Reaction of isonicotinanilide hydrochloride with phosphorus pentachloride and aniline. One half of the crude isonicotinanilide hydrochloride described in a preceding section (0.0288 mole) in 50 ml. of dry benzene was heated to 50° in a round-bottomed flask and 20 g. of phosphorus pentachloride was added slowly. The reaction mixture was then heated to 140° for 1 hr., all of the solvent distilling off. Aniline (0.1 mole) in 100 ml. of benzene was then added to the residue and the reaction mixture was heated on the steam bath for 45 min. and 10 ml. more of aniline was added. The mixture was cooled and filtered, the precipitate was taken up in 10% hydrochloric acid, treated with Norit, filtered, and taken to *p*H 4.0 with 5% sodium hydroxide. The precipitate which formed was recrystallized from ethyl alcohol to give 0.9 g. (10.4%) of *N,N'*-diphenylisonicotinamidine, melting at 192–193° (Fisher-Johns). A mixed melting point with the product from the Willgerodt reaction was not depressed.

Thiopicolinanilide (VIII); *2-(2-pyridyl)benzothiazole* (X); *and N,N'-diphenylpicolinamidine* IX. A suspension of 96.2 g. (3.0 g. atom) of sulfur, 93.1 g. (1.0 mole) of α-picoline, and 139.7 g. (1.5 moles) of aniline was heated under reflux for 16 hr., the inner temperature rising from 180–220°. The unreacted aniline and α-picoline were removed by distillation under a vacuum. Excess sulfur was removed by solution of the pot residue in 1500 ml. of alcohol, cooling, and filtering. The filtrate, after concentration to 600 ml. and chilling, deposited 15 g. of yellow crystals, m.p. 126–133°. One recrystallization out of alcohol gave a material, m.p. 133–135°; the mixed melting point with 2-(2-pyridyl)benzothiazole was not depressed.

After removal of the benzothiazole, the filtrate was concentrated and distilled under a vacuum at 1 mm. to give the following fractions:

(1) b.p. 140–170° (96 g.)
(2) b.p. 170–176° (54 g.)
(3) b.p. 176–185° (with slight decomposition) 8 g.

The first fraction, upon solution in warm alcohol (40°), yielded two crystalline solids: 2-(2-pyridyl)benzothiazole, m.p. 126–133°, 45 g., only slightly soluble in alcohol, and thiopicolinanilide, m.p. 51–53° (42 g.), which is more soluble and crystallized from the filtrate upon chilling.

The second fraction, upon solution in alcohol and chilling, yielded thiopicolinanilide, m.p. 51–53°.

The third fraction, upon solution in alcohol and chilling, yielded *N,N'*-diphenylpicolinamidine (IX), m.p. 93–95°, after recrystallization from absolute alcohol and ligroin.

Anal. Calcd. for $C_{18}H_{15}N_3$: C, 79.1; H, 5.5; N, 15.4; mol. wt., 273. Found: C, 79.4; H, 5.6; N, 15.1; mol. wt., 284.

2-(2-Pyridyl)benzothiazoline hydrochloride (XII). This isomer was prepared by the method just described for compound V from 2-pyridinecarboxaldehyde (Aldrich Chemical Co.). The bright yellow crystals melted, with decomposition, at 166–168°.

Anal. Calcd. for $C_{12}H_{11}ClN_2S$: C, 57.47; H, 4.42; N, 11.17. Found: C, 57.9; H, 4.4; N, 11.5.

2-(2-Pyridyl)benzothiazole (X). The oxidation of the benzothiazoline was accomplished by the procedure just described for compound I to give the benzothiazole, m.p. 133–135°. A mixed melting point with a sample from the Willgerodt reaction showed no depression.

Anal. Calcd. for $C_{12}H_8N_2S$: C, 67.90; H, 3.80; N, 13.20. Found: C, 67.9; H, 3.8; N, 13.2.

N,N'-Diphenylpicolinamidine (IX). Picolinanilide XIII, m.p. 72–74° was prepared by the method of Engler.[6] A suspension of 6.6 g. of picolinanilide in 25 ml. of dry benzene was treated with 10 g. of phosphorus pentachloride at 50°. The reaction mixture was then heated to 110° for 3 hr., all of the solvent distilling off. Aniline (10 ml.) in 60 ml. of dry benzene was then added to the residue and the reaction mixture was heated on the steam bath for 1 hr. The mixture was cooled, filtered, and the precipitate was dissolved in 100 ml. of 10% hydrochloric acid. This solution was treated with carbon, filtered, and taken to *p*H 6.0 with 10% sodium hydroxide solution. Upon cooling, a precipitate was formed which was recrystallized from alcohol, m.p. 93–95°. A mixed melting point with the product from the Willgerodt reaction was not depressed.

ROCHESTER 4, N. Y.

(6) C. Engler, *Ber.*, **27**, 1786 (1894).

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, RADIUM INSTITUTE, UNIVERSITY OF PARIS]

Tritylation of Some Phenols and Naphthols

NG. PH. BUU-HOÏ AND RICHARD RIPS

Received December 26, 1956

The Baeyer-Villiger condensation reaction of triphenylcarbinol with some phenols, naphthols, and dihydroxynaphthalenes is investigated, and the constitution of several of the resulting substitution products is discussed.

The Baeyer-Villiger condensation of triphenylcarbinol with phenols, phenol ethers, and naphthols to give tritylated products was extensively investigated by Hardy,[1] who found that condensation occurred only in the position *para* to a phenol or an ether group. In the case of β-naphthol, however, Hardy assigned the structure of 1-trityl-2-naphthol (I) to the monotritylated product, without offering any proof of constitution. Recently, Schönberg, Mustafa, and Shalaby[2] reported an unequivocal synthesis of 1-trityl-2-naphthol by reacting phenylmagnesium bromide with *o*-naphthofuchsone; the reaction product, m.p. 155°, differed from Hardy's substance, which melted at 228°. This observation led us to investigate anew the tritylation reaction of phenolic compounds, to ascertain whether there would be true instances of *ortho* substitution.

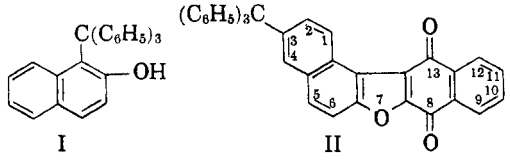
Repetition of Hardy's experiments with β-naphthol gave a tritylnaphthol melting at 230°, which condensed readily with 2,3-dichloro-1,4-naphthoquinone in pyridine to give a furanoquinone. This reaction proved that the position 1 adjacent to the hydroxy group was free,[3] thus confirming Schön-

(1) Hardy, *J. Chem. Soc.*, 1000 (1929).

(2) Schönberg, Mustafa, and Shalaby, *J. Am. Chem. Soc.*, **77**, 5756 (1955).

(3) *Cf.* Buu-Hoï, *J. Chem. Soc.*, 489 (1952); Buu-Hoï and Demerseman, *J. Chem. Soc.*, 4699 (1952).

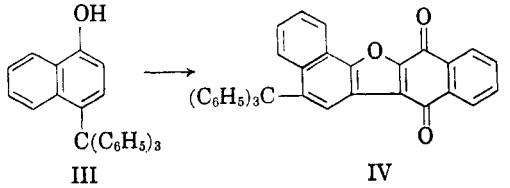
berg, Mustafa, and Shalaby's observations. Apart from position 1, the trityl group could have entered



I II

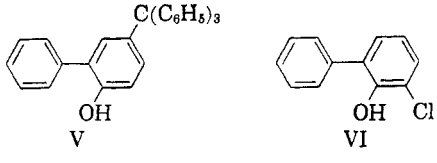
position 6 or 8; in view of similar results obtained in *tert.* alkylations[4] and cyclohexylation[5] of β-naphthol, the most probable structure of Hardy's compound is 6-trityl-2-naphthol, and that of the corresponding furanoquinone, 3-tritylidinaphtho[2,1-2',-3']furan-8,13-dione (II). These structures are further upheld by the failure of 6-bromo-2-naphthol to undergo tritylation.

In the reaction of triphenylcarbinol with α-naphthol, Hardy isolated a monosubstitution product which he formulated as 4-trityl-1-naphthol (III); because of the known ability of α-naphthol to undergo some degree of alkylation in position 2,[5] this formula needed some confirmation. This was now forthcoming in a successful condensation with 2,3-dichloro-1,4-naphthoquinone to a furanoquinone, which must be 5-tritylidinaphtho[1,2-2',3']furan-7,12-dione (IV).



III IV

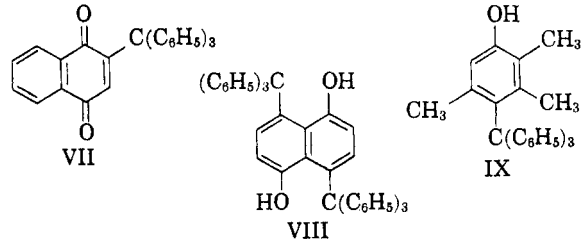
The resistance of trityl radicals to *ortho* substitution in Baeyer-Villiger reactions, already found by Hardy in several examples in the benzene series, was now further demonstrated in the biphenyl series by the behavior of 2- and 4-hydroxybiphenyl. The former compound readily yielded 2-hydroxy-5-tritylbiphenyl (V), while the latter failed to react; it is true that the reaction also failed with 6-chloro-



V VI

2-hydroxybiphenyl (VI), despite the presence of a free *para* position, but this could probably be attributed to the deactivating influence of the chlorine atom.

It does not ensue from the previously recorded failures that *ortho* substitution cannot take place in certain favorable circumstances. 1,4-Dihydroxynaphthalene, for instance, could be tritylated, although the primary substitution product underwent oxidation in the course of the reaction, to give 2-trityl-1,4-naphthoquinone (VII); with 1,5-dihydroxynaphthalene, disubstitution occurred as expected, to give a compound considered to be 1,5-dihydroxy-4,8-ditritylnaphthalene (VIII). In the case of 2,7-dihydroxynaphthalene,[6] a disubstitution product was also obtained, in which at least one of



VII VIII IX

the trityl groups occupied an α-position, as no furanoquinone was formed with 2,3-dichloro-1,4-naphthoquinone.

The preferential attack on *para* positions in Baeyer-Villiger reactions involving triphenylcarbinol does not seem due to steric hindrance, as 2,3,5-trimethylphenol, a compound whose *para* position is sterically hindered, readily underwent tritylation, to give 2,3,5-trimethyl-4-tritylphenol (IX). It should be noted that the presence of carbonyl groups inhibits tritylation completely, as is the case with 2,4-dihydroxybenzaldehyde, gallacetophenone, and lawsone (2-hydroxy-1,4-naphthoquinone).

EXPERIMENTAL

Tritylation of β-naphthol. To a solution of 12 g. of triphenylcarbinol and 12 g. of β-naphthol in 120 ml. of warm acetic acid, 20 g. of sulfuric acid was added portionwise with stirring, and the mixture left for three days at room temperature. The abundant precipitate which had by then formed (in Hardy's experiments the reaction mixture was left for one month) was collected, washed thoroughly with aqueous ethanol, dried, and recrystallized from ethanol. *6(?)-Trityl-2-naphthol* (I) was thus obtained as fine, colorless prisms, m.p. 230°; yield, 6 g. A similar experiment, performed with 6-bromo-2-naphthol, failed to give any substitution product even after 1 month.

3(?)-Tritylidinaphtho[2,1-2',3']furan-8,13-dione (II). A mixture of 3 g. of the foregoing naphthol, 1.8 g. of 2,3-dichloro-1,4-naphthoquinone, and 30 ml. of anhydrous pyridine was gently refluxed for 2 hr.; the precipitate which formed after cooling was collected, washed with aqueous ethanol, then with water, dried, and recrystallized from pyridine. Yield, 3 g. of silky golden-yellow needles, m.p. 347–348°, giving, with hot sulfuric acid, a greenish-blue coloration.

Anal. Calcd. for $C_{39}H_{24}O_3$: C, 86.7; H, 4.5. Found: C, 86.5; H, 4.5.

Tritylation of α-naphthol. A mixture of 13.5 g. of α-naphthol, 12 g. of triphenylcarbinol, and 120 ml. of warm acetic acid was treated with 20 g. of sulfuric acid and left

(4) Buu-Hoï, Le Bihan, Binon, and Rayet, *J. Org. Chem.*, **15**, 1060 (1950); Buu-Hoï, Le Bihan, and Binon, *J. Org. Chem.*, **16**, 185 (1951); Buu-Hoï, Le Bihan, Binon, and Xuong, *J. Org. Chem.*, **16**, 988 (1951).

(5) Alberti, *Ann.*, **450**, 309 (1926).

(6) For previous work on substitution reactions of 1,5- and 2,7-dihydroxynaphthalene, see Buu-Hoï and Lavit, *J. Chem. Soc.*, 1743 (1956); *J. Org. Chem.*, **20**, 1191 (1955).

overnight at room temperature. The yield was 14 g. of *4-trityl-1-naphthol*, crystallizing from ethanol in colorless prisms, m.p. 205°; this product, dissolved in hot ethanol, gave with ferric chloride a brown-violet coloration which faded on cooling.

Condensation of this naphthol with 2,3-dichloro-1,4-naphthoquinone in pyridine yielded *5-trityldinaphtho-[1,2-2',3]furan-7,12-dione* (IV), crystallizing from pyridine in silky golden yellow needles, m.p. 352–353°, giving, with sulfuric acid, a cobalt-blue halochromy; yield 80%.

Anal. Calcd. for $C_{39}H_{24}O_3$: C, 86.7; H, 4.5. Found: C, 86.3; H, 4.5.

2-Hydroxy-5-trityldiphenyl (V). A solution of 3 g. of 2-hydroxydiphenyl and 3 g. of triphenylcarbinol in 30 ml. of warm acetic acid was treated in the usual way with 5 g. of sulfuric acid, and the red mixture obtained was left for a week at room temperature. The precipitate (4 g.) was treated as above, and yielded on recrystallization from a mixture of benzene and ethanol, shiny, colorless, sublimable needles, m.p. 246–247°.

Anal. Calcd. for $C_{31}H_{24}O$: C, 90.3; H, 5.9. Found: C, 89.9; H, 6.1.

From similar experiments performed with 3-chloro-2-hydroxybiphenyl and 4-hydroxybiphenyl (1 month at room temperature), only the starting materials were recovered, along with some triphenylmethane.

2-Trityl-1,4-naphthoquinone (VII). A mixture of 3 g. of 1,4-dihydroxynaphthalene and 3 g. of triphenylcarbinol in 50 ml. of acetic acid was treated with 5 g. of sulfuric acid in the usual way. The precipitate (3 g.), obtained after 3 days on addition of water, was washed with water, and crystallized several times from a mixture of ethanol and benzene, to give *2-trityl-1,4-naphthoquinone* in the form of canary yellow prisms, m.p. 222–223°, giving a deep green coloration in sulfuric acid. This compound was insoluble in aqueous alkalis, and yielded phthalic acid on oxidation with potassium permanganate.

Anal. Calcd. for $C_{29}H_{20}O_2$: C, 87.0; H, 5.0. Found: C, 87.2; H, 5.2.

1,5-Dihydroxy-4,8-ditritylnaphthalene (VIII). A mixture of 3 g. of 1,5-dihydroxynaphthalene and 6 g. of triphenylcarbinol in 60 ml. of acetic acid was treated with 5 g. of sulfuric acid. The precipitate which formed after 2 days was washed with ethanol, then with hot dioxane, and recrystallized from tetralin, giving 3 g. of fine, colorless prisms, m.p. 429–430°.

Anal. Calcd. for $C_{48}H_{36}O_2$: C, 89.4; H, 5.6. Found: C, 89.2; H, 5.9.

2,7-Dihydroxy-1,x-ditritylnaphthalene. This compound, prepared from 2,7-dihydroxynaphthalene as for β-naphthol, crystallized from a mixture of ethanol and benzene in silky colorless needles, m.p. 318–320°; yield 60%.

Anal. Calcd. for $C_{48}H_{36}O_2$: C, 89.4; H, 5.6. Found: C, 89.1; H, 5.9.

This compound failed to give a furanoquinone on heating with 2,3-dichloro-1,4-naphthoquinone in pyridine medium.

2,3,5-Trimethyl-4-tritylphenol (IX). Prepared from 2,3,5-trimethylphenol (3 g.), this compound crystallized from ethanol in silky colorless needles (1 g.), m.p. 170–171°.

Anal. Calcd. for $C_{28}H_{26}O$: C, 88.9; H, 6.9. Found: C, 88.6; H, 6.6.

Similar experiments performed with *p-tert.* amylphenol, 2,4-dihydroxybenzaldehyde, gallacetophenone, and lawsone were completely negative.

PARIS (V^e^), FRANCE

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, RADIUM INSTITUTE, UNIVERSITY OF PARIS]

Friedel-Crafts Acylations of 3-Chloro-4-methoxybiphenyl

NG. PH. BUU-HOÏ, MICHEL SY, AND JEAN RICHÉ

Received December 26, 1956

Friedel-Crafts acylations of 3-chloro-4-methoxybiphenyl with aliphatic and aromatic acid chlorides are shown to give 4'-acyl-3-chloro-4-methoxybiphenyls, several of which were prepared and their reactions investigated. In the course of this work, a large number of new derivatives of 3-chloro-4-hydroxybiphenyl and its methyl ether (ketones, phenols, quinolines) were synthesized.

Substitution reactions in the biphenyl series present an interesting subject of research, because of the possibility for substitutions to be homonuclear or heteronuclear. For instance, 4-methoxybiphenyl has been shown to undergo Friedel-Crafts acylations[1] mainly at position 4', with some substitution at position 3. When the directing effect of the first substituent is weaker, as is the case with 4-alkyldiphenyls,[2] acylations have been found to occur almost exclusively at position 4'. It was now thought of interest to investigate similar Friedel-Crafts reactions with 3-chloro-4-methoxybiphenyl (I), a readily accessible molecule in which the position *ortho* to the methoxy group is deactivated by the chlorine atom present in the *meta* position. (It is known that bromination of 4-hydroxybiphenyl leads to a monobromo derivative, even in relatively drastic conditions.)[3]

The starting material, 3-chloro-4-hydroxybiphenyl, possesses to some extent the properties of a cryptophenol, and could be completely methylated with sodium hydroxide and dimethyl sulfate only in the presence of methanol or ethanol;[4] acylation of 3-chloro-4-methoxybiphenyl by acetyl chloride in the presence of aluminum chloride in nitrobenzene medium gave, in excellent yields, a ketone which must have been 4'-acetyl-3-chloro-4-methoxybiphenyl (II; R = H), as its demethylation afforded a substance which, since it did not show the proper-

(1) See Fieser and Bradsher, *J. Am. Chem. Soc.*, **58**, 1738, 2337 (1936).

(2) Buu-Hoï and Royer, *Rec. trav. chim.*, **70**, 825 (1951); *Bull. soc. chim. France*, **17**, 489 (1950).

(3) Bell and Robinson, *J. Chem. Soc.*, 1132 (1927).

(4) For other instances of methylation of cryptophenols. see Buu-Hoï and Lavit, *J. Chem. Soc.*, 2412 (1956).