

the above isocyanates. Difficulty was encountered in obtaining satisfactory analyses on compounds containing the isobutyl and the *t*-butyl radicals. Repeated purifications did not improve the analyses.

#### EXPERIMENTAL

A general procedure is given for the preparation of each type of compound. Physical and analytical data are listed in Tables I, II, and III.

*2-Methylpiperazine* was purchased from the Wyandotte Chemical Corporation.

*Chlorohydrins*. Tetramethylene chlorohydrin was prepared by the method of Starr and Hixon.<sup>3</sup> Trimethylene chlorohydrin and ethylene chlorohydrin were purchased from the Eastman Kodak Company.

*Alkyl and aralkyl halides*. With the exception of benzohydril chloride, alkyl and aralkyl bromides were used. They were purchased from the Eastman Kodak Company.

*4-(ω-Hydroxyalkyl)-2-methylpiperazines*. 2-Methylpiperazine (2.8 moles) was dissolved in 500 ml. of ethanol. The chlorohydrin (1.0 mole) was added and the mixture was shaken well. The mixture was then refluxed for 2 hr. Potas-

(3) D. Starr and R. Hixon, *J. Am. Chem. Soc.*, **56**, 1595 (1934).

sium hydroxide (1.1 moles) was added and after heating for 0.5 hr., approximately half of the ethanol was removed by distillation. The reaction mixture was cooled and filtered. The remainder of the ethanol and the unreacted 2-methylpiperazine were then removed by distillation. The 4-(ω-hydroxyalkyl)-2-methylpiperazines were then distilled using reduced pressure.

*1-Substituted-4-(2-hydroxyalkyl)-2-methylpiperazines*. 4-(ω-Hydroxyalkyl)-2-methylpiperazine (0.60 mole) was dissolved in 175 ml. of absolute ethanol. To this solution was added the aralkyl or the alkyl halide (0.60 mole). The reaction mixture was refluxed 6 to 10 hr. Sodium bicarbonate (0.75 mole) was added, the ethanol was removed by distillation, and 300 ml. of water was added. The reaction mixture was extracted with ether. The ether extracts were dried over anhydrous sodium sulfate and then filtered. After the removal of the ether, the products were distilled using reduced pressure.

*Urethanes of 1-substituted-4-(ω-hydroxyalkyl)-2-methylpiperazines*. The isocyanate (0.05 mole), dissolved in 20 ml. of hexane, was added to a solution of the 1-substituted-4-(ω-hydroxyalkyl)-2-methylpiperazine (0.05 mole) in 20 ml. of hexane. The two were mixed well and allowed to stand at room temperature. The solid urethanes were filtered and recrystallized from hexane or heptane. The oils were washed with hexane.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MICHIGAN STATE UNIVERSITY]

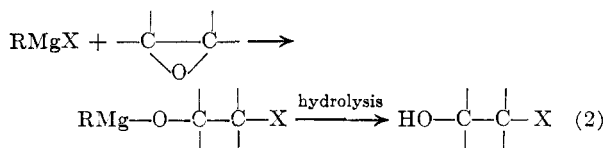
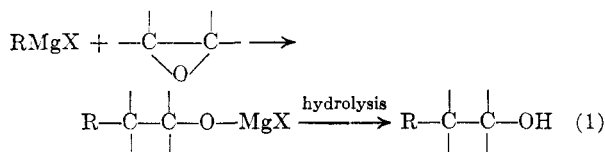
## The Reaction of Some Organomagnesium Iodides with 1,2-Epoxypropane

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Several Grignard reagents prepared by the reaction of an organic iodide with magnesium in the presence of anhydrous ether were treated with one and two molar equivalents of 1,2-epoxypropane to give an alcohol and an iodohydrin. In all cases, the yield of the iodohydrin was greater than that of the expected alcohol. Only when two molar equivalents of epoxide were present was the yield of alcohol significant. The reaction of the dioxane soluble portion of the Grignard reagent (R<sub>2</sub>Mg) with two molar equivalents of epoxide to yield an alcohol was also investigated.

It has been shown<sup>4-6</sup> that the reaction of a Grignard reagent with an epoxide occurs in such a manner that either the organo-magnesium bond or the magnesium-halide bond may be attacked by the epoxide (1,2). The resulting products are mixtures of an alcohol and a halohydrin.



(1) Abstracted from a thesis submitted by Francis E. Evans in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Michigan State University, March 1955.

When Grignard reagents obtained from organic chlorides,<sup>5</sup> bromides,<sup>6</sup> and iodides<sup>4</sup> were treated with epoxyethane (ethylene oxide) in equimolar quantities the products were predominately the expected alcohols, indicating mainly reaction at the organo-magnesium bond. Halohydrin, presumably formed by reaction at the magnesium-halide bond, was produced in all cases, but in surprisingly increased yields when Grignard reagents prepared from iodides were used. The yield of both the expected alcohol and the halohydrin were increased when the reaction was carried out between two moles of epoxyethane and one mole of the Grignard reagent.

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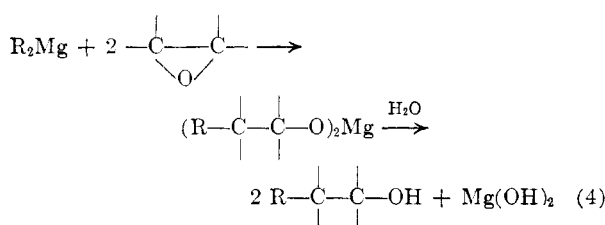
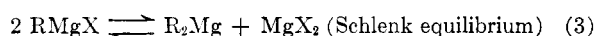
(4) R. C. Huston and A. A. Agett, *J. Org. Chem.*, **6**, 123 (1941).

(5) R. C. Huston and C. C. Langham, *J. Org. Chem.*, **12**, 90 (1947).

(6) R. C. Huston and H. M. D'Arcy, *J. Org. Chem.*, **18**, 16 (1953).

However, it was found<sup>7,8</sup> that when one mole of 1,2-epoxypropane (propylene oxide) was treated with either one or two moles of a Grignard reagent a halohydrin was the main product. Higher yields of the expected alcohols and lower yields of the halohydrin resulted from the reactions of 1,2-epoxypropane with Grignard reagents of organic chlorides,<sup>8</sup> than from those of corresponding bromides.<sup>7</sup>

Reaction of epoxides with the dioxane soluble portion of the Grignard reagent ( $R_2Mg$  resulting from the Schlenk equilibrium<sup>4,9</sup>) leads to the expected alcohol as the product of the reaction involving two moles of epoxide and one mole of dialkylmagnesium (3,4).



Good yields of the expected alcohols and only traces of halohydrins were obtained<sup>5,6</sup> from the reactions of epoxyethane and 1,2-epoxypropane with the dioxane-soluble portions of the Grignard reagents of organic chlorides and bromides.

This paper reports the results obtained when some Grignard reagents prepared from organic iodides and the dioxane-soluble portions of these Grignard reagents were caused to react with one and two moles of 1,2-epoxypropane.

Table I gives the yields of active species in certain Grignard reagents and in the dioxane-soluble portions of these reagents as determined

TABLE I

YIELDS<sup>a</sup> OF  $RMgX$  AND  $R_2Mg$  PRODUCED FROM ORGANIC IODIDES

Organic Iodide	% $RMgI^b$	% $R_2Mg^c$
Methyl	100	18
Ethyl	96	48
<i>n</i> -Propyl	93	64
<i>i</i> -Propyl	74	48
<i>n</i> -Butyl	92	42
<i>s</i> -Butyl	72	50
Phenyl	92	74

<sup>a</sup> Average values based on three or more similar Grignard preparations. <sup>b</sup> Per cent of active species in Grignard reagent calculated as  $RMgI$  and based on the amount of organic iodide used. <sup>c</sup> Per cent of active species in dioxane-soluble portion calculated as  $R_2Mg$  and based on the amount of  $RMgI$  found in the original Grignard solution.

(7) R. C. Huston and C. O. Bostwick, *J. Org. Chem.*, **13**, 331 (1948).

(8) R. C. Huston and H. E. Tiefenthal, *J. Org. Chem.*, **16**, 673 (1951).

(9) W. Schlenk and W. Schlenk, Jr., *Ber.*, **62**, 920 (1929).

by titration of aliquots (Gilman procedure<sup>10</sup>), the active species being calculated as  $RMgI$  for the total Grignard solutions, and as  $R_2Mg$  for the dioxane-soluble portions. The Grignard reagents were prepared in the usual fashion by reaction of organic iodides with magnesium in anhydrous ether. The dioxane-soluble portions were obtained as supernatant ether-dioxane solutions after precipitation by dioxane and subsequent centrifuging.

When Grignard reagents prepared from organic iodides were treated with equimolar quantities of 1,2-epoxypropane, the yields of the expected alcohols were of the order of 1-2% and were unaffected by varied reaction temperatures (5-25°) and reaction times (1-24 hours). Yields of the iodohydrin ranged from 18-80% depending on time and temperature of reaction. Iodohydrin yields were reproducible only when continuous agitation was employed and both reaction temperatures and reaction times were accurately controlled. Data in Table II show the effect of temperature and reaction times on the yield of iodohydrin.

Attempts to increase the yields of the alcohols by heating the reaction mixture were ineffective. Much decomposition was observed and the yield of iodohydrin was decreased.

In all reactions trace amounts of acetone were found. A possible mechanism has been previously discussed.<sup>7</sup> In many reactions traces of isopropyl alcohol were found and in the case of the reaction of phenylmagnesium iodide with 1,2-epoxypropane, benzene and diphenyl were isolated in considerable amounts. This was not unexpected since similar results are recorded in the literature.<sup>11</sup> Considerable quantities of the hydrocarbon that one might expect to obtain by hydrolysis of  $RMgI$  were isolated in all cases.

The yields of iodohydrin obtained from the reaction of organomagnesium iodides with equimolar quantities of 1,2-epoxypropane were remarkably similar (60-80%) at low temperatures (5°) and for short reaction times (1 hr.) (Table II). However, as both temperature and reaction time were increased, reactions involving compounds with branched or normal organic groups larger than methyl showed a definite decrease in iodohydrin yield.

It is apparent from a study of the series of reactions listed in Table II which were hydrolyzed at one, two, four, and six hours that reactions of the methyl and phenylmagnesium iodides with 1,2-epoxypropane showed little change in yield of iodohydrin with time. On the other hand, the *n*-propyl- and *n*-butylmagnesium iodides when reacted with 1,2-epoxypropane show an increased yield of iodohydrin up to two hours followed by a

(10) H. Gilman, P. D. Wilkinson, H. P. Fishel, and C. H. Meyers, *J. Am. Chem. Soc.*, **45**, 150 (1923).

(11) M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, Inc., New York, 1954, p. 59.

TABLE II

EFFECT OF TIME<sup>a</sup> AND TEMPERATURE<sup>b</sup> ON YIELDS<sup>c,d</sup> OF IODOHYDRIN FROM REACTION OF SEVERAL ORGANOMAGNESIUM IODIDES (RMgI) WITH 1 MOLE OF 1,2-EPOXYPROPANE<sup>e</sup>

Temperature, °C.	Time, Hr.	% Yields of Iodohydrin						
		Methyl	Ethyl	<i>n</i> -Propyl	<i>i</i> -Propyl	<i>n</i> -Butyl	<i>i</i> -Butyl	Phenyl
5	1	71	80	69	69	76	69	73
15	1	78	78	74	66	72	55	73
15	2	80	77	78	60	78	46	73
15	4	78	75	73	42	73	37	73
15	6	80	66	72	37	70	35	74
15	12	79	38	64	30	65	28	69
15	24	77	27	55	29	45	22	65
25	1	70	64	65	50	75	42	70
25	12	77	26	44	25	59	23	63
25	24	78	18	24	18	38	18	53

<sup>a</sup> Zero time was considered to be immediately after the addition of epoxide. <sup>b</sup> Temperature was controlled by a constant temperature water bath to  $\pm 1^\circ$ . <sup>c</sup> Actual yields were determined by hydrolysis of iodohydrin and titration of aliquots for iodide ion. Theoretical yields were calculated from determined amounts of RMgI assumed to react according to Equation 2. <sup>d</sup> The yield of the expected alcohols was in all cases 1-2%. <sup>e</sup> A material balance determined in the case of the *n*-propylmagnesium iodide accounted for 97% of the reacting materials.

TABLE III

EFFECT OF TIME<sup>a</sup> ON YIELDS OF IODOHYDRIN (% I) AND ALCOHOLS (% ALC.). REACTION OF RMgI WITH 2 MOLAR EQUIVALENTS OF 1, 2-EPOXYPROPANE<sup>c</sup>

Grignard Reagents	Zero Hr. <sup>b</sup>		<sup>1</sup> / <sub>4</sub> Hr. <sup>b</sup>		<sup>3</sup> / <sub>4</sub> Hr. <sup>b</sup>		3 Hr. <sup>b</sup>		18 Hr. <sup>b</sup>	
	% I	% Alc.	% I	% Alc.	% I	% Alc.	% I	% Alc.	% I	% Alc.
Methyl	94	10	97	16	91	16	86	24	87	26
Ethyl	94	11	100	12	99	16	86	23	71	33
<i>n</i> -Propyl	97	2	99	5	99	9	83	15	71	23
<i>i</i> -Propyl	100	7	91	9	79	11	63	16	59	18
<i>n</i> -Butyl	90	8	95	13	87	13	77	16	79	24
<i>s</i> -Butyl	85	2.6	80	3	70	3	59	7	53	8
Phenyl	95	9	100	12	92	22	83	24	80	30

<sup>a</sup> Temperature was held constant at  $15 \pm 1^\circ$ . <sup>b</sup> Reaction time after addition of the epoxide was complete (all additions took about 30 min.). <sup>c</sup> A material balance determined in the case of *n*-propylmagnesium iodide accounted for 88% of the reacting materials.

yield decrease. These results indicate that *n*-propyl- and *n*-butylmagnesium iodides react with 1,2-epoxypropane at a slower rate than do the methyl and ethylmagnesium iodides. The isopropyl- and secondary butylmagnesium iodides show a marked decrease in iodohydrin yield immediately, indicating that the maximum yield of iodohydrin was probably reached before hydrolysis of the reaction which was allowed to stand the minimum time of one hour.

When organomagnesium iodides were treated with two moles of 1,2-epoxypropane the yields of both the expected alcohol and the iodohydrin were increased. In many cases the yield of iodohydrin was almost quantitative (Table III). Hydrolysis of similar reactions at different set time intervals provided several interesting facts. In all cases except those of the isopropyl- and secondary butylmagnesium iodides, the yield of iodohydrin from interaction of one mole of organomagnesium halide and two moles of 1,2-epoxypropane reached a maximum and then decreased as the reaction time was extended. The reaction of isopropylmagnesium iodide with two moles of 1,2-epoxypropane gave a

100% yield of iodohydrin, while the yield of iodohydrin from secondary butylmagnesium iodide under similar conditions was 85%. In all cases the amount of the formed alcohol increased steadily over a period of about 18 hours, and became nearly constant thereafter (Table IV).

In contrast, however, when diorganomagnesium compounds were allowed to react with two moles of 1,2-epoxypropane, prolonging the reaction time beyond the point at which a Michler's ketone test for free Grignard reagent was negative gave a substantially increased yield of the expected alcohol in all cases (Table IV). This phenomenon was thought to be due to the slow formation of an intermediate complex between  $R_2Mg$  and the epoxide. Presumably such a complex, being more stable than the complex formed between  $R_2Mg$  and ether, might not be expected to react in the normal fashion with Michler's ketone.

When an organomagnesium iodide was treated with one mole of 1,2-epoxypropane little precipitate formed. However, when a second mole was added, a heavy precipitate slowly appeared. Analysis of the dried precipitate for magnesium



formation of polymeric compounds. The rate of its decomposition is faster at higher temperatures.

When a second mole of the epoxide is added (7) the slower reaction to yield the alcohol intermediate occurs to a degree and a thick white precipitate (F) is formed.

It is noteworthy that it was necessary to have the second mole of epoxide present in order to obtain an appreciable amount of the expected alcohol, and that *only* in the reaction of organomagnesium iodides with two moles of the epoxide did a heavy precipitate appear. Further, in the reaction of dialkylmagnesium with two moles of 1,2-epoxypropane a white precipitate appeared which continued to increase on standing even after a negative Michler's ketone test. This increase in precipitate paralleled an increased yield of alcohol that was observed in reactions allowed to stand for various time intervals.

TABLE V  
CHARACTERIZATION OF THE ALCOHOLS

Alcohol	B.P., °C. (atm.) <sup>a</sup>	$n_D^{25}$	Derivatives <sup>a,b</sup> M.P., °C.
2-Butanol	97-99	1.3937 <sup>12,13</sup>	75-76 <sup>14,15</sup>
2-Pentanol	117-119	1.4064 <sup>8,16</sup>	60.5-61.5 <sup>8,17</sup>
2-Hexanol	137-139	1.4152 <sup>8,18</sup>	37.5-38.0 <sup>8,19</sup>
4-Methyl-2-pentanol	128-130	1.4154 <sup>8,12</sup>	62.5-63.5 <sup>8,19</sup>
2-Heptanol	157-159	1.4225 <sup>17,18</sup>	48.8-49.5 <sup>14,17</sup>
4-Methyl-2-hexanol	151-153	1.4247 <sup>8,20</sup>	50-51 <sup>20</sup>
1-Phenyl-2-propanol	211-214	1.3264 <sup>21</sup>	87.8-88.2 <sup>21</sup>

<sup>a</sup> All boiling points and melting points are uncorrected.

<sup>b</sup> All derivatives are 3,5-dinitrobenzoates except in the case of 1-phenyl-2-propanol (phenylurethane).

#### EXPERIMENTAL

*Preparation of Grignard reagents.* Fifty g. (2.1 g.-atoms) of magnesium turnings was placed in a dry, 2-l., three-necked round bottomed flask which was fitted with a mercury sealed stirrer, a Hershberg dropping funnel (for precise control of flow), and an efficient condenser. The condenser and dropping funnel were fitted with drying tubes

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(17) G. B. Malone and E. E. Reid, *J. Am. Chem. Soc.*, **51**, 3426 (1929).

(18) L. M. Ellis and E. E. Reid, *J. Am. Chem. Soc.*, **54**, 1678 (1932).

(19) P. Sutter, *Helv. Chim. Acta*, **21**, 1269 (1938).

(20) J. Cymerman, I. M. Heilbron, and E. R. H. Jones, *J. Chem. Soc.*, 90 (1945).

(21) M. S. Newman, *J. Am. Chem. Soc.*, **62**, 2295 (1947); I. M. Heilbron, *Dictionary of Organic Compounds*, Oxford University Press, New York, 1953, Vol. III, p. 318

filled with a calcium chloride-soda lime mixture. The flask was swept with dry nitrogen before addition of the reactants. Provision was made for external cooling of the flask as needed.

Anhydrous ethyl ether (100 ml.) and redistilled organic iodide (5-10 g.) were added to start the reaction. More ether (500 ml.) was then added and the remainder of the 2 moles of organic iodide in 300 ml. of ether was added through the dropping funnel. External cooling was required. After addition was complete agitation was continued for an hour; the Grignard reagents were immediately analyzed according to the procedure described by Gilman,<sup>10</sup> and then treated at once with 1,2-epoxypropane. Neither allowing the Grignard reagents to stand overnight nor refluxing them for up to 6 hr. appreciably increased the yields.

*Analysis of the Grignard reagent.* The Grignard reagent was transferred through a glass tube fitted with a glass wool filter by means of nitrogen pressure into a graduated mixing cylinder which had been fitted with an inlet tube, a safety tube, and an outlet tube reaching to the bottom of the cylinder. The volume of the solution was measured and a 1-ml. aliquot was analyzed by the Gilman procedure<sup>10</sup> with phenolphthalein as the indicator. Another 1-ml. aliquot was analyzed for iodide by the Volhard method.

*Reaction of 1 mole of Grignard reagent with 1 mole of 1,2-epoxypropane.* About one third of a mole of the Grignard reagent was transferred by means of nitrogen pressure to a dry 1-l., three-necked, round bottomed flask which had been swept with dry nitrogen. The flask was fitted with a condenser, a glycerol sealed stirrer, a dropping funnel, and a thermometer. Both the condenser and the dropping funnel were fitted with drying tubes filled with a calcium chloride-soda lime mixture. An equimolar amount of 1,2-epoxypropane was diluted with an equal volume of anhydrous ether and added slowly to the Grignard reagent. The reaction temperature was maintained at 15° by external cooling and the reaction mixture was agitated continuously. After addition of the epoxide was completed (12-15 min.), the reaction mixture was maintained at the desired temperature by placing the flask in a constant temperature bath (controlled to  $\pm 1^\circ$ ) and agitation was continued.

At the end of the reaction period, the reaction mixture was hydrolyzed by dropwise addition of a saturated solution of ammonium iodide. External cooling was necessary. Forty to 60 ml. of ammonium iodide solution were required to cause complete precipitation of the magnesium salts and leave a clear ether solution. Vigorous agitation was necessary during hydrolysis in order to obtain a smooth decomposition. The precipitate was separated by decantation and washed thoroughly with ether. Water was then added to the precipitate to form a pasty mass which was extracted once with ether.

The combined ether solutions of organic products were dried over sodium sulfate. The ether was removed by distillation through an 18-in. Vigreux column until the temperature in the pot reached 50°. (Careful control of pot temperature was necessary to prevent decomposition of product.)

The residue remaining after removal of the ether was analyzed for iodohydrin according to a previously described procedure.<sup>8</sup>

The ether was removed from the dried mixture of organic products by distillation as before to a pot temperature of 50°. The residue was then fractionated through either an 8-in. column packed with glass helices or a 9-in. Vigreux column fitted with a total reflux, partial take-off type head. After the initial fractionation, all similar runs were combined and refractionated before physical constants were determined and derivatives were prepared.

*Reaction of 1 mole of Grignard reagent with 2 moles of 1,2-epoxypropane.* The calculated amount of 1,2-epoxypropane in ether was added at a temperature of 15° to the Grignard reagent as described in the above procedure (time, ca. 30 min.). Then the reaction mixture was placed in a constant temperature bath maintained at 15°  $\pm$  1° and agitated

constantly. The reaction was characterized by progressive formation of a white precipitate which in some cases became a gel.

At the end of the prescribed reaction period the reaction mixture was hydrolyzed with 70–90 ml. of saturated  $\text{NH}_4\text{I}$  solution and the products were estimated or isolated as described above.

*Reaction of diorganomagnesium compounds with 1,2-epoxypropane.* The supernatant dioxane-ether solution<sup>4,22,23</sup> (containing for the most part diorganomagnesium compounds and essentially iodide free as shown by hydrolysis and analysis for iodide ion) was then transferred to a flask set up as described for the reaction of Grignard reagent with 1,2-epoxypropane. The calculated amount of 1,2-epoxypropane dissolved in an equal volume of anhydrous ether was added dropwise with stirring at 15° over a period of 10 min. The reaction flask was placed in a constant temperature bath (15°) and agitated for the balance of the reaction period.

Hydrolysis of the reaction mixture was carried out with 25–35 ml. of the saturated  $\text{NH}_4\text{I}$  solution. The hydrolyzed mixture was processed and fractionated as previously described.

*Preparation of 1-iodo-2-propanol.* The magnesium iodide etherate<sup>24</sup> (0.5 g.-atom) was prepared with equipment similar to that used in the preparation of the Grignard reagents and was transferred by means of nitrogen pressure to a dry nitrogen-swept 1-l., three-necked, round bottomed flask equipped as described above. One mole of 1,2-epoxypropane in 100 ml. of anhydrous ether was added over a period of 1 hr. with stirring. A dense white precipitate formed as the epoxide was added. The reaction flask was placed in a constant temperature water bath and agitated for 24 hr. at 15°. The reaction mixture was hydrolyzed in the usual manner with 80–90 ml. of saturated  $\text{NH}_4\text{I}$  solution. The ether solution of organic reaction products (mainly 1-iodo-2-propanol) was dried over sodium sulfate and the ether was removed by distillation. The amount of iodohydrin present in the residue was then determined as previously described.<sup>5</sup>

The yield was 75–83% based on the amount of iodine used in preparing the magnesium iodide.

A quantity of 1-iodo-2-propanol was distilled (41–43° at 3 mm.) and its physical properties were determined.

*Refractive Index.* Lit.:<sup>25</sup>  $n_D^{30}$ : 1.5365. Found.  $n_D^{20}$ : 1.5453,  $n_D^{30}$ : 1.5417.

(22) L. F. Fieser, *Experiments in Organic Chemistry*, Part II, 2nd ed., D. C. Heath and Co., Boston, 1941.

(23) C. R. Noller and W. R. White, *J. Am. Chem. Soc.*, **59**, 1354 (1937).

(24) R. Stewart and A. R. Ubbelohde, *J. Chem. Soc.*, 2649 (1949).

*Density.* Lit.:<sup>25</sup>  $d_4^{20}$ : 1.8999. Found:  $d_4^{30}$ : 1.9359.

*Molecular Refraction.* Calcd. 30.39. Found: 30.40. The values found for both the refractive index and density remained constant upon repeated fractionation of the compound.

The per cent iodine in 1-iodo-2-propanol was determined by both alkali decomposition<sup>8</sup> and sodium peroxide fusion. Both methods gave the same results.

*Anal.* Calcd. for  $\text{C}_3\text{H}_7\text{OI}$ : I, 68.2%. Found: I, 67.9%.

The iodohydrin produced in the reaction of organomagnesium iodides or magnesium iodide with 1,2-epoxypropane could be either 1-iodo-2-propanol or 2-iodo-1-propanol or a mixture of the two. Analysis using the infrared method of Stewart and Vanderwerf<sup>25</sup> indicated that at least 90% of the iodohydrin was present as 1-iodo-2-propanol.

An attempt to prepare the 3,5-dinitrobenzoate of 1-iodo-2-propanol failed. However, an attempt to prepare the  $\alpha$ -naphthylurethane derivative was successful.<sup>14</sup> The product resulting from this reaction was recrystallized from ligroin until a constant melting point of 131.8–132.9° was obtained.

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{14}\text{O}_2\text{NI}$ : C, 47.50; H, 3.97; N, 3.94; I, 35.60. Found: C, 48.00; H, 4.12; N, 3.87; I, 34.97.

*Identification of products.* The alcohols were identified by their boiling points, their refractive indices, and by the melting points of their 3,5-dinitrobenzoates. In the case of 1-phenyl-2-propanol the phenylurethane was used instead of the 3,5-dinitrobenzoate for purpose of characterization.

The preparation of derivatives was accomplished by following standard procedures.<sup>14,15</sup> The derivatives are listed in Table V.

There appears to have been some error in reporting the melting point of the 3,5-dinitrobenzoate of 4-methyl-2-hexanol in earlier studies.<sup>7,8</sup> The melting point of 50–51° obtained for this derivative in this study agrees with the value reported by Cymerman, Heilbron, and Jones.<sup>20</sup>

*Calculation of yields.* The alcohols were isolated by fractionation. The per cent yield of each alcohol was calculated by taking the ratio of the moles of alcohol produced to the moles of organic radical present in the original Grignard reagent.

The yields of 1-iodo-2-propanol were determined by alkaline decomposition and Volhard titration of the iodide ion produced and on the basis of iodide found in the original Grignard reagent.

*Acknowledgment.* The authors' thanks are due to Drs. R. L. Guile and R. M. Herbst for their interest and encouragement throughout this investigation.

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(25) C. A. Stewart and C. A. Vanderwerf, *J. Am. Chem. Soc.*, **76**, 1259 (1954).