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, soldified 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, $n^{25}\text{D}$ 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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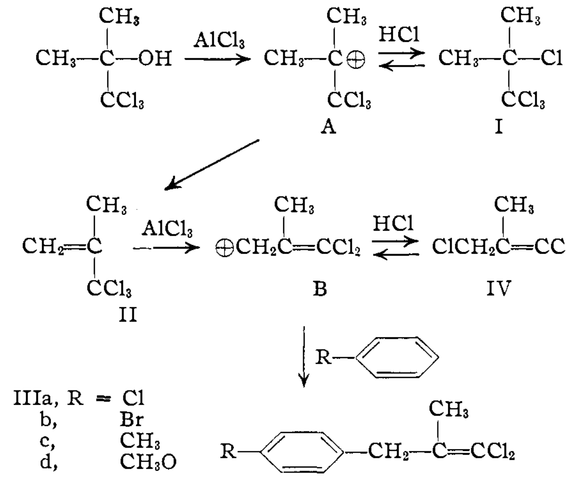
(1) Presented in part before the 123rd, 1952, Meeting of The American Chemical Society. This paper represents part of a dissertation submitted by Huey Pledger, Jr., in partial fulfillment of the requirements for the Ph.D. degree at Kansas State College.

(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).



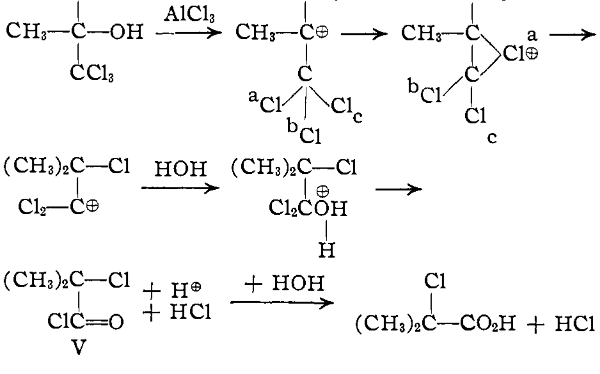
3,3,3-Trichloro-2-methyl-1-propene (TMP) (II), 1,1,3-trichloro-2-methyl-1-propene (allyl TMP) (IV) and 1,1,1,2-tetrachloro-2-methylpropane (I) were treated under typical reaction conditions (Table I, A). In each case a significant amount of 3-(*o*- and *p*-chlorophenyl)-1,1-dichloro-2-methyl-1-propene (IIIa) was obtained. Thus, each of these possible intermediates can give carbonium ion B, which reacts to give the products found (IIIa-d).

The facile and rapid rearrangement of II to IV (allyl-TMP) in essentially quantitative yields when catalyzed by various Friedel–Crafts catalysts is shown in Table III. Very little polymerization occurred.

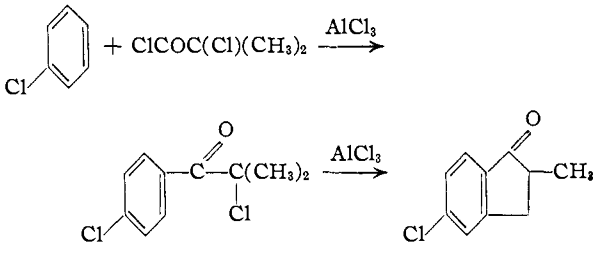
Aluminum chloride appears to abstract a chloride ion, facilitating the rearrangement, and then to react with the resulting carbonium ion (B), to replace the chlorine and form allyl-TMP. Neither boiling at 136–138° for three hours, nor the presence of hydrochloric acid causes the rearrangement. A trace of a Lewis acid, such as listed in Table III, must be present.

Further evidence for the existence of carbonium ion A is given by the isolation of small amounts of I from the reaction mixture in two cases (*cf.* Table I, B).

The reactions of hydrated trichlorobutanol with chlorobenzene and bromobenzene in the presence of aluminum chloride yielded α-chloroisobutyric acid in both cases. This was evidently the result of intermediate formation of α-chloroisobutyryl chloride, which hydrolyzed *in situ* during the reaction. This is assumed to be a migration of the pinacol–pinacolone type in which a chlorine atom is migrating with its electrons. In the reaction between hydrated trichlorobutanol and anisole, phenol was liberated and reacted with the intermediate acid chloride to give phenyl α-chloroisobutyrate.



When anhydrous trichlorobutanol was condensed with chlorobenzene, 5-chloro-2-methyl-1-indanone was obtained. This is assumed to result from reaction of the intermediate acid chloride V with chlorobenzene.



The indanone was identified by independent synthesis from chlorobenzene and α-chloroisobutyryl chloride (V) and by mixed melting point of the 2,4-dinitrophenylhydrazones.

Condensation of the anhydrous alcohol with bromobenzene gave a significantly high yield (27%) of trichloro-*t*-butyl α-chloroisobutyrate. The reaction here appears to be

$$\text{V} + \text{HO—C(CH}_3)_2\text{CCl}_3 \longrightarrow (\text{CH}_3)_2\text{C(Cl)C(=O)O—C(CH}_3)_2\text{CCl}_3 + \text{HCl}$$

The structures of the 3,3-dichloro-2-methylallylbenzenes (IIIa-d) were established by synthesis from independently prepared allyl-TMP, aluminum chloride and the corresponding benzenes. Three of these syntheses are included in Table I-A and I-C. The structures were further supported by the infrared spectra, which showed a strong band at 6.19 μ typical for the $\text{Cl}_2\text{C=C—}$ group. The analyses are reported in Table II.

Experimental

Melting and boiling points are uncorrected.

1,1;1,2-Tetrachloro-2-methylpropane (I).—Ten moles (1864 g.) of anhydrous 1,1,1-trichloro-2-methyl-2-propanol was dissolved in 3575 ml. (49.3 moles) of thionyl chloride. To this solution 133 g. (1 mole) of anhydrous aluminum chloride was added cautiously with stirring. The resultant solution remained at room temperature 36 hours. The excess thionyl chloride was removed at reduced pressure and room temperature, and the final traces were destroyed with methanol. The remaining slush was poured over crushed ice (stirring). Filtration gave 1917 g. of brown solid, which was crystallized from ethyl alcohol–acetone. After treatment with Norit, in carbon tetrachloride, a total of 1132 g. (57.7%) of white crystals, m.p. 178.0–178.7°, was obtained (lit. m.p. 178.6–179.6°).[4] This synthesis differs from any previously reported.

3,3,3-Trichloro-2-methyl-1-propene (TMP).—This was prepared as previously described[5] with either purified thionyl chloride or Hooker Electrochemical Co. partly refined thionyl chloride containing small amounts of ferric chloride. The TMP was obtained in about 90% yield[5] in both cases. It was collected at b.p. 131.6–138.0° (740 mm.), $n^{20}\text{D}$ 1.4795 ± 0.0005, d^{20}_4 1.297–1.300 and used for the reactions reported herein. The infrared spectrum was characterized by a strong

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(4) A. O. Rogers and R. E. Nelson, THIS JOURNAL, **58**, 1207 (1936).

(5) D. G. Kundiger, H. Pledger, Jr., and L. E. Ott, *ibid.*, **77**, 6659 (1955), where yields and method are reported with purified thionyl chloride not containing small amounts of ferric chloride, and with eleven other catalysts.

TABLE I

	Aliphatic	Aromatic	Molar ratio[a]	Temp., °C.	Time, hr.	Products (yield)[b]
A	$(CH_3)_2C(CCl_3)Cl$	C_6H_5Cl	0.5:5:0.02	90–98.5	1.25	IIIa (28)
	$Cl_2C{=}C(CH_3)CH_2Cl$	C_6H_5Cl	.3:1:0.04	95–100	1	IIIa (57.9)
	$H_2C{=}C(CH_3)CCl_3$	C_6H_5Cl	6.6:21:0.2	95–100	4	IIIa (58)
B	$(CH_3)_2C(CCl_3)OH$[c]	C_6H_5Cl	10:20:5	95–100[d]	5	IIIa (25), I (5.7), α-chloroisobutyric acid (37.5)[e]
	$(CH_3)_2C(CCl_3)OH$[f]	C_6H_5Cl	1:5:1	95–100	2	IIIa (1.76), 5-chloro-2-methyl-1-indanone (20)[g]
	$(CH_3)_2C(CCl_3)OH$[c]	C_6H_5Br	1:1.8:0.36	95–110	5	IIIb (14), α-chloroisobutyric acid (22.6)
	$(CH_3)_2C(CCl_3)OH$[f]	C_6H_5Br	11.7:23.3:2.4	92	5.5	IIIb (6), I (5.7), trichloro-*t*-butyl α-Cl-isobutyrate (26.8)[i]
	$(CH_3)_2C(CCl_3)OH$[c]	$C_6H_5CH_3$	2:4:0.7	90–95	2.7	IIIc (19.5), α-chloroisobutyl *p*-methylphenyl ketone[j]
	$(CH_3)_2C(CCl_3)OH$[c]	$C_6H_5OCH_3$	1.8:4.4:1	85–90	2.1	IIId (4), phenyl α-chloroisobutyrate (3.7)
C	$Cl_2C{=}C(CH_3)CH_2Cl$	$C_6H_5CH_3$	2:8:0.04	60–65	2	IIIc (57.8)
	$Cl_2C{=}C(CH_3)CH_2Cl$	$C_6H_5OCH_3$	5:20:0.9	87	4.5	IIId (65.6)[k]

[a] The ratio of aliphatic to aromatic to aluminum chloride. [b] Based on aliphatic. R is *o* and *p*. [c] Hydrated trichlorobutanol, m.p. 77.3–78.2°. [d] Stood 20 hours at 27° after reaction. [e] B.p. 40–42.5° (0.5 mm.), $n^{20}\text{D}$ 1.4350. [f] Anhydrous trichlorobutanol, m.p. 96–97°. [g] These yields are approximations based on the yield of DNP from a center cut. The mixture had b.p. 80.5–82.5° (0.4 mm.), $n^{20}\text{D}$ 1.5688–1.5745. [h] B.p. 50–51.5° (0.1 mm.), $n^{20}\text{D}$ 1.4345–1.4360. [i] B.p. 51–52° (0.2 mm.), $n^{20}\text{D}$ 1.4730–1.4751. [j] A third unidentified constituent was present in this mixture. The yield is from material $n^{20}\text{D}$ 1.5433. [k] Also obtained 4-(3,3-dichloro-2-methylallyl)-phenol, m p. 91–93°. The reactions between $Cl_2C{=}C(CH_3)CH_2Cl$ and phenols are reported in another publication.

In each case of an isolated substituted dichloromethylallylated benzene, only one product fraction was obtained as a mixture of ortho and para isomers. These could not be separated by fractionation. The position isomers were shown by infrared analysis. Only traces of meta isomer (1 to 2%) were indicated present. Oxidation with alkaline permanganate of the substituted 3,3-dichloro-2-methylallylbenzenes gave 35–40% yields of the pure para substituted benzoic acids with the correct m.p.'s. The oxidation studies indicated that about as much ortho isomer was present as para isomer, and this agreed with approximate indications from infrared spectra. In each recrystallization of the mixed ortho and para substituted acids from oxidation, a part of the high yield of the crude acid was lost in purification by recrystallization. The ortho substituted benzoic acids are so many more times soluble in water than the para acids, for example, ortho chlorobenzoic acid is five times more soluble in water than the para acid, that the ortho acid was lost in the solvent water during purification.

TABLE II

PHYSICAL CONSTANTS AND ANALYTICAL RESULTS FOR SUBSTITUTED 3,3-DICHLORO-2-METHYLALLYLBENZENES

R	B.p., °C.	Mm.	$n^{20}\text{D}$	d^{20}_4	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Chlorine, % Calcd.	Found	Formula
p-Chloro	88	0.5	1.5605	1.283	50.99	50.85	3.85	3.89	45.20	44.47	$C_{10}H_9Cl_3$
p-Bromo	110	0.9	1.5799	1.508	42.89	42.57	3.24	3.30	25.33	25.4	$C_{10}H_9BrCl_2$
p-Methoxy	105	1.1	1.5505	1.211	57.16	57.10	5.23	5.26	30.68	30.70	$C_{11}H_{12}Cl_2O$
p-Methyl	60	0.09	1.5457	1.162	61.41	61.34	5.62	5.76	32.96	32.84	$C_{11}H_{12}Cl_2$

TABLE III

THE CATALYTIC REARRANGEMENT OF 3,3,3-TRICHLORO-2-METHYL-1-PROPENE TO 1,1,3-TRICHLORO-2-METHYL-1-PROPENE (ALLYL-TMP)

Catalyst	Reflux time in minutes[c]	Product[a] b.p., °C.	Yield, %
$AlCl_3$[b]	0–1	152–157	95.6
$FeCl_3$	0–1	155.5–159	88.3
$Fe(NO_3)_3$	0–1	154–159	89.1
$SnCl_4$	0–1	153.5–159	92.7
$ZnCl_2$	7	153.5–159	87.2
H_2SO_4 (95%)	10	152–157	91.7
$MgCl_2$	70	152–158	84.0
None[d]	180	132–136	..

[a] Work in our laboratory has shown that material b.p. 152–160° is greater than 98% pure 1,1,3-trichloro-2-methyl-1-propene. [b] The rearrangement is highly exothermic with this catalyst. The heat from rearrangement caused the solution temperature to rise from 30° to 121° in 30 seconds. [c] The reflux time is the needed minimum time for the rearrangement determined at the point the vapor temperature in the head reached at least 152°. [d] No product allyl-TMP was obtained by refluxing 3 hours. HCl also was added and no allylic rearrangement occurred.

band at 5.61 μ and no band at 6.19 μ. A very small fraction was collected at b.p. 153.5–156.5° (738 mm.), $n^{20}\text{D}$ 1.4990 ± 0.0003, d^{20}_4 1.346. It was pure 1,1,3-trichloro-2-methyl-1-propene (allyl-TMP). Infrared analysis on this material showed a sharp band at 6.19 μ and no band at 5.61 μ.

3,3-Dichloro-2-methylallylbenzenes.—The same general procedure was employed in all reactions reported in Table I. The reactants were mixed and maintained at the desired temperature while anhydrous aluminum chloride was added portionwise and with stirring throughout the reaction period. The alternative procedure of adding a solution of the reactants to the aluminum chloride was used in some instances, with no change in results. The reaction mixture was poured over crushed ice containing 10% of hydrochloric acid. The organic products were extracted with ether and the ethereal extract dried over anhydrous magnesium sulfate. After removal of the ether, the residual liquid was distilled through a glass helices packed column (120 mm. long and 20 mm. diameter). Analytical samples of the various compounds were obtained by taking a center fraction of the series of fractions which had a constant refractive index during a particular distillation. Analytical results are summarized in Table II.

The isomeric mixture of 3-(*o* and *p*-methoxyphenyl)-1,1-dichloro-2-methyl-1-propene was previously obtained[6] without separation of the isomers by condensing TMP and anisole with the aid of HF. The yield, however, was smaller than that obtained in the present investigation.

The Catalytic Rearrangement of 3,3,3-Trichloro-2-methyl-1-propene to 1,1,3-Trichloro-2-methyl-1-propene (Allyl-TMP).—The key data and results are reported in Table III. The general procedure was as follows: About 30 g. of 3,3,3-trichloro-2-methyl-1-propene, b.p. 131.6–138°, was placed in a 100-ml. flask attached to a vacuum jacketed head. The head was fitted with an Adjustotherm thermometer and a Friedrich condenser. A connection for venting any gases was made between the condenser and the receiver.

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[6] C. C. Price and H. D. Marshall, *J. Org. Chem.*, **7**, 532 (1943).

Then 0.1 to 0.2 mole per cent. of desired catalyst was added and the liquid heated rapidly. The vapor temperature was measured as the vapor front moved up the head by adjusting the thermometer. If the temperature was at least 152°, the liquid was distilled. If the vapor temperature was less than 152°, the heat was adjusted such that the vapor refluxed in the head just below the side-arm. When the temperature reached 152°, the time interval was recorded, the heat increased, and the allyl-TMP was distilled. The accounting of material was 100%; the yields of distilled allyl-TMP (figured as conversion of starting-material) are shown in Table III.

Trichloro-*t*-butyl α-Chloroisobutyrate (VII).—This compound (26.8%) resulted as a by-product from the aluminum chloride catalyzed reaction between anhydrous trichlorobutanol and bromobenzene. A sample, b.p. 60.0° (0.45 mm.), n^{20}_{D} 1.4730, d^{20}_{4} 1.312, was used for ultimate and infrared analyses.

Anal. Calcd. for $C_8H_{12}Cl_4O_2$: MR_D, 60.0; C, 34.1; H, 4.3; Cl, 50.3. Found: MR_D, 60.3; C, 34.38; H, 4.46; Cl, 49.75.

The structure was also established by the infrared spectrum: ester carbonyl stretch, 5.72(S); carbon–chlorine stretch of trichloromethyl group, 12.52(VS); C–C stretch involving carbonyl group and other carbons, 7.81(S), 8.66(VS), 8.95(S).

α-Chloroisobutyric Acid.—This compound was produced as a by-product in the condensation between hydrated trichlorobutanol and chlorobenzene. A sample, b.p. 51.7° (1.0 mm.), n^{20}_{D} 1.4340, d^{20}_{4} 1.179, was used for analyses.

Anal. Calcd. for $C_4H_7ClO_2$: MR_D, 27.0; Cl, 28.9; neut. equiv., 122.5. Found: MR_D, 27.2; Cl, 28.95; neut. equiv., 122.

This acid was hydrolyzed with 20% sodium hydroxide to α-hydroxyisobutyric acid, m.p. 78.6–80° (lit. m.p. 79°); mixed m.p. with authentic acid gave no depression.

α-Chloroisobutyric acid reacted with aniline in benzene and gave silvery needles, m.p. 100–101°, somewhat soluble in ether, of the aniline α-chloroisobutyrate salt.

Anal. Calcd. for $C_{10}H_{14}O_2ClN$: Cl, 16.47; neut. equiv., 215.5. Found: Cl, 16.61; neut. equiv., 215.7.

5-Chloro-2-methyl-1-indanone.—Two moles (224 g.) of chlorobenzene and 67 g. (0.5 mole) of anhydrous aluminum chloride were heated to 65°. The solution was stirred and maintained at 65–68° while adding 56.4 g. (0.4 mole) of α-chloroisobutyryl chloride dropwise during one hour. After standing 16 hours at room temperature, the reaction mixture was poured over ice containing hydrochloric acid. The organic layer was separated, the aqueous layer extracted with ether, the organic layer and ether extract combined, dried over magnesium sulfate, filtered and the ether removed. The residual liquid was fractionated through a glass helices packed column to give 34.1 g. (47%) of 5-chloro-2-methyl-1-indanone, b.p. 78–81.7° (0.3 mm.), n^{20}_{D} 1.5694, d^{20}_{4} 1.240. The 2,4-dinitrophenylhydrazone of this indanone was prepared[7] in 79% (5.1 g.) yield, m.p. 226–226.8°.

Anal. Calcd. for $C_{16}H_{13}ClO_4N_4$: C, 53.27; H, 3.63; N, 15.53. Found: C, 53.23; H, 3.9; N, 15.78.

Acknowledgment.—We gratefully acknowledge the grants from The Dow Chemical Co. which supported this research. We appreciate the interpretations of infrared spectral analyses by Dr. Alvin W. Baker of The Dow Chemical Co. and by Professor Ellis R. Lippincott of Kansas State College.

[7] S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1947, p. 199.

MANHATTAN, KANSAS

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

Dichloromethylallyl Compounds. II. The Catalytic and Non-catalytic Substitution of Certain Chloroallylic Groups in the Ring and on the Oxygen in Phenols

BY D. G. KUNDIGER AND H. PLEDGER, JR.[1]

RECEIVED OCTOBER 5, 1955

The four allylic chlorides; 1,1,3-trichloro-2-methyl-1-propene, 1,3-dichloro-2-butene, 1,3-dichloro-2-methyl-1-propene and 1-chloro-2-(dichloromethylene)-cyclohexane were found to substitute into the nucleus of phenols in the absence of catalysts. 3,3,3-Trichloro-2-methyl-1-propene reacted with phenols in the absence of catalysts and yielded both C and O substituted products. The aluminum chloride catalyzed reaction between 1,1,3-trichloro-2-methyl-1-propene and phenols gave the same substitution products as the uncatalyzed reaction. Twelve substituted phenyl 3,3-dichloro-2-methylallyl ethers were synthesized.

In a previous paper,[2] the aluminum chloride catalyzed reactions between 3,3,3-trichloro-2-methyl-1-propene (TMP) and also between 1,1,3-trichloro-2-methyl-1-propene (allyl-TMP) and certain substituted benzenes were reported. This work showed that allyl-TMP did not react with substituted benzenes in a way analogous to allyl chloride. Nenitzescu and Isacescu[3] showed that allyl chloride reacted with benzene when aluminum chloride was present and gave 1,2-diphenylpropane, not allylbenzene. However, we were able to isolate dichloromethylallylbenzenes.[2] Also, allyl-TMP underwent very little polymerization in the presence of aluminum chloride.[2] These facts led us to believe that the dichloromethylallyl group could be introduced into the phenolic ring. The results in Tables I and II show that this was done.

During the investigation of the catalytic reactions between allyl-TMP and phenols, it was discovered that allyl-TMP reacted with phenols in the absence of catalysts. This type of reaction was extended to include TMP, 1,3-dichloro-2-butene and 1-chloro-2-(dichloromethylene)-cyclohexane (allyl-TMC). The new phenols which were produced are summarized in Table I. The properties and the results of analyses are summarized in Table II.

Both the catalytic and the non-catalytic reaction between phenol and allyl-TMP resulted in *ortho* and *para* substitution (Table I). However, the primary purpose of this work was to study the method of introduction of the dichloromethylallyl

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[1] This paper represents part of a thesis submitted by H. Pledger, Jr., to The Graduate School, Kansas State College, in partial fulfillment of the requirements of the degree Doctor of Philosophy. This work was supported in full by The Dow Chemical Co.

[2] D. G. Kundiger and H. Pledger, Jr., THIS JOURNAL, **78**, 6098 (1956).

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