoöctane ($[\alpha]^{24}_{\mathrm{D}}$ + 30.03, d^{24}_{4} 1.101, n^{23}_{D} 1.4488), it was refluxed for sixty-five hours. After the solution had been cooled with a xylene–Dry Ice-bath, dilute hydrochloric acid was added, in order to decompose excess Grignard reagent. The organic layer was separated, washed with water, dried with calcium chloride, and distilled over sodium. The product (8.7 g., b. p. 66.5–67° (13 mm.), n^{25}_{D} 1.4252) still gave a positive Beilstein test, so it was redistilled over sodium. This time the hydrocarbon was free from halogen; b. p. 68.5–69° (15 mm.), $[\alpha]^{25}_{\mathrm{D}}$ 0.748, n^{25}_{D} 1.4246.

Anal. (by M. Hines). Calcd. for $C_{11}H_{22}$: C, 85.62; H, 14.38. Found: C, 85.92; H, 13.90.

(+)1-Phenyl-2-Methylbutane by Grignard Reaction.—An ether solution of benzylmagnesium chloride was prepared from 76.0 g. (0.600 mole) of benzyl chloride and 18.3 g. (0.750 g. atom) of magnesium. It was siphoned from excess magnesium and refluxed for thirty-five hours under a nitrogen atmosphere with 21.2 g. (0.155 mole) of 2-bromobutane (b. p. 90.5–91.5°, $[\alpha]^{25}_{\mathrm{D}}$ − 16.80, d^{25}_{4} 1.244). The excess Grignard reagent was then decomposed with dilute hydrochloric acid, and the ether layer washed with water, dried with calcium chloride and distilled over sodium. Two fractions were collected; b. p. 80–88° (25 mm.), 1.1 g.; b. p. 88–89° (25 mm.), 3.8 g. (17% yield). The latter fraction was redistilled over sodium to give a product with, $[\alpha]^{25}_{\mathrm{D}}$ + 0.64, d^{25}_{4} 0.857, n^{25}_{D} 1.4871. The diacetamido derivative was prepared by the procedure of Ipatieff and Schmerling.[19] Only one diacetamido derivative was isolated; m. p. 197–198°. It did not depress the melting point of an authentic sample of 1-(diacetamidophenyl)-2-methylbutane.[3]

Action of Silver Nitrate on Active Amyl Bromide Sample.—A 10-g. sample of 2-methyl-1-bromobutane[4] ($[\alpha]^{25}_{\mathrm{D}}$ 3.92) was shaken for ten minutes with 100 cc. of 0.1 N aqueous silver nitrate. A precipitate formed immediately upon mixing the reagents. The organic layer obtained from the filtrate was washed with cold concd. sulfuric acid, water and 5% sodium carbonate solution, and dried over potassium carbonate. Distillation yielded 3 g. bromide; $[\alpha]^{25}_{\mathrm{D}}$ + 4.02, d^{25}_{4} 1.2205.

(+) 4-Methyldecane and Treatment with Ozone.—A sample of 4-methyl-1-decene (3.0 g., $[\alpha]^{25}_{\mathrm{D}}$ 4.79) was dissolved in methanol and reduced at 25° with hydrogen at thirty-pounds pressure, platinum being used as the catalyst. A 93% yield (2.8 g.) 4-methyldecane was obtained; $[\alpha]^{25}_{\mathrm{D}}$ + 1.39, d^{25}_{4} 0.7396, n^{22}_{D} 1.4175. This hydrocarbon was dissolved in ethyl acetate and treated with ozone for a period of three hours. The recovered hydrocarbon had the same physical constants as the initial material; therefore, ozone did not cause any racemization. In view of this result, it seems highly improbable that any racemization would have occurred during the ozonolysis of 4-methyl-1-decene.

Summary

Optically active 4-methyl-1-decene was pre-

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[15] Nystrom and Brown, THIS JOURNAL, **69**, 1198 (1947).

[16] "Organic Syntheses," Coll. Vol. II, 2nd edition, John Wiley and Sons, Inc., New York, N. Y., p. 247.

[17] *Ibid.*, Coll. Vol. II, p. 323.

[18] Johnson, Blizzard and Carhart, THIS JOURNAL, **70**, 3664 (1948).

[19] Ipatieff and Schmerling, *ibid.*, **60**, 1476 (1938).

pared in good yields by the reactions of allylsodium and allylmagnesium bromide with optically active 2-bromoöctane. Samples of 3-methylnonane were prepared by the degradation of the optically active 4-methyl-1-decene and by synthesis from active 2-methyl-1-bromobutane. From a comparison of the rotations of these compounds, it was concluded that the allylmetallic condensations took place with inversion of configuration with less than 21% and more than 13% racemization.

Benzylmagnesium chloride reacted with (−)2-bromobutane to give a low yield of extensively racemized 1-phenyl-2-methylbutane.

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[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Systems of Boron Trifluoride with Phosphine, Arsine and Hydrogen Bromide

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Introduction

From the reviews of the coördination compounds of the boron halides by Booth[1] and Martin,[2,3] certain problems become apparent.

In Group 5a of the periodic classification, the following compounds of boron trifluoride with ammonia and phosphine have been reported: $NH_3\cdot BF_3$, $(NH_3)_2\cdot BF_3$, $(NH_3)_3\cdot BF_3$, $PH_3\cdot BF_3$ and $PH_3\cdot(BF_3)_2$.[1] The existence of the last compound has been questioned by Wiberg and Heubaum.[4] It was decided to study the system boron trifluoride–phosphine inasmuch as there is no analogous compound formed by boron trifluoride with ammonia, nor by the other boron halides with phosphine (only $PH_3\cdot BCl_3$, $PH_3\cdot BBr_3$ and $PH_3\cdot BI_3$? are reported[2]).

No compounds have been reported in which boron trifluoride is coördinated to an arsenic atom in any of its compounds, although $AsH_3\cdot BCl_3$[2] and $AsH_3\cdot BBr_3$[3] are known. Therefore, it was decided to investigate the system boron trifluoride–arsine.

Similarly, no compounds have been reported in which boron trifluoride is coördinated to a bromine atom in any of its compounds. Fluoboric acid is well known, but hydrogen chloride and boron trifluoride do not coördinate,[5] so it was of interest to see if this trend extended to hydrogen bromide. Therefore the system boron trifluoride–hydrogen bromide was investigated.

Experimental

Source of Reactants

Boron Trifluoride.—Gaseous boron trifluoride was obtained in a steel cylinder from the Harshaw Chemical Company, Cleveland, Ohio.

Arsine.—Sodium arsenide was prepared by fusing stoichiometric quantities of metallic sodium and metallic arsenic in a covered Hessian crucible. The reaction does not take place until the temperature is raised somewhat above the melting point of sodium. The reaction is very violent and lasts only for one or two seconds.

The apparatus used in the preparation of arsine consisted of a one-liter filter flask which served as a generator. A 250-ml. separatory funnel was attached to the generator with a one-hole rubber stopper. The side arm of the generator led to a safety manometer, and then in the order: a trap cooled with Dry Ice, a drying tube containing lumps of barium oxide, and a trap cooled with liquid air. A stopcock on the end of the last trap permitted the removal of any non-condensable gases present, the evacuation of the apparatus, or the withdrawal of the product. The Dry Ice-trap was used to remove most of the moisture from the generated gases and the barium oxide tube completed the desiccation. The product condensed in the liquid air trap.

The sodium arsenide was placed in the dry generator, and the apparatus was evacuated before any water was added to the generator through the separatory funnel. These precautions are necessary, because some free sodium may be present in the sodium arsenide. At least 30 ml. of liquid arsine was collected from 200 to 250 g. of sodium arsenide.

Phosphine.—The generating apparatus employed to prepare arsine was used also to synthesize phosphine. Crystalline phosphorous acid was placed in the generator and nitrogen added to the evacuated system until the pressure was 400 to 500 mm. Upon heating, the phosphine came off readily and smoothly. At lower pressures, the phosphorous acid failed to disproportionate and distilled into the Dry Ice-trap. About 40 ml. of liquid phosphine was obtained from about 400 g. of phosphorous acid.

A closed system, free of air, must be used for handling phosphine. The spontaneous combustion of phosphine in the apparatus does not harm the apparatus under low pressure, but leaves a reddish-orange deposit on the surface of the glass.

Hydrogen Bromide.—Hydrogen bromide was obtained in a steel cylinder from the Matheson Company, Joliet, Illinois.

Purification.—All gases used in the investigation were purified by fractional distillation as previously described.[6,7] They were stored in steel cylinders from which samples were withdrawn as needed.

Thermal Analyses.—The apparatus for establishing the mole fractions and to determine the freezing points of the various solutions was the same as previously described[5,8] except for the elimination of the use of polarized light in determining freezing points.

System: Boron Trifluoride–Phosphine.—The freezing point of the purified boron trifluoride used in this study was found to be −127.0 ± 0.3°. The purified phosphine was observed to freeze at −133.0 ± 0.3°. This value is

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(1) H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949, Chapter 4.

(2) D. R. Martin, *Chem. Revs.*, **34**, 461-473 (1944).

(3) D. R. Martin, *ibid.*, **42**, 581-599 (1948).

(4) E. Wiberg and U. Heubaum, *Z. anorg. Chem.*, **225**, 270-272 (1935).

(5) H. S. Booth and D. R. Martin, THIS JOURNAL, **64**, 2198-2205 (1942).

(6) D. R. Martin, *ibid.*, **67**, 1088 (1945).

(7) D. R. Martin and J. P. Faust, *J. Phys. Coll. Chem.*, **53**, 1255 (1949).

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