

[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORP.]

Uncatalyzed Thermal *ortho*-Alkylation of Phenols

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Received June 10, 1958

A method has been found for preparing *o*-alkyl phenols thermally, in the absence of a catalyst. When phenol and certain olefins are heated to about 320° under pressure for several hours, the reaction product is largely an *ortho* monosubstituted phenol. Thus, isobutene yields *o*-*t*-butylphenol, 1-butene yields *o*-*sec*-butylphenol, and cyclohexene the *o*-cyclohexyl isomer. Lower olefins such as ethylene and propylene yield a spectrum of products including di- and tri-substituted phenols and phenol ethers. Possible mechanisms for the reaction are discussed.

A study of the uncatalyzed, thermal alkylation of phenol with olefins to give *o*-alkylphenols, in particular *o*-*tert*-butylphenol, is reported in this paper.

o-*tert*-Alkylphenols have only recently been obtained in appreciable yields from phenol alkylations. They are readily isomerized by the usual alkylation catalysts so that even if initially formed they are largely converted to the less hindered *para* derivatives. Recently, however, milder acid catalysts and reaction conditions have been used to give products containing substantial proportions of *o*-*tert*-alkylphenols. *Ortho* isomer yields of 20–61% are reported from the alkylation of phenols with olefins in the presence of 0.6% phosphorus oxychloride at 38–55°.¹ Isobutene and phenol passed over a silica-alumina catalyst at 120–200° reportedly give a high ratio of *ortho* to *para* *t*-butylphenol.^{2,3}

Benzyl halides and tertiary alkyl chlorides also give *ortho* alkylation of phenol under special conditions. In the presence of potassium carbonate, nuclear alkylation of phenols with α -phenylethyl chloride gave mainly *ortho* substituted phenols⁴; by contrast, the uncatalyzed reaction with *tert*-alkyl and benzyl halides gave only *para* alkyl derivatives.⁵ Likewise, gels obtained by treating drying oils with boron trifluoride are reported to catalyze the *ortho* alkylation of phenol with *tert*-butyl chloride to give monoalkylate containing up to 67% *o*-*tert*-butylphenol.⁶

In contrast to *tert*-alkylphenols, *sec*-alkylphenols obtained by catalytic alkylation of phenol often contain substantial proportions of *ortho* isomers.⁷ Selective uncatalyzed thermal alkylation giving *o*-*sec*-alkylphenols has also been known for some

time. Skraup and Beifuss⁸ reported 30% conversions of phenol and *p*-cresol to *o*-cyclohexylphenols by heating with cyclohexene at 300° for 75 hours. Two patents issued to Skraup *et al.*^{9,10} describe the uncatalyzed alkylation of *m*-cresol with propylene to give thymol. Yields of 50–60%, based on reacted *m*-cresol, were obtained after 70 hours at 370°. Contrary to our results, Schaad¹¹ reported that propylene and phenol did not react in 4 hours at 300°, but that reaction did occur in the presence of calcium acid phosphate.

Since the completion of our work, Stroh¹² *et al.* and Kolka *et al.*¹³ have both reported on the aluminum phenoxide catalyzed *ortho* and di-*ortho* alkylation of phenols. Thermal alkylation of phenols with olefins containing 7–22 carbon atoms has also been described.¹⁴

Results. Most of our alkylations were carried out by heating olefins with phenols for 2–3 hours at 315–330° in rocking autoclaves. The 70-hour reaction period used by Skraup *et al.*^{8–10} was found unnecessary. Glass liners were used in some initial experiments, but were omitted later when it was found that the reaction was apparently unaffected by the 304 stainless steel reactor (18% Cr, 8% Ni, 2% Mn, 1% Si).

Thermal alkylations of phenol with isobutene were the most promising of those screened and, therefore, received most attention. Table I summarizes some of the experiments. The best results show 25–34% conversions of phenol to *tert*-butylphenol in 3 hours at 330° at 114–183 atmospheres pressure. In these experiments, the monoalkylate was 87–98% *o*-*tert*-butylphenol with minor amounts of *para* isomer. Yields at these conversions were 91–98% based on phenol and 32–53% based on isobutene. Diisobutylene and a small amount of

(1) British Patent 725,873 (March 9, 1955).

(2) W. A. Schulze and C. E. Stoops, U. S. Patent 2,514,419 (July 20, 1954).

(3) W. C. Offutt, U. S. Patent 2,516,152 (July 25, 1950).

(4) H. Hart and H. S. Eleuterio, *J. Am. Chem. Soc.*, **76**, 516 (1954).(5) H. Hart and J. H. Simons, *J. Am. Chem. Soc.*, **71**, 345 (1949).

(6) C. J. Plank and J. F. Socolofsky, U. S. Patent 2,460,793 (Feb. 1, 1949).

(7) C. C. Price, *Org. Reactions*, **3**, 1 (1942).(8) S. Skraup and W. Beifuss, *Ber.*, **60B**, 1070 (1927).

(9) British Patent 293,753 (Sept. 6, 1928).

(10) S. Skraup, K. Schöllkopf, and A. Serini, U. S. Patent 1,886,311 (Nov. 1, 1932).

(11) R. E. Schaad, U. S. Patent 2,371,550 (March 13, 1945).

(12) R. Stroh, R. Seydel, and W. Hahn, *Angew. Chem.*, **69**, 699 (1957).(13) A. J. Kolka, J. P. Napolitano, A. H. Filbey, and G. G. Ecke, *J. Org. Chem.*, **22**, 642 (1957).

(14) British Patent 746,407 (March 14, 1956).

TABLE I
THERMAL ALKYLATION OF PHENOL BY ISOBUTENE

Experiment No.	1	2	3	4	5	6	7	8	9	10 ^a	11
Reactants, moles											
Phenol	10.0	5.0	5.02	5.0	5.0	5.0	5.0	5.02	2.0	5.0	<i>o-t</i> -Butylphenol, 0.45
Isobutene	16.0	8.0	8.0	8.0	8.0	11.95	8.0	4.0	5.87	11.95	
Other materials							H ₂ O, 1	H ₂ O, 25	<i>n</i> -Pentane, 5.0	Sulfur, 0.062	
Reactor capacity, Liters	4.73	2.68	4.09 ^b	4.73	4.73	2.68	4.73	4.73	4.73	2.68	0.25
Temperature, °C.											
Initial	318	318	330	331	268	260	316	316	332	315	316
Final	330	331	330	332	263	264	321	320	333	333	330
Total pressure, atm.											
Initial	140	114	95	75	52.5	95	87	145	75	183	7.8
Final	115	95	87	68	47.5	97	81.5	151	73	143	43
Reaction time, hr.	3	3	2	6	3	12.7	3	1	3	3.1	5.3
Product, moles											
Phenol	7.20	3.49	4.16	4.02	4.12	3.98	4.40	3.90	1.94	3.73	0.32
<i>t</i> -Butylphenols	2.30	1.36	0.73	0.74	0.88	1.14	0.66	0.58	Nil	1.58	0.12
Di- <i>t</i> -butylphenols ^c	0.093	0.034	0.073	0.068	0.023	0.033	0.049	—	—	0.12	—
Polymer (as isobutene)	1.81	1.25	0.71	—	0.30	0.44	0.77	—	—	3.14	—
<i>Ortho</i> isomer in butylphenol fraction, %	98.3	90.7	^d	94.3	100	97.8	^d	53	—	86.6	—
Phenol converted, %	25.3	28.5	16.3	16.7	17.6	23.4	3.9	—	Nil	34.0	27
Yield, ^e based on:											
Phenol converted, %	96	98	91	92	97	97	93	—	—	91	—
Isobutene converted, %	53	51	46	—	72	69	43	—	—	32	—

^a Sulfur contaminated bomb. ^b Glass liner used. ^c Small bottoms fraction assumed to be di-*t*-butylphenol. ^d Mainly *ortho*. ^e Calculated on a no loss basis. ^f *o-t*-Butylphenol remaining after equilibration.

TABLE II
MISCELLANEOUS THERMAL ALKYLATIONS

Experiment No.	19	20	21	22	23	24	25	26
Reactants, moles								
Phenol	5.0	5.0	2.78	5.0	5.0	5.0	5.0	<i>o</i> -Cresol, 4.0
Alkylating agent	Ethylene, <i>ca.</i> 10	Propylene, 10	Butene-1, 8.0	Pentene-2, 5.55	Di-isobutene, 2.5	Cyclohexene, 10.0	<i>t</i> -Butyl alco- hol, 5.0	Isobutene, 4.0
Reactor capacity, liters	4.73	4.73	4.73	2.68	4.73	4.73	2.68	4.73
Temperature, °C.								
Initial	320	316	323	325	325	315	316	310
Final	334	340	332	334	333	332	320	317
Pressure, atm.								
Initial	248	99	49	68	34	41	102	54
Final	230	78.5	47	69.7	41	46	92	54
Reaction time, hr.	3.2	3.2	2.67	2.75	3.6	3.67	2.87	3.0
Products, moles								
Phenol	2.40	3.49	4.37	2.60	4.46	4.12	4.14	3.34 ^c
Monoalkylphenol	1.24	0.70	0.45	0.10	0.10 ^a	0.25	0.83	0.35 ^d
Dialkylphenol	0.47	0.01	0.07	0.01	0.03 ^b	0.05	0.04	0.09 ^e
Trialkyl phenol	0.16	0.04				—		
Phenyl alkyl ether	—	0.14				0.168		
Alkylphenyl alkyl ether	0.14	0.03						
Dialkylphenyl alkyl ether	0.12	0.03						
Trialkylphenyl alkyl ether	0.14							
Yield, based on phenol con- sumed:								
Monoalkylphenols, %	47.8	46.3	71.4	55.5	18.6	28.4	96.4	53.0
Total alkylphenols, %	72.0	49.6	82.5	61.2	24.0	34.1	101	66.7

^a *t*-Butylphenol. ^b Octylphenols and di-*t*-butylphenol. ^c *o*-Cresol. ^d *t*-Butylcresol. ^e Di-*t*-butylcresol.

high boiling product were also obtained. Lowering the temperature slowed the isobutene polymerization more than the alkylation and increased the yields based on isobutene to about 70%.

The suspected reversibility of the alkylation was definitely established by starting with pure *o*-*tert*-butylphenol (Experiment 11, Table I). Twenty-seven per cent of the alkylphenol charged was recovered after 5.3 hours at 316–330°. Approximate calculations were made assuming that equilibrium had been reached in this experiment. The conversions actually obtained fall short of this limit. Higher phenol conversions should be possible at lower temperatures, but the rate of approach to equilibrium drops off rapidly with decreasing temperature.

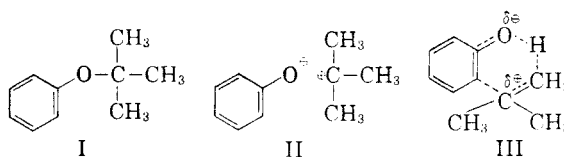
The conversion of phenol was decreased appreciably by addition of water to the reaction mix. The amount of *para* alkylation was greatest, amounting to 47% of the *tert*-butylphenol isolated, when a large amount of water was present, and appeared to be least when the concentration of isobutene in the liquid phase was highest.

Dilution with *n*-pentane essentially stopped the reaction. The presence of a small amount of sulfur had no apparent inhibiting effect.

Trial thermal alkylations with other reactants are shown in Table II. These were carried out as single experiments at 315–334° under pressures from 34 to 248 atmospheres. Phenol alkylation occurred with ethylene, propylene, 1-butene, 2-pentene, cyclohexene, diisobutylene, and *tert*-butyl alcohol. As the concentrations of the reactants in the liquid phase are not known, the olefin reactivity order cannot be established from our data. However, the results indicate that ethylene and other olefins have reactivities of the same magnitude as isobutene, rather than differing by several powers of 10 as they do in many reactions. Ethylene and propylene gave complex mixtures of mono and polysubstituted phenols and phenol ethers, while the higher olefins gave predominantly *o*-monoalkylphenols and little or no ethers. Isobutene reacted with *o*-cresol to give *ortho* substituted product, but did not react with aniline.

Discussion. The *ortho* and *para* positions of phenol each receive about the same activation from the hydroxyl group. On this basis, substitution in the nucleus should give at least one-third *para* products. Steric effects would tend to increase the proportion of *para* isomer formed initially. Any product isomerization that might occur would also increase the proportion of *para* at the expense of *ortho* isomer. These effects would be expected particularly with *tert*-alkyl groups; but we found that the uncatalyzed thermal alkylation of phenol with isobutene gave *o*-*tert*-butylphenol and very little *para* isomer. Therefore, the phenolic hydroxyl group must participate directly in some way to account for the unexpected experimental results.

Three possible intermediates (I, II) or transition state (III) in the isobutene alkylation, which involve direct participation of the hydroxyl group, are:



o-Alkylation is also the predominant result with ethylene and with other olefins. Similar possible structures can be written for these.

o-Alkylation *via* the alkyl phenyl ether (I) is unlikely. *tert*-Butyl phenyl ether rearranges readily on heating to give *para*-, not *ortho*-*tert*-butylphenol.^{13,15} We found that *n*-butyl phenyl ether was unaffected under our alkylation conditions. Therefore, it is improbable that *o*-ethylphenol is formed by rearrangement of ethyl phenyl ether. Wheland¹⁶ regards the evidence on mechanism of rearrangement of alkaryl ethers as conflicting. He favors dissociation and recombination, or, in some cases, direct alkyl transfer to another molecule. Neither of these processes would be expected to give selective *ortho* alkylation. Hart and Simons⁵ studied the uncatalyzed alkylation of phenol by *tert*-butyl chloride and were unable to find ethers in their products. They concluded, therefore, that if ethers were formed this step would have to be rate controlling. Under these circumstances, *p*-cresol should alkylate as rapidly as phenol. Instead they found that it reacted at only one-eighth the rate for phenol per *ortho* position, as might be expected for direct nuclear alkylation.

The second intermediate shown (II) represents complete transfer of a proton from phenol to the olefin to form an ion pair, which, because of the low dielectric constant of the medium, would remain closely associated until reaction occurred. There is not much difference between II and III where isobutene is concerned, and either one, or both, may be involved in this *ortho* alkylation. However, primary and secondary carbonium ions which would be required for alkylations with ethylene and other olefins are much less stable. Therefore, a very large difference in rate would be expected for *ortho* alkylation of phenol with ethylene and isobutene by way of type II intermediates. Instead, these rates are of the same order of magnitude. With type II intermediates, ether formation would also probably compete more effectively with alkylation than is observed.

The carbonium ion intermediate (II), however, probably does play a more important part in tertiary alkylation in high dielectric media. Our data

(15) R. A. Smith, *J. Am. Chem. Soc.*, **55**, 3718 (1933).

(16) G. W. Wheland, *Advanced Organic Chemistry*, second edition, John Wiley and Sons, New York, N. Y., 1949, p. 555.

for isobutene alkylation show the highest percentage of *p*-*tert*-butylphenol obtained in the presence of a large amount of water. Here dissociation of the ion pair is favored, and *para* as well as *ortho* alkylation is to be expected. A similar, but smaller, effect is noted at high phenol concentrations. This may again reflect a greater ionizing effect of the medium or possibly a greater opportunity for intermolecular reaction of the intermediate with another phenol molecule.

A concerted process involving a transition state of type III appears best able, of those considered, to explain uncatalyzed *ortho* alkylation of phenols with ethylene, isobutene, and olefins of intermediate types. In this, alkylation and transfer of the proton occur through a transitory six-membered ring.

Although the possible intermediates and transition state shown are pictured as formed from one molecule of phenol and one molecule of olefin, it is quite possible that two or more molecules of phenol are involved in the intermediate complex. This would result in a large effect of phenol concentration on rate. Our data, such as the strong inhibiting effect of pentane dilution on the reaction (Experiment 9, Table I) suggest that such an affect may exist. Hart and Simons⁵ found the uncatalyzed alkylation of phenol with *tert*-butyl chloride to be first order in alkyl halide but *second to sixth order in phenol*, depending on the solvents used.

EXPERIMENTAL

Apparatus and procedure. The thermal alkylations were carried out in 2.7- and 4.7-liter stainless steel rocking autoclaves. The reactors were charged at room temperature, heated to the desired reaction temperatures, and shaking started. At the conclusion of each run, the reactor was depressured through a wet-test-meter while holding at 38–65°. Volatile materials remaining in the reaction mixtures were trapped during subsequent distillation of the products. These distillations were carried out at atmospheric pressure using a 3-foot "zigzag" fractionating column.¹⁷

Materials. Baker's c.p. phenol was used without further purification. Isobutene was Phillips 99 mole %. Cyclohexene and 2-pentene were Phillips 95 mole %. The other olefins were of equivalent purity. *tert*-Butyl alcohol was Eastman White Label, and the *o*-cresol, Eastman Practical Grade.

Product analyses and material balances for isobutene reactions. Crystalline product boiling about 183° was assumed to be pure phenol. Phenol in precuts was separated from diisobutylene by alkali extraction, and the extracts analyzed for phenol by bromination. Transition cuts boiling between phenol and *o*-*tert*-butylphenol were assumed to contain only these components. The phenol contents were estimated by bromination analyses of the aqueous phases after treating the mixtures with aqueous sodium hydroxide and extracting with ether to remove the less acidic *o*-*tert*-butylphenol. The amounts of the latter substance were estimated from the distillation curves. For purposes of calculation, the small amounts of distillation residues were assumed to be di-*tert*-butylphenols, although these products were not actually isolated.

Isobutene polymers were not determined directly. They

(17) M. J. Schlatter, *J. Am. Chem. Soc.*, **76**, 4952 (1954), footnote 26.

were present in the phenol precuts and probably to some extent in the transition cuts between the phenol and *o*-*tert*-butylphenol plateaus. The weight of polymer was estimated as the difference between the weight of total liquid product and the weights of phenol and alkylphenols. Isobutene material balances were obtained from measurements of the amounts of gas recovered on depressuring the reactor, the Dry Ice condensates from the product distillations, and the differences in weights between the total liquid products and the phenol charged.

Purification and properties of *o*-*tert*-butylphenol. Solution of the *o*-*tert*-butylphenol prepared in all experiments in Claisen's alkali¹⁸ and extraction with mixed hexanes gave less than 1% of neutral products, indicating that negligible amounts of ethers and olefin polymers were present. The basic solution was acidified, the phenol taken up in benzene, washed, dried, and distilled at 100-mm. pressure through a 4-foot "zigzag" column. Center-cut, constant boiling, constant refractive index product was taken as pure *o*-*tert*-butylphenol. It had the following properties: b.p. 224.6° at 760 mm., 154.0° at 100 mm.; n_D^{20} 1.5238; d_4^{20} 0.9820; aryloxyacetic acid derivative, m.p. 144.0–145.6°. These values are nearly identical with those reported by Kolka *et al.*¹³ and Rosenwald *et al.*¹⁹ The infrared spectrum confirmed the *o*-alkylphenol structure. Heating the material with a little sulfuric acid rearranged it to *p*-*tert*-butylphenol, m.p. 99–100°; aryloxyacetic acid derivative m.p. 86.5°. ²⁰

Effect of time on the reaction of isobutene with phenol at 330°. A sealed glass tube containing 470 g. of phenol was placed in a 2.5-liter rocking autoclave. After adding 750 ml. of liquid isobutene, the autoclave was heated to 330° and the glass tube broken by starting the shaker. Liquid samples were drawn at intervals. After removal of volatiles boiling below phenol, weighed samples were dissolved in benzene. The phenol was extracted with alkali and was determined by bromination. Phenol conversion leveled off at about 30% conversion in 1.5–2.0 hr.; half of this value was reached in 21 min.

Thermal dissociation of *o*-*tert*-butylphenol. Pure *o*-*tert*-butylphenol was heated in a small bomb at 315–332°. The pressure built up to 49 atm. over a period of 5 hr. and appeared to be leveling off. This does not necessarily indicate that equilibrium was attained, as polymerization of isobutene occurs under these conditions. Analysis of the products showed that all but 27% of the *o*-*tert*-butylphenol charged had dissociated into phenol and isobutene.

Other thermal alkylations. 1. Phenol and ethylene. The total reaction product was partitioned with Claisen's alkali and mixed hexanes. The resulting phenolic and neutral products were distilled separately, and compositions were estimated from the distillation curves. The monoalkylate (b.p. 205–218°, 96.1 g.) was largely *o*-ethylphenol. This was confirmed by preparation of the aryloxyacetic acid derivative, m.p. 139–139.6° (Lit. m.p. 140–141°, ²⁰ m.p. *p*-ethyl derivative, 96–97° ²⁰).

Anal. Calcd. for C₁₀H₁₂O₂: C, 68.02; H, 7.27. Found: C, 68.01, 68.06; H, 7.21, 7.19.

The diethylphenol fraction (52.7 g.) was collected from 227–231°, n_D^{20} 1.5238. This is probably 2,4-diethylphenol (Lit. b.p. 227–230°, ²¹ n_D^{25} 1.5218²²). Triethylphenols dis-

(18) Claisen's alkali is prepared by dissolving 350 g. of potassium hydroxide in 250 ml. of water and diluting to 1 liter with methanol.

(19) R. H. Rosenwald, J. R. Hoatson, and J. A. Chenicek, *Ind. Eng. Chem.*, **42**, 162 (1950).

(20) E. H. Huntress and S. P. Mulliken, *Identification of Pure Organic Compounds, (Order I)*, John Wiley and Sons, New York, N. Y., 1941.

(21) K. von Auwers and W. Mauss, *Ann.*, **460**, 240 (1928).

(22) J. E. Copenhaver and E. E. Reid, *J. Am. Chem. Soc.*, **49**, 3157 (1927).

tilled at about 248°. The best fraction (11.8 g.) was collected from 242–249°, n_D^{20} 1.5164 (Lit. b.p. 244–246°²¹).

2. *Phenol and propylene*. Distillation of the reaction product gave two cuts which were largely *o*-isopropylphenol: (a) 19.9 g., b.p. 210–215°, n_D^{20} 1.5208, (b) 43.7 g., b.p. 215–217°, n_D^{20} 1.5267 (Lit. b.p. 214.5°, n_D^{20} 1.5263, *m*-isopropylphenol b.p. 228°, *p*-isomer b.p. 228.2°).²³ The aryloxyacetic acid derivative crystallized as white fluffy needles from mixed hexanes, m.p. 131.4–132.4° (Lit. 130° uncorr.).²⁴

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 66.65; H, 6.72. Found: C, 66.65, 66.54; H, 6.90, 6.79.

The transition and higher boiling cuts were partitioned between Claisen's alkali and mixed hexanes to separate neutral products. Distillation of the phenolic fraction gave additional *o*-isomer and two di-alkylphenol cuts: (a) 6 g., b.p. 226–242°, n_D^{20} 1.5182, (b) 13 g., b.p. 242–248°, n_D^{20} 1.5146. These are probably mixtures of 2,4- and 2,6-diisopropylphenols. There was no inflection in the distillation curve to indicate the presence of *p*-isopropylphenol.

Distillation of the neutral fraction gave 19 g. of isopropylphenyl ether, less than 1 g. of transition cuts, 5 g. of product distilling from 223–240°, which was mainly the isopropyl ether of *o*-isopropylphenol, and 7 g. of higher boiling products.

3. *Phenol and 1-butene*. The product was mainly *o*-butylphenol. This was collected in two cuts: (a) 24.9 g., b.p. 227.0–227.5°, n_D^{20} 1.5231, (b) 17.9 g., b.p. 227.5–228°, n_D^{20} 1.5227 (Lit. b.p. 228°).¹⁹ Infrared analysis based on a strong band at 13.3 μ showed the product to be largely *o*-alkylphenol. The structure was confirmed by preparation of the aryloxyacetic acid derivative, m.p. 111.0–111.6° (Lit. 111°).¹⁹

(23) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

(24) J. B. Niederl and E. A. Storch, *J. Am. Chem. Soc.*, **55**, 284 (1933).

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.75. Found: C, 69.21, 69.30; H, 7.68, 7.73.

4. *Phenol and cyclohexene*. After removal of phenol and some unidentified low boiling material by distillation, the product was partitioned with Claisen's alkali. Distillation of the phenolic fraction gave solid *o*-cyclohexylphenol, b.p. 151° at 17 mm., m.p. 55° (Lit. 55°).⁸

5. *Phenol and diisobutylene*. The product was treated as described for the ethylene experiment. Distillation of the phenolic fraction gave 10.7 g. of *o*-*tert*-butylphenol and 4.0 g. of the *p*-isomer. It was assumed that the bottoms (5.1 g.) were octylphenols.

6. *Phenol and tert-butyl alcohol*. This product was worked up as described for the isobutene experiments.

7. *Phenol and isopropyl ether*. Very little alkylation occurred. Distillation of the product gave 4.2 g. of material, b.p. 181–214°, 0.4 g. b.p. 214–220° and 0.5 g., b.p. 220–230°. However, 6% of the ether decomposed during reaction and was recovered as a mixture of propylene and propane.

8. *o*-Cresol and isobutene. The composition of the product was estimated from the distillation curve and by infrared analyses of the distillation cuts. The principal phenolic component boiling in the range of 234–242° was a 1,2,3-trisubstituted benzene, probably 2-methyl-6-*tert*-butylphenol. Approximately 14% of the material was a 1,2,4-trisubstituted benzene; this was probably 2-methyl-4-*tert*-butylphenol.

9. *Aniline and isobutene*. No reaction occurred when 47 g. of aniline and 60 g. of isobutene were heated at 315–327° for 3 hr.

Thermal rearrangement of phenyl n-butyl ether. This ether was recovered unchanged after heating for 3 hr. at 315–327°.

Acknowledgment. This work was supported by The Oronite Chemical Co.

RICHMOND, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Addition of Halogens and Halogen Compounds to Allylic Chlorides.

I. Addition of Hydrogen Halides¹

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Received September 10, 1956

The addition of hydrogen chloride to allylic chlorides was found to be extremely difficult under the conditions employed, except in the case of allyl chloride. 3,3-Dichloropropene isomerized instead to give 1,3-dichloropropene. 3,3,3-Trichloropropene isomerized to 1,1,3-trichloropropene in the presence of hydrogen chloride, with no addition observed.

The addition of hydrogen iodide to allylic chlorides was found to be accompanied by halogen exchange, reduction, and allylic isomerization. The addition products observed were: 2-iodo-1-chloropropene for allyl chloride, 2-iodo-1,1-dichloropropene for 3,3-dichloropropene, 3-iodo-1,1,1-trichloropropene for 3,3,3-trichloropropene, 1-iodo-1,3-dichloropropene for 1,3-dichloropropene, and 1-iodo-1,1,3-trichloropropene for 1,1,3-trichloropropene.

The addition of hydrogen halides to allylic chlorides has been studied by Kharasch and co-

workers,^{3–5} including both allyl chloride and a trichloropropene. In order to gain a better understanding of the mechanism of electrophilic attack on unsaturated compounds, Swindale, Swedlund, and Robertson⁶ compared halogen addition to allylic halides with halogen substitution in benzyl halides.

Early work on the nitration of benzylic chlo-

(1) This is an abstract of a part of the doctoral thesis submitted by Lieng-huang Lee.

(2) Present address: Research Division, Dow Chemical Company, Midland, Mich.

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