1.5538 and a carbonyl band, probably that of VIII, had appeared in the infrared spectrum. Refractionation appeared to increase the proportion of Ihb in these samples.

Pyrolyses of Phenylacetaldehyde Dimethylacetal (II).—When II was distilled slowly from a flask containing potassium hydroxide and calcium carbonate through a heated tube containing a 7″ column of nichrome helices, the conversion to I was *ca.* 40%. Twenty-one grams of the above distillate was heated for two days in the same column so that the head temperature was below 205°. The temperature was then raised and 10–11 g. of clear product was obtained while *ca.* 6 g. remained in the pot. The product was treated with sodium carbonate and calcium chloride. From its refractive index, it appeared that most of the acetal had been consumed. Both I were present. Except for traces of VIII in the head and II in the tail fractions, a high quality mixture of I was obtained on distillation.

Other preparative methods will be described briefly. Sealed tubes containing II and activated alumina or silica gel exploded at 220° (presumably dimethyl ether had formed from methanol). Sealed tubes at 220° containing II and freshly ignited calcium oxide gave I. When II was heated with quinoline or activated alumina in a nitrogen (oxygen-free) atmosphere, compound I was obtained. In all cases the products contained both isomers. The prior removal of peroxides from II with adsorption alumina appeared to have no effect on the outcome of these experiments.

Oxidation Products of β-Methoxystyrene (I).—When mixtures of I were allowed to stand exposed to light and air for several weeks the odor of VIII was apparent. In one case several crystals had formed on the walls of the flask. These were fished out singly. The highest melting point found was 121–122° of several in the range 115–122°. By a similar procedure the highest mixed melting point with an authentic sample of benzoic acid (IV) was undepressed at 120–121°.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Alkenylphenols Related to the Poison Ivy Principle. An Improved Method of Synthesis Involving the Na–Butanol Cleavage of Benzyl Ethers

BY BERNARD LOEV[1] AND CHARLES R. DAWSON

RECEIVED APRIL 13, 1956

Because of their acid labile properties, the synthesis of alkenylphenols, such as are found in the poison ivy principle, has involved the problem of developing a method of protecting the phenolic hydroxyl groups while the olefinic side chain is introduced. It has been found that benzyl ethers of phenols are cleaved readily by sodium and butanol under conditions which do not effect an isolated olefinic bond. However, the benzyl ethers of styrene-type phenols are simultaneously cleaved and reduced by sodium and butanol, a fact which is advantageous in the Grignard synthesis of both alkyl and alkenyl phenols. An improved synthesis of *o*-pentadecylphenol and 3-pentadecylcatechol (hydrourushiol) is described.

The allergenic principles of the poison ivy plant and the Japanese lac tree have both been shown to be mixtures of compounds having a normal 15 carbon chain attached in the 3-position of catechol.[2–4] In both cases, less than 5% of the mixture is 3-pentadecylcatechol (hydrourushiol). More than 95% of the mixture consists of three olefinic components,[5] differing only in the degree and positions of unsaturation in the 15 carbon side chain.[3,4]

Whereas the minor and saturated component, 3-pentadecylcatechol, has for several years been available (synthetically) for clinical study,[6] the individual olefinic components of the poison ivy principle have only recently been separated in the form of their dimethyl ethers.[3] In the methylated form the components are clinically inactive, and demethylation is not possible in the case of the olefinic components. Thus to make the major poison ivy components available for clinical study, either a new method of separation must be developed which will yield the olefins in their active and free phenolic form, or a method of synthesis must be devised. This communication is concerned with one of the problems in the synthesis.

Hydrourushiol has been synthesized by methods involving, as the final step, aluminum chloride[7] or hydrochloric acid[8] cleavage of the hydrourushiol dimethyl ether. Such methods, however, cannot be used in the synthesis of the olefinic components of urushiol, because alkenylphenols are sensitive to heat and to acids,[9] *i.e.*, they undergo extensive and rapid polymerization. Mason[10] has considered this aspect of the problem of synthesizing alkenylcatechols and has advocated the use of the diphenylmethylene ether as a means of protecting the phenolic groups during synthesis. He found that the diphenylmethylene ether of model alkylcatechols could be cleaved under mildly acidic conditions, but he apparently did not investigate the stability of alkenylcatechols under these same conditions. No one has reported the synthesis of an alkenylphenol utilizing the diphenylmethylene ether derivative, and experience in this Laboratory with olefinic phenols would indicate that even mild acidic conditions should be avoided. For this reason, it has seemed advisable to consider other means of protecting the phenolic hydroxyl groups.

It has been found in the present investigation that benzyl ethers of phenols can be cleaved readily by treatment with sodium and butyl alcohol. Thus benzylhydrocardanol (I) has been converted into hydrocardanol (II), and dibenzylhydrourushiol (XIII) has been converted into hydrourushiol (XIV).

Although the catalytic hydrogenolysis of benzyl

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(1) This paper is based on a portion of the thesis submitted by Bernard Loev in 1952 to Columbia University in partial fulfillment of the requirements for the Ph.D. degree in chemistry.

(2) R. Majima and co-workers, *Ber.*, **55**, 172 (1922), and preceding papers.

(3) W. F. Symes and C. R. Dawson, THIS JOURNAL, **76**, 2959 (1954).

(4) S. V. Sunthankar and C. R. Dawson, *ibid.*, **76**, 5070 (1954).

(5) For nomenclature see B. Loev and C. R. Dawson, *ibid.*, **78**, 1180 (1956).

(6) H. Keil, D. Wasserman and C. R. Dawson, *J. Allergy*, **16**, 275 (1945).

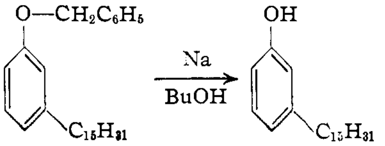
(7) C. R. Dawson, D. Wasserman and H. Keil, THIS JOURNAL, **68**, 534 (1946).

(8) H. S. Mason, *ibid.*, **67**, 1538 (1945).

(9) R. Majima, *Ber.*, **42**, 1418 (1909).

(10) H. S. Mason, THIS JOURNAL, **66**, 1156 (1944).

ethers is well known, and the cleavage by bulk sodium and sodium in liquid ammonia has been reviewed,[11] the use of sodium and alcohol as a means of cleavage of benzyl ethers has received scant attention. The Na–butanol reaction has apparently not been used heretofore for the cleavage of benzyl ethers of phenols.



I II

Debenzylation by catalytic hydrogenolysis serves well for the conversion of I to II, but it cannot be used in the synthesis of an olefinic phenol because of the simultaneous reduction of the olefinic bond(s). Aromatic olefins of the styrene type (double bond conjugated with the ring) are reduced by treatment with sodium and alcohol,[12] but isolated double bonds are not affected. This fact has made possible the successful synthesis of urushenol, the monoölefinic component of the poison ivy principle.[13]

The benzyl ether cleavage by means of sodium and butyl alcohol was first explored in the synthesis of *o*-pentadecylphenol, because this compound had previously been synthesized[14] and the intermediates, 2-(1′-hydroxypentadecyl)-phenol (III) and 2-(pentadecenyl-1′)-phenol(IV) were available as reference compounds. Conversion of III to its benzyl ether VI followed by dehydration gave the same olefin (VII) as was obtained by direct benzylation of IV. Reduction of VII with sodium and butyl alcohol resulted in simultaneous reduction of the conjugated double bond and cleavage of the benzyl ether, giving *o*-pentadecylphenol (V). Anhydrous ethanol was also used; however, the yield of cleaved product was much lower.[15] The phenolic olefin (IV) was also reduced directly to V, using sodium and butanol.

Because of the marked sensitivity of olefinic catechols to acids and heat, the benzyl ether cleavage proved to have greater significance in the synthesis of hydrourushiol (see Fig. 1). It has been pointed out,[14] that although the route III → IV → V (discussed above) can be used successfully for the synthesis of alkyl monohydric phenols, such a route cannot be used for the synthesis of alkyl dihydric phenols because the carbinol intermediate corresponding to III cannot be directly dehydrated. Thus all attempts to dehydrate IX directly resulted only in polymer. However, the dehydration of the corresponding dibenzyl ether XI occurred readily to give XII. VIII can be benzylated *before* the Grignard reaction, thereby saving two-thirds of the Grignard reagent required using route VIII → IX → XI (Fig. 1). XII was simultaneously reduced and cleaved to give hydrourushiol (XIV) in 78% yield from IX, and a 64% over-all yield from X.

Catalytic hydrogenation of XI gave IX[15] and catalytic hydrogenation of XII gave dibenzyl hydrourushiol (XIII) or hydrourushiol (XIV), depending on the conditions. Although catalytic reduction of XII can be used for the synthesis of hydrourushiol, it would be of no value for the synthesis of alkenylphenols, for any isolated double bonds in the side chain would be reduced along with the double bond conjugated with the benzene ring.

Preparation of X by means of treating the sodium salt of VIII with benzyl bromide,[16] gave yields in the order of only 5%. An attempted preparation by refluxing the catechuic aldehyde with benzyl bromide and potassium carbonate in acetone[17] also was unsuccessful. Only a high melting condensation product of undetermined structure was obtained. When methanol was used as the solvent, no product was obtained.[15] X was finally prepared in good yield when the temperature of the benzyl bromide–potassium carbonate reaction was increased by the use of butanol as the solvent.

The hydrourushiol prepared by the procedures described in this paper not only is obtained in better yield but is of somewhat better quality than that prepared by the acidic cleavage of the dimethyl ether.[7,8] Whereas satisfactory yields can be obtained in the acid cleavage step in small scale operations, the demethylation often is incomplete and gives trouble in purifying the product when larger amounts of the dimethyl ether are hydrolyzed.

The sodium–butanol–benzyl ether reaction cannot be either a thermal cleavage[18] or a base-catalyzed cleavage[19–21] for when dibenzyl hydrourushiol was heated with sodium butoxide under the same conditions that prevail during the reductive cleavage, the uncleaved ether was recovered quantitatively. No attempt has been made to isolate the other product of the sodium–butanol cleavage reaction. However, one would expect this other product to be toluene. There is evidence that this sodium–alcohol cleavage of benzyl ethers can also be applied to the protection of alcoholic groups, for 6-benzyloxy-1-hexanol gave a small yield of hexamethylene glycol on such treatment.[15]

Experimental[22]

Benzylhydrocardanol (I).—A 30-g. (0.1 mole) sample of hydrocardanol,[23] was dissolved in 100 cc. of acetone containing 15 cc. of benzyl bromide (hood!), and 38 g. of powdered, anhydrous potassium carbonate. The brown mixture, on refluxing, gradually became much lighter. After 24 hours of refluxing, the salts were filtered and the acetone removed by distillation. The residual reddish-brown liquid was poured into water, extracted with ether, and then

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[11] R. L. Burwell, *Chem. Revs.*, **54**, 615 (1954).

[12] A. Klages, *Ber.*, **35**, 2633, 2646 (1902).

[13] B. Loev and C. R. Dawson, to be published.

[14] B. Loev and C. R. Dawson, THIS JOURNAL, **78**, 4083 (1956).

[15] Details of these investigations are available in the dissertation of B. Loev, a microfilm of which may be obtained from the Columbia University Library.

[16] W. S. Rapson and R. Robinson, *J. Chem. Soc.*, 1533 (1935).

[17] L. Claisen and O. Eisleb, *Ann.*, **401**, 21 (1913).

[18] C. N. Lowe, *ibid.*, **241**, 374 (1887).

[19] D. Y. Curtin and S. Leskowitz, THIS JOURNAL, **73**, 2630 (1951).

[20] C. R. Hauser and S. W. Kantor, *ibid.*, **73**, 1436 (1951).

[21] Wittig and Löhmann, *Ann.*, **550**, 260 (1942).

[22] All melting points are corrected. The ultraviolet spectra were taken on a Cary recording spectrophotometer in 95% ethanol. Microanalysis was performed by Tiedcke Laboratory, Teaneck, N. J., and Micro-Tech Laboratories, Skokie, Ill.

[23] Kindly supplied by the Irvington Varnish and Insulator Co., Irvington N. J.

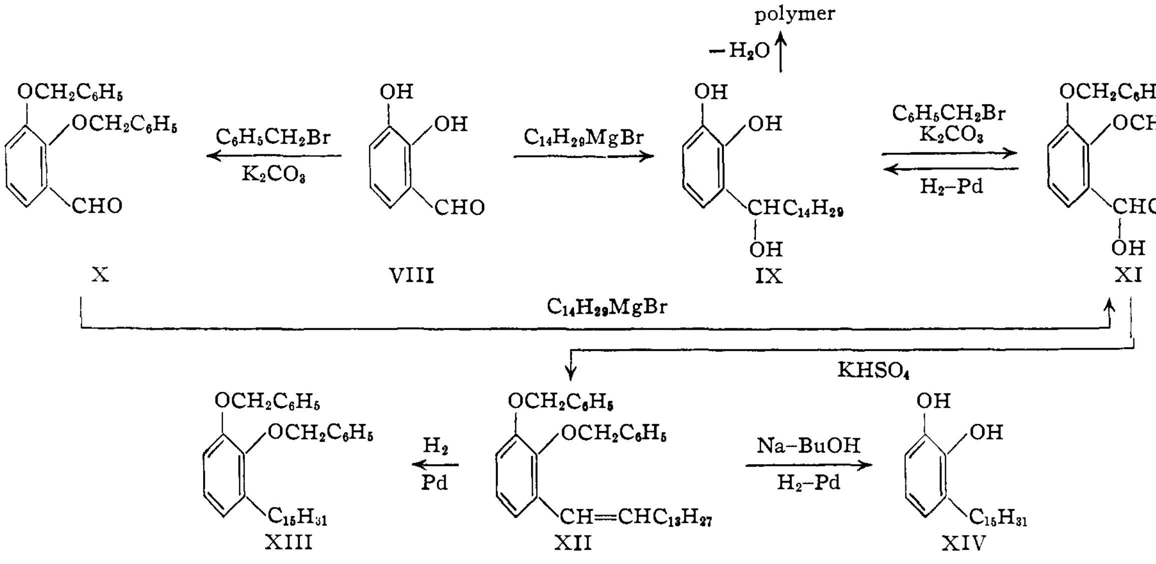

Fig. 1.—Synthesis of hydrourushiol.

washed twice with Claisen solution. The ethereal layer was dried and the solvent removed. The residual brown liquid, on cooling and stirring, solidified to a brown solid. After crystallization from an acetone–ethanol mixture, there was obtained 34 g. (86.2% yield) of benzylhydrocardanol, a white solid, m.p. 39–40°. Further recrystallization from ethanol raised the melting point to 40–40.2°.

Anal. Calcd. for $C_{28}H_{42}O$: C, 85.22; H, 10.73. Found: C, 85.18; H, 10.83.

Hydrocardanol (II.)—Sodium, 3 g., was added rapidly but in small pieces, to a hot solution of 5 g. of benzylhydrocardanol in 50 cc. of anhydrous butanol. The solution which was originally a light yellow, gradually turned almost colorless. After the sodium had all reacted, a small amount of cold water was added, then cold, dilute hydrochloric acid. The organic layer was washed with saturated sodium chloride, dried, and the solvent removed *in vacuo*. The light yellow oil solidified on cooling to room temperature. Recrystallization from petroleum ether gave hydrocardanol, m.p. 50–51°; the melting point was not depressed when mixed with an authentic sample of hydrocardanol.

Dibenzylhydrourushiol (XIII).—Hydrourushiol[24] (18 g.) dissolved in 60 cc. of acetone containing 15 cc. of benzyl bromide and 50 g. of anhydrous potassium carbonate was refluxed for 24 hours. The dibenzylhydrourushiol was isolated as described above for benzylhydrocardanol. Recrystallization from acetone–ethanol gave 20.8 g. (74.5% yield), colorless, m.p. 52.4–53.0°.

Anal. Calcd. for $C_{35}H_{48}O_2$: C, 83.95; H, 9.66. Found: C, 83.48; H, 9.76.

Hydrourushiol (XIV) by Reductive Cleavage of XIII.—Sodium, 4.35 g. (0.205 mole), was added rapidly, in small pieces, to a hot solution of 10 g. (0.0205 moles) of dibenzylhydrourushiol in 80 cc. of anhydrous butanol. On the addition of the first few pieces of sodium, the solution turned dark red-brown, then gradually became lighter until finally it became pale yellow (after about 3 g. of the sodium had been added). As the solution cooled at the end of the reaction, it became dark again. Cold water, containing a little sodium hydrosulfite was slowly added and then 50% acetic acid. The color of the solution gradually turned light red, orange, and finally yellow. The organic layer was washed with dilute bicarbonate solution, dried, and the solvent removed *in vacuo*. The residual oil was dissolved in anhydrous methanol, and treated with an excess of a methanol solution containing 1.2 g. of lead acetate trihydrate per 10 cc. The dense white precipitate of lead salt was filtered off, washed with ether, and dried; weight corresponded to a 57.5% yield of hydrourushiol.

The lead salt was suspended in methanol and treated with hydrogen sulfide. The lead sulfide was removed by filtration and the solvent evaporated leaving a pale yellow oil which solidified at room temperature. The solid was sublimed *in vacuo*, and the hydrourushiol was isolated as a pure white solid, m.p. 58–58.5°, showing no depression when a mixed melting point was taken with an authentic sample.

Anal. Calcd. for $C_{21}H_{36}O_2$: C, 78.69; H, 11.32. Found: C, 78.56; H, 10.99.

o-Benzyloxyphenyltetradecylcarbinol (VI).—A 4-g. sample of 2-(1′-hydroxypentadecyl)-phenol (III), prepared as previously described,[14] was converted to the benzyl ether in the manner described above for benzylhydrocardanol, giving a 58.5% yield of the benzyl ether as a white, granular solid, m.p. 37–37.5° (from petroleum ether).

Anal. Calcd. for $C_{28}H_{42}O_2$: C, 81.90; H, 10.31. Found: C, 81.50; H, 10.29.

2-(Pentadecenyl-1′)-phenol Benzyl Ether (VII). (a) Dehydration of VI.—A mixture of 3 g. of the carbinol VI and 0.5 g. of fused potassium bisulfate was heated at 150° for five minutes and then at 170° for 30 minutes (until all spattering ceased). The resulting oil was dissolved in ether, washed, dried, and the solvent removed, giving an 85.5% yield of VII, as a yellow oil. Distillation at 0.1 mm. produced an almost colorless oil, b.p. 168–170°, $n^{18}D$ 1.5290.

Anal. Calcd. for $C_{28}H_{40}O$: C, 85.65; H, 10.27. Found: C, 85.20; H, 10.37.

(b) Benzylation of IV.—A 15-g. sample of 2-(pentadecenyl-1′)-phenol (IV), prepared as previously described,[14] was converted to the benzyl ether in the manner described above for benzyl hydrocardanol. Removal of solvents, *in vacuo*, gave a 77% yield of VII, as a golden yellow oil, $n^{26}D$ 1.5267; insoluble in ethanol. The ultraviolet absorption spectra of VII prepared by both of these methods was identical.

o-Pentadecylphenol (V). (a) Reductive Cleavage of VII.—A 7-g. sample of VII dissolved in 60 cc. of butanol was treated with 5 g. of sodium as described under hydrocardanol. The crude o-pentadecylphenol was purified by sublimation, giving a 30% yield of white crystals, m.p. 47.5–49.5°, showing no depression of melting point when mixed with a sample of V prepared by other means.[14]

(b) Reduction of IV Using Sodium and Butanol.—A 5-g. sample of IV dissolved in 50 cc. of butanol was treated with 3 g. of sodium in the same manner as the reductive cleavage of benzyl ethers was carried out (described under hydrocardanol). The crude o-pentadecylphenol was recrystallized from petroleum ether giving a 30% yield of white crystals, showing no depression when a mixed melting point was taken with a known sample.[14]

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[24] Prepared as described elsewhere.[7]

2,3-Dihydroxybenzaldehyde Dibenzyl Ether (X).—A mixture of 25 g. of pyrocatechuic aldehyde, 50 cc. of benzyl bromide, 50 cc. of butanol and 60 g. of anhydrous potassium carbonate was refluxed with vigorous stirring for 24 hours. The mixture, now dark brown, was poured into water, and extracted with ethyl acetate and ether. The organic layer was washed several times with saturated salt solution and then with 5% sodium hydroxide, until the basic wash water was colorless. Removal of the solvent left a viscous, dark, brown oil that soon solidified. This residue was extracted repeatedly with boiling ligroin. Chilling of these extracts caused precipitation of X as fine, white, fibrous crystals, m.p. 91–91.2° (55% yield). A sample recrystallized for analysis melted 92–93.2° (λ_{max} 256 mμ).

Anal. Calcd. for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70. Found: C, 79.23; H, 5.80.

2,3-Dibenzyloxyphenyltetradecylcarbinol (XI). (a) **Benzylation of IX.**—A solution of 12 g. of (0.0358 mole) of IX,[14] 12.2 g. (0.0716 mole) of benzyl bromide and 10 g. of powdered, anhydrous potassium carbonate, in 20 cc. of acetone, was refluxed for 24 hours. The solution, originally of an olive drab color, soon changed to pale brown. The solvent was distilled, and the residual oil and precipitated salts were poured into water, extracted with ether, dried, and all volatile material removed *in vacuo*. The residual oil, on stirring, solidified to a tan solid, giving no ferric chloride test. The solid was dissolved in hot petroleum ether, decolorized with Norite, and the solution cooled, giving 12.5 g. of white solid, m.p. 53–57°. On further recrystallization from petroleum ether the melting point rose to 59.5–60.5° (55.5% yield).

Anal. Calcd. for $C_{35}H_{48}O_5$: C, 81.35; H, 9.36. Found: C, 80.78; H, 8.50.

(b) **Grignard Reaction on X.**—The Grignard reagent was prepared from 6.6 g. (0.022 mole) of freshly distilled tetradecyl bromide and 0.53 g. (0.022 mole) of magnesium. To the light gray ethereal solution of the Grignard reagent, was slowly added a solution of 7 g. (0.022 mole) of chromatographed dibenzyl ether of pyrocatechuic aldehyde (X) in ether containing sufficient anhydrous benzene to bring the aldehyde into solution. No visible reaction occurred. After refluxing for several hours, the solution became pale yellow and a granular white dispersion formed. The solution was hydrolyzed by pouring it into cold, dilute, acetic acid. The colorless ethereal layer was washed with bicarbonate solution and then the solvent was removed. The residual golden yellow oil was taken up in about 25 cc. of boiling ethanol; on chilling, a small amount of octacosane precipitated, and was filtered, 0.8 g. The ethanol was distilled, and the residual yellow oil slowly solidified at room temperature. The solid was dissolved in hot petroleum ether and treated with Norite. On cooling, a white, granular precipitate of XI slowly formed; 9.1 g. (82% yield) showing no depression of melting point when mixed with the material prepared under (a). XI was also prepared starting with tetradecyl chloride. In this case, however, the halide must be very pure, and even then the reaction required eight hours of refluxing for the Grignard reagent to form. The yield of XI in this case was 71%.

2′,3′-Dibenzyloxyphenylpentadecene-1 (XII).—A 10-g. sample of the carbinol XI was dehydrated by heating with 1 g. of potassium bisulfate at 155°, in the manner already described under the preparation of VII. The product, formed in quantitative yield, was a pale tan liquid, $n^{25}D$ 1.5455. On standing, the liquid crystallized, m.p. 37–40°. Recrystallization from alcohol–acetone gave XII as white crystals, m.p. 40.5–42°, insoluble in alcohol. A small sample was hydrogenated in ethyl acetate using 10% palladium-on-carbon catalyst. The hydrogenation was stopped as soon as the theoretical quantity of hydrogen had been absorbed. Removal of the solvent gave hydrourushiol dibenzyl ether, m.p. 50.5–51.5°, showing no depression of melting point when mixed with a known sample.

Hydrourushiol (XIV) by Reductive Cleavage of XII.—Nitrogen was bubbled through a solution of 4.5 g. of XII in 100 cc. of anhydrous butanol warmed to 70–80°. The nitrogen was stopped and 9 g. of sodium was rapidly added in small pieces. A rapid succession of color changes occurred—first dark blue-green, then light yellow green, light orange, and finally pale yellow. When all of the sodium had reacted, 20 cc. of water and 50 cc. of 20% acetic acid, each containing several grams of sodium hydrosulfite, were added. The color was now pink. A small amount of HCl was added and the solution became colorless. The solution was separated and the top organic layer was washed with water containing some sodium hydrosulfite, and dried. Removal of the solvent, *in vacuo*, left 2.65 g. of yellow oil that rapidly solidified to a light pink solid, soluble in alcohol, and giving a dark green ferric chloride test. The solid readily recrystallized from petroleum ether, giving 2.3 g. (78.4% yield) of white, crystalline hydrourushiol, m.p. 57.5–58.5°.

Acknowledgment.—The authors are indebted to the Lederle Laboratories Division of the American Cyanamid Co. for a grant to Columbia University for support of this investigation. They also wish to thank Dr. V. J. Paul for technical aid.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

Dichloromethylallyl Compounds. I. 3,3-Dichloro-2-methylallylbenzenes[1,2]

BY DONALD G. KUNDIGER AND HUEY PLEDGER, JR.

RECEIVED AUGUST 1, 1955

Substituted benzenes were allowed to react with both hydrated and anhydrous 1,1,1-trichloro-2-methyl-2-propanol in the presence of aluminium chloride. Substituted dichloromethylallylated benzenes were obtained from the hydrated 1,1,1-trichloro-2-methyl-2-propanol. Also, α-chloroisobutyric acid was isolated as a by-product in yields up to 37% because of rearrangement of 1,1,1-trichloro-2-methyl-2-propanol to α-chloroisobutyryl chloride with loss of HCl and attendant hydrolysis. Other derivatives were identified that showed the presence of α-chloroisobutyryl chloride as an intermediate in the reaction, particularly when anhydrous 1,1,1-trichloro-2-methyl-2-propanol was used.

From the reaction of trichlorobutanol (1,1,1-trichloro-2-methyl-2-propanol) with benzene, toluene and *p*-xylene in the presence of anhydrous aluminum chloride, Willgerodt and Genieser[3] reported the isolation of small amounts of compounds in which the chlorine atoms and the hydroxyl of trichlorobutanol were replaced. We have re-investigated this reaction with toluene, and with chlorobenzene, bromobenzene and anisole and have not obtained the expected replacement products. Instead, 3,3-dichloro-2-methylallylbenzenes (IIIa-d) have been obtained, indicating dehydration and rearrangement.

Possible intermediates in the reaction are shown in the formula chart.

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(1) Presented in part before the 123rd, 1952, Meeting of The American Chemical Society. This paper represents part of a dissertation submitted by Huey Pledger, Jr., in partial fulfillment of the requirements for the Ph.D. degree at Kansas State College.

(2) This investigation was supported by a research grant from The Dow Chemical Co., Midland, Mich.

(3) C. Willgerodt and A. Genieser, *J. prakt. Chem.*, [2] **37**, 371 (1888).