

NITRO DERIVATIVES OF PHLOROGLUCINOL

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A literature review reveals that no adequate method is available for the direct nitration of phloroglucinol to mononitro and dinitro derivatives, although several procedures are listed for the trinitro compound.

This paper deals with: (a) the direct nitration of phloroglucinol to produce mono-, di-, and tri-nitrophloroglucinols; (b) ultraviolet and infrared absorption spectra of these compounds; and (c) a procedure for obtaining the trimethyl ether derivatives directly from the nitrophloroglucinols. The properties of these ethers agree with those prepared indirectly from mononitrophloroglucinol and diazomethane (1), and from dinitro- and trinitro-tribromobenzenes and sodium methoxide (2, 3).

DISCUSSION OF RESULTS

The ultraviolet spectra show the similarity in structure of the mono-, di-, and tri-nitrophloroglucinols (Fig. 1), with a maximum at 353, 404, and 390 $m\mu$, respectively. Phloroglucinol has a maximum at 268 $m\mu$ and the curve compares favorably with that recorded in methanol on a Cary recording instrument (4).

A greater similarity is also noted in the infrared spectra (Fig. 2), where hydroxyl absorption is indicated at 3.20 μ ; —C=C— at 6.05 μ ; and nitro groups at 6.25, 6.43, and 7.65 μ . A Nujol mull of phloroglucinol reveals an hydroxyl absorption at 3.13 μ , Nujol at 6.84 μ and 7.28 μ and in general compares favorably with a spectrum of phloroglucinol obtained photographically (5). The assignments indicated above for the various absorption maxima are those which seem logical for the compounds involved, following assignments ascribed by other workers on similar compounds (5). Hydroxyl absorption decreases in the series of increasing nitro groups and is absent altogether in the trinitrophloroglucinol, confirming the opinion that all the hydroxyl groups are completely chelated with the nitro groups of the latter compound. It is interesting to note the disappearance of the C—H absorption (3.2 μ) as the nitration increases. Also the lack of absorption at 5.8–5.9 μ might suggest that no carbonyl groups are present in the structure of phloroglucinol molecules. This fact is noteworthy because many textbooks discuss a keto-enol equilibrium for this compound.

EXPERIMENTAL

Absorption spectra. Ultraviolet absorption spectra were obtained with a model DU Beckman quartz spectrophotometer. Infrared absorption spectra were obtained from a recording Baird spectrophotometer Model B (NaCl prism).

Mononitrophloroglucinol (I). Anhydrous phloroglucinol (4 g.) was swirled with 60 ml. of dilute sulfuric acid (1:1) for three minutes. A mixture of 4.2 ml. of concentrated nitric acid and 20 ml. of dilute sulfuric acid (1:1) was cooled to 20° and added slowly. The solution darkened as it was stirred for one hour, and a rust-colored product formed. The mixture was then poured onto 80 g. of crushed ice. The precipitate was filtered and mixed with 30 g. of crushed ice, allowed to stand for 15 minutes, filtered, dried, and recrystallized. Yield 3.8 g. of red-orange needles, m.p. 183–185°.

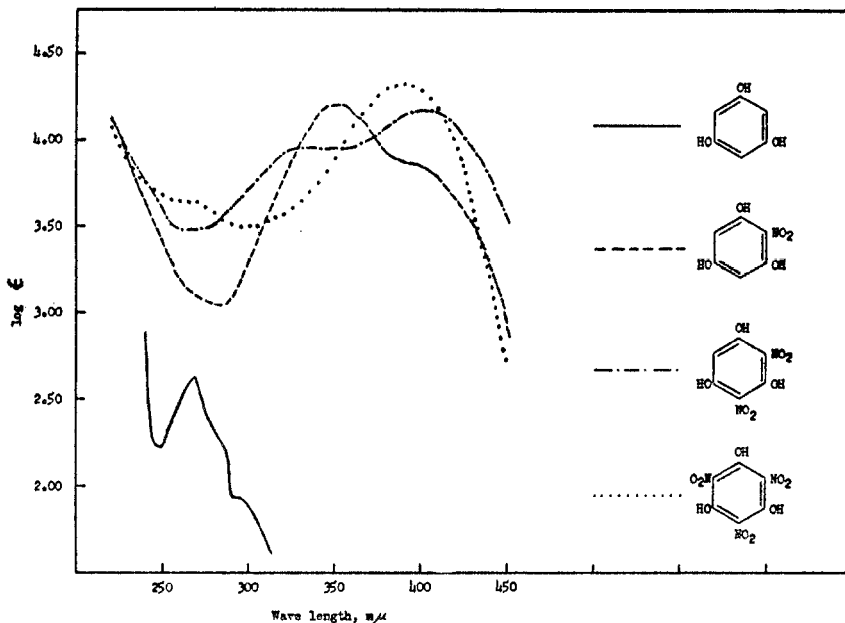


FIG. 1. ULTRAVIOLET ABSORPTION SPECTRA OF NITROPHLOROGLUCINOLS.

Anal. Calc'd for $C_6H_6NO_6$: C, 42.2; H, 2.9; N, 8.2.

Found: C, 42.0; H, 2.9; N, 8.1.

Dinitrophenol (II). Anhydrous phenol (50 g.) was mixed with 2.5 liters of dilute sulfuric acid (1:1) and stirred for three minutes. Then a mixture of 51 ml. of concentrated nitric acid and 250 ml. of concentrated sulfuric acid was added in small portions with stirring. In 35 minutes there was an increased evolution of gas and the solution changed to a deep ruby-red color. After stirring for five hours it was poured onto 800 g. of crushed ice. The filtered brown precipitate was made into a paste with ice-water and filtered. Any unreacted mononitro derivative was removed by boiling with 200 ml. of water and filtering while hot; this left behind 36 g. of a tan residue. Recrystallization from 4.5 liters of boiling water yielded 18 g. of light yellow needles, m.p. 205–206°.

Anal. Calc'd for $C_6H_4N_2O_7$: C, 33.3; H, 1.85; N, 12.9.

Found: C, 33.7; H, 1.8; N, 12.6.

Trinitrophenol (III). Following directions previously reported (6) we obtained 3 g. of the trinitrophenol; yellow needles, m.p. 165–166°.

Trimethyl ethers of the nitrophenols. The respective nitrophenol (5 g.) was mixed with 12.5 g. of sodium carbonate and 100 ml. of methyl sulfate, and the mixture was heated in an oil-bath at 125° for 45 minutes, with stirring. The resulting dark liquid was poured into cold water, made alkaline with sodium hydroxide solution, heated just below boiling, and cooled to room temperature. The filtered precipitate was treated with 30 ml. of acetone to extract the trimethyl ether. The ethers were recrystallized from methanol to give yellow needles.

| Trimethyl Ether of | Observed m.p., °C. | Reported m.p., °C. | Literature Reference |
|--------------------|--------------------|--------------------|----------------------|
| I | 152 | 151 | (1) |
| II | 164 | 165 | (2) |
| III | 76 | 75 | (3) |

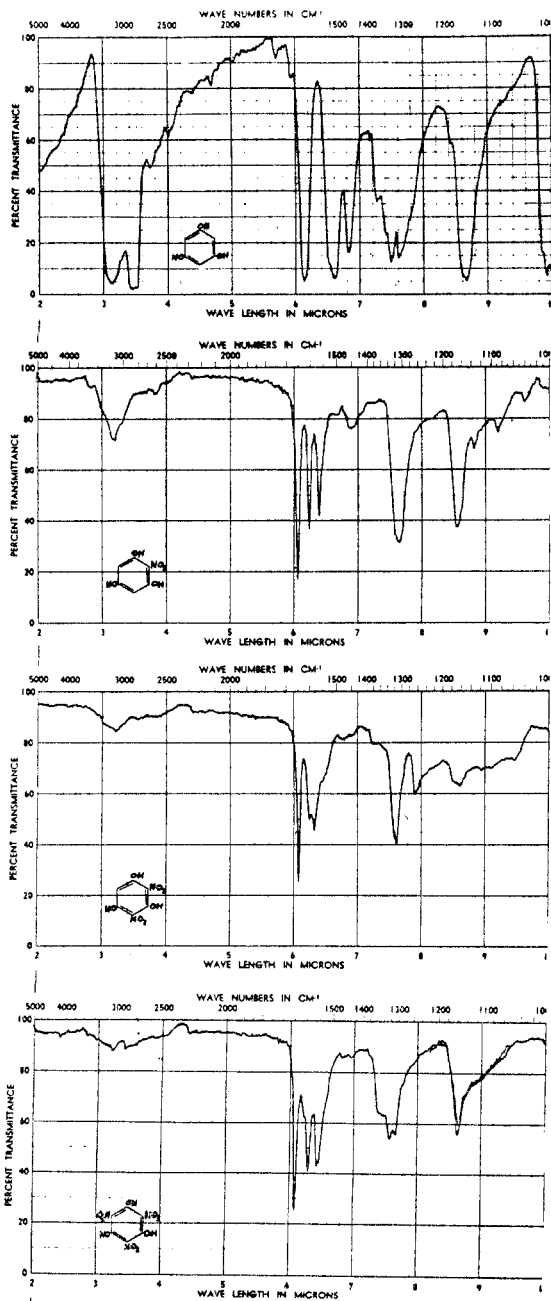


FIG. 2. INFRARED ABSORPTION SPECTRA OF NITROPHLOROGLUCINOLS.

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