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

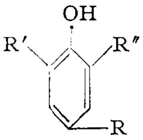
[1] This paper represents part of a thesis submitted by H. Pledger, Jr., to The Graduate School, Kansas State College, in partial fulfillment of the requirements of the degree Doctor of Philosophy. This work was supported in full by The Dow Chemical Co.

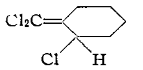
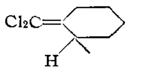
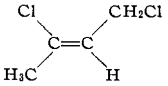
[2] D. G. Kundiger and H. Pledger, Jr., THIS JOURNAL, **78**, 6098 (1956).

[3] C. D. Nenitzescu and D. A. Isacescu, *Ber.*, **66**, 1100 (1933).

TABLE I

SYNTHESIS OF PHENOLS,

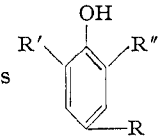


	Catalyst	Halide employed	Ratio[a]	R	R′	R	Reacn. temp., °C.	Reacn. time, hr.	Yield, %
1	$AlCl_3$	$Cl_2C{=}C(CH_3)CH_2Cl$	1/1/1.2	H	$Cl_2C{=}C(CH_3)CH_2-$	H	54–60	1/2	31.8
1				$Cl_2C{=}C(CH_3)CH_2-$	H	H			25.8
2	$AlCl_3$	$Cl_2C{=}C(CH_3)CH_2Cl$	1/1/0.3	H	$Cl_2C{=}C(CH_4)CH_2-$	H	55–60	5/6	18.1
2				$Cl_2C{=}C(CH_3)CH_2-$	H	H			15.0
3	None	$Cl_2C{=}C(CH_3)CH_2Cl$	2/1/0	H	$Cl_2C{=}C(CH_3)CH_2-$	H	143–167	7	26.7
3				$Cl_2C{=}C(CH_3)CH_2-$	H	H			15.4
4	None	$Cl_3C{-}C(CH_3){=}CH_2$	1/1/0	H	$Cl_2C{=}C(CH_3)CH_2-$	H	65–110	1/2	16.4[b]
4				$Cl_2C{=}C(CH_3)CH_2-$	H	H			1.7
5	$AlCl_3$	$Cl_2C{=}C(CH_3)CH_2Cl$	1/1/0.2	Cl	$Cl_2C{=}C(CH_3)CH_2-$	H	40–45	2 1/6	27.4
6	$AlCl_3$	$Cl_2C{=}C(CH_3)CH_2Cl$	1/1/0.4	Cl	$Cl_2C{=}C(CH_3)CH_2-$	H	65–72	1/2	17.4
6				Cl	$Cl_2C{=}C(CH_3)CH_2-$	$Cl_2C{=}C(CH_3)CH_2-$			31.8
7	$AlCl_3$	$Cl_2C{=}C(CH_3)CH_2Cl$	1/1/0.2	Cl	$Cl_2C{=}C(CH_3)CH_2-$	H	65–70	1 3/4	30.3
7				Cl	$Cl_2C{=}C(CH_3)CH_2-$	$Cl_2C{=}C(CH_3)CH_2-$			36.0
8	None	$Cl_2C{=}C(CH_3)CH_2Cl$	3/1/0	Cl	$Cl_2C{=}C(CH_3)_2CH_2-$	H	135–199	5 1/2	65.0
9	$AlCl_3$	$Cl_3C{-}C(CH_3){=}CH_2$	2/1/0.1	CH_3	$Cl_2C{=}C(CH_3)CH_2-$	H	40–45	1 5/6	39.0
10	None	$Cl_3C{-}C(CH_3){=}CH_2$	1/1/0	CH_3	$Cl_2C{=}C(CH_3)CH_2-$	H	78–83; 187	1/3; 1/2	23.6[c]
11	None	$Cl_2C{=}C(CH_3)CH_2Cl$	2/1/0	CH_3	$Cl_2C{=}C(CH_3)CH_2-$	H	150–168	7	40.7
12	None	$Cl_2C{=}C(CH_3)CH_2Cl$	3/1/0	Isopropyl	$Cl_2C{=}C(CH_3)CH_2-$	H	155–187	7	67.7
13	None	$Cl_2C{=}C(CH_3)CH_2Cl$	1.9/1/0	*t*-Butyl	$Cl_2C{=}C(CH_3)CH_2-$	H	154–165	8	41.2
14	$FeCl_3$	$Cl_2C{=}C(HC_3)CH_2Cl$	3/1/0.005	*t*-Butyl	$Cl_2C{=}C(CH_3)CH_2-$	Cl	140	12	61.3
15	None		2/1/0	CH_3		H	69–71	1/3	18.9
16	None		2/1/0	CH_3	$ClC(CH_3){=}CHCH_2$	H	111–112	1	41.2[d]

[a] The molar ratio of phenolic compound to halide to catalyst. [b] An 8.4% yield to phenyl 3,3-dichloro-2-methylallyl ether also resulted. [c] A 5.8% yield to *p*-methylphenyl 3,3-dichloro-2-methylallyl ether also resulted. [d] Used 0.027 mole of hydroquinone in reaction mixture.

TABLE II

PROPERTIES OF SYNTHESIZED PHENOLS



R	R′	R″	M.p., °C.	B.p., °C.	B.p., Mm.	Analyses, % Calcd. C	Calcd. H	Calcd. Cl	Found C	Found H	Found Cl
H	$Cl_2C{=}C(CH_3)CH_2-$	H	....	100.0	0.4	55.32	4.64	...	55.59	4.46	...
$Cl_2C{=}C(CH_3)CH_2-$	H	H	91–93	...	..	55.32	4.64	32.66	55.12	4.53	32.91
Cl	$Cl_2C{=}C(CH_3)CH_2-$	H	....	136.0	.8	47.55	3.59	42.11	47.29	3.39	41.81
CH_3	$Cl_2C{=}C(CH_3)CH_2-$	H	52.5–53.7	...	..	57.25	5.34	30.7	57.42	5.19	30.44
t-Butyl	$Cl_2C{=}C(CH_3)CH_2-$	H	....	128–130	.6	61.54	6.64	...	61.75	6.35	...
Isopropyl	$Cl_2C{=}C(CH_3)CH_2-$	H	....	113.5–114	.25	60.23	6.22	27.36	60.70	5.85	26.99
t-Butyl	$Cl_2C{=}C(CH_3)CH_2-$	Cl	....	113	.2	54.63	5.57	...	54.32	5.44	...
Cl	$Cl_2C{=}C(CH_3)CH_2-$	$Cl_2C{=}C(CH_3)CH_2-$	....	175.0	.12	44.9	3.5	47.3	45.27	3.52	47.3

group into the phenolic ring. Therefore, phenols were used which contained substituents in the *para* position so that position isomers would be minimized.

The non-catalytic method when applied to phenol and TMP gave *o*- and *p*-dichloromethylallylphenols and the phenyl dichloromethylallyl ether. The ether was obtained in low yield (8.4%) No TMP was recovered but instead allyl-TMP was isolated. The formation of allyl-TMP is explained by assuming that some of the ether was cleaved by liberated hydrogen chloride to give this compound and phenol. At the relatively low temperature used, very little of the allyl-TMP so formed could react with phenol, so that the allyl-TMP was isolated. Whenever aluminum chloride was used as a catalyst in the reaction between TMP and *p*-cresol, no ether was found (Table I), because the aluminum chloride promotes the complete cleavage of the ether by hydrogen chloride. Also, some of the allyl-TMP formed by this cleavage probably reacted to give dichloromethylallylated *p*-cresol.

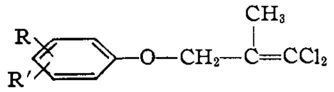
Whenever allyl-TMP was allowed to react non-catalytically with phenols, ethers were not isolated, because of their cleavage at the higher reaction temperature.[4] Bert and Andor showed that phenyl 3-chloroallyl ether reacts with bromine in chloroform at 0° to give phenol, *p*-bromophenol, 3-bromo-1-chloro-1-propene and *p*-bromophenyl 3-chloroallyl ether.

The course of the non-catalytic reaction between

[4] L. Bert and E. Andor, *Compt. rend.*, **194**, 722 (1932).

TABLE III

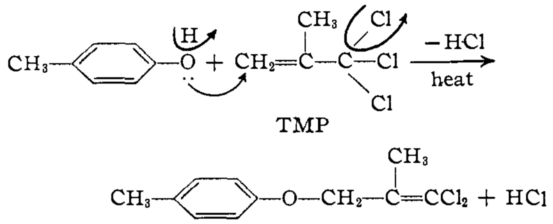
SUBSTITUTED PHENYL 3,3-DICHLORO-2-METHYLALLYL ETHERS[a]



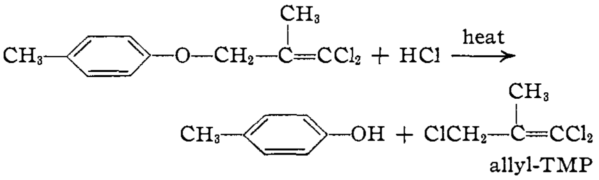
R =	R' =	B.p. °C.	Mm.	M.p., °C.	n^{20}_D range	d^{20}_4 range	Yield, %
H	H	76–83	0.3	....	1.5468–1.5471	1.215–1.227	61.7
4-Cl	H	97–105	0.4	....	1.5570–1.5591	1.325	66.8
2-Cl	H	106–109	0.4–0.6	....	1.5587–1.5612	1.347–1.355	77.4
2-CH_3[b]	H	93.5–95.3	0.7	....	1.5429–1.5442	1.214–1.206	56.5
4-CH_3[c]	H	93.0–95.5	.6	....	1.5419–1.5421	1.195–1.208	63.8
4-Br	H	118–120	.4	....	1.5769–1.5778	1.547–1.555	63.4
4-NO_2	H	....	......	47.5–49.3	....	....	22.7
4-Phenyl	H	....	......	87.5–89.5	....	....	95.9
2-Cl	4-Cl	....	......	46.5–48.0	....	....	71.7
Penta-Cl	..	....	......	148–149	....	....	84.3
4-Phenyl	2-Cl	....	......	52–55	....	....	68.7
2-CO_2CH_3	H	118.5–121	0.2–0.18	....	1.5510–1.5513	1.266–1.268	29.5

[a] The quantities of reagents were 0.5 mole of phenolic compound, 0.5 mole of allyl-TMP and 0.6 mole of potassium carbonate. [c] 0.45 mole of *o*-cresol. [b] 0.45 mole of *p*-cresol.

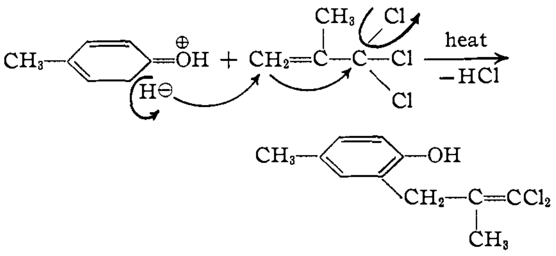
phenols and TMP is exemplified by the equations below for *p*-cresol.



Some of the ether is cleaved thus



also simultaneously



This S_N2' type of reaction is in keeping with previous results.[5] The reactions between allyl-TMP and phenols probably proceed by a normal S_N2 reaction mechanism.

The nature of the products from these reactions leaves no doubt that the dichloromethylallylated phenols are not formed by an *ortho*-Claisen rearrangement of the ethers. Since inversion is necessary during such a rearrangement, the phenols formed would possess two allylic chlorines, rather than the two vinylic chlorines found in the present work. The *ortho* Claisen rearrangement is hindered because the vinylic chlorines oppose the necessary shift of π-electrons; the literature contains no record of the reversibility of the rearrangement of TMP to allyl-TMP. Work in our laboratory also substantiates the irreversibility of this rearrangement.[2]

The structures of the phenolic products were further evidenced by their infrared spectra. The characterizing band for the $Cl_2C{=}C$ group was at 6.15 to 6.20 μ.

Results with 1,3-dichloro-2-butene show that polymers result unless hydroquinone is present. Thus, one vinylic chlorine is not sufficient to stabilize the double bond against addition reactions. The stabilizing effect of two vinylic chlorines is again shown by the yield of monomeric phenol from 1-chloro-2-(dichloromethylene)-cyclohexane.

The twelve phenoxy ethers listed in Table III and IV were prepared in anhydrous acetone. All reactions were conducted for five hours so that the effect of phenolic acidity might be correlated with yields of ethers. *p*-Phenylphenol was run seven hours to show that the yields could be increased by using a longer reaction time. The yields (Table III) indicate that the acidity of the phenol is not the sole factor influencing the reaction rates. The factors that affect reaction rates were not studied, but solubilities appear to be important. No side reactions occurred except with *p*-nitrophenol and with methyl salicylate.

Acknowledgment.—We wish to thank The Dow Chemical Co. for the analyses. We are indebted to Dr. A. W. Baker, The Dow Chemical Co., for many of the infrared analyses and for his interpretations.

Experimental[6]

Substituted Phenols. (a) Non-catalytic Reactions.—A mixture of the desired phenol and halide was heated at the desired temperature and for the time given in Table I. The reaction mixture was then distilled through either a Claisen head or a column (120 mm. high and 20 mm. diameter) packed with glass helices.

In some cases the phenolic products were obtained as supercooled liquids and seeding was necessary to promote crystallization. Solid phenols were purified by recrystallizing from petroleum ether, b.p. 60–70°, or from a mixture of petroleum ethers, b.p. 30–40° and b.p. 60–70°.

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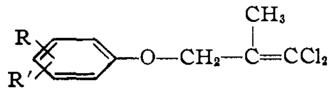
(5) P. B. D. De La Mare and C. A. Vernon, *J. Chem. Soc.*, 3628 (1952).

(6) All boiling and melting points are uncorrected.

TABLE IV

PROPERTIES OF SUBSTITUTED PHENYL-3,3-DICHLORO-2-METHYLALLYL ETHERS



R =	R′ =	B.p., °C.	B.p., Mm.	M.p., °C.	$n^{20}D$	d^{20}_4	MRD Calcd.	MRD Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found
H	H	76.0	0.3	....	1.5470	1.227	55.7	55.8	55.3	55.3	4.65	4.78	32.7	32.5
4-Cl	H	104–105	.4	....	1.5590	1.325	60.6	61.1	47.74	47.41	3.61	3.64	42.28	42.52
2-Cl	H	107.5	.6	....	1.5612	1.355	60.6	60.2	47.74	47.90	3.61	3.64	42.28	42.19
2-CH_3	H	93.5–95.3	.7	....	1.5440	1.210	60.3	60.2	...	...	..	..	30.70	30.52
4-CH_3	H	93.0–95.5	.6	....	1.5420	1.205	60.3	60.2	...	...	..	..	30.70	30.49
4-Br[a]	H	119.5–120	.4	....	1.5769	1.548	63.5	63.3	40.6	40.98	3.07	3.18	23.95	23.88
4-NO_2[b]	H	....	..	51.0–52.5	....	...	..	..	45.8	46.2	3.46	3.53	27.1	26.1
4-Phenyl	H	....	..	87.7–88.3	....	...	..	..	65.6	65.6	4.82	4.98	24.3	24.1
2-Cl	4-Cl	....	..	51.0–52.0	....	...	..	..	42.0	42.22	2.82	2.7	49.6	49.45
Pentachloro	..	....	..	148.0–149.0	....	...	..	..	...	...	..	..	63.75	63.1
4-Phenyl	2-Cl	....	..	56.5–57.0	....	...	..	..	...	...	..	..	32.5	32.77
2-CO_2CH_3	H	118.5–120	.2	....	1.5513	1.266	66.5	69.5	...	...	..	..	25.85	25.6

[a] Analysis for bromine: calcd. 27.00, found 26.32. [b] Analysis for nitrogen: calcd. 5.35, found 5.15.

Center cuts from the distillation were used for analyses (Table II).

(b) **Aluminum Chloride Catalyzed Reactions.**—With constant stirring, anhydrous aluminum chloride was added to the melted phenol. After HCl evolution ceased, the halide was added dropwise under the conditions shown in Table I. After reaction, the mixture was cooled and poured over crushed ice containing hydrochloric acid. Ether extraction procedures were used and the ethereal solution was dried (magnesium sulfate). After removal of ether, the residue was distilled as given in a.

Demethylation of 1,1-Dichloro-3-(*p*-methoxyphenyl)-2-methyl-1-propene.—This ether was synthesized in 66.5% yield.[2] The following procedure of ether cleavage utilized the method of Stone and Shechter.[7] To 79 g. of phosphorus pentoxide was added with stirring, 202 ml. of 85% phosphoric acid and the mixture cooled. Potassium iodide, 445 g. (2.7 mole), and 177.9 g. (0.77 mole) of 1,1-dichloro-3-(*p*-methoxyphenyl)-2-methyl-1-propene were added. The mixture was heated at 93° for five hours and the product phenol extracted with 5% sodium hydroxide. The base extract was acidified to congo red. The oil was separated, cooled, and the solid filtered. Crystallization from hot petroleum ether (b.p. 60–70°) gave 32.7 g. of crystals. A second crop, 16.06 g., of pink needles was obtained. These two crops were combined and gave 48.75 g. (31.4%) of 4-(3,3-dichloro-2-methylallyl)-phenol (II), m.p. 84.5–91.5°.

Another reaction by the same procedure using only one hour heating gave a 21.8% yield of II, m.p. 92–95.3°. These crystals had m.p. 94.3–95.7° when recrystallized from Skelly B and represented analytically pure II.

1-Chloro-2-(dichloromethylene)-cyclohexane (Allyl-TMC).—To 374 g. (1.72 moles) of 1-trichloromethyl-1-cyclohexanol (cryst. pt. 57.5°) was added slowly 100 ml. of a total of 610 ml. (8.4 moles) of thionyl chloride. The remaining 510 ml. of thionyl chloride was added after the evolution of hydrogen chloride had subsided. After standing 19 hours, the solution was heated at 63° for five hours. The excess thionyl chloride was removed by distillation. Further distillation at reduced pressure gave 204.5 g. (59.5%) of 1-chloro-2-(dichloromethylene)-cyclohexane, b.p. 107° (13 mm.), $n^{20}D$ 1.5310, d^{20}_4 1.314; infrared spectrum showed $Cl_2C{=}C$ group (6.20 μ), cyclohexyl (3.40, 3.50 and 3.73 μ).

2-(3-Chloro-3-methylallyl)-4-methylphenol (XI).—Two moles (216.2 g) of *p*-cresol, 125 g. (1.0 mole) of distilled 1,3-dichloro-2-butene (b.p. 126.0–126.5°, $n^{20}D$ 1.4722) and 3 g. (0.027 mole) of hydroquinone were mixed and heated from 119 to 132° in 50 minutes while sweeping the mixture with nitrogen. The evolution of hydrogen chloride was rapid during most of this time. Distillation under nitrogen gave unreacted halide (12.41 g.) and unreacted *p*-cresol (125.7 g.). The residual liquid was rapidly distilled through a Claisen head. The cut, b.p. 101° (0.03 mm.) −194° (0.25 mm.), 114.2 g., was redistilled through the same apparatus. 2-(3-Chloro-3-methylallyl)-4-methylphenol (XI) was collected as three fractions, b.p. 91 (0.1 mm.)−98° (0.09 mm.), 63.7 g. (32.7%), $n^{20}D$ 1.5525 to 1.5540.

Substituted Phenyl 3,3-Dichloro-2-methylallyl Ethers.—The following general procedure was used to prepare the ethers listed in Table III. A flask of appropriate size was fitted with a condenser carrying a calcium chloride drying tube and a motor driven stirrer. Acetone (500 ml.) was added and the desired amounts of 1,1,3-trichloro-2-methyl-1-propene (allyl-TMP) and substituted phenol were dissolved in the acetone. The stirrer was started and a slight molar excess of anhydrous potassium carbonate was added. The contents were refluxed five hours while stirring.

After cooling to room temperature the reaction mixture was treated in one of several ways.

If there appeared to be acetone-insoluble product present, the mixture was filtered. The filter cake was washed several times with acetone and then with water to remove potassium salts. The filtrate was diluted with one liter of water and any additional phenoxy ether was removed by filtration. The product was purified by crystallization from ethanol.

If the reaction mixture appeared to have only insoluble potassium salts, it was poured into twice its volume of water. If solid ether precipitated, it was filtered; if not, separation and ether extraction procedures were used. The product was purified by distillation through a packed column if it was a liquid.

The unreacted potassium carbonate and the potassium chloride were removed by filtration followed by several acetone washes. The filtrate was distilled to remove acetone and the residue was treated as its properties dictated.

Table III contains a summary of the syntheses of twelve ethers. The yield which is reported for a given ether is for the material falling within the boiling point and corresponding refractive index range given. Analytical results are reported in Table IV.

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[7] H. Stone and H. Shechter, *J. Org. Chem.*, **15**, 491 (1950).