Communications

See Editorial, *J. Org. Chem.*, **37**, No. 19, 4A (1972).

Friedel–Crafts Reactions of Amino Compounds. New Method for the Preparation of 1-Amino-4-hydroxyanthraquinone[1]

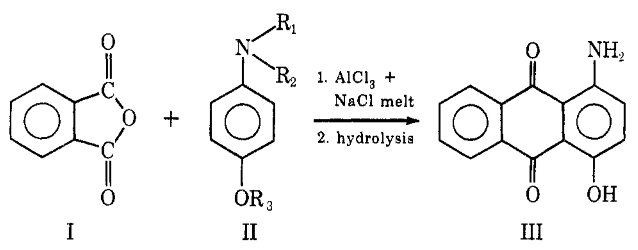
Summary: Friedel–Crafts reaction of substituted amines has resulted in a new method for the preparation of 1-amino-4-hydroxyanthraquinone.

Sir: The Friedel–Crafts acylation and cyclization reactions have been used for the direct synthesis of anthraquinones and related compounds.[2-5] However, no aminoanthraquinones have yet been prepared by this method where amino derivatives are directly involved as reaction species.

We wish to report the direct synthesis of 1-amino-4-hydroxyanthraquinone (III), commercially known as Celliton Fast Pink B and used as dye for all classes of fibers.[6] The dye has been prepared earlier from anthraquinone derivatives.[7-9]

The reaction of 4-aminophenol and its derivatives was studied in detail where aminophenols IIa–e were condensed with phthalic anhydride I in presence of $AlCl_3$–NaCl melt (Scheme I).

Scheme I



IIa, $R_1 = R_2 = R_3 = H$
b, $R_2 = R_3 = H$; $R_1 = COCH_3$
c, $R_2 = R_3 = H$; $R_1 = COC_6H_5$
d, $R_1 = R_2 = R_3 = COC_6H_5$
e, $R_1 = R_2 = R_3 = COCH_3$

The reactions were carried out at various temperature ranges, between 170 and 210°, and time durations, 15 to 45 min, yielding compound III, 3% from 4-aminophenol (IIa), 10% from *N*-acetyl-4-aminophenol (IIb), 15% from *N*-benzoyl-4-aminophenol (IIc), 20% from tribenzoyl-4-aminophenol (IId), and 45% from triacetyl-4-aminophenol (IIe).

1-Amino-4-hydroxyanthraquinone (III) from IIe.—An intimate slurry of IIe (4 g) and I (4 g) was gradually added with stirring to a clear melt of anhydrous $AlCl_3$ (40 g) and NaCl (10 g) at 170–180°. The mixture was further stirred at 200–210° for 45 min, cooled, and digested with 2 *N* hydrochloric acid. The reaction product was thoroughly washed with water and dried and its benzene extract was chromatographed over silica gel. The pink band obtained, after eluting the column with benzene–acetone mixture (90:10), and on crystallization from benzene gave pink plates III, 2.5 g, mp 215°. The purity of the compound was checked by tlc (R_f 0.32; silica gel–benzene), analytical data (Calcd for $C_{14}H_9O_3N$: C, 70.29; H, 3.76; N, 5.85. Found: C, 70.42; H, 3.69; N, 5.78.) and spectral results [ir ν_{max} 3500, 3400, 1640, 1600, 1540, 1470, 1250, 1190, 840, 800, 740 cm^{-1}; mass spectrum ($M\cdot^+$) *m/e* 239, 212, 211, 183, 182, 107, 100, 76].

It was observed that fully protected amino groups yield better results as is evident from reactions with IId and IIe. It is interesting to note that IIe gave the best yield (45%) of the anthraquinone III. The lesser yield of III with IId may possibly be due to steric factor, the benzoyl group shielding the reactive center.

Acknowledgments.—We are indebted to Professor R. C. Kapoor for providing facilities and to Professor Paul J. Scheuer, University of Hawaii, for spectral analysis.

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Received December 1, 1972

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[1] Presented in part at the Chemists Convention Bombay, India, 1971.

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Preparation of 7-*cis*-Ionyl and -Ionylidene Derivatives and Other Sterically Hindered Olefins by One-Way Sensitized Geometric Isomerization[1]

Summary: Quantitative preparations of many sterically hindered olefins have been achieved by selective triplet sensitization.

Sir: The severe steric hindrance (methyl–methyl or methyl–hydrogen interaction) present in the 7- and 11-cis isomers of vitamin A and carotenoids once cast doubt on their possible existence,[3] but, since then, 11-cis vitamin A (the less hindered of the two) and other compounds with similar steric interactions have been routinely prepared by selective hydrogenation of the corre-

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[1] Photochemistry of Polyenes. III. The material on which this communication is partially based was presented in a plenary lecture at the 23rd IUPAC Congress, Boston, Mass, July 1971. The proceedings of this congress have been published.[2]

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