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THE REACTION OF GRIGNARD REAGENTS WITH 3,4-EPOXY-1-BUTENE. I. 1-NAPTHYLMAGNESIUM BROMIDE

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INTRODUCTION

The addition of Grignard reagents to 3,4-epoxy-1-butene is of interest because the unsaturated alcohols formed in the reaction are promising intermediates. For example, dehydration would lead to substituted butadienes. Semeniuk and Jenkins have reported the reaction of 3,4-epoxy-1-butene with the methyl Grignard (1). From the acidic hydrolysis of the adduct of 3,4-epoxy-1-butene with methylmagnesium iodide, they obtained 2-penten-1-ol. The structure was assumed on evidence of the boiling point only. Based upon this result, they advanced analogous structures for the reaction products with cyclohexylmagnesium chloride, phenylmagnesium bromide, 1-naphthylmagnesium bromide, and *o*-ethoxyphenylmagnesium chloride. They further advanced reasons "...to explain the fact that alcohols of but one isomeric form could be isolated". Work in progress in our laboratories with methylmagnesium bromide indicates that a mixture of alcohols is obtained, rather than an "... alcohol of one isomeric form". Thus far, three different isomeric alcohols have been isolated and characterized (to be reported later).

Upon reviewing the literature concerning the reactions of the oxirane ring with Grignard reagents, it was found that a variety of courses had been observed. These are briefly reviewed here.

Ethylene oxide reacts with a Grignard reagent to form an adduct, which, upon hydrolysis, yields mainly a primary alcohol (2, 3) and a small quantity of secondary alcohol (4). The course of the reaction is set forth as proceeding through a complex which rearranges to give (upon hydrolysis) the alcohol. The rearrangement occurs when the ether, in which the reaction is run, is removed; the increased temperature effects the rearrangement.

Substitution in the oxirane ring causes the reaction to proceed differently. With 1,2-epoxypropane, ring cleavage occurs with formation of a secondary alcohol (5). Replacing a hydrogen of the methyl group of 1,2-epoxypropane with chlorine or with a methoxy group or a phenoxy group leads to the same result, namely, the secondary alcohol (6, 7, 8, 9). Substitution of an ethyl group on the oxirane ring also gives the secondary alcohol; Levene and Walti obtained 3-heptanol from *n*-propylmagnesium bromide and 1,2-epoxybutane and analogous products from isopropyl and phenyl Grignard reagents (10).

Disubstitution on the oxirane ring results in the formation of products which are dependent upon the location of the substitents. Thus, 1,2-epoxy-2-methyl-

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propane (isobutylene oxide) gives 3-methyl-2-butanol which appears to have resulted from initial isomerization of the oxide to an aldehyde followed by normal addition (12, 13).

Disubstitution involving both carbons of the oxirane ring results in apparent isomerization to a ketone. Thus, with 2,3-epoxybutane, methylmagnesium bromide gives 2-methyl-2-butanol (14). Henry also found that 2,3-epoxy-2-methylbutane gives 2,3-dimethyl-2-butanol with the methyl Grignard reagent (11). That this is a case of initial isomerization to the ketone followed by addition and not due to a normal ring cleavage was demonstrated by Norton and Hass when they obtained 2,3-dimethyl-3-pentanol from the oxide and the ethyl Grignard (15). The ethyl Grignard and 2,3-dimethyl-2,3-epoxybutane also react through isomerization to the ketone to give 2,2,3-trimethyl-3-pentanol (15).

Another epoxide which has been investigated extensively is 1-phenyl-1,2-epoxyethane (styrene oxide). Tiffeneau and Fourneau found that organomagnesium compounds gave the product resulting from addition to phenylacetaldehyde, presumably formed by initial isomerization of styrene oxide (16). Kharasch and Clapp, however, found that the order of addition of reagents determines the products formed in the reaction with aryl Grignards. Thus, from styrene oxide and phenylmagnesium bromide, addition of the oxide to the Grignard gave 2,2-diphenylethanol (no isomerization), while addition of the Grignard to the oxide gave 1,2-diphenylethanol (initial isomerization to phenylacetaldehyde) (17). Similar results were obtained with *p*-anisylmagnesium bromide. Golumbic and Cottle found that this same oxide gave 1-phenyl-2-propanol with methylmagnesium iodide, the result of apparent initial isomerization to the aldehyde (18).

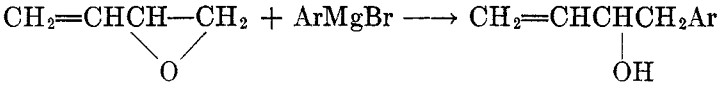
Tiffeneau observed that 1,2-epoxy-2-phenylpropane gives a secondary alcohol with phenylmagnesium bromide (apparent isomerization) (19). This same phenomenon was observed by Khaletzkii using the Grignard reagent from *tert*-butyl chloride (20).

It has been observed generally that the reaction of epoxides with dialkyl- or diaryl-magnesium compounds gives products resulting only from normal opening of the ring without attendant isomerization (15, 18, 21).

RESULTS AND DISCUSSION

The addition of 1-naphthylmagnesium bromide to 3,4-epoxy-1-butene or butadiene monoxide, in diethyl ether, followed by hydrolysis of the adduct gave a viscous, colorless liquid product (I) (assumed at this point), b.p. 147.5–153°/0.2 mm., in 55–58% yield. This compound slowly decolorized bromine in carbon tetrachloride and rapidly reduced potassium permanganate in acetone. It gave a 1-naphthylurethan (VI), m.p. 103–104.5°, and a xanthate (VII), m.p. 180.5–181.8° (dec.). It did not form an acid phthalate. Its analysis for carbon and hydrogen was in accord with one of the isomeric carbinols expected.

From the Introduction it is seen that several structures are feasible for this carbinol:



$$\mathrm{CH_2{=}CH\overset{}{CH}{-}CH_2} \ (\text{epoxide, O}) + \mathrm{ArMgBr} \longrightarrow \mathrm{CH_2{=}CH\underset{\underset{OH}{|}}{C}HCH_2Ar}$$

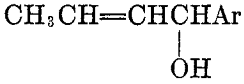
I

$$\mathrm{CH_2{=}CH\underset{\underset{Ar}{|}}{C}HCH_2OH}$$

II

$$\mathrm{CH_2{=}CHCH_2\underset{\underset{OH}{|}}{C}HAr}$$

III



$$\mathrm{CH_3CH{=}CH\underset{\underset{OH}{|}}{C}HAr}$$

IV

$\mathrm{HOCH_2CH{=}CHCH_2Ar}$ Ar = 1-Naphthyl

V

I and II would result from cleavage of the oxirane ring without attendant isomerization. III would result from initial isomerization to an aldehyde with subsequent normal Grignard addition. IV would result from isomerization to the aldehyde, as in III, followed by an allylic shift of the double bond with subsequent normal Grignard addition. This does not seem unlikely, since isocrotonaldehyde is not known; syntheses leading to it result in crotonaldehyde (22). V would result from formation of I followed by an allylic shift of the hydroxyl group or by an attack of the negative aryl group at the 1-position followed by shift of the double bond and opening of the oxirane ring to give the primary alcohol.

Since neither the isolated carbinol nor its isomers had been reported in the literature, experiments were undertaken to determine the position of the hydroxyl and 1-naphthyl groups by degradation and synthesis.

Hydrogenation of the carbinol was carried out over palladium on charcoal. The product (VIII) gave a xanthate (IX), m.p. 175–176° (dec.), which depressed the melting point, 180.5–181.8° (dec.), of the xanthate (VII) prepared from the unsaturated carbinol.

An Oppenauer oxidation was performed on VIII. A product (X) was obtained in 52.5% yield. It gave no 2,4-dinitrophenylhydrazone. However, it did give a positive von Bitto test (an alkaline nitroprusside solution) indicating the presence of the carbonyl group. Negative fuchsin and Tollens tests indicated that the compound was probably a ketone. A semicarbazone (XI) was obtained, m.p. 165–167°, with some difficulty.

The probable presence of a keto group eliminated structures II and V from consideration since oxidation of these carbinols would result in the formation of aldehydes. To confirm elimination of II, the compound (X) was subjected to a Clemmensen reduction. The product (XII) gave a picrate (XIII), m.p. 104°, which corresponds with that of 1-*n*-butylnaphthalene (104–106°) (23). The melting point of 1-(1-methylpropyl)naphthalene picrate is 76° (24).

The synthesis of the carbinol III was carried out in 94% yield from allylmagnesium chloride and 1-naphthaldehyde. The carbinol gave a xanthate (XIV), m.p. 163.8–165° (dec.), which depressed the melting point of the xanthate (VII), m.p. 180.5–181.8° (dec.), and a 1-naphthylurethan (XV), m.p. 115.5–117°, which depressed the melting point of the urethan (VI), m.p. 103–104.5°.

Therefore, structure III involving isomerization to vinylacetaldehyde followed by normal addition is eliminated. A further consideration in the elimination of III is the relative stability of the known carbinol as compared with the product from the Grignard reaction with the epoxide (see Experimental).

IV was synthesized by the addition of 1-naphthylmagnesium bromide to crotonaldehyde. The structure of the product was assumed, in view of the work of Stevens (25, 26) which demonstrated that phenylmagnesium bromide adds 1,2 to the α,β-unsaturated system in crotonaldehyde. All attempts to prepare the 1-naphthylurethan, acid phthalate, and potassium xanthate failed. Wherever the application of heat was necessary, the product was converted to a polymeric mass. None of the oily residues crystallized after standing two years. The ease with which this carbinol dehydrates upon heating and the inability to prepare derivatives of it, contrasts markedly with the behavior of the unknown carbinol.

Synthesis of I did not appear feasible since the Grignard reagent prepared from 1-chloromethylnaphthalene added to acrolein would not give an unambiguous reaction product. Delaby reported that the analogous reaction between acrolein and benzylmagnesium chloride gave only 5% of the carbinol expected by 1,2-addition (27). Thus, the synthesis of 1-(1-naphthyl)-2-butanone (X) was attempted since the ketone derived from I had given a semicarbazone.

1-(1-Naphthyl)-2-butanone was synthesized by adding ethylmagnesium bromide to 1-naphthaleneacetonitrile. This ketone gave a semicarbazone (XVI) m.p. 166–167.5°, which did not depress the melting point of the semicarbazone XI.

Therefore, the major product resulting from the reaction of 3,4-epoxy-1-butene with 1-naphthylmagnesium bromide is the carbinol, 1-(1-naphthyl)-3-buten-2-ol (I).

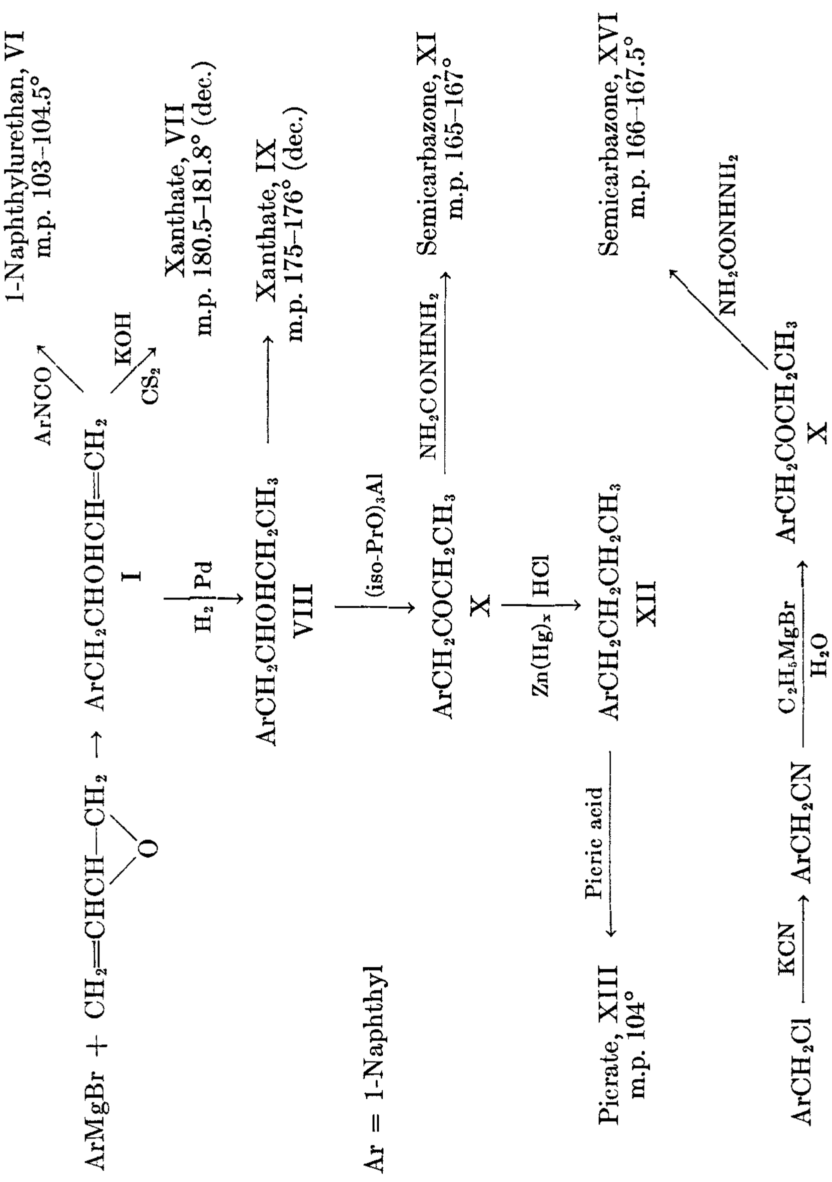
The steps leading to this conclusion are outlined in Chart I.

MECHANISM

The opening of an unsymmetrically substituted oxirane ring by means of the Grignard reagent, in general, takes place at the terminal carbon atom leading to a secondary alcohol. Thus, the addition of the Grignard reagent to 1,2-epoxypropane (10, 13, 15, 28–31), epichlorohydrin (7, 8, 32–42), 1,2-epoxy-3-methoxypropane (6, 9), and 1,2-epoxybutane (10) all give secondary alcohols. Only in the one instance, in which styrene oxide was added to the Grignard reagent, was the ring opened to give a primary alcohol (17).

Since the Grignard reagent is a strong base, other base-catalyzed reactions should be analogous. Kadesch has observed that the sodium methoxide-catalyzed methanolysis of 3,4-epoxy-1-butene results in the secondary alcohol (43). In the hands of Bartlett and Ross this result was verified, although a small quantity of the isomeric product was obtained (44). More recently, Swern and co-workers have reported similar results with allyl alcohol (45). Russell and Vander Werf have shown that the same ring opening is noticed with 3,4-epoxy-1-butene in the reaction with sodium ethyl malonate (46). Finally

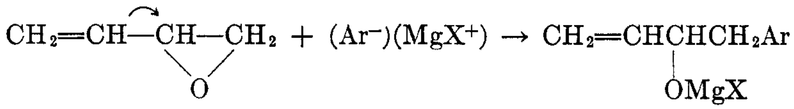
CHART I


ArMgBr + CH₂=CHCH—CH₂ (O) → ArCH₂CHOHCH=CH₂
I
ArNCO
1-Naphthylurethan, VI
m.p. 103–104.5°
KOH
CS₂
Xanthate, VII
m.p. 180.5–181.8° (dec.)
H₂ | Pd
ArCH₂CHOHCH₂CH₃
VIII
Xanthate, IX
m.p. 175–176° (dec.)
Ar = 1-Naphthyl
(iso-PrO)₃Al
ArCH₂COCH₂CH₃
X
NH₂CONHNH₂
Semicarbazone, XI
m.p. 165–167°
Zn(Hg)ₓ | HCl
ArCH₂CH₂CH₂CH₃
XII
Picric acid
Picrate, XIII
m.p. 104°
ArCH₂Cl
KCN
ArCH₂CN
C₂H₅MgBr
H₂O
ArCH₂COCH₂CH₃
X
NH₂CONHNH₂
Semicarbazone, XVI
m.p. 166–167.5°

Trevoy and Brown have shown that lithium aluminum hydride also effects opening of the oxirane ring at the terminal carbon (47).

From these results it seems reasonable that the reaction examined here is an ionic one and probably proceeds in the following way: The vinyl group donates electrons to the carbon to which it is attached, rendering it relatively negative to the distal carbon atom. The electron density is thus lower at the far carbon atom, so that the attack of the carbanion takes place there.

From steric considerations, also, the bulky 1-naphthyl group should militate for addition at the terminal position, which is less sterically hindered.



EXPERIMENTAL

All temperatures are uncorrected.

Starting materials. Ethyl bromide (b.p. 38°, n_D^{20} 1.4239), allyl chloride[2] (b.p. 45°, n_D^{20} 1.4154), and crotonaldehyde (b.p. 103–105°, n_D^{20} 1.4360) were distilled before use.

3,4-Epoxy-1-butene. The commercial product[3] was dried over Drierite and fractionated through a total reflux, partial take-off column [packed section (6-mm. Pyrex helices) 126 cm. long, 2.2 cm. o.d., 1.8 cm. i.d.]. After removing a small amount of a water azeotrope (48), the product distilled at 66.4–66.6°/760, n_D^{25} 1.4152 [reported, b.p. 65–65.8°/739, n_D^{20} 1.4170 (43); b.p. 67°, n_D^{25} 1.4151 (44); b.p. 67.6°/760, $n_D^{20.5}$ 1.4167 (48)].

1-Bromonaphthalene. Direct bromination of naphthalene according to Clarke and Brethen (49) gave the product in 73% yield, b.p. 132°/12, n_D^{20} 1.6582.

Addition of 1-naphthylmagnesium bromide to 3,4-epoxy-1-butene. Several preliminary experiments were carried out to determine the optimum conditions for forming the product. The temperature of the reaction was varied by replacing the ethyl ether with isopropyl ether and also by replacing part of the ethyl ether with benzene until the temperature of the reaction mixture was 70°. It was necessary to remove scrupulously all traces of acid from all apparatus in order to minimize dehydration during distillation of the product. The following experiment represents one which gave the best results.

1-Naphthylmagnesium bromide was prepared under nitrogen from 6.08 g. (0.25 atom) of magnesium turnings and 51.8 g. (0.25 mole) of 1-bromonaphthalene in 175 ml. of absolute ethyl ether (50). A solution of 17.5 g. (0.25 mole) of 3,4-epoxy-1-butene in 50 ml. of ether was added dropwise with stirring at such a rate as to maintain a vigorous reflux (about 45 minutes is required). Stirring was continued for eight hours after the reflux and then the reaction mixture was allowed to stand at room temperature for twelve hours.

The solution was hydrolyzed with 100 ml. of 2.5 *N* hydrochloric acid and 200 g. of ice, the ether layer separated, and the water layer extracted with ether; the combined ether extracts were washed with water until neutral. After drying the ether layer over potassium carbonate, filtering, and concentrating it at reduced pressure, it was steam-distilled at reduced pressure to remove naphthalene. During this codistillation, which required 2 l. of water, the vapor temperature did not exceed 50°. The residue was extracted with ether and dried twice with fresh potassium carbonate. After distillation of the ether, distillation of the residue gave 27.2–28.6 g. (0.137–0.145 mole; 55–58%) of the carbinol (I), b.p. 147.5–153°/0.2, d_4^{20} 1.094. Some dehydration accompanied the distillation.

The carbinol evolved hydrogen slowly when treated with sodium. It slowly decolorized

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[2] Kindly supplied by the Shell Development Corporation, Emeryville, California.

[3] Kindly supplied by the Columbia Chemicals Division of the Pittsburgh Plate Glass Company, Pittsburgh 13, Pa.

bromine in carbon tetrachloride, but rapidly decolorized potassium permanganate in acetone.

1-Naphthylurethan (VI). A mixture of 0.65 g. of the carbinol and 0.55 g. of 1-naphthylisocyanate was heated on a steam-bath for fifteen minutes. Upon cooling, an oil appeared which did not solidify after standing five days in a refrigerator. Extraction of the reaction mixture with 10 ml. of hot Skellysolve C (petroleum ether, b.p. 85–100°) gave a solution of the product from which 0.82 g. (68%) of the crude urethan, m.p. 101.4–104°, was obtained. Two more recrystallizations raised the melting point to 103–104.5°.

Xanthate (VII). The procedure was a modification of that of Whitmore and Lieber (51). A solution of 0.47 g. of the carbinol and 0.11 g. of pulverized potassium hydroxide was prepared by heating the mixture on a steam-bath. The supernatant liquid was decanted from undissolved alkali and, after cooling, was diluted with an equal volume of dry ether. Upon the addition, with stirring, of 0.18 ml. of carbon disulfide, the cream-colored xanthate precipitated and was filtered after dilution of the mixture with twice its volume of ether. The crude xanthate (0.12 g., 20% yield) was slurried with ether and filtered. After purification by precipitation with ether from absolute alcohol the xanthate had m.p. 180.5–181.8° (dec.).

Attempted preparation of the acid phthalate. The procedure of Goggans and Copenhaver was employed (52). A solution of the carbinol (0.5 g.) and phthalic anhydride (5 g.) in pyridine (3 ml.) was heated on a steam-bath for ten minutes and then cooled. After extracting with ether to remove excess anhydride, heating with water at 60°, extracting with chloroform to leave behind residual phthalic acid, and drying over sodium sulfate, attempts to crystallize the oily residue from chloroform or benzene-petroleum ether were unsuccessful. The product was still a viscous, brown oil after standing in a refrigerator for two years.

PROOF OF STRUCTURE

Hydrogenation of I to 1-(1-Naphthyl)butan-2-ol (VIII). Ten grams (0.050 mole) of I in a mixture of 100 ml. of methanol and 100 ml. of toluene over 0.5 g. of 5% palladium on charcoal took up the theoretical amount of hydrogen, 1290 ml., in 19 minutes. However, because the rate at the end of that time was as rapid as that at the beginning, a total of 1395 ml. (8.1% excess) of hydrogen was added. The total time consumed was 22 minutes. Upon filtering and distilling at reduced pressure, there was obtained 7.9 g. (0.039 mole; 78%) of product (VIII), b.p. 136–139°/0.3 which did not decolorize permanganate solution.

Xanthate (IX). The xanthate was prepared, as previously described, from the saturated product. The crude xanthate (14% yield) had m.p. 174–176° (dec.) and upon recrystallization this was raised to 175–176° (dec.). A mixed melting point with xanthate VII was depressed to 168° (dec.).

Oxidation to 1-(1-Naphthyl)-2-butanone (X). An Oppenauer oxidation was carried out in a manner similar to that investigated by Adkins and Franklin (53). A mixture of 5.9 g. (0.03 mole) of VIII, 7 g. of aluminum isopropoxide (redistilled Eastman Kodak Technical grade), 100 ml. of distilled methyl ethyl ketone, and 50 ml. of dry benzene was refluxed for 18 hours. After adding 3 ml. of water to the hot solution, the mixture was filtered with suction and the precipitate of aluminum hydroxide washed with four 5-ml. portions of ether. The combined filtrates were dried quickly over potassium carbonate, residual water being removed by azeotropic distillation with 50 ml. of benzene, and distilled at reduced pressure to give 3.1 g. (0.016 mole; 52.5%) of product (X), b.p. 142–143°/0.5.

The product gave no precipitate with phenylhydrazine or 2,4-dinitrophenylhydrazine. A positive von Bitto test (54) was obtained by adding 1 ml. of 0.5% sodium nitroprusside solution to the product in distilled carbonyl-free methanol. Upon making the solution alkaline with sodium hydroxide solution, a yellow-red color was obtained.

Fuchsin-aldehyde and Tollens tests were negative. Attempts to prepare a 2,4-dinitrophenylhydrazone by the usual methods (55) were unsuccessful. An attempt to prepare it by heating the carbonyl compound in a glacial acetic acid solution of the reagent was also unsuccessful.

Semicarbazone (XI). The ketone X (0.25 ml.) was dissolved in 2 ml. of ethanol (56). The solution was made turbid with water, and 0.25 g. of semicarbazide hydrochloride and 0.4 g. of sodium acetate were added and the mixture was agitated. It was heated in boiling water, allowed to cool, and then placed in a refrigerator. After four days, the semicarbazone (XI), (0.23 g.; 41%), was obtained. After recrystallization from 50% ethanol, XI had m.p. 165–167°.

Clemmensen reduction of X *to n-butylnaphthalene* (XII). According to Martin's procedure (57), 4 g. of granulated zinc was shaken with a mixture of 6 ml. of water, 0.2 ml. of concentrated hydrochloric acid, and 0.4 g. of mercuric chloride. The aqueous solution was decanted after 5 minutes and 3 ml. of water, 7 ml. of concentrated hydrochloric acid, 4 ml. of toluene, 1.2 g. of 1-(1-naphthyl)-2-butanone (X), and 0.2 ml. of glacial acetic acid were added to the residue in that order. The mixture was refluxed for 27 hours with 6 ml. of concentrated hydrochloric acid added in three portions at 6-hour intervals. After cooling the mixture, it was extracted with ether, the ether solution dried over potassium carbonate, and the solution concentrated under reduced pressure on a steam-bath. The residual brown oil was treated with a saturated solution of picric acid. A yellow picrate deposited, m.p. 104°.

RELATED SYNTHESES

1-Chloromethylnaphthalene was prepared by the method of Grummitt and Buck (58) in 55% yield, n_D^{20} 1.635.

1-Naphthaldehyde. An attempt was made to convert 1-chloromethylnaphthalene to 1-naphthaldehyde by oxidation with hexamethylenetetramine according to Badger (59) (acetic acid as solvent). The method was attractive due to the stated reaction time of 1 minute. However, troublesome emulsions were encountered so that the procedure of Ruggli and Preuss (60) was modified for this synthesis and is herein given.

In a 3-necked, 5-l. flask equipped with stirrer, thermometer, and reflux condenser, a mixture consisting of 112 g. (0.63 mole) of 1-chloromethylnaphthalene, 89.6 g. (0.64 mole) of hexamethylenetetramine, and 2560 ml. of 60% alcohol was refluxed for six hours. The alcohol was removed under reduced pressure and the brown oil which separated was extracted with two 100-ml. portions of ether. The ether solution was cooled to 5° and 200 ml. of a saturated sodium bisulfite solution was slowly added with stirring. The bisulfite addition product was filtered and washed successively with water and benzene. Heating the addition product on the steam-bath with the calculated amount of 2.5 *N* hydrochloric acid solution was followed by extraction of the resulting brown oil with 100 ml. of ether, drying over potassium carbonate, and finally distillation to give 62.9 g. [0.403 mole; 63.6%; reported yield (60) 45–50%] of colorless oil, b.p. 117–121°/2.4.

1-(1-Naphthyl)-3-buten-1-ol (III). The Grignard reaction was carried out by the method of Arnold and Coyner (61). To a mixture of 6.05 g. (0.25 atom) of magnesium in 150 ml. of ether was added 2 ml. of allyl chloride. After the reaction was started, a solution of 24.4 ml. (total, 25.7 g.; 0.34 mole) of allyl chloride and 28.9 g. (0.185 mole) of 1-naphthaldehyde in 75 ml. of ether was added dropwise over 25 minutes. The mixture was stirred at room temperature for twelve hours, and then was allowed to stand for nine hours. After decomposing the mixture with 100 ml. of 2.5 *N* hydrochloric acid and 200 g. of scraped ice, extracting with three 50-ml. portions of ether, washing the combined ether extracts with water until neutral, and concentrating to 100 ml., the residual water layer was separated. The ether layer was dried over potassium carbonate and distilled to give 34.5 g. [0.174 mole; 94%; recalculation of the reported yield (61) indicated 86% had been obtained] of III, b.p. 141.5–143.5°/0.8, n_D^{25} 1.6099 [reported (61) b.p. 150–151°/5].

Xanthate (XIV). The derivative was prepared from 1.41 g. of carbinol III, 0.33 g. of pulverized potassium hydroxide, and 0.54 ml. of carbon disulfide according to the earlier directions. Recrystallization from ethanol gave the xanthate XIV (0.35 g.; 19%), m.p. 163.8–165° (dec.). A mixed melting point with xanthate VII was depressed to 152° (dec.).

1-Naphthylurethan (XV). The derivative was prepared from 0.65 g. of the carbinol III and 0.55 g. of 1-naphthylisocyanate according to the earlier directions. Recrystallization from petroleum ether gave the urethan XV (0.90 g.; 74%), m.p. 115.5–117°. A mixed melting point with urethan VI was depressed to 90°.

1-(1-Naphthyl)-2-buten-1-ol (IV). Preliminary experiments indicated the extreme sensitivity of the reaction product to heat and traces of acid. The following procedure was finally adopted as giving the best results. 1-Naphthylmagnesium bromide was prepared in the usual manner from 6.08 g. (0.25 atom) of magnesium and 51.8 g. (0.25 mole) of 1-bromonaphthalene in 175 ml. of ether. Crotonaldehyde (17.5 g., 0.25 mole) in 50 ml. of ether was added over thirty minutes. After stirring for eight hours and standing for eight more, the mixture was hydrolyzed with 100 ml. of 2.5 *N* hydrochloric acid and 200 g. of ice, and extracted with three 50-ml. portions of ether. The combined ether extracts were washed with water until neutral, dried over potassium carbonate, concentrated, and distilled with steam at reduced pressure under nitrogen. When naphthalene ceased codistilling the residue was extracted with 150 ml. of ether in three portions, the ether solution concentrated to 50 ml., dried over potassium carbonate, and distilled under nitrogen at reduced pressure from a modified Claisen flask to give 40 g. (0.20 mole; 80%) of IV, b.p. 147–148°/0.55.

Attempts to prepare the 1-naphthylurethan, acid phthalate, and potassium xanthate were unsuccessful. In all cases, oils resulted which appeared to be polymeric in nature. None of the residues crystallized after standing two years.

1-Naphthaleneacetonitrile. The procedure of Adams and Thal (62) for the preparation of benzyl cyanide was modified for the synthesis of 1-naphthaleneacetonitrile. Sodium cyanide (36 g., 0.74 mole) and 32 ml. of water were placed in a 500-ml. flask equipped with a dropping-funnel and reflux condenser. The mixture was heated on a steam-bath to dissolve the cyanide, and a solution of 100 g. (0.57 mole) of 1-chloromethylnaphthalene in 71 g. of 95% ethanol was added dropwise over one-half hour. The mixture was refluxed on a steam-bath for four hours, cooled, filtered to remove sodium chloride, and the salt washed with a small portion of alcohol. As the filtrate was concentrated on a steam-bath, the nitrile layer separated and was then distilled from a modified Claisen flask to give 59 g. (0.35 mole, 62%) of a colorless oil, b.p. 158–160°/2, 136–137°/0.5; n_D^{25} 1.6173 [reported, b.p. 175–185°/11–14 (63), b.p. 150–152°/1.5 (64)].

1-(1-Naphthyl)-2-butanone. In a preliminary experiment in which the reaction mixture was immediately hydrolyzed with ammonium chloride after addition of the Grignard reagent, no ketone was obtained and a 79% recovery of nitrile was effected. The procedure finally utilized follows.

The Grignard reagent was prepared in the usual way from 4.1 g. (0.17 atom) of magnesium, 18.5 g. (0.17 mole) of ethyl bromide, and 100 ml. of anhydrous ether. A solution of 30 g. (0.18 mole) of 1-naphthaleneacetonitrile in 50 ml. of ether and 50 ml. of benzene was added dropwise over 75 minutes. The mixture was refluxed for two hours, 200 ml. of benzene was added, and the solution distilled until the vapor temperature reached 70°. Refluxing was continued for three hours and the mixture was allowed to stand at room temperature overnight. During the addition of the nitrile a yellow-orange precipitate formed which changed to a viscous, immobile mass after the refluxing period. After decomposing the precipitate with a dilute hydrochloric acid and ice mixture, the organic layer was separated and the aqueous layer extracted with ether. Neutralization of the aqueous acidic layer with ammonium hydroxide gave rise to troublesome emulsions during the extraction with ether. The ether extracts were combined, dried, and the ether removed. No residual imine was found.

The original organic layer was dried, and the ether and benzene evaporated leaving a viscous black oil. Distillation from a Claisen flask gave 5.3 g. (0.027 mole; 16%) of product, b.p. 119–134°/0.5, and a large polymeric residue. On removing the polymeric material from the flask with benzene, a white solid was obtained which did not melt below 300°. No further work was done on this substance.

Semicarbazone (XVI). The derivative was prepared from 0.25 ml. of the ketone and 0.25 g. of semicarbazide hydrochloride according to the earlier directions. Recrystallization gave the semicarbazone; yield 54%, m.p. 166–167.5°. A mixed melting point with semicarbazone XI showed no depression.

TABLE I

PHYSICAL CONSTANTS AND ANALYSES OF COMPOUNDS

COMPOUND	B.P., °C.	MM.	n_D (°C.)	M.P., °C.	ANALYSES					
					Calc'd			Found		
					C	H	N	C	H	N
I	147.5–153	0.2	1.6166(27)		84.81	7.12		84.40	7.18	
VI				103–104.5	81.72	5.76	3.81	81.46	5.77	3.79
VII				180.5–181.8(dec.)	57.65	4.19	2.05(S)	57.18	4.25	2.16(S)
VIII	136–139	0.3			83.97	8.05		84.05	8.01	
IX				175–176(dec.)	57.28	4.81	2.04(S)	56.75	4.42	2.09(S)
XI				165–167	70.56	6.71	16.46	70.25	6.62	16.63
XIII				104						
1-Naphthaldehyde	117–121[a]	2.4	1.6551(20)		84.59	5.16		84.32	5.18	
III	141.5–143.5	0.8	1.6099(25)		84.81	7.12		84.62	7.12	
XIV				163.8–165(dec.)	57.65	4.19	2.05(S)	57.22	4.24	2.09(S)
XV				115.5–117			3.81			3.69
IV	147–148	0.55	1.6185(30)		84.81	7.12		84.56	7.19	
XVI				166–167.5	70.56	6.71	16.46	70.88	6.69	16.69

[a] Previously reported by Ruggli and Preuss (60), b.p. 156–157°/14 mm.; Badger (59), b.p. 150°/13 mm.

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SUMMARY

The major product of the reaction of 1-naphthylmagnesium bromide with 3,4-epoxy-1-butene is 1-(1-naphthyl)-3-buten-2-ol. This was demonstrated in two ways: (a) reduction to 1-(1-naphthyl)-butan-2-ol, oxidation to 1-(1-naphthyl)-2-butanone, reduction to 1-(1-naphthyl)butane, and preparation of the known picrate of the hydrocarbon; (b) comparison of the semicarbazone of the 1-(1-naphthyl)-2-butanone so prepared and that prepared from the same ketone resulting from an unequivocal synthesis.

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BIBLIOGRAPHY

(1) SEMENIUK AND JENKINS, *J. Am. Pharm. Assoc., Sci. Ed.*, **37**, 118 (1948).
(2) GRIGNARD, *Bull. soc. chim.*, (3) **29**, 944 (1903).
(3) GRIGNARD, *Compt. rend.*, **136**, 1260 (1903).
(4) COTTLE AND HOLLYDAY, *J. Org. Chem.*, **12**, 510 (1947).
(5) HENRY, *Compt. rend.*, **145**, 453 (1907).
(6) BOYD AND VINEALL, *J. Chem. Soc.*, 1622 (1929).
(7) KOELSCH AND MCELVAIN, *J. Am. Chem. Soc.*, **51**, 3390 (1929).
(8) KOELSCH AND MCELVAIN, *J. Am. Chem. Soc.*, **52**, 1164 (1930).
(9) RIBAS, *Anales soc. españ. fís. y quím.*, **26**, 122 (1928).
(10) LEVENE AND WALTI, *J. Biol. Chem.*, **90**, 81 (1931).
(11) HENRY, *Compt. rend.*, **144**, 308 (1907).
(12) HENRY, *Compt. rend.*, **145**, 21 (1907).
(13) HENRY, *Compt. rend.*, **145**, 154 (1907).
(14) HENRY, *Compt. rend.*, **145**, 406 (1907).
(15) NORTON AND HASS, *J. Am. Chem. Soc.*, **58**, 2147 (1936).
(16) TIFFENEAU AND FOURNEAU, *Compt. rend.*, **146**, 697 (1908).
(17) KHARASCH AND CLAPP, *J. Org. Chem.*, **3**, 355 (1938).
(18) GOLUMBIC AND COTTLE, *J. Am. Chem. Soc.*, **61**, 996 (1939).
(19) TIFFENEAU, *Compt. rend.*, **140**, 1458 (1905).
(20) KHALETZKII, *J. Gen. Chem. (U.S.S.R.)*, **6**, 1 (1936); *Chem. Abstr.*, **30**, 4844 (1936).
(21) COTTLE AND POWELL, *J. Am. Chem. Soc.*, **58**, 2267 (1936).
(22) WHITMORE, *Organic Chemistry*, Van Nostrand Company, New York, 1937, p. 274.
(23) BEILSTEIN, 4th edition, **6**, 273.
(24) TSUKERVANIK AND TERENT'EVA, *J. Gen. Chem. (U.S.S.R.)*, **7**, 637 (1937); *cf. Elsevier's Encyclopedia of Organic Chemistry*, edited by F. Radt, vol. 12 B, Elsevier Publishing Company, Amsterdam, Holland, 1948, p. 123.
(25) STEVENS, *J. Am. Chem. Soc.*, **56**, 1425 (1934).
(26) STEVENS, *J. Am. Chem. Soc.*, **57**, 1112 (1935).
(27) DELABY, *Compt. rend.*, **194**, 1248 (1932).
(28) HESS, *Ber.*, **46**, 3113 (1913).
(29) LEVENE AND WALTI, *J. Biol. Chem.*, **94**, 367 (1931).
(30) NEWMAN, *J. Am. Chem. Soc.*, **62**, 2295 (1940).
(31) SHAREFKIN AND RITTER, *J. Am. Chem. Soc.*, **63**, 1478 (1941).
(32) FOURNEAU AND TIFFENEAU, *Bull. soc. chim.*, (4) **7**, 1227 (1907).

(33) Iotsitch, *J. Russ. Phys.-Chem. Soc.*, **34,** 96 (1902); *cf. Bull. soc. chim.*, (3) **28,** 920 (1902).

(34) Iotsitch, *J. Russ. Phys.-Chem. Soc.*, **35,** 554 (1903); *cf. Bull. soc. chim.*, (3) **32,** 704 (1904).

(35) Iotsitch, *J. Russ. Phys.-Chem. Soc.*, **36,** 6 (1904); *cf. Bull. soc. chim.*, (3) **34,** 185 (1904).

(36) Kling, *Bull. soc. chim.*, (3) **31,** 14 (1904).

(37) Magrane and Cottle, *J. Am. Chem. Soc.*, **64,** 484 (1942).

(38) Normant, *Compt. rend.*, **219,** 163 (1944).

(39) Ribas and Tapia, *Anales soc. españ. fís. y quím.*, **28,** 636 (1930).

(40) Riedel, German Patent 183,361 (1907); *Chem. Zentr.*, 1607 I (1907).

(41) Stahl and Cottle, *J. Am. Chem. Soc.*, **65,** 1782 (1943).

(42) Tapia and Hernandez, *Anales soc. españ. fís. y quím.*, **28,** 691 (1930).

(43) Kadesch, *J. Am. Chem. Soc.*, **68,** 41 (1946).

(44) Bartlett and Ross, *J. Am. Chem. Soc.* **70,** 926 (1948).

(45) Swern, Billen, and Knight, *J. Am. Chem. Soc.*, **71,** 1152 (1949).

(46) Russell and Vander Werf, *J. Am. Chem. Soc.*, **69,** 11 (1947).

(47) Trevoy and Brown, *J. Am. Chem. Soc.*, **71,** 1675 (1949).

(48) Whitmore and Krems, *J. Am. Chem. Soc.*, **71,** 2427 (1949).

(49) Clarke and Brethen, *Org. Syntheses*, Coll. Vol. I, 2nd ed., 121 (1941).

(50) Gilman, St. John, and Schulze, *Org. Syntheses*, Coll. Vol. II, 425 (1943).

(51) Whitmore and Lieber, *Ind. Eng. Chem., Anal. Ed.*, **7,** 127 (1935).

(52) Goggans and Copenhaver, *J. Am. Chem. Soc.*, **61,** 2909 (1939).

(53) Adkins and Franklin, *J. Am. Chem. Soc.*, **63,** 2381 (1941).

(54) von Bitto, *Merck Index*, 5th ed., Merck and Company, Inc., Rahway, N. J., 1940, p. 649.

(55) Shriner and Fuson, *Systematic Identification of Organic Compounds*, 3rd edition, John Wiley and Sons, Inc., New York, 1948, p. 171.

(56) Shriner and Fuson, Ref. 55, p. 170.

(57) Martin, *J. Am. Chem. Soc.*, **58,** 1438 (1936).

(58) Grummitt and Buck, *Org. Syntheses*, **24,** 30 (1944).

(59) Badger, *J. Chem. Soc.*, 535 (1941).

(60) Ruggli and Preuss, *Helv. Chim. Acta*, **24,** 1350 (1941).

(61) Arnold and Coyner, *J. Am. Chem. Soc.*, **66,** 1543 (1944).

(62) Adams and Thal, *Org. Syntheses*, Coll. Vol. I, 2nd ed., 107 (1941).

(63) Cambron, *Can. J. Research*, **17 B**, 10 (1939).

(64) Manske and Ledingham, *Can. J. Research*, **17 B,** 14 (1939).