having marked reducing power revealed that the displacement was accompanied by reductive cleavage to give dimesitylmethane.[2] The reductive cleavage, which is analogous to that observed earlier in the reaction of dioxolones with *t*-butylmagnesium chloride,[3] has been realized also with triphenylmethyl acetate and with 3,3-diphenylphthalide. Both triphenylmethane and 1,1,1-triphenyl-2,2-dimethylpropane were isolated when triphenylmethyl acetate was treated with *t*-butylmagnesium chloride; and a small amount of *o*-benzohydrylbenzoic acid was obtained when the phthalide was treated with the same reagent. 9-Acetoxyanthracene reacted with the *t*-butyl reagent to give anthracene in a yield of 27%.

A dioxolone was prepared from benzaldehyde and mandelic acid and treated with *t*-butylmagnesium chloride. Reductive cleavage was not observed, however.

Experimental

Triphenylmethyl Acetate.—When triphenylmethyl acetate was treated with the *t*-butyl reagent, triphenylmethane and 1,1,1-triphenyl-2,2-dimethylpropane were obtained in yields of 10 and 20%, respectively. The melting point of the triphenyl derivative corresponded to that given by Gomberg, 185–187°.[4]

Anal. Calcd. for $C_{23}H_{24}$: C, 91.95; H, 8.05. Found: C, 92.02; H, 8.28.

3,3-Diphenylphthalide.—The reaction of *t*-butylmagnesium chloride with 3,3-diphenylphthalide, made by the interaction of phthalyl chloride and diphenylcadmium,[5] was carried out in the usual manner. The reaction mixture, in this case, turned a deep red when the phthalide was added to the Grignard reagent, the color persisting throughout the reaction. *o*-Benzohydrylbenzoic acid was obtained in a 14% yield when the alkaline wash solutions were acidified. The acid, melting at 160–162°, was identical with an authentic sample.[6] From the neutral portion a 60% recovery of phthalide was made.

9-Acetoxyanthracene.—To a Grignard reagent, prepared from 9.3 g. of *t*-butyl chloride and 2.4 g. of magnesium in 100 ml. of ether, was added a solution of 2.4 g. of 9-acetoxyanthracene in 40 ml. of ether. The reaction mixture was heated under reflux for an hour before being decomposed with an ice–hydrochloric acid mixture. The ether layer was washed with sodium carbonate solution and dried over anhydrous magnesium sulfate. Removal of the ether left 0.48 g. of red-orange crystals melting at 200–215°. Recrystallization of the compound from benzene raised the melting point to 214–217°; the melting point was not depressed when these crystals were mixed with an authentic sample of anthracene.

Preparation of 9-Acetoxyanthracene.—Fifty grams of acetic anhydride was added slowly to a solution of 12 g. of anthrone in 150 ml. of pyridine. After being heated under reflux for 15 minutes, the reaction mixture was cooled and poured into 500 ml. of ice-cold water. Treatment of the crystalline product with Darco and numerous recrystallizations from ethanol gave light yellow needles, m.p. 133–134°, yield 7.2 g. (44%).

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.32; H, 4.94.

Preparation of the Dioxolone from Benzaldehyde and Mandelic Acid.—When the procedure for acetone–mandelic acid[2] was applied to mandelic acid and benzaldehyde, the dioxolone was obtained in a yield of 50%, m.p. 104–105°.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 74.98; H, 5.04. Found: C, 74.90; H, 5.21.

The infrared spectrum of this dioxolone contains an absorption band at 1780 cm.$^{-1}$, assignable to a carbonyl group.

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The Reaction between Propylene Oxide and the *t*-Butyl Grignard Reagent[1]

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The product of the interaction of the Grignard reagent and an epoxy compound may result from cleavage of the ring in either of the two possible directions or may evolve from an initial isomerization of the epoxide to an aldehyde or ketone, followed by the usual addition of the reagent to the carbonyl group. The actual course of any specific reaction is determined by the structures of the epoxide and the Grignard reagent, and in some cases by the reaction conditions.[2]

The reaction between *t*-butylmagnesium halides and propylene oxide has been the subject of conflicting reports. Stevens and McCoubrey[3] reported that the reaction of *t*-butylmagnesium chloride with the oxide gives 2,2-dimethyl-3-pentanol as well as propylene chlorohydrin. Huston and his co-workers, without referring to the earlier work, reported that the reaction with *t*-butylmagnesium bromide[4] as well as with the chloride[5] yields 4,4-dimethyl-2-pentanol.[6] The present investigation was undertaken to clarify this discrepancy.

Results

The mixture from the reaction of *t*-butylmagnesium chloride and propylene oxide, after decomposition with an aqueous ammonium salt and destruction of propylene chlorohydrin with concentrated alkali, yields an alcoholic component (I) which has proved to be 2,2-dimethyl-3-pentanol (II). This proof is based on the comparison of the physical and chemical properties of I to authentic samples of II and 4,4-dimethyl-2-pentanol (III). In addition, I was oxidized with chromic acid to a ketone (IV) and the physical and chemical properties compared to authentic samples of 2,2-dimethyl-3-pentanone (V) and 4,4-dimethyl-2-pentanone (VI).

The authentic products were prepared by unequivocal methods. II was prepared by the reaction of *t*-butylmagnesium chloride with propionaldehyde and III was prepared by the reduction of VI with lithium aluminum hydride. V was prepared by the reaction of the ethyl Grignard reagent with pivalamide and VI was prepared by the chromic acid oxidation of diisobutylene.

The 3,5-dinitrobenzoates, 1-naphthylurethans and phenylurethans of I, II and III and the 2,4-dinitrophenylhydrazones and semicarbazones of

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[1] Abstracted from the M.S. Thesis of L. D. Caul, Canisius College June, 1954.

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[6] A summary of the conflicting evidence is given in reference 2, p. 430.

IV, V and VI were compared. The identity of I with II and IV with V is obvious from the melting points and mixed melting points given in the Experimental section. Therefore, the alcoholic product from the reaction of propylene oxide and the *t*-butyl Grignard reagent is 2,2-dimethyl-3-pentanol, probably arising from the rearrangement of the oxide to propionaldehyde, followed by normal Grignard addition.

Experimental

Reaction of *t*-Butylmagnesium Chloride with Propylene Oxide.—A total of 2200 ml. of ether solution containing 4.22 moles of *t*-butylmagnesium chloride (by analysis) was treated with 489 g. (8.44 moles) of propylene oxide in 500 ml. of ether over a period of 3 hours. Stirring was continued for an additional hour and the mixture was allowed to stand overnight. After an additional 4 hours stirring the reaction mixture was allowed to stand in a dark cabinet without stirring for 7 weeks. The mixture was decomposed with a saturated ammonium sulfate solution, extracted with ether and the ether solution washed until neutral. The ether solution was refluxed with 320 g. of sodium hydroxide and one liter of water for 6 hours to decompose the chlorohydrin. The ether was distilled through a fractionating column after which all volatile material was distilled as rapidly as possible through a Vigreux column using aspirator vacuum and a Dry Ice receiver. The volatile fraction, b.p. 30–190°, was fractionated through a 45-cm. packed column to yield 24 g. of material up to 52° (26 mm.), 125 g. (25% yield) at 52–56.5° (26 mm.) and 9.8 g. up to 88° (26 mm.). The main fraction (I), after redistillation, had freezing point −5°, n^{20}_{D} 1.4230, d^{20}_{4} 0.8246 (reported[5] b.p. 135.4° (742 mm.), n^{20}_{D} 1.4241), MR_{D} 35.89 (calcd. 36.05).

In another preparation of this same alcohol, using 2.84 moles of the Grignard reagent and 5.68 moles of propylene oxide, an 18% yield of I was recovered. In this preparation ammonium chloride was used in the hydrolysis after the mixture had been at room temperature for 52 days and benzene was used to wash the aqueous portion.

The 3,5-dinitrobenzoate of I had m.p. 94–95° (reported m.p. 92.5–93.0°[3] and 92–93°[7]), mixed melting point with derivative of II, m.p. 92.8–94°, mixed melting point with derivative of III, m.p. 71–72°.

The 1-naphthylurethan of I had m.p. 107–108° (reported[3] m.p. 107–108°), mixed melting point with derivative of II, m.p. 107.0–108.8°, mixed melting point with derivative of III, m.p. 77.1–78.2°.

The phenylurethan of I had m.p. 85–86°, mixed melting point with derivative of II, m.p. 84.0–85.6°, mixed melting point with derivative of III, m.p. 35–42°.

2,2-Dimethyl-3-pentanol (II).—Propionaldehyde (308 g., 5.3 moles) in an equal volume of ether was added over 1.5 hours to *t*-butylmagnesium chloride prepared over an 8-hour period from 484 g. (5.3 moles) of *t*-butyl chloride and 130 g. (5.3 moles) of magnesium in 2600 ml. of ether. The reaction mixture was refluxed for an additional hour and poured over a mixture of cracked ice and 5% sulfuric acid. The ether layer and ether extracts of the aqueous layer were washed with dilute sodium bisulfite solution, dilute sodium hydroxide and water, and dried over anhydrous sodium sulfate. Fractional distillation gave 4 g. of material at 45–53.5° (25 mm.) and 176 g. (28% yield) of II, b.p. 53.5–54.5° (25 mm.), freezing point 5°, n^{20}_{D} 1.4238, d^{20}_{4} 0.8281 (reported b.p. 136–137°, d^{20}_{20} 0.826[8] and b.p. 44–45° (15 mm.), n^{20}_{D} 1.4218[9]), MR_{D} 35.79 (calcd. 36.05).

The 3,5-dinitrobenzoate of II had m.p. 93.6–94.8° (reported[3] m.p. 92.5–93°).

The 1-naphthylurethan of II had m.p. 107.2–108.6° (reported m.p. 107–108°[3] and 109–110°[9]).

The phenylurethan of II had m.p. 82.2–83.5° (reported[10] m.p. 83°).

4,4-Dimethyl-2-pentanol (III).—An ethereal solution of lithium aluminum hydride was prepared by refluxing 6.5 g. (0.17 mole) of the complex hydride with 500 ml. of ether for 1.25 hours. 4,4-Dimethyl-2-pentanone (VI) (50 g., 0.44 moles) in 75 ml. of ether was added over 30 minutes and the mixture was refluxed for an additional 0.75 hours. The reaction mixture was hydrolyzed with 6.5 ml. of water, 6.5 ml. of 15% sodium hydroxide and 19.5 ml. of water. The granular precipitate was filtered, washed with ether and the ether solution was dried and evaporated. Fractionation gave 32.4 g. (63% yield) of III, b.p. 50.5–57.5° (25 mm.). Redistillation gave 24.1 g. at 57.0–57.5° (25 mm.), freezing point −60°, n^{20}_{D} 1.4188, d^{20}_{4} 0.8133 (reported[11] b.p. 137–137.5°, n^{20}_{D} 1.4188, d^{20}_{4} 0.8115).

The 3,5-dinitrobenzoate of III had m.p. 93.5–94.5° (reported m.p. 95–96°[3] and 95.2–95.7°[11]).

The 1-naphthylurethan of III had m.p. 86.1–87.0° (reported[11] m.p. 86.5–87°).

The phenylurethan of III did not crystallize on standing at room temperature even after several recrystallizations from petroleum ether in a Dry Ice–acetone freezing mixture. The liquid was distilled and collected at 115° (0.1 mm.) and left at room temperature for several days to crystallize. The product was recrystallized from petroleum ether, m.p. 51–53.5° (reported[12] m.p. 52–53°).

Oxidation of I.—I (23.0 g., 0.20 moles), mixed with 32 ml. of water and 8 ml. of concentrated sulfuric acid in a 250-ml. flask equipped with a stirrer and dropping funnel, was cooled to 10°. A chromic acid solution containing 20 g. (0.07 mole) of potassium dichromate in 32 ml. of water and 8 ml. of concentrated sulfuric acid was cooled to 10° and added dropwise with vigorous agitation while maintaining the temperature below 15°. The mixture was left at room temperature for 48 hours, diluted with 110 ml. of water and steam distilled. The organic layer was dried and distilled to yield 13.8 g. (60% yield) of IV, b.p. 122–127°. On redistillation IV had b.p. 125–127°, freezing point −45°, n^{20}_{D} 1.4065, d^{20}_{4} 0.8118, MR_{D} 34.59 (calcd. 34.54).

The 2,4-dinitrophenylhydrazone of IV had m.p. 121.4–122.0°, mixed melting point with derivative of V, m.p. 119.2–120.4°, mixed melting point with derivative of VI, m.p. 81–82°.

The semicarbazone of IV had m.p. 145.5–146.5°, mixed melting point with derivative of V, m.p. 144.2–145.6°, mixed melting point with derivative of VI, m.p. 130–133°.

2,2-Dimethyl-3-pentanone (V).—Trimethylacetyl chloride was prepared in 72% yield by heating 51 g. (0.50 mole) of trimethylacetic acid with 140.5 g. (1.00 mole) of benzoyl chloride.[13]

Trimethylacetamide, m.p. 152–153°, was prepared in 75% yield by adding 43 g. of trimethylacetyl chloride to 75 ml. of concentrated ammonium hydroxide.

Trimethylacetamide (125.4 g., 0.25 moles) in 500 ml. of ether was added over one hour to ethylmagnesium bromide prepared from 164 g. (1.5 moles) of ethyl bromide and 37 g. (1.5 moles) of magnesium in 550 ml. of ether. The mixture was refluxed for 16 hours and decomposed with cracked ice and dilute hydrochloric acid. The ether layer was dried and distilled to yield 14.5 g. (50% yield) of V at 60–62° (70 mm.), freezing point −49°, n^{20}_{D} 1.4057, d^{20}_{4} 0.8098 (reported[14] b.p. 123–124°, n^{20}_{D} 1.4052), MR_{D} 34.61 (calcd. 34.54).

The 2,4-dinitrophenylhydrazone of V had m.p. 121.2–122.2° (reported[15] m.p. 143.5–144.5° should probably refer to semicarbazone).

Anal. Calcd. for $C_{13}H_{18}N_4O_4$: C, 53.05; H, 6.17; N, 19.04. Found: C, 53.36; H, 6.01; N, 18.83.

The semicarbazone of V had m.p. 144.6–145.8° (reported[16] m.p. 144°).

4,4-Dimethyl-2-pentanone (VI).—The attempted oxidation of 2,4,4-trimethyl-1-pentene, b.p. 100–101°, obtained by fractionation of diisobutylene, with dilute chromic acid, was unsuccessful. The preparation of VI by the procedure

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of Mosher and Cox[17] using concentrated chromic acid gave a 48% yield of product, b.p. 123.5–127°, freezing point $-64°$, $n^{20}\mathrm{D}$ 1.4060, $d^{20}{}_4$ 0.8165 (reported[18] b.p. 122–124°, $n^{20}\mathrm{D}$ 1.4040), MR_D 34.35 (calcd. 34.54).

The 2,4-dinitrophenylhydrazone of VI had m.p. 97.1–98.2° (reported[19] m.p. 100°).

The semicarbazone of VI had m.p. 173–174° (reported m.p. 173.5–175.5°[20] and 176°[21]).

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The Direct Preparation of Benzyllithium

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No direct synthesis of benzyllithium has been reported but a number of indirect methods[1–4] which in every case require several intermediate steps, has been described. Consequently, it was desirable to find a method by which benzyllithium might be made directly from a benzyl halide and lithium. Also, because of its high order of reactivity as compared to the corresponding Grignard reagent and because of its value as a synthetic intermediate, benzyllithium could prove to be an extremely useful synthetic tool if it were possible to prepare by a simple, direct method.

Benzyllithium has been obtained in trace amounts in a metalation reaction and in a halogen-metal interconversion reaction. In the former case toluene was metalated laterally to give a very small yield of benzyllithium.[5] In the latter case benzyl chloride reacted with ethyllithium at $-50°$ to give a trace amount of phenylacetic acid upon carbonating the reaction mixture.[6] In another similar reaction it was found that benzyl bromide and phenyllithium reacted to form an almost quantitative yield of bibenzyl.[7]

In this Laboratory we have been able to synthesize benzyllithium directly though in small yields by the reaction of benzyl chloride with lithium ribbon in purified dioxane. As in previous work, the

$$C_6H_5CH_2Cl + 2Li \longrightarrow C_6H_5CH_2Li + LiCl$$

main difficulty encountered in this investigation was that the benzyllithium reacted rapidly with excess benzyl chloride to yield bibenzyl. To minimize this side-reaction, conditions were varied and different

$$C_6H_5CH_2Li + C_6H_5CH_2Cl \longrightarrow C_6H_5CH_2CH_2C_6H_5 + LiCl$$

solvents were tried. Of the various solvents used, benzyllithium could be prepared only in purified dioxane. Also, of the two types of lithium tried, namely ribbon and wire, benzyllithium was formed only when the ribbon was employed. This may have been due to the fact that the cuttings of the lithium ribbon afforded a greater surface area than the cuttings of lithium wire.

Despite the high dilution, the large excess of lithium ribbon and a relatively low temperature, the coupling reaction could not be diminished to any great extent.

The low yield of benzyllithium, as determined by carbonation, may have been partly due to the ineffectiveness of the carbonation. This difficulty arises because of the high freezing point of dioxane. In most cases the reaction mixture solidified in contact with the Dry Ice–ether slurry. In an attempt to alleviate this difficulty, the reaction mixture was diluted with ether prior to carbonation. This modification appeared to improve the facility of the carbonation but not enough to increase the yield appreciably.

A greater lithium surface should increase the yield of benzyllithium and decrease the yield of coupling products. This finds experimental support in the improved yields of some other RLi compounds when lithium dispersion is used.[8] The excess of lithium ribbon that can be used is limited, since beyond a certain quantity the lithium ribbon interferes with the stirring efficiency which is also very important.

Experimental[9]

Reaction of Benzyl Chloride with Lithium Ribbon.—To a 500-ml., three-necked flask fitted with a thermometer, nitrogen inlet, mechanical stirrer and addition funnel were added 7.25 g. (1.04 gram atoms) of lithium ribbon ($^1/_4'' \times {}^1/_{32}''$), cut into approximately $^1/_4''$ squares and 40 ml. of anhydrous ether. After washing the lithium ribbon with two additional such portions of ether, the ether was replaced with 100 ml. of purified dioxane.[10] To the rapidly stirred lithium ribbon suspension was added dropwise 6.0 g. (0.047 mole) of benzyl chloride dissolved in 50 ml. of dioxane over a period of 1.5 hours. The addition was continued at room temperature until a lemon-yellow color was evident at which time the reaction mixture was cooled to 10° by means of an ice-bath and the remaining benzyl chloride was added at this temperature. After about 10 ml. of the benzyl chloride solution had been added, the reaction mixture turned brown. The reaction mixture was stirred at 10° for 15 minutes upon completing the addition of the benzyl chloride and then it was carbonated by pouring the mixture jetwise through a glass wool plug alternately in two 1000-ml. beakers containing Dry Ice–ether slurries which were constantly being stirred. Prior to the carbonation Color Test I[11] was strongly positive. During the carbonation it was necessary to add anhydrous ether intermittently in order to prevent freezing of the carbonated mixture. After the carbonated mixtures were allowed to warm to room temperature, they were hydrolyzed with water. Subsequently, the solutions were combined and to the resulting solution was added about 10 ml. of 5% sodium hydroxide. The aqueous layer was separated and subsequently extracted with ether for 20 hours in a 1-liter, liquid–liquid extractor. The aque-

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