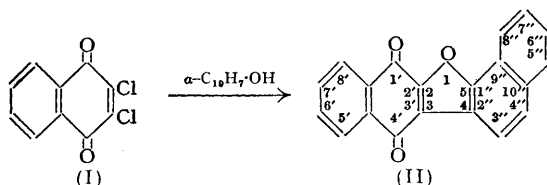


917. The Condensation of 2 : 3-Dichloro-1 : 4-naphthaquinone with α -Naphthols.

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α -Naphthol and 2 : 3-dichloro-1 : 4-naphthaquinone give dinaphtho-(2' : 3'-2 : 3)(1'' : 2''-5 : 4)furan-1' : 4'-quinone, and the reaction has been extended to a number of 4-substituted 1-naphthols. Some alkylation and arylalkylation reactions of α -naphthol have been investigated.

EISTERT (*Ber.*, 1944, **80**, 52) found that 2 : 3-dichloro-1 : 4-naphthaquinone (I) reacted with β -naphthol in pyridine, giving dinaphtho(2' : 3'-2 : 3)(1'' : 2''-4 : 5)furan-1' : 4'-quinone, and one of us showed this cyclisation reaction to be characteristic of 2-naphthols having the adjacent α -position free (Buu-Hoï, *J.*, 1952, 489). The reaction of 2 : 3-dichloro-1 : 4-naphthaquinone with 1-naphthols has now been investigated. α -Naphthol reacted readily with one mol. of the quinone (I), to yield a yellow substance which gave with sulphuric acid a bluish colour reminiscent of that displayed by dinaphtho-(2' : 3'-2 : 3)(1'' : 2''-5 : 4)furan-1' : 4'-quinone; this fact and the analytical results showed that this substance was the isomeric dinaphtho(2' : 3'-2 : 3)(1'' : 2''-5 : 4)furan-1' : 4'-quinone (II).



For testing the generality of this reaction, some substituted 1-naphthols were required. Whereas such reactions have been repeatedly studied with β -naphthol (see Price, "Organic Reactions," 1946, Vol. III, New York, p. 1; Contractor, Peters, and Rowe, *J.*, 1949, 1993; Buu-Hoï *et al.*, *J. Org. Chem.*, 1950, **15**, 1060; 1951, **16**, 185, 988), little has been recorded for α -naphthol, mostly benzylation. 4-Benzyl-1-naphthol, first obtained by Bakunin and Barberio (*Gazzetta*, 1903, **33**, II, 470), was conveniently prepared by Dziewoński and Dziecielewski's method (*Bull. Intern. Acad. Polon.*, 1927, *A*, 275), condensing α -naphthol with benzyl chloride in the presence of zinc chloride in chloroform; repetition yielded, in addition to 4-benzyl-1-naphthol, a dibenzyl-1-naphthol in which one benzyl group was evidently in the position 4 as the compound was also obtained from 4-benzyl-1-naphthol.

4-Benzyl-1-naphthol and 2 : 3-dichloro-1 : 4-naphthaquinone gave 4''-benzyldinaphtho-(2' : 3'-2 : 3)(1'' : 2''-5 : 4)furan-1' : 4'-quinone, a substance of properties similar to the non-substituted quinone; 2-benzyl- and 2-allyl-1-naphthol, on the other hand, failed to give that reaction.

Condensation of α -naphthol with *p*-methylbenzyl chloride gave a monosubstituted and a disubstituted product. The former must be 4-*p*-methylbenzyl-1-naphthol, as it reacted with (I) to give a brasanquinone, probably 4''-*p*-methylbenzyldinaphtho(2' : 3'-2 : 3)(1'' : 2''-5 : 4)furan-1' : 4'-quinone; the disubstituted product was a 4 : *x*-di-*p*-methylbenzyl-1-naphthol. Alkylation of α -naphthol with *tert*-butyl bromide in conditions similar to the *para*-benzylation yielded a liquid monosubstituted product, which was certainly not the *ortho*-compound as it gave with (I) a brasanquinone [possibly 4''-*tert*-butyldinaphtho(2' : 3'-2 : 3)(1'' : 2''-5 : 4)furan-1' : 4'-quinone], and a disubstituted product, possibly 4 : *x*-di-*tert*-butyl-1-naphthol.

EXPERIMENTAL

Dinaphtho(2' : 3'-2 : 3)(1'' : 2''-4 : 5)furan-1' : 4'-quinone (II).—A solution of α -naphthol (1.5 g.) and 2 : 3-dichloro-1 : 4-naphthaquinone (2.3 g.) (Ullmann and Ettisch, *Ber.*, 1921, **54**, 259) in anhydrous pyridine (15 c.c.) was gently refluxed for 12 hours; the precipitated product (3 g.) obtained on dilution with methanol crystallised from toluene as golden-yellow, sublimable

needles, m. p. 231°, which distilled *in vacuo* without decomposition and gave an intense blue colour with sulphuric acid (Found : C, 80.4; H, 3.3. $C_{20}H_{10}O_3$ requires C, 80.5; H, 3.4%).

Benzylation of α -Naphthol.—To α -naphthol (159 g.) and freshly fused powdered zinc chloride (150 g.) in dry chloroform (500 c.c.), redistilled benzyl chloride (126 g.) was added in small portions; when the spontaneous boiling had subsided, gentle refluxing was applied for 2 hours. The cooled mixture was shaken with water, and the chloroform layer washed with dilute hydrochloric acid, then with water, and dried ($CaCl_2$); after evaporation, the residue was vacuum-fractionated, giving, apart from 4-benzyl-1-naphthol, b. p. 242°/11 mm., m. p. 125° (Dziewoński and Dziecielewski, *loc. cit.*), 4 : x-dibenzyl-1-naphthol (30 g.), b. p. 303—305°/11 mm., leaflets (from cyclohexane), m. p. 117° (Found : C, 88.6; H, 6.4. $C_{24}H_{20}O$ requires C, 88.9; H, 6.2%). For comparison, benzyl 4-benzyl-1-naphthyl ether was prepared from the sodio-derivative of 4-benzyl-1-naphthol and benzyl chloride in aqueous medium, and was a pale yellow, viscous oil, b. p. 292—294°/11 mm. (Found : C, 88.8; H, 6.5%).

4''-Benzylidinaphtho(2' : 3'-2 : 3)(1'' : 2''-5 : 4)furan-1' : 4'-quinone.—Prepared as was the non-substituted product from 4-benzyl-1-naphthol (2.3 g.) and the quinone (I) (2.3 g.) in pyridine, this furan formed from benzene golden-yellow needles (3.2 g.), m. p. 265°, giving a blue-violet colour with sulphuric acid (Found : C, 83.2; H, 4.2. $C_{27}H_{18}O_3$ requires C, 83.5; H, 4.1%).

Condensation of α -Naphthol with p-Methylbenzyl Chloride.— α -Naphthol (60 g.), p-methylbenzyl chloride (50 g.), and zinc chloride (80 g.) in chloroform (150 c.c.) gave 4-p-methylbenzyl-1-naphthol (80%), b. p. 251°/11 mm., prisms (from cyclohexane), m. p. 132° (Found : C, 87.0; H, 6.8. $C_{18}H_{16}O$ requires C, 87.1; H, 6.5%), and 4 : x-di-p-methylbenzyl-1-naphthol, b. p. 308—310°/11 mm., leaflets (from cyclohexane), m. p. 144° (Found : C, 88.4; H, 6.8. $C_{28}H_{24}O$ requires C, 88.6; H, 6.8%).

4''-p-Methylbenzylidinaphtho(2' : 3'-2 : 3)(1'' : 2''-5 : 4)furan-1' : 4'-quinone formed from benzene golden-yellow prisms, m. p. 241°, giving a blue-violet colour with sulphuric acid (Found : C, 83.3; H, 4.6. $C_{28}H_{18}O_3$ requires C, 83.6; H, 4.5%).

tert.-Butylation of α -Naphthol.— α -Naphthol (160 g.), tert.-butyl bromide (140 g.), and zinc chloride (140 g.) in chloroform (500 c.c.) were gently refluxed for 2 hours. The usual treatment yielded after repeated vacuum-fractionation a liquid tert.-butyl-1-naphthol (30 g.), b. p. 160°/2 mm., n_D^{20} 1.5905 (Found : C, 84.2; H, 8.2. $C_{14}H_{16}O$ requires C, 84.0; H, 8.0%), and a solid di-tert.-butyl-1-naphthol (30 g.), b. p. 190—192°/2 mm., needles (from cyclohexane), m. p. 145° (Found : C, 84.3; H, 9.5. $C_{18}H_{24}O$ requires C, 84.4; H, 9.4%).

4''(?) -tert.-Butylidinaphtho(2' : 3'-2 : 3)(1'' : 2''-5 : 4)furan-1' : 4'-quinone crystallised from benzene as golden-yellow, sublimable needles, m. p. 233°, giving a blue-violet colour with sulphuric acid (Found : C, 81.3; H, 5.0. $C_{24}H_{18}O_3$ requires C, 81.4; H, 5.1%).

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