[Contribution from the Kedzie Chemical Laboratory,
Michigan State College]

ALKYLATION OF PHENOL WITH *t*-BUTYL ALCOHOL IN THE PRESENCE OF PERCHLORIC ACID

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Received August 25, 1947

The alkylation of phenol has been realized by the use of *t*-butyl alcohol or isobutylene in the presence of such catalysts as aluminum chloride, zinc chloride mixed with small amounts of aluminum chloride, phosphoric, and sulfuric acids (1, 2, 3, 4, 5, 6).

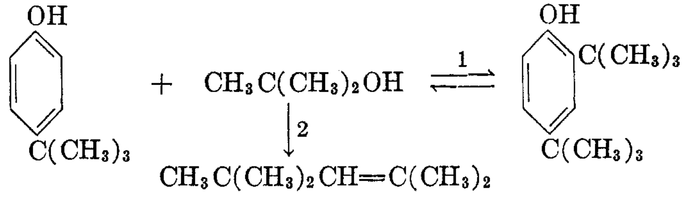
Perchloric acid has a very high hydrogen ion activity (7) and the fact that it retains this activity in the presence of organic compounds (8) should make it an effective catalyst in some organic reactions. The lack of investigation in this field is probably due to the hazardous nature of perchloric acid-organic mixtures (9).

With these facts in mind the effect of perchloric acid catalysis in alkylation of phenol with *t*-butyl alcohol was investigated, first on very small amounts of the reactants (50 mg.). The quantities of the reactants were successively increased until the amounts presented in the experimental data were reached. Such precautions should always be observed when using perchloric acid with organic materials.

Relatively good yields of 2,4-di-*t*-butylphenol (see Table I) are obtained in the presence of perchloric acid, whereas by other means of catalysis the main product is the 4-*t*-butylphenol.

Apparently the reaction is in equilibrium (A); 1 being a fast reaction, 2 being slow.

(A)



The di-substituted product is less soluble in perchloric acid than the mono product. Therefore, the shift in equilibrium, which may occur only at the point of contact of the di-*t*-butylphenol and perchloric acid phases, is very slow.

In the ten-minute runs small amounts of the mono product and di-isobutylene were obtained. In the sixty-minute runs proportionately greater amounts of the mono product and di-isobutylene were obtained and in the twenty-hour run 4-*t*-butylphenol was isolated by merely extracting the organic layer and distilling off the di-isobutylene.

Acknowledgement. The author wishes to express sincerest thanks to Dr. Frederick R. Duke who suggested this problem, and whose advice and encouragement throughout the investigation made this paper possible.

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EXPERIMENTAL

Runs were made in 1:1, 1:2, and 1:3 molar ratios; the quantity of phenol was kept constant while that of the *t*-butyl alcohol was varied. Two complete runs were made under the same conditions and with the same treatment of the products. The time intervals were for ten minutes and sixty minutes. A third run was also made with the 1:3 molal ratio for a period of twenty hours.

I. *The reaction of phenol with t-butyl alcohol in the presence of perchloric acid.* To a stirred solution (the sixty-minute and twenty-hour runs were put on a mechanical shaker) of 24 g. (0.25 mole) of phenol, 30 cc. of water, and 100 cc. of 70% perchloric acid, 15 cc. (0.25 mole) of *t*-butyl alcohol was slowly added. The temperature was carefully observed and did not rise above 60° in any case. At the end of the time interval the mixture was transferred to a separatory funnel and the aqueous layer extracted three times with petroleum ether (60–70°). The combined ethereal solutions were then washed with water and separated. The organic layer was washed twice with a saturated solution of potassium bicarbonate[2] and, finally, again washed with water.

II. *4-t-Butylphenol.* The ethereal solution (I) from above was extracted with four different portions of a 10% potassium hydroxide solution. The combined extracts were acidified with hydrochloric acid and the mixture transferred to a separatory funnel. The aqueous layer was extracted two times with petroleum ether. 4-*t*-Butyl phenol was obtained from the ether solution. The impure product was recrystallized from ligroin, white needles, m.p. 99°.

TABLE I

YIELD OF PRODUCTS, %

	MONO			DI		
	1:1	1:2	1:3	1:1	1:2	1:3
10 min. runs	5	10	16	5	21	44
60 min. runs	26	32	21	5	27	28
20 hr. run	—	—	48			

Anal. Calc'd for $C_{10}H_{14}O$: C, 80.00; H, 9.33.
Found: C, 80.02; H, 9.24.

2,4-Di-t-butylphenol. The original ethereal solution (I) was next extracted with four different portions of Claisen solution (10). The combined extracts were treated the same as the 10% potassium hydroxide extracts. 2,4-Di-*t*-butylphenol was obtained from this fraction. The impure product was purified with ligroin, white crystals, m.p. 54°.

Anal. Calc'd for $C_{14}H_{22}O$: C, 81.55; H, 10.63.
Found: C, 81.34; H, 10.01.

The twenty-hour run was made the same as above, up to II. At this point the solution was transferred to a distilling flask, the ether and di-isobutylene (b.p. 101–102°, n_D 1.415, readily adds bromine) were distilled off and the 4-*t*-butyl phenol crystallized on cooling. The impure product was recrystallized from ligroin; m.p. 99°.

Anal. Calc'd for $C_{10}H_{14}O$: C, 80.00; H, 9.33.
Found: C, 80.10; H, 9.54.

4-t-Butylphenyl benzoate. Two 5-cc. portions of benzoyl chloride were added slowly, with vigorous shaking, to 0.5 g. of 4-*t*-butylphenol dissolved in 10 cc. of anhydrous pyridine. The solution was set aside for five hours then poured into cold water. The water mixture

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[2] The potassium salt of perchloric acid is very insoluble in organic materials, whereas the sodium salt is appreciably soluble.

was extracted with ether and the ethereal solution was separated and evaporated. The benzoate which remained was recrystallized from alcohol, m.p. 83°.

Anal. Calc'd for $C_{17}H_{18}O_2$: C, 80.03; H, 7.08.
Found: C, 80.00; H, 7.01.

2,4-Di-t-butylphenyl benzoate. The benzoate of the di-substituted product was obtained by the procedure given above, m.p. 98°.

Anal. Calc'd for $C_{21}H_{26}O_2$: C, 81.29; H, 8.38.
Found: C, 81.21; H, 8.27.

SUMMARY

Perchloric acid is presented as an effective and rapid catalyst for the alkylation of phenol with *t*-butyl alcohol.

A method to obtain relatively good yields of 2,4-di-*t*-butylphenol is presented.

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