evolved hydrogen chloride and developed a yellow color when it was digested on a steam-bath. After thirty minutes the excess of thionyl chloride was evaporated and the residue dissolved in ether. The fluorenone derivative crystallized in stout pale yellow needles and it melted at 183°. The yield was 4.6 g.

Anal. Calcd. for $C_{25}H_{16}O$: C, 90.4; H, 4.8; mol. wt., 332. Found: C, 90.2; H, 5.0; mol. wt., 321.

1,3,9-Triphenyl Fluorenol, IX.—The tertiary alcohol was obtained without difficulty by treating the ketone with phenylmagnesium bromide. It crystallizes from ether–petroleum ether in colorless needles and melts at 207°.

Anal. Calcd. for $C_{31}H_{22}O$: C, 90.7; H, 5.4. Found: C, 90.3; H, 5.6.

1,3,9-Triphenyl Fluorene, XI.—The hydrocarbon was first obtained in an attempt to reduce triphenyl benzohydrol with hydrogen iodide. It is formed equally rapidly by the action of other halogen acids on the secondary alcohol. It crystallizes in colorless needles and it melts at 149°.

Anal. Calcd. for $C_{31}H_{22}$: C, 94.4; H, 5.6. Found: C, 94.4; H, 5.8.

1,3-Diphenyl Triphenylphenyl Fluorene, XIII.—The hydrocarbon was obtained by the action of hydrogen iodide on hexaphenyl benzohydrol. It crystallizes in minute needles and melts at 221°.

Anal. Calcd. for $C_{49}H_{34}$: C, 94.5; H, 5.5. Found: C, 94.4; H, 5.6.

Summary

A comparison of a series of derivatives of triphenylbenzene with the corresponding derivatives of mesitylene shows that while the former are uniformly less reactive than the latter there is no conspicuous difference in behavior which can be attributed to a difference in space relations.

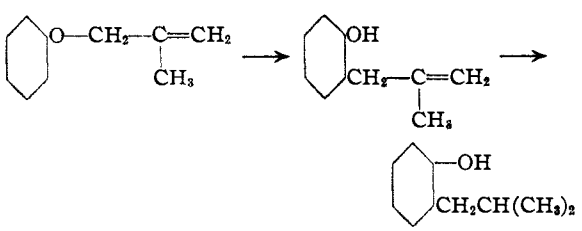
CAMBRIDGE, MASS. RECEIVED DECEMBER 4, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Introduction of Isobutyl Groups into Phenols, Cresols and Homologous Compounds

BY QUENTIN R. BARTZ,[1] RICHARD F. MILLER AND ROGER ADAMS

Pyman[2] demonstrated that the introduction of a higher alkyl group into phenol, cresol or one of the homologs, greatly enhanced the antiseptic action of the molecule. Numerous methods of preparation[3] for various types of alkylated phenols have been described in recent years, but none of these is suitable for the introduction of the isobutyl group. The isobutyl derivatives may be formed conveniently by rearrangement of the proper methylallyl phenol ether to the corresponding methylallyl phenol, followed by catalytic reduction.



Through the kindness of Dr. H. W. Cronwell of the Abbott Laboratories, North Chicago, Illinois, the various isobutyl and diisobutyl phenols were tested bactericidally. These phenols are only slightly soluble in water; the more complex ones give clear solutions at 37° only in dilutions of 1:10,000 or higher. The phenol with the highest bactericidal value was 2-isobutyl-4,5-dimethylphenol. By the F. D. A. method with *staphylococcus aureus* at 37°—transfer method—the product showed kills in five minutes, diln. 1:1000, 1:2000 and 1:5000, but not in 1:10,000 in fifteen minutes. It is obvious that the isobutyl derivatives are not so effective as the corresponding *n*-butyl or higher alkylated analogs.

Methylallyl chloride reacts similarly to allyl halides in the formation of phenol ethers,[4] though with certain phenols it is found preferable to substitute a Williamson synthesis for the potassium carbonate and acetone method used by Claisen and Eisleb. In general, the yields were not as great as those of the allyl ethers.

The methylallyl phenyl ethers rearrange more rapidly than the allyl phenyl ethers either by direct pyrolysis or by heating in a solvent. The

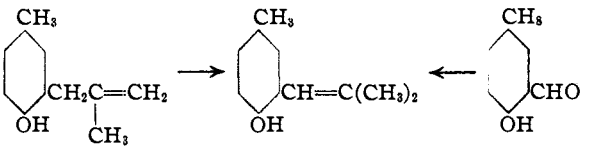
(1) Submitted as part of a thesis for the Degree of Doctor of Philosophy in Chemistry.

(2) Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 281 (1930). See also Johnson and Lane, THIS JOURNAL, **43**, 348 (1921); Dohme, Cox and Miller, *ibid.*, **48**, 1688 (1926).

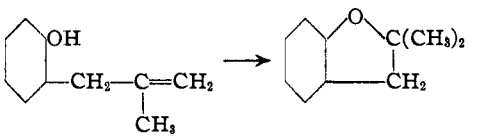
(3) Rosenmund and Schnurr, *Ann.*, **460**, 56 (1928); Rosenmund, Bushwald and Deligiannis, *Arch. pharm.*, **271**, 342 (1933); Read, Reddish and Burlingame, THIS JOURNAL, **56**, 1377 (1934); Niederl and Storch, *ibid.*, **53**, 272, 1928 (1931); **54**, 1063 (1932); Sowa, Hinton and Nieuwland, *ibid.*, **54**, 2019 (1932); Smith, *ibid.*, **55**, 849, 3718 (1933); Natelson, *ibid.*, **56**, 1583 (1934).

(4) Claisen and co-workers, *Ber.*, **45**, 3157 (1912); **58**, 275 (1925); **59**, 2344 (1926); *Ann.*, **401**, 21 (1913); **418**, 69 (1919); **442**, 210 (1925); **449**, 81 (1926); *Z. angew. Chem.*, **36**, 478 (1923).

methylallyl group, like the allyl, enters the position ortho to the hydroxyl as demonstrated by the ring formation between the methylallyl and hydroxyl groups which may occur only if the groups are in adjacent positions. If an ortho position is not vacant, the methylallyl group enters the para position. The rearranged product from the methylallyl ether of *p*-cresol was isomerized with alkali to 2-isobutenyl-*p*-cresol, a product identical with that previously prepared by von Auwers[5] by the action of isopropylmagnesium bromide on *p*-homo-salicylaldehyde followed by dehydration.



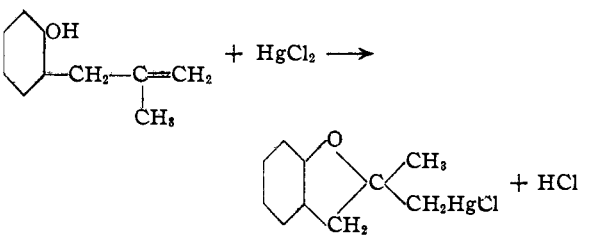
In the reaction mixture from the rearrangement of methylallyl ethers, alkali-insoluble by-products were always present and if the heating was continued too long were present in very appreciable quantities—8–10% in the case of *o*-cresol, 14–15% in the case of *m*- or *p*-cresol, and approximately 20% in the case of *p*-chlorophenol. The by-product proved to be a dimethyldihydrobenzofuran, undoubtedly produced by isomerization of the methylallylphenol, since it was observed that the tendency for certain of these latter compounds to isomerize is so great that the mere standing at room temperature of a low-boiling petroleum ether solution containing anhydrous magnesium sulfate results in the formation of dimethyldihydrobenzofurans. Heating of the methylallylphenols accomplishes the same results. These products were identical with those formed by the action of pyridine hydrochloride on methylallylphenols. Curiously enough the pyrolytic rearrangement never proceeded quantitatively, but generally to a maximum of 40%, after which it was necessary to remove the dihydrobenzofuran before more phenol would isomerize. The process, however, was not an equilibrium reaction, since attempts by the same method to reconvert the dimethyldihydrobenzofuran to methylallylphenol resulted in failure.



(5) Von Auwers, *Ber.*, **47**, 2339 (1914).

Claisen observed a by-product amounting to 4–6% of dihydrobenzofuran when rearranging allyl phenyl ether. He assumed this to be due to isomerization of the phenol. In a later investigation, however, he studied the reaction of α, γ-dimethylallyl bromide and phenols in acetone with potassium carbonate. As part of the product he isolated substituted dihydrobenzofurans and concluded that since allyl phenols were converted to dihydrobenzofurans only in the presence of acid reagents and not in neutral or alkaline solution, the dihydrobenzofurans must have formed directly from the original phenol and α,γ-dimethylallyl bromide. The ease of rearrangement of methylallyl phenyl ethers and the ease of isomerization of the resulting phenols make it probable that the mechanism in Claisen's reactions proceeded also through these two intermediate steps.

Methylallylphenols show properties analogous to allylphenols—catalytic reduction yields isobutylphenols; concentrated aqueous alkali converts them to isobutenylphenols; heating with pyridine hydrochloride results in the formation of dimethyldihydrobenzofurans; addition of mercuric salts produces mercurated dimethyldihydrobenzofurans.



Claisen found that the allyl ethers of the allylphenols rearranged to give from 10–30% of diallylphenols. The methylallyl ethers of methylallylphenols may be rearranged either by pyrolysis or by heating in diethylaniline as a solvent. Under the latter conditions di-methylallylphenols are produced in 70–80% yields.

Experimental

Preparation of Methylallyl Ethers

Method 1.—A mixture of 1 mole of phenol, 1.1 moles of anhydrous potassium carbonate and 1.1 moles of methylallyl chloride (b. p. 73–73.5 (746 mm.)) and 125 cc. of acetone was heated under reflux on a steam-bath for twenty-four hours. After cooling, 500 cc. of water was added and the aqueous layer separated and extracted with 200 cc. of petroleum ether. The petroleum ether extract and water-insoluble layer were mixed and extracted with 10% aqueous sodium hydroxide. After the usual washing and

drying over anhydrous magnesium sulfate, the products were fractionated.

In preparing the methylallyl ethers of 2-methylallyl-*o*- or *p*-cresols, it was an advantage to remove the petroleum ether before alkaline extraction.

In the preparation of resorcinol di-methylallyl ether a by-product of the mono-methylallyl ether of resorcinol was obtained. The di-ether was synthesized by the general procedure described above except that two moles of potassium carbonate and two moles of methylallyl chloride were used for each mole of resorcinol. The aqueous sodium hydroxide extract was made acid to Congo red with hydrochloric acid and the oil extracted with toluene. After evaporation of the toluene, the residue was washed several times with hot water to remove unchanged resorcinol. Dilute hydrochloric acid aids in breaking the emulsion. The oil was finally dried in toluene and then distilled.

Method 2.—A solution of 0.2 mole of sodium ethylate in 60 cc. of absolute ethyl alcohol and 0.2 mole of phenol was warmed in an oil-bath (bath temp. 85–90°) and 0.22 mole of methylallyl chloride was added slowly. The mixture was heated for about fifteen hours, cooled and diluted with 350 cc. of water. The oily layer was separated and mixed with a petroleum ether extract of the aqueous layer. After drying, the petroleum ether was removed by distillation and the residual oil extracted with 10% aqueous sodium hydroxide, then dried and distilled.

Rearrangement of Methylallyl Phenyl Ethers to Methylallylphenols

Method 1.—The methylallyl phenyl ethers were heated under an air condenser with a thermometer suspended in the liquid. The flask was placed in a Woods metal bath previously heated to 245°. The ether boiled around 200° and gradually increased in the course of thirty minutes until it reached a maximum of 230–240°, after which it began to drop slowly. At this point the reaction was assumed to be complete. After cooling, the product was extracted with 240 cc. of 10% potassium hydroxide solution in three equal portions and then the alkaline solution was extracted with low-boiling petroleum ether to remove any unchanged methylallyl phenyl ether. The aqueous solution was made acid to Congo red and the oil extracted with petroleum ether, dried and distilled.

When the phenols were dried in petroleum ether over anhydrous magnesium sulfate, they were not allowed to stand for over ten hours, since cyclization slowly takes place under these conditions.

The rearrangement of the methylallyl ether of guaiacol and of the di-methylallyl ether of resorcinol in contrast to most of the others is markedly exothermic. As a consequence, the bath was held at 205° instead of at 245°.

Apparently the drop in temperature after the maximum is reached is due to isomerization to dihydrobenzofurans and consequently the reaction must be stopped as soon as that point is reached. As an example may be cited the rearrangement of the methylallyl ether of *m*-cresol. If the heating is stopped when the temperature starts to drop (thirty to thirty-five minutes) the yield is 60–70%, but if heating is continued for forty-five minutes the yield is only 30%.

Method 2.—The rearrangement in diethylaniline was used for all the higher-boiling methylallyl ethers.

A mixture of methylallyl ether with half its weight of diethylaniline was heated under an air condenser in a bath held at about 245°. The temperature of the boiling mixture increased from about 210° to 230–235° (about twenty minutes) where it remained constant for about ten minutes. The product was cooled, diluted with petroleum ether and extracted with cold dilute sulfuric acid to remove the diethylaniline. It was next extracted with several portions of alcoholic potassium hydroxide (3.5 KOH:2.5 H_2O:9 CH_3OH). The alkaline extract was diluted with water and then extracted with petroleum ether to obtain the phenol.

The derivatives of the xylenols were obtained in about 50–60% yields, those of the methylallyl cresols in 70–80% yields. The greater solubility of the former products in aqueous sodium hydroxide and hence the tendency not to be completely precipitated on dilution accounted for the lower yields in the former case. If the diluted methyl alcoholic alkaline solutions are acidified to Congo red before extracting, the yields may be increased to 60–70%.

Preparation of Isobutenyl Derivatives.—The same procedure was employed here as used by Claisen[6] for homologous compounds. The yields were about 80%.

Preparation of Isobutyl Derivatives.—The methylallylphenols were reduced with platinum oxide catalyst and hydrogen at 2–3 atm. pressure in alcohol solution. The reductions were complete for 15–20 g. of material in five minutes. The yields were essentially quantitative. The higher melting solids were crystallized from dilute ethyl alcohol.

Preparation of the Aryloxyacetic Acids.—The procedure of Koelsch was used.[7] The products were purified by crystallization from high-boiling petroleum ether.

Preparation of *p*-Nitrobenzoates.—These were formed from *p*-nitrobenzoyl chloride in pyridine solution. The best solvent for purification of the products was high-boiling petroleum ether.

Preparation of Acetates.—Several hours of refluxing of acetic anhydride (2 moles) and of phenol (1 mole) was used.

Preparation of Dimethyldihydrobenzofurans.—These were obtained in several ways: (1) as alkali-insoluble products in the formation of methylallylphenols by rearrangement of the methylallyl ethers of the phenols (yields 10–20%); (2) by heating the methylallylphenols for a few hours at the boiling temperature—temperature gradually dropped as rearrangement took place (yields variable, generally 30–40%); (3) by heating the methylallylphenols with 2 moles of pyridine hydrochloride (bath temp. 235–245°) for two hours, cooling, washing, extracting with 10% aqueous alkali to remove unchanged phenol (yields 80%); (4) many of the methylallylphenols when dissolved in moist petroleum ether to which anhydrous magnesium sulfate was added, gradually isomerized. In ten days, 6-methylallyl-3-methylphenol under these conditions gave 45% of dihydrobenzofuran.

Preparation of Mercurated Dimethyldihydrobenzofurans.—An aqueous solution of 0.55 mole of mercuric

(6) Claisen and Eisleb, *Ann.*, **401**, 21 (1913).
(7) Koelsch, THIS JOURNAL, **53**, 304 (1931).

TABLE I

CONSTANTS OF ARYL-METHYLALLYL ETHERS

No.	Methylallyl ether of	Method of prepn.	B. p., °C.	Mm.	d_{20}^{20}	$n^{20}D$	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
1	Phenol	1	70	8	0.9638	1.5168	$C_{10}H_{12}O$	81.08	8.17	80.65	8.11
2	2-Methylphenol	1	82.5	5	.9537	1.5225	$C_{11}H_{14}O$	81.43	8.70	81.61	8.69
3	3-Methylphenol	1	85.5	4	.9496	1.5143	$C_{11}H_{14}O$	81.43	8.70	81.52	8.86
4	4-Methylphenol	1	84	3	.9499	1.5142	$C_{11}H_{14}O$	81.43	8.70	81.60	8.95
5	2,4-Dimethylphenol	2	90	3	.9453	1.5139	$C_{12}H_{16}O$	81.77	9.14	81.85	9.28
6	2,5-Dimethylphenol	2	88.5	4	.9430	1.5135	$C_{12}H_{16}O$	81.77	9.14	82.01	9.22
7	3,4-Dimethylphenol	1	98.5	4	.9520	1.5185	$C_{12}H_{16}O$	81.77	9.14	82.00	9.25
8	2-Methoxyphenol	1	107.5	9	1.0334	1.5270	$C_{11}H_{14}O_2$	74.12	7.92	74.08	7.87
9	4-Chlorophenol	1	101.5	8	1.0979	1.5304	$C_{10}H_{11}OCl$	65.94	6.06	66.39	6.59
10	2-Isopropyl-5-methylphenol	2	105.6	6	0.942	1.5080	$C_{14}H_{20}O$	82.35	9.80	82.38	9.90
11	2-Methylallylphenol	2	104	4	.9440	1.5198	$C_{14}H_{18}O$	83.16	8.91	83.03	8.99
12	2-Methyl-6-methylallylphenol	1	106	5		1.5133	$C_{15}H_{20}O$	83.33	9.27	83.43	9.45
13	2-Methylallyl-5-methylphenol	2	120	4	.9409	1.5200	$C_{15}H_{20}O$	83.33	9.27	83.24	9.27
14	2-Methylallyl-4-methylphenol	1	118	4	.9401	1.5225	$C_{15}H_{20}O$	83.33	9.27	83.60	9.44
15	Resorcinol (monoether)	1	128	3	1.077	1.5451	$C_{10}H_{12}O_2$	73.12	7.37	73.12	7.47
16	Resorcinol (diether)	1	147	6	0.9937	1.5222	$C_{14}H_{18}O_2$	77.03	8.30	77.05	8.40

TABLE II

CONSTANTS OF METHYLALLYLPHENOLS

No.	Phenol	Method of prepn.	Time of heating for rearrg., min.	Max. temp., °C.	B. p. °C.	B. p. Mm.	d_{20}^{20}	$n^{20}D$	Color in alc. ferric chloride	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
1	2-Methylallyl	1	120	224	95	9	1.0068	1.5534	Red	$C_{10}H_{12}O$	81.08	8.17	80.86	8.24
2	2-Methylallyl-6-methyl	1	60	228	87	4	0.9821	1.5324	Brown	$C_{11}H_{14}O$	81.43	8.70	81.58	8.77
3	2-Methylallyl-5-methyl-	1	35	234	98	7	.991	1.5382	Green	$C_{11}H_{14}O$	81.43	8.70	81.65	8.90
4	2-Methylallyl-4-methyl	1	35	235	101	7	.986	1.5370	Green	$C_{11}H_{14}O$	81.43	8.70	81.50	8.81
5	2,4-Dimethyl-6-methylallyl	2	45	229.5	103	6	.972	1.5302	Brown	$C_{12}H_{16}O$	81.77	9.14	81.91	9.26
6	2,5-Dimethyl-6-methylallyl	2	45	230	100	6	.981	1.5336	Green (dil.) Brown (concd.)	$C_{12}H_{16}O$	81.77	9.14	81.82	9.18
7	3,4-Dimethyl-6-methylallyl	2	40	233	116	7	.988	1.5400	Green	$C_{12}H_{16}O$	81.77	9.14	82.03	9.16
8	2-Methylallyl-6-methoxy	1	23	248.5	115	8	1.049	1.5368	Green	$C_{11}H_{14}O_2$	74.12	7.92	74.23	7.94
9	2-Methylallyl-4-chloro	1	13	246.5	113	8	1.145	1.5622	Green	$C_{10}H_{11}OCl$	65.71	6.06	65.68	6.30
10	2-Isopropyl-5-methyl-6-methylallyl	2	20	231	110	6	0.954	1.5225	Green	$C_{14}H_{20}O$	82.35	9.80	82.24	9.99
11	2,6-Dimethylallyl	2	32	228	110	2	.979	1.5360	Green	$C_{14}H_{18}O$	83.16	8.91	83.02	8.93
12	2,4-Dimethylallyl-6-methyl	2	37	237.5	134	7	.958	1.5319	Green	$C_{15}H_{20}O$	83.33	9.27	83.42	9.27
13	2,6-Dimethylallyl-5-methyl	2	30	235.5	130	7	.962	1.5315	Brown	$C_{15}H_{20}O$	83.33	9.27	83.41	9.35
14	2,6-Dimethylallyl-4-methyl	2	45	235.5	127	7	.957	1.5323	Brown	$C_{15}H_{20}O$	83.33	9.27	83.28	9.29
15	4,6-Dimethylallyl resorcinol	1	40		145	3	1.053	1.5550	Pink (turbid)	$C_{14}H_{18}O_2$	77.03	8.30	76.73	8.40

chloride[8] was mechanically stirred and 0.05 mole of a methylallylphenol added drop by drop. Stirring was continued for five hours. The oil which separated soon after the reaction was started, solidified in this time in a single lump. It was broken up and stirred for several hours longer. The product was then filtered and purified from ethyl alcohol.

The corresponding bromides and iodides may be made from the chlorides by suspending the chloride (3 g. in 200 cc. of water) in water, adding potassium iodide or bromide and heating on a steam-bath for two hours. The bromides or iodides were purified from ethyl alcohol.

(8) Adams, Roman and Sperry, THIS JOURNAL, **44**, 1781 (1922); Mills and Adams, *ibid.*, **45**, 1842 (1923).

TABLE III

CONSTANTS OF ISOBUTYLPHENOLS

No.	Phenol	B. p., °C.	Mm.	$n^{20}D$	d_{20}^{20}	Color in alc. ferric chloride	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
1	2-Isobutyl	86	6	M. p. 21		Red	$C_{10}H_{14}O$	80.53	8.72	80.48	8.76
2	2-Isobutyl-6-methyl	100	9	M. p. 41–42		Orange	$C_{11}H_{16}O$	80.49	9.76	80.53	9.93
3	2-Isobutyl-4-methyl	106	9	1.5221	0.964	Green	$C_{11}H_{16}O$	80.49	9.76	80.67	9.88
4	2-Isobutyl-5-methyl	105	8	1.5229	.966	Green	$C_{11}H_{16}O$	80.49	9.76	80.60	9.84
5	2,4-Dimethyl-6-isobutyl	M. p.	69–70				$C_{12}H_{18}O$	80.85	10.16	80.67	9.91
6	2,5-Dimethyl-6-isobutyl	M. p.	73–74				$C_{12}H_{18}O$	80.85	10.16	81.08	10.26
7	3,4-Dimethyl-6-isobutyl	107	3	1.5254	.968		$C_{12}H_{18}O$	80.85	10.16	81.04	10.17
8	2-Isopropyl-5-methyl-6-isobutyl	111	2	1.5110	.936	Brown	$C_{14}H_{22}O$	81.47	10.75	81.63	10.78
9	2,6-Di-isobutyl	118	6	1.5300	.958	Red	$C_{14}H_{22}O$	81.47	10.75	81.16	10.66
10	2,4-Di-isobutyl-6-methyl	121	2	M. p. 48–49			$C_{15}H_{24}O$	81.82	10.91	81.86	11.24
11	2,6-Di-isobutyl-5-methyl	120	4	1.5070	.924		$C_{15}H_{24}O$	81.82	10.91	82.06	11.10
12	2,6-Di-isobutyl-4-methyl	121	2	1.5050	.915		$C_{15}H_{24}O$	81.82	10.91	81.70	11.02

TABLE IV

CONSTANTS OF ISOBUTENYLPHENOLS

No.	Phenol	B. p., °C.	Mm.	$n^{20}D$	d_4^{20}	Color in alc. ferric chloride	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
1	2-Isobutenyl	81	6	1.5590	1.0119	Red	$C_{10}H_{12}O$	81.08	8.17	80.87	8.38
		M. p.	22								
2	2-Methyl-6-isobutenyl	112	18	1.5356	0.982	Red	$C_{11}H_{14}O$	81.43	8.70	81.41	8.74
3	2-Isobutenyl-5-methyl	127	17	1.5442	.993	Green	$C_{11}H_{14}O$	81.43	8.70	81.60	8.72
4	2-Isobutenyl-4-methyl	102	8	1.5510	.991	Green	$C_{11}H_{14}O$	81.43	8.70	81.34	8.82

TABLE V

ARYLOXYACETIC ACIDS (WHITE NEEDLES)

No.	Phenol used	M. p., °C.	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
1	2-Methylallyl-4-methyl	116–117	$C_{13}H_{16}O_3$	70.91	7.23	70.67	7.30
2	2-Methylallyl-5-methyl	77–78	$C_{13}H_{16}O_3$	70.91	7.23	70.72	7.75
3	4-Methyl-6-isobutyl	99	$C_{13}H_{18}O_3$	70.27	8.10	70.36	8.08
4	4-Methyl-6-isobutenyl	79–80	$C_{13}H_{16}O_3$	70.91	7.23	70.56	7.76

TABLE VI

ACETATES

No.	Phenol used	B. p., °C.	Mm.	$n^{20}D$	d_{20}^{20}	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
1	2-Methylallyl	98	6	1.5177	1.008	$C_{12}H_{14}O_2$	75.78	7.41	75.65	7.57
2	2-Methyl-6-methylallyl	116	12	1.5093	1.002	$C_{13}H_{16}O_2$	76.47	7.91	76.52	7.99
3	2-Methylallyl-4-methyl	115	5	1.5122	1.006	$C_{13}H_{16}O_2$	76.47	7.91	76.55	7.98
4	2-Methylallyl-5-methyl	123	5	1.5103	1.006	$C_{13}H_{16}O_2$	76.47	7.91	76.40	8.01

TABLE VII

p-NITROBENZOATES

No.	Phenol used	M. p., °C.	Character of product, needles	Formula	Nitrogen analyses, % Calcd.	Found
1	2-Methylallyl	42	White	$C_{17}H_{15}O_4N$	4.71	4.45
2	2-Methylallyl-4-methyl	66–67	White	$C_{18}H_{17}O_4N$	4.50	4.58
3	2,4-Dimethyl-6-isobutyl	100–101	White	$C_{19}H_{21}O_4N$	4.28	3.96
4	2,4-Di-isobutyl-6-methyl	103–104		$C_{22}H_{27}O_4N$	3.80	4.29
5	2,6-Di-isobutyl-5-methyl	130.5	Yellow	$C_{22}H_{27}O_4N$	3.80	3.96
6	2,6-Di-isobutyl-4-methyl	87–88	White	$C_{22}H_{27}O_4N$	3.80	3.76
7	2-Isobutyl-3-methyl-6-isopropyl	128.5	Yellow	$C_{21}H_{25}O_4N$	3.95	4.02
8	2-Isobutenyl	64	Yellow	$C_{17}H_{15}O_4N$	4.71	4.60
9	4-Methyl-6-isobutenyl	69.5	Yellow	$C_{18}H_{17}O_4N$	4.50	4.58

TABLE VIII

CONSTANTS OF THE 1,2-DIHYDROBENZOFURANS

No.	1,2-Dihydrobenzofuran	Method of prepn.	B. p., °C.	Mm.	d_{20}^{20}	$n^{20}D$	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
1	1,1-Dimethyl	1, 2, 3	62	7	0.996	1.5190	$C_{10}H_{12}O$	81.08	8.17	80.08	8.37
2	1,1,6-Trimethyl	1, 3, 4	74	8	.983	1.5150	$C_{11}H_{14}O$	81.43	8.70	81.56	8.70
3	1,1,5-Trimethyl	1, 2, 3, 4	87	11	.978	1.5167	$C_{11}H_{14}O$	81.43	8.70	81.50	8.73
4	1,1,4-Trimethyl	1, 3, 4	88	10	.978	1.5151	$C_{11}H_{14}O$	81.43	8.70	81.53	8.70
5	1,1-Dimethyl-4-chloro	1	96	5	1.135	1.5300	$C_{10}H_{11}OCl$	65.93	6.06	65.52	6.24

TABLE IX

CONSTANTS OF THE MERCURATED 1-METHYL-1,2-DIHYDROBENZOFURANS

No.	1,2-Dihydrobenzofuran	M. p., °C.	Formula	Mercury analyses, % Calcd.	Found
1	1-Chloromercurimethyl-1-methyl	81	$C_{10}H_{11}OClHg$	52.35	51.90
2	1-Chloromercurimethyl-1,6-dimethyl	72.5	$C_{11}H_{13}OClHg$	50.53	50.32
3	1-Chloromercurimethyl-1,4-dimethyl	102.4	$C_{11}H_{13}OClHg$	50.53	50.60
4	1-Iodomercurimethyl-1,4-dimethyl	73	$C_{11}H_{13}OIHg$	40.98	40.78
5	1-Bromomercurimethyl-1,4-dimethyl	93–94	$C_{11}H_{13}OBrHg$	45.48	45.05

Summary

1. Methylallyl phenyl ethers rearrange upon heating to give *o*-methylallylphenols.

2. *o*-Methylallylphenols (a) on heating or (b) by treatment with pyridine hydrochloride, give dimethyldihydrobenzofurans, (c) by catalytic reduction give isobutylphenols, (d) by action of sodium hydroxide give isobutenylphenols, (e) by addition of mercuric salts give mercurated dimethyldihydrobenzofurans.

3. The isobutyl group does not enhance the antiseptic action of the phenols as much as the *n*-butyl or higher molecular weight alkyl groups.

URBANA, ILLINOIS RECEIVED DECEMBER 5, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE UNIVERSITY OF MONTANA]

The Addition of Chloroform and Bromoform to *o*-Chlorobenzaldehyde

BY JOSEPH W. HOWARD AND IRWIN CASTLES

Introduction

Previous work has shown that benzaldehyde is one of the few aldehydes to which chloroform and bromoform will add forming the corresponding trichloromethyl and tribromomethyl carbinols.[1,2,3]

The present work was undertaken in order to ascertain whether or not chloroform and bromoform would add in a similar manner to *o*-chlorobenzaldehyde. It was found that such a reaction did take place. In addition the acetates, propionates, butyrates, and benzoates of the resulting carbinols have been prepared and studied.

Experimental Part

Preparation of Trichloromethyl-*o*-chlorophenylcarbinol.—To a mixture of 46 g. of freshly distilled *o*-chlorobenzaldehyde and 60 g. of dry chloroform was added with constant stirring 4 g. of powdered potassium hydroxide over a one-hour period. The mixture was allowed to stand for three hours, ether was added, and the resultant mixture filtered. The filtrate was distilled until the temperature of 130° at 6 mm. was reached. The residue was then steam distilled to remove the last traces of *o*-chlorobenzaldehyde and *o*-chlorobenzoic acid. It was washed with dilute sodium carbonate solution, extracted with ether, dried over sodium sulfate and the ether distilled off. The carbinol was then removed by distillation, coming over at 170–171° at 6–7 mm. The yield was 20 g. of d_{20}^{20} 1.580.

Anal. Calcd. for $C_8H_6OCl_4$: Cl, 54.58. Found: Cl, 54.61.

Preparation of Tribromomethyl-*o*-chlorophenylcarbinol.—The above procedure was followed with the substitution of 130 g. of bromoform for 60 g. of chloroform. This compound boils at 195–196° at 8 mm. The yield was 29 g. of d_{20}^{20} 2.117.

Anal. Calcd. for $C_8H_6OClBr_3$: Cl, 9.01; Br, 60.96. Found: Cl, 9.04; Br, 60.80.

Both of these carbinols are insoluble in water but readily soluble in carbon bisulfide, ethyl alcohol, methyl alcohol, benzene, acetone, ether, chloroform and carbon tetrachloride.

(1) Jocicz, *Chem. Centr.*, **68**, I, 1013 (1897).
(2) Siegfried, *ibid.*, 1, 606 (1899).
(3) Howard, THIS JOURNAL, **47**, 455 (1925); **52**, 5059 (1930).