

the solution was made homogeneous. The ketone was racemized and the gross material now had $[\alpha]^{25}_D$ 4.9°. Since the average yield of ketone is 83.4%, the ketonic part of the product had $[\alpha]^{25}_D$ 7.2°. A portion of the product was passed through a column of Fisher alumina. The hydroxylic material recovered from the column had $[\alpha]^{25}_D$ 14.5°.

The deamination products of both *erythro*- and *threo*-III

were analyzed by gas-liquid chromatography.¹⁷ The chromatogram of the ketonic fraction indicated the presence of only one substance. It was found that 1% of *p*-tolyl α -methylbenzyl ketone in the presence of IV could be detected. Therefore, no methyl migration takes place.

(17) A Burrell Kromo-Tog model K-1, fitted with a 1/4-inch column backed with Apiezon supported on Kromat-F-13, was used.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

Steric Hindrance as a Factor in the Alkylation of Ambident Anions: The Alkylation of Potassium 2,6-Di-*t*-butylphenoxide^{1,2}

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The reactions of potassium 2,6-di-*t*-butylphenoxide provide a particularly clear demonstration of the importance which steric effects may assume in the alkylation of ambident anions: methyl iodide gives an 88% yield of ether and 6% carbon alkylation; ethyl iodide gives an 11% yield of ether and 66% carbon alkylation; isopropyl iodide gives exclusively carbon alkylation.

In an earlier paper it was emphasized that steric hindrance is one of the prime factors in considering the alternate reaction paths available to an ambident anion.⁴ The present study, which employs the 2,6-di-*t*-butylphenoxide ion, a well defined and relatively inflexible structure, provides a demonstration that under the proper auspices steric hindrance is an overriding factor. As can be seen from Table I, on treatment with a set of alkyl halides of increasing steric requirement an unmistakable shift from oxygen to carbon alkylation occurs.^{4a}

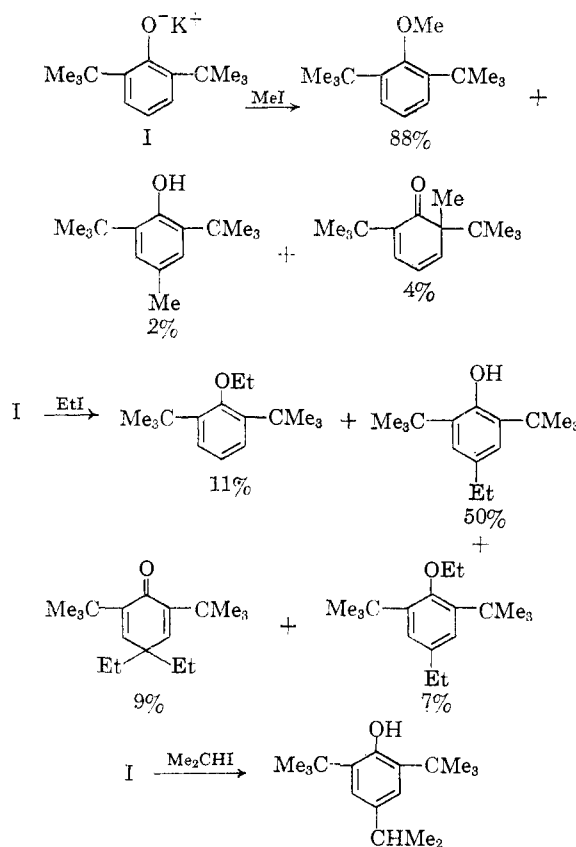
TABLE I
ALKYLATION OF POTASSIUM 2,6-DI-*t*-BUTYLPHENOXIDE

Alkyl iodide	O-Alkylation, %	C-Alkylation, %
Methyl	88	6
Ethyl	11	66 ^a
Isopropyl ^b	0	100

^a This is a conservative figure almost certainly too low by at least 8% (*cf.* Experimental). ^b Here only 28% of the alkyl halide undergoes substitution; elimination of hydrogen iodide accounts for the remainder.

The detailed accounting of products is of some interest in its own right and is summarized in the following equations; structure proofs are discussed in the Experimental section.

In a study which antedated ours, Coffield, Filbey, Ecke and Kolka⁵ called attention to significant differences in behavior in the reactions of 2,6-diisopropylphenol and 2,6-di-*t*-butylphenol. Of particular interest is the difference observed on treating the sodium salts of these phenols with benzoyl chloride; the diisopropylphenoxide gives a 65%



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(2) Paper III in the series, "The Chemistry of Ambident Anions."

(3) XR Fellow of the Purdue Research Foundation 1958-1960.

(4) N. Kornblum and A. P. Lurie, *J. Am. Chem. Soc.*, **81**, 2705 (1959).

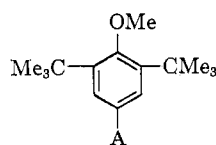
(4a) As anticipated, the reaction of methyl, ethyl or isopropyl iodide with potassium phenoxide under the identical conditions employed with potassium 2,6-di-*t*-butylphenoxide gives, in each instance, 75-85% yields of the pure ether and no carbon alkylation product could be isolated. We are indebted to Mr. Richard Derby of this Laboratory for these experiments.

(5) T. H. Coffield, A. H. Filbey, G. G. Ecke and A. J. Kolka, *ibid.*, **79**, 5019 (1957).

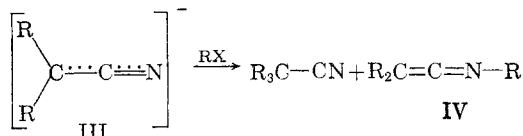
yield of 2,6-diisopropylphenyl benzoate whereas with the di-*t*-butylphenoxide none of the corresponding ester is isolated; instead the product is 2,6-di-*t*-butyl-4-benzoylphenol (24% yield). Also of interest is the observation of Cohen⁶ that the methyl ethers (II) can be prepared in 58-65% yields by treatment of the sodium salts of the corresponding phenols with methyl iodide.

The importance of steric hindrance in controlling the course of ambident anion alkylations has been recognized for several other types of anions. Thus,

(6) L. A. Cohen, *J. Org. Chem.*, **22**, 1333 (1957).

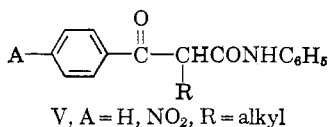
II, A = CH₃, CN, CO₂C₂H₅

alkylation of the ambident anion derived from nitriles (III) ordinarily occurs on carbon. But in 1956, Prober, employing trimethylchlorosilane as the alkylating agent, discovered several examples of ketenimine (IV) formation and explained this N-alkylation mainly on steric grounds.⁷



Recently, Newman, Fukunaga and Miwa have reported that the anion of diisopropylacetone, on alkylation with isopropyl iodide, yields moderate amounts of ketenimine and that in the case of *t*-butylisopropylacetone only ketenimine is obtained⁸; they emphasized the importance of steric factors in controlling the ratio of carbon to nitrogen alkylation of nitriles. Still more recently, Rabjohn and Stapp⁹ have obtained ketenimines on alkylating hindered nitriles and have correlated the enhanced proportion of N-alkylation with steric hindrance.

Steric factors also have been found to operate in the alkylation of the salts of monoalkylated benzoylacetonilides (V). C-Alkylation is favored when

V, A = H, NO₂, R = alkyl

the entering group is methyl, while O-alkylation gradually predominates as the bulk of the entering group is increased to *n*-propyl or isopropyl.¹⁰

It is clear, then, that steric hindrance must be taken into account when considering the factors which influence the course of ambident anion reactions.

Experimental^{11,12}

All reactions were conducted under nitrogen. All gas chromatographic analyses were carried out on a Perkin-Elmer Vapor Fractometer using a 1-m. silicone oil column (GE SF96). Ethyl Corporation¹³ 2,6-di-*t*-butylphenol was

(7) M. Prober, *J. Am. Chem. Soc.*, **78**, 2274 (1956).

(8) M. S. Newman, T. Fukunaga and T. Miwa, *ibid.*, **82**, 873 (1960).

(9) N. Rabjohn and P. R. Stapp, *J. Org. Chem.*, **26**, 45 (1961).

(10) A. L. Searles and D. Ressler, *J. Am. Chem. Soc.*, **80**, 3656 (1958).

(11) Analyses are by Dr. C. S. Yeh and Mrs. B. Groten, Purdue University, and Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(12) The infrared absorption spectra were determined by Mrs. W. Dilling on a Perkin-Elmer model 21 spectrophotometer. Spectra were determined using the pure liquid or the molten low melting solid; with high melting solids, solutions in carbon tetrachloride were employed. Ultraviolet absorption spectra were determined on a Cary model 14 spectrophotometer in absolute ethanol.

(13) We are grateful to the Ethyl Corp. for a generous gift of this phenol.

recrystallized from aqueous ethanol; m.p. 37–38°. Koppers 2,6-di-*t*-butyl-4-ethylphenol¹⁴ and 2,6-di-*t*-butyl-4-isopropylphenol¹⁴ were also recrystallized from aqueous ethanol; m.p. 42–44° and 39–41°, respectively. *t*-Butyl alcohol was allowed to stand over calcium hydride and distilled as needed; only the center cut was used (b.p. 82.8–83°). Tetraethylene glycol dimethyl ether (Ansul Chemical Co.) was allowed to stand over calcium hydride or lithium aluminum hydride and distilled as needed; only the center cut was used (b.p. 105° (1 mm.)).

Methyl Iodide with Potassium 2,6-Di-*t*-butylphenoxide.—To 20.0 g. (0.097 mole) of 2,6-di-*t*-butylphenol dissolved in 50 ml. of *t*-butyl alcohol was added 105 ml. (0.101 mole) of a 0.963 *N* solution of potassium *t*-butoxide in *t*-butyl alcohol. A light green precipitate formed which was dissolved by the addition of 50 ml. of tetraethylene glycol dimethyl ether. To the resulting green solution was added 25.0 ml. (0.398 mole) of methyl iodide (*n*_D²⁰ 1.5317) and the reaction was allowed to proceed at 25°. As the reaction progressed the green color changed to yellow; no precipitation was observed. The reaction was over in 9 hours after which the product was poured into water and extracted with petroleum ether (35–37°). The extract was washed several times with water and dried over anhydrous sodium sulfate. Removal of the petroleum ether at room temperature gave 20.9 g. of crude product which was a yellow liquid.

(a) **2,6-Di-*t*-butylanisole.**—Three grams of the crude product was diluted with an equal volume of petroleum ether (35–37°) and placed on a column of basic alumina (Merck). Elution with graded mixtures of diethyl ether–petroleum ether (up to 40% diethyl ether) gave 2.54 g. (88% yield) of a colorless liquid, which proved to be 2,6-di-*t*-butylanisole, as six fractions having *n*_D²⁰ 1.5042–1.5044 (A). Further increases in the proportion of diethyl ether did not remove anything more from the column until the eluent was *ca.* 70% diethyl ether. At this point 0.13 g. of a red liquid (B) came off the column. Finally, by using pure diethyl ether as the eluent 0.18 g. of a red liquid (C) was obtained.

The 2.54 g. of colorless liquid (A) exhibits infrared absorption at 7.98 μ (ether linkage) and shows no absorption in the region 2.75 μ (hindered OH) and no absorption in the region 6.00 μ –6.10 μ (dienone), and it possesses the composition of 2,6-di-*t*-butylanisole.

Anal. Calcd. for C₁₈H₂₄O: C, 81.76; H, 10.98. Found: C, 81.69; H, 11.26.

(b) **Cleavage of 2,6-Di-*t*-butylanisole.**—To 200 ml. of liquid ammonia was added a solution of 2.00 g. (0.0091 mole) of the 2,6-di-*t*-butylanisole obtained above in 5 ml. of anhydrous diethyl ether. Approximately 1.4 g. (0.036 mole) of potassium metal was added whereupon the solution turned dark blue. The reaction flask was fitted with a Dry Ice condenser, and the solution was stirred under reflux for 6 hours after which the ammonia was allowed to evaporate, and then 20 ml. of absolute ethanol was added followed by 200 ml. of water. A yellow oil formed which was extracted with petroleum ether (35–37°); the extract was washed with water, dried, and the petroleum ether was removed. The 1.81 g. of residual liquid was chromatographed on basic alumina (Merck). Elution with petroleum ether (35–37°) gave 0.08 g. of 2,6-di-*t*-butylanisole. (Its infrared spectrum was identical with that of A.) Further elution with diethyl ether gave 1.72 g. of a yellow solid, m.p. 32–38°. A portion of the solid, 0.50 g., was rechromatographed over basic alumina. Elution with petroleum ether gave 0.49 g. (94% yield) of 2,6-di-*t*-butylphenol, m.p. 37–38°; mixed m.p. with authentic 2,6-di-*t*-butylphenol, 37–38°.

(c) **2,6-Di-*t*-butyl-6-methyl-2,4-cyclohexadienone.**—The 0.13 g. of red liquid B obtained in part a, *n*_D²⁰ 1.4995, did not absorb in the infrared at 2.75 μ (OH) but showed a doublet at 6.05 and 6.10 μ . The ultraviolet spectrum exhibited a maximum of 310 m μ . These are the spectral characteristics of 2,6,6-trialkylated-2,4-cyclohexadienones.¹⁵

Rechromatographing of 0.07 g. of B on basic alumina (Merck) using petroleum ether (35–37°) gave nothing in the eluate; with diethyl ether–petroleum ether (1:9) 0.05 g. of a

(14) We are grateful to the Koppers Co. for generous gifts of these phenols.

(15) D. Y. Curtin and R. J. Crawford, *Chemistry and Industry*, 313 (1956); D. Y. Curtin and R. R. Fraser, *ibid.*, 1358 (1957); D. Y. Curtin, R. J. Crawford and M. Wilhelm, *J. Am. Chem. Soc.*, **80**, 1391 (1958); H. Conroy and R. A. Firestone, *ibid.*, **78**, 2290 (1956); F. Kalberer and H. Schmid, *Helv. Chim. Acta*, **40**, 779 (1957).

yellow orange liquid was obtained; this had an infrared absorption spectrum identical with that of B. The yield of dienone is, therefore, 0.13 g. (4%).

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 82.10; H, 11.00.

(d) **2,6-Di-*t*-butyl-4-methylphenol.**—The 0.18 g. of red liquid, fraction C of section (a), had an infrared spectrum identical with that of a mixture of 2,6-di-*t*-butylphenol and 2,6-di-*t*-butyl-4-methylphenol. At 12.60 μ , 2,6-di-*t*-butylphenol has a strong band which is absent in 2,6-di-*t*-butyl-4-methylphenol. The latter has a strong band at 13.04 μ which is not exhibited by 2,6-di-*t*-butylphenol. Using known mixtures of these two phenols, standard Beer's law plots were prepared from which it was established that the mixture C consisted of 32% 2,6-di-*t*-butyl-4-methylphenol and 62% 2,6-di-*t*-butylphenol. Thus, the yield of 2,6-di-*t*-butyl-4-methylphenol was 0.05 g. (2%).

Ethyl Iodide with Potassium 2,6-Di-*t*-butylphenoxide.—To 20.0 g. (0.097 mole) of 2,6-di-*t*-butylphenol dissolved in 25 ml. of *t*-butyl alcohol was added 91 ml. (0.097 mole) of a 1.07 *N* solution of potassium *t*-butoxide in *t*-butyl alcohol and then 50 ml. of tetraethylene glycol dimethyl ether. To the resulting green solution was added 25.0 ml. (0.298 mole) of ethyl iodide (n_D^{20} 1.5129). As the reaction proceeded, precipitation was observed, and the reaction mixture turned red. After 24 hours at 25° the reaction mixture was poured into water and extracted with petroleum ether (35–37°). The petroleum ether extract was washed several times with water and dried over anhydrous sodium sulfate. Removal of the petroleum ether at room temperature gave 22.3 g. of a red liquid which was dissolved in 20 ml. of petroleum ether (60–70°), and to this solution was added ca. 10 g. of sodium hydride suspended in 20 ml. of petroleum ether (60–70°). The mixture was stirred under nitrogen; as the reaction proceeded a green solid precipitated, and after 16 hours at 25° the contents of the flask were filtered in a dry-box under a nitrogen atmosphere. The filtrate was washed with water and then dried over anhydrous sodium sulfate. Removal of the petroleum ether at room temperature gave 7.53 g. of a yellow liquid (A). Methanol was added cautiously to the solid on the funnel until hydrogen evolution ceased. About 250 ml. of water then was added, and the yellow oil which formed was isolated by extraction with petroleum ether (35–37°). The petroleum ether solution was washed with water and dried over anhydrous sodium sulfate. Removal of the petroleum ether at room temperature gave 13.7 g. of a red liquid B.

(a) **2,6-Di-*t*-butylphenetole and 2,6-Di-*t*-butyl-4-ethylphenetole.**—A 2.00-g. portion of (A) was diluted with an equal volume of petroleum ether (35–37°) and placed on a basic alumina (Merck) column. Elution with petroleum ether (35–37°) gave 1.05 g. of a colorless liquid (I) followed by 0.52 g. of a light yellow solid, m.p. 29–31° (II). Finally, elution with diethyl ether gave 0.40 g. of a red liquid (III).

The infrared spectrum of fraction I was free of bands at 2.75 μ (phenolic) and 6.00–6.10 μ (dienone) but showed ether absorption at 7.95 μ . By gas chromatographic analysis fraction I was found to consist of 59% 2,6-di-*t*-butylphenetole and 41% 2,6-di-*t*-butyl-4-ethylphenetole. Thus, 0.62 g. (11% yield) of 2,6-di-*t*-butylphenetole and 0.43 g. (7% yield) of 2,6-di-*t*-butyl-4-ethylphenetole were formed.

(b) **2,6-Di-*t*-butyl-4,4-diethyl-2,5-cyclohexadienone.**—The infrared spectrum of fraction II (m.p. 29–31°) isolated in section a was devoid of phenolic absorption, and showed a doublet at 6.00 and 6.06 μ . The ultraviolet spectrum exhibited a maximum at 242 $m\mu$. This is what would be expected for a 2,6-di-*t*-butyl-4,4-disubstituted 2,5-cyclohexadienone.¹⁶ The yield of 2,6-di-*t*-butyl-4,4-diethyl-2,5-cyclohexadienone is, therefore, 0.52 g. (9%). Additional evidence for the structure assigned to fraction II (m.p. 29–31°) derives from the identity of this compound with the dienone prepared from potassium 2,6-di-*t*-butyl-4-ethylphenoxide and ethyl iodide (*vide infra*).

Anal. Calcd. for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found: C, 82.51; H, 11.32.

(c) **Fraction III.**—The 0.40 g. of red liquid labeled III in section a exhibits phenolic absorption at 2.77 μ and has a

strong band at 12.99 μ characteristic of 2,6-di-*t*-butyl-4-ethylphenol. Also, there is a doublet at 6.02 and 6.10 μ signifying the presence of a dienone. The ultraviolet spectrum has a peak at 277 $m\mu$ (aromatic absorption) and a peak at 310 $m\mu$ (a substituted 2,4-cyclohexadienone). Thus, spectral data indicate that III is probably a mixture of 2,6-di-*t*-butyl-4-ethylphenol and 2,6-di-*t*-butyl-6-ethyl-2,4-cyclohexadienone and/or 2,6-di-*t*-butyl-4,6-diethyl-2,4-cyclohexadienone. In view of the structural uncertainty this material was not included in the accounting of Table I but it should be noted that, in any event, it represents carbon alkylation.

(d) **2,6-Di-*t*-butyl-4-ethylphenol.**—All but 1.20 g. of fraction B, *i.e.*, 12.5 g., when molecularly distilled at room temperature gave 11.2 g. of a light yellow oily distillate. A viscous residue (1.21 g.) remained in the pot. The infrared spectrum of the distillate was identical with that of a mixture of 2,6-di-*t*-butyl-4-ethylphenol and 2,6-di-*t*-butylphenol. At 12.60 μ 2,6-di-*t*-butylphenol exhibits a strong band absent in 2,6-di-*t*-butyl-4-ethylphenol. The latter has a strong band at 12.99 μ absent in 2,6-di-*t*-butylphenol. Using known mixtures of these two phenols standard Beer's law plots were prepared from which it was established that 84% of the distillate was 2,6-di-*t*-butyl-4-ethylphenol and 16% 2,6-di-*t*-butylphenol. As a check, a known mixture was prepared having this composition and its infrared spectrum was found to be superimposable on that of the unknown. Thus, the yield of 2,6-di-*t*-butyl-4-ethylphenol was 10.1 g. (50%).

One gram of the light yellow distillate was chromatographed on silica gel (Davison-200 mesh) with petroleum ether (35–37°) to give 0.64 g. of 2,6-di-*t*-butyl-4-ethylphenol, m.p. 42–44°; mixed m.p. with an authentic sample of 2,6-di-*t*-butyl-4-ethylphenol, 42–44°; lit.¹⁷ m.p. 44°.

Anal. Calcd. for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 82.01; H, 11.39.

The residue, 1.21 g., from the molecular distillation, once recrystallized from 95% ethanol, gave 0.54 g. of yellow crystals, m.p. 136–138°. A second recrystallization did not change the melting point. The infrared spectrum showed weak OH absorption at 2.75 μ and strong absorption at 6.02 and 6.08 μ (dienone). The ultraviolet spectrum shows very weak absorption at 275 $m\mu$ (aromatic absorption) and a strong band at 237 $m\mu$, presumably arising from an α,β -unsaturated carbonyl. These data suggest that this is a mixture of the *dimer* of 2,6-di-*t*-butyl-6-ethyl-2,4-cyclohexadienone and 2,6-di-*t*-butyl-4-ethylphenol. Here, as in part c, this material was not included in the accounting of Table I even though it represents carbon alkylation.

Anal. Calcd. for $C_{16}H_{26}O$: C, 81.99; H, 11.18; mol. wt., 234. Found: C, 81.96; H, 10.93; mol. wt. (cryoscopic in camphene), 362, 386.

Preparation of 2,6-Di-*t*-butyl-4-ethylphenetole and 2,6-Di-*t*-butyl-4,4-diethyl-2,5-cyclohexadienone.—To 5.00 g. (0.021 mole) of 2,6-di-*t*-butyl-4-ethylphenol dissolved in 10 ml. of *t*-butyl alcohol was added 23 ml. (0.023 mole) of a 1.02 *N* solution of potassium *t*-butoxide in *t*-butyl alcohol solution. A yellow precipitate formed which dissolved on the addition of 20 ml. of tetraethylene glycol dimethyl ether. To the resulting orange solution was added 10.0 ml. (0.119 mole) of ethyl iodide (n_D^{20} 1.5131). After 19 hours at room temperature (no precipitation) the clear solution was poured into water and extracted with petroleum ether (35–37°). The petroleum ether phase was washed several times with water and dried over anhydrous sodium sulfate. Removal of the solvent at room temperature gave 5.57 g. of crude product as a yellow liquid.

Part of the crude, 2.00 g., was chromatographed on basic alumina (Merck) using petroleum ether (35–37°). This gave 0.78 g. (39% yield) of a white solid I, m.p. 46–47°, followed by 0.98 g. (50% yield) of II, a light yellow solid, m.p. 30–32°. Finally, elution with benzene gave 0.24 g. of a yellow liquid III. The infrared spectrum of I showed neither phenolic nor dienone absorption, but there is an ether band at 7.95 μ . Gas chromatographic analysis showed only one peak. *Anal.* Calcd. for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found: C, 82.44; H, 11.72. The white solid I is, therefore, the ethyl ether of 2,6-di-*t*-butyl-4-ethylphenol. It was employed as a standard in the gas chromatographic analysis

(16) (a) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1439 (1957); (b) W. R. Hatchard, R. D. Lipscomb and F. W. Stacey, *J. Am. Chem. Soc.*, **80**, 3636 (1958); also see W. S. Johnson and H. Wyeberg, *J. Org. Chem.*, **24**, 1424 (1959).

(17) G. H. Stillson, D. W. Sawyer and C. K. Hunt, *J. Am. Chem. Soc.*, **67**, 305 (1945).

of fraction I in section a of the experiment entitled "Ethyl Iodide with Potassium 2,6-Di-*t*-butylphenoxide."

The light yellow solid II, m.p. 30–32°, had an infrared spectrum devoid of phenolic absorption, but showed a doublet at 6.00 and 6.06 μ (dienone). The ultraviolet spectrum exhibited a maximum at 242 $m\mu$ (cross-conjugated dienone).¹⁸ Gas chromatographic analysis showed a single peak. *Anal.* Calcd. for C₁₅H₂₀O: C, 82.38; H, 11.52; mol. wt., 267. Found: C, 82.25; H, 11.71; mol. wt. (cryoscopic in camphene), 248, 250. Thus II is 2,6-di-*t*-butyl-4,4-diethyl-2,5-cyclohexadienone. A mixed m.p. with the dienone, m.p. 29–31°, isolated in section b of the experiment "Ethyl Iodide with Potassium 2,6-Di-*t*-butylphenoxide," was undepressed. Furthermore, the infrared and ultraviolet absorption spectra of these two dienones are identical.

The yellow liquid III exhibited phenolic absorption at 2.75 μ and a doublet at 6.05 and 6.10 μ (dienone). The ultraviolet spectrum showed absorption at 283 $m\mu$ (aromatic absorption) and at 318 $m\mu$. The doublet in the infrared and the peak at 318 $m\mu$ suggest the presence of the 2,6-di-*t*-butyl-4,6-diethyl-2,4-cyclohexadienone.

Preparation of 2,6-Di-*t*-butylphenetole.—Prior to carrying out the experiment "Ethyl Iodide with Potassium 2,6-Di-*t*-butylphenoxide" as described above, a run was made with the purpose of obtaining a pure sample of 2,6-di-*t*-butylphenetole. After treatment with sodium hydride a neutral fraction corresponding to A was obtained. On chromatographing 2.00 g. of this neutral material on basic alumina (Merck) with petroleum ether (35–37°), there was isolated 0.48 g. of a white solid, m.p. 50–57°. On rechromatographing, this gave 0.12 g. of white crystals, m.p. 57–58.5°. The infrared spectrum was devoid of phenolic and dienone absorption, but exhibited ether absorption at 7.95 μ . Also, gas chromatographic analysis showed only one peak.

Anal. Calcd. for C₁₅H₂₀O: C, 81.99; H, 11.18. Found: C, 81.98; H, 11.12.

Isopropyl Iodide with Potassium 2,6-Di-*t*-butylphenoxide.—To 20.0 g. (0.097 mole) of 2,6-di-*t*-butylphenol dissolved in 25 ml. of *t*-butyl alcohol was added 93 ml. (0.097 mole) of a 1.05 *N* solution of potassium *t*-butoxide in *t*-butyl alcohol and 50 ml. of tetraethylene glycol dimethyl ether. To the resulting green solution was added 50.0 ml. (0.45 mole) of isopropyl iodide (n_D^{20} 1.4994). As the reaction proceeded precipitation occurred and the solution turned orange. The reaction was allowed to proceed for 29 hours at room temperature, and a slow stream of nitrogen was bubbled through the reaction mixture. The exit gases passed, in turn, through two ice-cooled traps each containing 5 ml. (0.098 mole) of bromine in 75 ml. of methylene chloride and then

an empty trap, cooled to –80°. After 29 hours the reaction mixture was poured into 250 ml. of distilled water and extracted with petroleum ether (35–37°). The extract was washed several times with distilled water and dried over anhydrous sodium sulfate. Removal of the petroleum ether gave 21.2 g. of crude product as a red liquid (I). Titration of the aqueous layer for iodide ion showed the reaction to be complete.

The contents of the traps were combined and washed with aq. sodium sulfite until the methylene chloride layer was colorless. The methylene chloride phase then was washed with aq. sodium bicarbonate, distilled water and dried over anhydrous magnesium sulfate. Removal of the solvent left 11.0 g. of a residue as a yellow liquid (II).

Gas chromatographic analysis of I showed only two peaks and quantitative studies showed that 68% of the mixture was 2,6-di-*t*-butylphenol and 32% 2,6-di-*t*-butyl-4-isopropylphenol. This corresponds to 14.4 g. (0.070 mole) of 2,6-di-*t*-butylphenol and 6.80 g. (0.027 mole) of 2,6-di-*t*-butyl-4-isopropylphenol. Thus, 28% alkylation occurred, and proceeded quantitatively to give the *p*-isopropylated phenol. Furthermore, the infrared spectrum of a synthetic mixture of these two phenols is identical with that of I. A 1.00-g. sample of I was chromatographed on silica gel (Davison 200-mesh) with petroleum ether to give 0.14 g., m.p. 39–41°, 2,6-di-*t*-butyl-4-isopropylphenol; mixed m.p. with authentic 2,6-di-*t*-butyl-4-isopropylphenol 39–41°, lit.¹⁶ m.p. 38–42°.

Anal. Calcd. for C₁₇H₂₂O: C, 82.20; H, 11.36. Found: C, 82.00; H, 11.18.

Six grams of II was made up to 100 ml. in methylene chloride. Quantitative gas chromatographic analysis showed that 5.25 g. of 1,2-dibromopropane was present. Since the reaction of isopropyl iodide with potassium 2,6-di-*t*-butylphenoxide went to completion (see above), and since only 28% alkylation was achieved, 72% elimination must have occurred. The 5.25 g. of dibromopropane corresponds to 49% elimination, *i.e.*, to a 68% yield. Distillation of 5.00 g. of II gave a 0.50-g. forerun of a yellow liquid (b.p. 110–130°) and then 3.76 g. of pure 1,2-dibromopropane, b.p. 136–138°, n_D^{20} 1.5189–1.5190; lit.¹⁹ b.p. 139–142°, n_D^{20} 1.5194.

Anal. Calcd. for C₃H₆Br₂: C, 17.84; H, 3.00; Br, 79.16. Found: C, 17.86; H, 3.17; Br, 79.15.

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Small-Ring Compounds. XXXV. Studies of Rearrangements in the Nitrous Acid Deaminations of Methyl-substituted Cyclobutyl-, Cyclopropylcarbinyl- and Allylcarbinylamines^{1a,b}

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The compositions of the alcohol mixtures formed in nitrous acid deaminations of cyclopropylmethylcarbinylamine, (2-methylcyclopropyl)-carbinylamine, 2-methylcyclobutylamine, 3-methylcyclobutylamine, crotylcarbinylamine and allyl-methylcarbinylamine have been determined. These results and the behavior of the corresponding alcohols under isomerization conditions in strongly acidic media may be explained by assuming formation of three non-equivalent, unsymmetrical, non-classical cationic intermediates analogous to those previously proposed for the carbonium ion reactions of other small-ring derivatives.

Introduction

The pattern of reaction products from carbonium ion-type reactions of cyclobutyl, cyclopropylcarbinyl and allylcarbinyl derivatives cannot be

satisfactorily explained by assuming formation of the highly symmetrical "tricyclobutonium ion" intermediate (I).² However, the experimental

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