

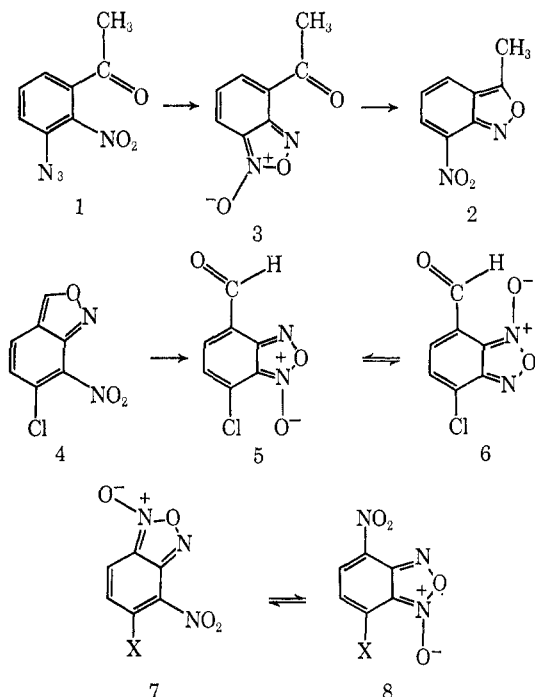
Heterocyclic Rearrangements. XII.¹
The Formation of a Formylbenzofurazan
Oxide from a Nitroanthranil

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A few years ago a new anthranil synthesis was reported, in the decomposition of the nitroazidoacetophenone (1) to form 3-methyl-7-nitroanthranil (2), via the presumed intermediate acetylbenzofurazan oxide (3).²



We now find that nitration of 6-chloroanthranil leads to its 7-nitro derivative 4, which rearranges on heating to 7-chloro-4-formylbenzofurazan oxide (5). The nmr spectrum of 4 (in acetone) shows, as expected, an AB system (τ_A 1.80, τ_B 2.63, J_{AB} = 9.5 Hz) and a singlet (τ -0.02). Compound 5, on the other hand, gives at room temperature a very broad, indistinct spectrum, owing to the tautomerism of the furazan oxide ring, which places the formyl and ring protons in rapidly changing environments. On cooling to 0°, 5 shows two distinct AB spectra (τ_A 1.77, τ_B 2.31, J_{AB} = 8.0 Hz; $\tau_{A'}$ 2.01, $\tau_{B'}$ 2.12, $J_{A'B'}$ = 7.0 Hz) and two singlets from the aldehyde groups (τ -0.30; τ' -0.50), while at 80° one AB and a singlet are observed. The ratio of tautomers (5:6) was ca. 3:4 at 0°, the assignment of spectra to isomers (primed symbols refer to

structure 6) being made on the basis of the chemical shifts of the formyl protons (that in 6 is expected to be deshielded owing to the proximity of the N-oxide group) and of the aromatic protons.³

The rearrangement of nitrobenzofurazan oxides (7 \rightleftharpoons 8) has been described, and the apparent completeness of the conversion of 7 (X = Cl) into 8 (X = Cl) was suggested to be due to steric inhibition of resonance of the nitro group with the ring in 7.^{4,5} The present work establishes the first example of a benzofurazan oxide being formed by a rearrangement of this type from a system other than another benzofurazan oxide; probably steric inhibition again provides the energy to drive the rearrangement in the unexpected direction.

Experimental Section

Melting points are uncorrected. Nmr spectra of acetone solutions were measured on a Perkin-Elmer R10 60-MHz instrument with a variable-temperature probe.

6-Chloro-7-nitroanthranil (4).—6-Chloroanthranil⁶ (1.0 g, 0.065 mol), mp 64° (lit.⁶ mp 65°), was carefully dissolved in 10 cc of cold (0°), concentrated sulfuric acid. To the stirred solution at -5° was added dropwise a solution of potassium nitrate (0.9 g, 0.1 mol) in 20 cc of H₂SO₄. The mixture was stirred at 0° for 1/2 hr, then at 50° for a further 0.5 hr. The red solution was poured onto ice and extracted with methylene chloride. The organic layer was washed with water, dilute Na₂CO₃ solution, and again with water and then dried (Na₂SO₄). Removal of the solvent left a dark orange solid which was carefully crystallized from ethanol as orange plates (0.5 g, 40%): mp 96–97°; ir (Nujol) 1642 (anthranil), 1530, and 1350 cm⁻¹ (NO₂).

Anal. Calcd for C₇H₃ClN₂O₂: C, 42.3; H, 1.5. Found: C, 42.0; H, 1.5.

7-Chloro-4-formylbenzofurazan Oxide (5 \rightleftharpoons 6).—6-Chloro-7-nitroanthranil (0.9 g) was heated 30 min under reflux in 20 ml of glacial acetic acid. The solution was cooled, and an equal volume of water was added. The precipitated solid was crystallized from aqueous ethanol as yellow prisms (0.7 g, 77%): mp 103–104°; ir (Nujol) 1692 (C=O), 1618, 1580, 1545, and 1490 cm⁻¹ (benzofurazan oxide).⁷

Anal. Found: C, 42.5; H, 1.2.

Registry No.—4, 22950-43-2; 5, 22950-44-3.

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Reaction of Substituted 2-Carboethoxyacetyl-
aminopyridines and Similar Compounds with
Triethyl Orthoformate and Zinc Chloride

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In an attempt to prepare the ethoxymethylene derivative of 2-(carboethoxyacetyl-amino)-5-chloropyr-

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