[Contribution from the Department of Organic Chemistry, Radium Institute, University of Paris, and the Research Laboratories of the "Société Belge de L'Azote", Liege]

ALKYLATION OF PHENOLS AND NAPHTHOLS WITH SOME SYMMETRICAL TERTIARY ALCOHOLS

NG. PH. BUU-HOÏ, HENRI LE BIHAN, FERNAND BINON,
AND PIERRE MALEYRAN

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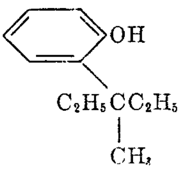
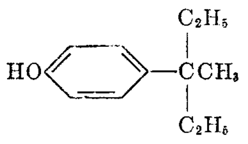
The study of the alkylation of phenols and naphthols with higher tertiary alcohols presents a twofold interest. In the practical field, many *tert*-alkylphenols and their derivatives are currently used as germicides (1), and certain *tert*-alkylnaphthols, such as 6-*tert*-butyl-1-chloro-2-naphthol, are efficient anthelmintics and fungicides (2). From the theoretical viewpoint, it is interesting to ascertain whether and to what extent the use of higher tertiary alcohols in alkylation reactions brings about fragmentation of their molecules under the influence of the catalyst. Such secondary reactions had been observed by Gilman and his associates in the alkylation of methyl 5-bromo-2-furoate with alkyl groups having more than four carbon atoms (3), by Norris and Sturgis in the *tert*-butylation of benzene (4), and by Huston and his associates in alkylations with certain highly ramified octanols (5).

The present work deals with the reaction of phenols and naphthols with some symmetrical tertiary alcohols not yet studied from that point of view. The condensation-catalyst used throughout was phosphoric acid (6).

Methyldiethylcarbinol underwent condensations without fragmentation, and gave with phenol a mixture of a low-boiling liquid (methyldiethyl)methylphenol, probably the *ortho*-derivative (I), and a high-boiling crystallized isomer

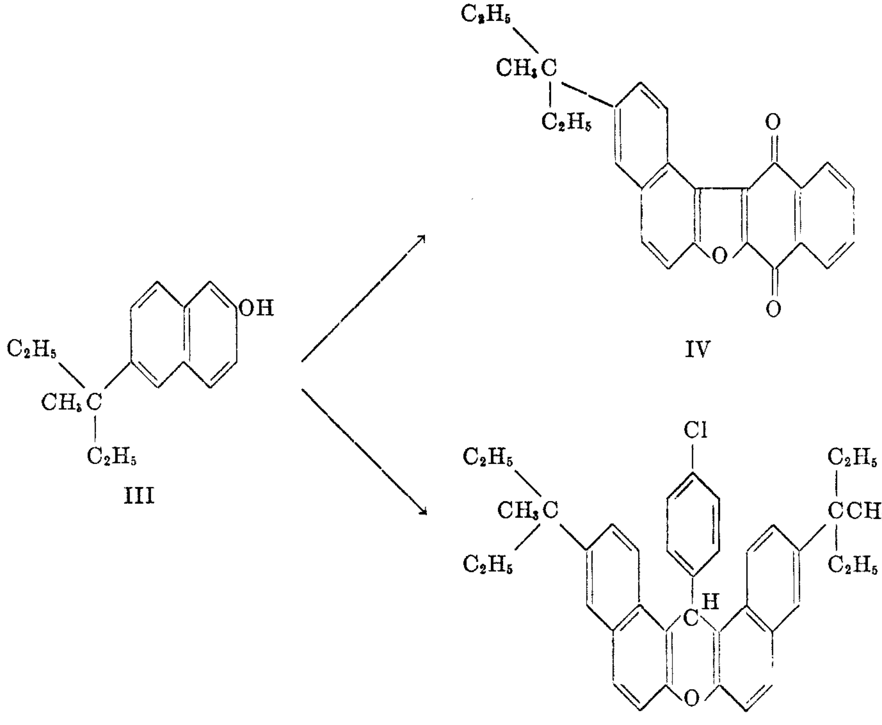


I



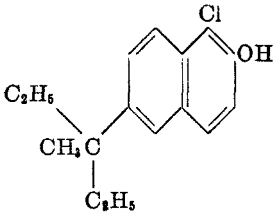
II

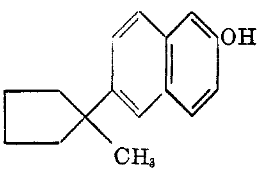
apparently *p*-(methyldiethyl)methylphenol (II). The reaction proved also successful with the three cresols, liquid monoalkylation-products being obtained in all three cases. Similar monoalkylation of β-naphthol could *a priori* affect either position 1 or position 6. The reaction product isolated was shown to be 6-(methyldiethyl)methyl-2-naphthol (III) by the formation with 2,3-dichloro-1,4-naphthoquinone



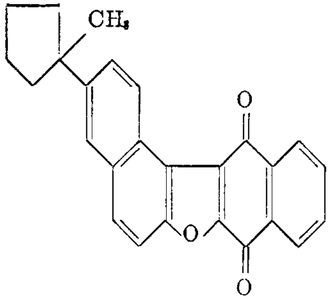
(7) of a brazanquinone of formula (IV), and with 4-chlorobenzaldehyde, of the well-crystallized xanthene derivative (V); the formation of these heterocyclic compounds is characteristic of β-naphthols having a reactive hydrogen in the adjacent α-position (8). Monochlorination of the naphthol (III) could be effected with sulfuryl chloride, 1-chloro-6-(methyldiethyl)methyl-2-naphthol (VI) being obtained.

The condensation with β-naphthol of another hexaätomic tertiary alcohol, 1-methyl-1-cyclopentanol, could also be effected without fragmentation, to give a monosubstitution product, which must be 6-(1-methylcyclopentyl)-2-naphthol (VII),

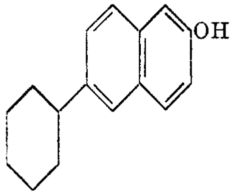

VI


VII

as it readily yielded with 2,3-dichloro-1,4-naphthoquinone the brazanquinone (VIII). Fragmentation was encountered with 1-*n*-propyl-1-cyclohexanol, which condensed with β-naphthol to give 6-cyclohexyl-2-naphthol (IX).



VIII



IX

EXPERIMENTAL

Condensation of methyldiethylcarbinol with phenol. Methyldiethylcarbinol was prepared from ethyl acetate and ethylmagnesium bromide, according to Henry (9). A mixture of 65 g. (0.7 mole) of phenol, 51 g. (0.5 mole) of methyldiethylcarbinol, and 90 g. of phosphoric acid (*d*, 1.85) was refluxed for 12 hours. The hot reaction product was poured into water, and the organic layer was taken up in benzene, washed with a 10% aqueous solution of sodium carbonate, then with water, dried over sodium sulfate, and the solvent evaporated. Vacuum-distillation of the residue yielded a portion b.p. 120–160°/15 mm. (61 g.), which gave on fractionation a liquid product (15 g.), b.p. 147°/17 mm., and a solid product (40 g.), b.p. 148–153°/15 mm. The colorless, fluid liquid with a pleasant fruity odor, probably *o-(methyldiethyl)methylphenol* (I), had n_D^{25} 1.52039; no crystallized derivative could be obtained therefrom.

Anal. Calc'd for $C_{12}H_{18}O$: C, 80.9; H, 10.1.

Found: C, 80.6; H, 10.2.

The solid crystallized from petroleum ether (b.p. 40–60°) as silky colorless prisms, m.p. 40–42°, also with a pleasant odor, and was probably *p-(methyldiethyl)methylphenol* (II) (10).

Anal. Calc'd for $C_{12}H_{18}O$: C, 80.9; H, 10.1.

Found: C, 80.9; H, 10.2.

Condensation of methyldiethylcarbinol with the cresols. (a) With *o*-cresol: this was performed with 75 g. of *o*-cresol, 51 g. of the alcohol, and 90 g. of phosphoric acid as above, and gave after vacuum-fractionation of the reaction-product, *(methyldiethyl)methyl-o-cresol* as a pale yellow oil (44 g.), b.p. 145–146°/13 mm., n_D^{25} 1.5200; this was probably a mixture of the *o*- and *p*-isomers.

Anal. Calc'd for $C_{13}H_{20}O$: C, 81.3; H, 10.4.

Found: C, 81.2; H, 10.5.

(b) With *m*-cresol: the yield was 30 g. of *(methyldiethyl)methyl-m-cresol,* forming a pale yellow oil, b.p. 150–155°/15 mm., n_D^{25} 1.51741 (probably a mixture of the two possible isomers).

Anal. Calc'd for $C_{13}H_{20}O$: C, 81.3; H, 10.4.

Found: C, 81.4; H, 10.5.

(c) With *p*-cresol: the yield was 35 g. of *(methyldiethyl)methyl-p-cresol,* forming a pale yellow oil, b.p. 145–147°/14 mm., n_D^{25} 1.51842.

Anal. Calc'd for $C_{13}H_{20}O$: C, 81.3; H, 10.4.

Found: C, 81.3; H, 10.5.

6-(Methyldiethyl)methyl-2-naphthol (III). A mixture of 100 g. (0.74 mole) of β-naphthol, 61 g. (0.6 mole) of methyldiethylcarbinol, and 100 g. of phosphoric acid was treated in the usual way. Vacuum-fractionation of the reaction-product yielded, together with recovered β-naphthol and a resinous polyalkylated portion b.p. 250–310°/15 mm., 46 g. of a portion b.p. 215–230°/15 mm., which solidified and gave on recrystallization from cyclohexane silky, colorless needles, m.p. 103°.

Anal. Calc'd for $C_{16}H_{20}O$: C, 84.2; H, 8.8.
Found: C, 84.0; H, 8.8.

6-(Methyldiethyl)methyl-2-naphthol methyl ether, prepared with methyl sulfate and sodium hydroxide, had b.p. 198–204°/15 mm., and crystallized from methanol as colorless prisms, m.p. 38°.

Anal. Calc'd for $C_{17}H_{22}O$: C, 84.3; H, 9.1.
Found: C, 84.2; H, 9.1.

2-p-Tolylamino-6-(methyldiethylmethyl)naphthalene. This secondary amine was prepared by heating at 180° for 12 hours a mixture of 4.8 g. of *p*-toluidine, 10 g. of the naphthol (III), and 0.2 g. of iodine. The reaction product was taken up in benzene, washed with an aqueous solution of sodium hydroxide, and purified by vacuum-distillation (b.p. 270–280°/15 mm.); it crystallized from ligroin as silky colorless needles, m.p. 79° (Yield, 10 g.).

Anal. Calc'd for $C_{23}H_{27}N$: C, 87.1; H, 8.5.
Found: C, 87.0; H, 8.6.

1-Chloro-6-(methyldiethyl)methyl-2-naphthol (VI). To a cooled solution of 5 g. of the naphthol (III) in 30 ml. of dry chloroform, 3 g. of sulfuryl chloride was added in small portions; the mixture was kept overnight, then washed with an aqueous solution of sodium carbonate, then with water, and dried over sodium sulfate. After evaporation of the solvent, the residue was vacuum-distilled (b.p. 230–240°/15 mm.), giving 3 g. of a substance which crystallized from ligroin as silky colorless prisms, m.p. 66°.

Anal. Calc'd for $C_{16}H_{19}ClO$: C, 73.1; H, 7.2.
Found: C, 73.4; H, 7.5.

3-(Methyldiethyl)methyldinaphtho[2,1,2',3']furan-8,13-dione (IV). A solution of 2 g. of the naphthol (III) and 3 g. of 2,3-dichloro-1,4-naphthoquinone in 8 ml. of anhydrous pyridine was gently refluxed for 12 hours. After cooling, methanol was added, and the precipitate obtained was recrystallized from benzene, yielding silky orange-yellow needles, m.p. 231°; sulfuric acid produced a deep blue coloration characteristic of brazanquinones.

Anal. Calc'd for $C_{26}H_{22}O_3$: C, 81.7; H, 5.8.
Found: C, 81.4; H, 6.0.

3,11-Di-(methyldiethyl)methyl-14-p-chlorophenyl-14H-dibenzo[a,j]xanthene (IV). To a boiling solution of 2 g. of the naphthol (III) and 1 g. of *p*-chlorobenzaldehyde in 10 ml. of acetic acid, a few drops of hydrochloric acid were added. After cooling, methanol was added, and the precipitate obtained recrystallized from ethyl acetate, giving colorless prisms, m.p. 203°.

Anal. Calc'd for $C_{39}H_{41}ClO$: C, 83.4; H, 7.3.
Found: C, 83.2; H, 7.3.

6-(1-Methylcyclopentyl)-2-naphthol (VII). 1-Methyl-1-cyclopentanol was prepared from cyclopentanone and methylmagnesium iodide (11); a mixture of 48 g. of this alcohol, 70 g. of β-naphthol, and 100 g. of phosphoric acid was refluxed for 16 hours. The reaction product, worked up in the usual way, yielded 25 g. of a portion b.p. 230°/15 mm., crystallizing from cyclohexane as silky colorless needles, m.p. 111°.

Anal. Calc'd for $C_{16}H_{18}O$: C, 85.0; H, 8.0.
Found: C, 84.8; H, 8.1.

3-(1-Methylcyclopentyl)dinaphtho[2,1,2',3']furan-8,13-dione (VIII) crystallized from benzene as orange-yellow needles, m.p. 239°, with decomposition above 222°; deep blue coloration with sulfuric acid.

Anal. Calc'd for $C_{26}H_{20}O_3$: C, 82.1; H, 5.3.
Found: C, 82.0; H, 5.2.

Condensation of 1-n-propyl-1-cyclohexanol with β-naphthol. 1-*n*-Propyl-1-cyclohexanol was prepared from cyclohexanone and *n*-propylmagnesium bromide (12); its condensation with β-naphthol, performed in the usual way, yielded a product b.p. 225–230°/16 mm., which gave on recrystallization from cyclohexane, silky colorless needles, m.p. 162°, alone, or mixed with 6-cyclohexyl-2-naphthol (13).

Anal. Calc'd for $C_{16}H_{18}O$: C, 85.0; H, 8.0.
Found: C, 84.9; H, 8.1.

SUMMARY

1. Methyldiethylcarbinol, 1-methyl-1-cyclopentanol, and 1-*n*-propyl-1-cyclohexanol have been condensed with phenols and β-naphthol, and fragmentation was encountered with the last alcohol.

2. Several new phenols and naphthols and their derivatives are described.

PARIS V^e, FRANCE

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