Phenol was alkylated with propylene at 230–240° and 200–500 p.s.i. over a two-hour period to yield 61% of 2,6-diisopropylphenol (m.p. 19°, b.p. 136° and 30 mm., n_D^{20} 1.5134; *Anal.* Calc'd for $C_{12}H_{20}O$: C, 80.85; H, 10.18. Found: C, 80.8; H, 10.2). The structure was established by chlorination with sulfuryl chloride to yield 2,6-diisopropyl-4-chlorophenol, an authentic sample of which was independently synthesized for comparison. Although small amounts of ethers were present in both the ethylene and propylene alkylation products, no *para*-alkylphenols were isolated.

The alkylation of phenol with isobutylene at 105–115° and 30–100 p.s.i. over a four-hour period gave 5% of recovered phenol, 46% of 2-*tert*-butylphenol (b.p. 120° at 30 mm., n_D^{20} 1.5239),[4] 1% of 4-*tert*-butylphenol, 36% of 2,6-di-*tert*-butylphenol (m.p. 36.5°, b.p. 147° at 30 mm.),[4] and higher-boiling products.

It has been found that the products of the isobutylene alkylation may be varied widely by changes in reaction times, pressures, and temperatures, and products containing from zero to 80% of 2,6-di-*tert*-butylphenol have been obtained. A rudimentary study of the kinetics and thermodynamics of the process has been completed and appears to explain these anomolies.

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(4) Pardee and Weinrich, *Ind. Eng. Chem.*, **36**, 596 (1944) have reported 2-*tert*-butylphenol, b.p. 122° at 30 mm. and 2,6-di-*tert*-butylphenol, m.p. 39°.

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Some New Reactions of Nitrogen Iodide with Organic Compounds[1]

Sir:

Although several reactions of nitrogen iodide with organic compounds have been described in the literature,[2,3,4] our preliminary studies with this reagent indicate that some of its most interesting and unusual reactions have thus far escaped attention. For example, although reaction with methyl ketones in aqueous ammonia has been reported to give mainly iodoform,[3] we have been able to isolate as significant products, in the cases of all monofunctional ketones studied, symmetrically substituted pyrazines. Cyclohexanone, 3-pentanone, propiophenone and acetone yield octahydrophenazine (I), 2,5-diethyl-3,6-dimethylpyrazine (II), 2,5-dimethyl-3,6-diphenylpyrazine (III), and 2,5-dimethylpyrazine (IV), respectively. Ethyl acetoacetate, with nitrogen iodide, gives diiodoacetamide (V). Reaction with tyrosine affords 3,5-diiodotyrosine (VI), or a separable mixture of VI and 3-iodotyrosine (VII), depending upon the proportions of reactants employed. Methyl pyruvate yields only iodoform, whereas no reaction is observed with benzene, naphthalene, diethyl ether, ethyl acetate, and acetamide.

Octahydrophenazine (I) was obtained in the following manner. A mixture of 65 g. of iodine and 250 ml. of concentrated aqueous ammonia was stirred mechanically for 10–15 minutes. The supernatant liquid then was decanted from the black solid nitrogen iodide. Next 250 ml. of fresh concentrated aqueous ammonia was added, stirring was resumed, and 27 g. of cyclohexanone was added dropwise over the course of 10–15 minutes with external ice cooling. After the reaction mixture was completely decolorized, stirring was continued for 8 hours and the mixture then was allowed to stand overnight. After addition of 25 g. of sodium bisulfite, the mixture was steam-distilled and the solid thus obtained was filtered from the distillate. Upon vacuum sublimation, 0.72 g. (2.8%[5] based on cyclohexanone) of I, m.p. 106.2–108.0° (uncorr.) was obtained. *Anal.* Calc'd for $C_{12}H_{16}N_2$: C, 76.6; H, 8.6; N, 14.9. Found: C, 76.2; H, 8.6; N, 15.1.

In similar fashion, we obtained II (8–14%) [b.p. 81° (7.6 mm.), n_D^{23} 1.4752, Calc'd for $C_{10}H_{16}N_2$: C, 73.1; H, 9.8; N, 17.1. Found: C, 72.8; H, 10.3; N, 17.0], III (23%) [m.p. 124° (corr.), Calc'd for $C_{18}H_{16}N_2$: C, 83.0; H, 6.2; N, 10.8. Found: C, 82.6; H, 5.9; N, 11.3], and IV [b.p. 58° (21 mm.), isolated as the mercuric chloride adduct or the picrate, in low yield]. Elemental analyses and absorption in the region 3330–3400 cm^{-1} indicate that I, II, and III are contaminated with the corresponding dihydropyrazines.

In the reaction of ethyl acetoacetate with nitrogen iodide, V, m.p. 219–220° (decomp.), (Calc'd for $C_2H_3I_2NO$: C, 7.7; H, 1.0; N, 4.5; I, 81.5. Found: C, 8.0; H, 1.1; N, 4.7; I, 80.8) was obtained in 26% yield, together with an impure solid, m.p. 245–248° (decomp.) which analyzed as a mixture of triiodoacetamide with a small amount of V.

With a 2:1 molar ratio of iodine to tyrosine, we obtained nearly quantitative conversion of tyrosine to VI, m.p. 206° (uncorr.). With a 1:1 ratio, a mixture containing approximately equal amounts of VI and VII, m.p. 204° (uncorr.) was obtained

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(1) One of us (S.H.W.) is indebted to the University of Kansas for a University Research Grant under which this work was done.

(2) A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), **4**, 1458 (1934); *Chem. Abstr.*, **29**, 3651^5 (1935).

(3) F. D. Chattaway and R. R. Baxter, *J. Chem. Soc.*, **103**, 1986 (1913).

(4) C. Willgerodt, *J. prakt. Chem.*, [II] **37**, 446 (1888).

(5) In these preliminary studies no effort was made to obtain maximum yields.

in a total yield of 38%.[6] The latter was separated from VI and characterized chromatographically.[7]

Nitrogen iodide also reacts with numerous other compounds, *e.g.*, ethyl malonate, *n*-butyraldehyde, cyclohexene, anisole, and pyridine, but the reactions appear to be more complex than those already described and the results have not as yet been fully elucidated. Details of these and other reactions of nitrogen iodide will be reported later.

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[6] Essentially this same reaction, with but slight modifications, has recently been reported as an excellent simple method for the synthesis of VII. See R. Pitt-Rivers, *Chemistry and Industry*, 21 (1956).

[7] We wish to thank Dr. David V. Cohn, Veterans Administration Hospital, Kansas City, Missouri, for performing the chromatographic separation and identification of VII.