The Nitration and Sulfonation of 2, 4, 6-Triphenyl-1, 3, 5-triazine[1]

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There are many examples of the preparation of cyaphenine, including the trimerization of benzonitrile with acidic,[2,3] basic[4,5] or organometallic catalysts[6,7], or by the high pressure technique.[8,9] It has also been reported that the formation of cyaphenine is possible by way of such condensations as the reaction of benzoyl

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chloride with potassium cyanate,[10] benzaldehyde with tetrasulfur tetranitride,[11] benzonitrile with benzoyl chloride,[12] benzene with cyanogen chloride,[13] ethyl benzimidate with its hydrochloride,[14] 4, 6-diphenyl-1,2,3,5-oxathiodiazine-2-dioxide with benzamidine,[15] and benzamide with phosphorous pentasulfide.[16] It has also been reported that methyl *m*- or *p*-nitrobenzimidate derived from the corresponding nitrobenzonitrile may be converted to 2, 4, 6-tris(*m*- or *p*-nitrophenyl)-1, 3, 5-triazine by an acid catalyst.[17] However, very little information is available on the electrophilic substitutions of cyaphenine.

The present paper will describe our data on the nitration and sulfonation of cyaphenine. The structure of the products was confirmed by infrared spectroscopy and chemical analysis, i. e., by estimations of the nitrogen content in the nitrated cyaphenine and of the sulfonyl group in the cyapheninesulfonic acid.

Experimental

Materials.—Cyaphenine was prepared according to the Cook-Jones procedure.[2] The product was purified by two recrystallizations from toluene (yield, 68.4%), m. p. 233.0—234.0°C (lit.[2] m. p. 232°C). The wave numbers (cm^{-1}) of the characteristic infrared absorption bands of cyaphenine (KBr disk) were 1590, 1530, 1450, 1370, 840, 740 and 680 cm^{-1}. Cyaphenine had an ultraviolet absorption band (λ_{max}) at 272 mμ ($\log \varepsilon = 4.22$) in 95% aqueous ethanol.

The Nitration of Cyaphenine.—A mixed acid, that is, a mixture of aqueous nitric acid (sp. wt. of 1.42, 0.09—0.63 mol.) and concentrated sulfuric acid (sp. wt. of 1.84, 0.09 mol.), was added, drop by drop and at 0°C, to a solution of cyaphenine (0.02 mol., 6.18 g.) in 95% sulfuric acid (29 ml.). The reaction mixture was then continuously stirred under the conditions listed in Table I. The crystals separated after the completion of reaction were washed with cold water and recrystallized from nitrobenzene. The number of nitiro groups per molecule of the resulting nitrocyaphenine (n_{NO_2}) was determined by infrared spectrophotometry (the concentration of nitrocyaphenine in the KBr disk: 0.25%); it was then calculated by means of the following equation:

$$n_{NO_2} = 0.89 \frac{T_{1350} - T_{1420}}{T_{1370} - T_{1420}}$$

where the T's are the transmittances (%) at the subscripted wave numbers and where the coefficient of "0.89" is a correction factor obtained from standard nitrated cyaphenine, for which the n_{NO_2} value was calculated by the estimation of the nitrogen content according to the Dumas method.

The Sulfonation of Cyaphenine.—A mixture of 50% oleum (7 g.) and cyaphenine (1.5 g.) was reacted while being stirred under the conditions listed in Table III. The resulting yellow viscous liquid was then poured into a mixture of ice and water and neutralized with sodium carbonate. The slurry, obtained on the evaporation of water, had 95% ethanol added, until the concentration of ethanol became 50%. The separated sodium sulfate was then filtered off, the filtrate being evaporated to dryness. The residue was extracted with 50% aqueous ethanol. The extract was then evaporated to dryness and extracted again with 70% aqueous ethanol. The extract was condensed, and a considerable amount of 95% aqueous ethanol was added. The precipitate of a colorless crystaline product, sodium cyapheninesulfonate, was collected by filtration, washed with ethanol, and dried. For the determination of sulfonyl groups in the resulting sodium cyapheninesulfonate, the isolated sulfonate was converted into the acid with cation exchange resin, Amberlite IR 120 (H^+); the sulfonic acid solution thus obtained was titrated with a standard aqueous solution of sodium hydroxide.

Results and Discussion

The Nitration of Cyaphenine.—Cyaphenine which had been prepared from benzonitrile according to the Cook-Jones method[2] was nitrated with a mixture of sulfuric and nitric acids. The nitrations under various conditions (i. e., reaction time, temperature, and concentrations of reactants) are listed in Table I. It is obvious that the nitration of cyaphenine is rather difficult because of the electron-attracting

Table I. Nitration of cyaphenine with a mixture of nitric and sulfuric acids

(HNO_3)/(Cyaphenine) mol. : mol.	Temp. °C	Time hr.	Yield g.	Number of NO_2[a]
4.5	0	3	8.2	1.4
22.5	0	3	8.6	1.7
31.5	0	3	8.6	1.8
4.5	20	0.5	8.2	1.1
4.5	20	1	7.9	1.5
4.5	20	2	8.2	1.3
4.5	20	5	8.5	1.5
4.5	20	7	7.9	1.7
4.5	20	10	8.0	1.4
4.5	−20	3	8.4	1.1
4.5	−10	3	8.2	1.2
4.5	10	3	8.2	1.4
4.5	40	3	7.8	1.7
4.5	60	3	7.0	1.1

a) The number of NO_2 group per molecule of product.

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nature of triazine, yielding a product with no more than two nitro groups. Trinitrocyaphenine is not obtained because of the deactivation of a residual phenyl group by the presence of two nitro groups as well as the triazine ring.

The nitrated cyaphenine shows new infrared absorptions (KBr disk), at 1350 (s), 820 (w), and 800 (s) cm^{-1}, not found in the spectrum of original cyaphenine. The absorption bands at 800 and 820 cm^{-1} correspond to meta- and para-substituted benzenes respectively; the band at 1350 cm^{-1} is assigned to the nitro group. Since the band at 820 cm^{-1} (para) is weak, the *p*-nitrocyaphenine content in the product should be much lower than that of the *m*-isomer.

The Decomposition of Cyaphenine and Nitrocyaphenine with Hydrochloric Acid.—Frankland and Evans reported, without a detailed description, the conversion of cyaphenine to benzoic acid and ammonia[6] by heating cyaphenine with concentrated hydrochloric acid in a sealed tube to 250°C. Our experiment to confirm this decomposition gave benzoic acid in a 93.2% yield under suitable conditions, as is indicated in Table II. However, cyaphenine was not converted to benzoic acid when heated in an acidic aqueous solution (2.9% sulfuric acid), even in the presence of potassium permanganate at 100°C for 24 hr.

Table II. Decomposition of cyaphenine with aqueous hydrochloric acid in a sealed tube at 250°C for 6 hr.

Cyaphenine g.	35%HCl ml.	Yield of $PhCO_2H$ g.	Conversion %
0.31	1	0.201	55.0
0.16	1	0.157	85.3
0.51	1	0.170	93.2

In the case of nitrocyaphenine, a similar decomposition was unsuccessful; green or brown solid materials of an unknown structure were obtained, but no nitrobenzoic acid was isolable.

The Sulfonation of Cyaphenine.—The sulfonation of cyaphenine with oleum under varying conditions are listed in Table III. Cyaphenine-trisulfonic acid was obtained by heating it at 100°C for 0.5 hr. However, a part of the introduced sulfonyl groups may be eliminated when the reaction mixture is kept standing after the completion of the reaction.

Absorption bands at 790 (s), 1040 (s), and 1100 (s) cm^{-1} in the infrared spectrum (KBr disk) of sodium cyaphenine-trisulfonate may be assigned to the meta-substituted phenyl group. In addition, the lack of absorption at 800—820 cm^{-1} shows the absence of the para-substituted phenyl group. Therefore, the sulfonation of cyaphenine is different from the nitration in that there is no para-substitution.

Table III. Sulfonation of cyaphenine with oleum (50% SO_3)

Temp. °C	Time hr.	Yield g.	Number of SO_3H[a]
40	6	1.7	2.6
60	6	2.7	2.6
100	6	2.4	2.3
100	0.35	2.0	2.7
100	0.5	2.0	3.0
100	1.2	2.2	2.8
100	2	2.1	2.8
100	4	2.4	2.7

a) The number of sulfonyl group per molecule of product.

Summary

The nitration of cyaphenine (2, 4, 6-triphenyl-1, 3, 5-triazine) with a mixture of nitric and sulfuric acids has been found to give products with mostly meta- and partly para-substituted benzene rings. The composition of products varies with the varying reaction conditions. *m, m'*-Dinitrocyaphenine is the product of the highest number of nitro groups. The sulfonation of cyaphenine with oleum gives trisulfonated cyaphenine at meta-positions of benzene rings; it suffers desulfonation when left standing in the reaction mixture for a long time.

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