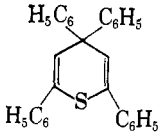
converted to sulfoxide. The shifted position for the ring hydrogens could then be due to a direct chemical shift by the electron-attacting sulfoxide group. The downfield shift for the methyl group may be analogous to that observed by Morin[4] in penicillin sulfoxide and indicates that the 2-methyl group is *cis* to the sulfoxide oxygen.[5]

The crystalline tetraphenylthiopyran, m.p. 157°, reported earlier[6] has been confirmed as the 2,4,4,6 isomer (IV) by n.m.r. bands at 2.87 and 4.00 τ in the ratio of 10:1.[6] Efforts to isolate a pure sample of the 2,2,4,6 isomer from the yellow oily residues after crystallization of IV were unsuccessful.[7]



IV

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The Polynitration of Indolines. 5,7-Dinitration

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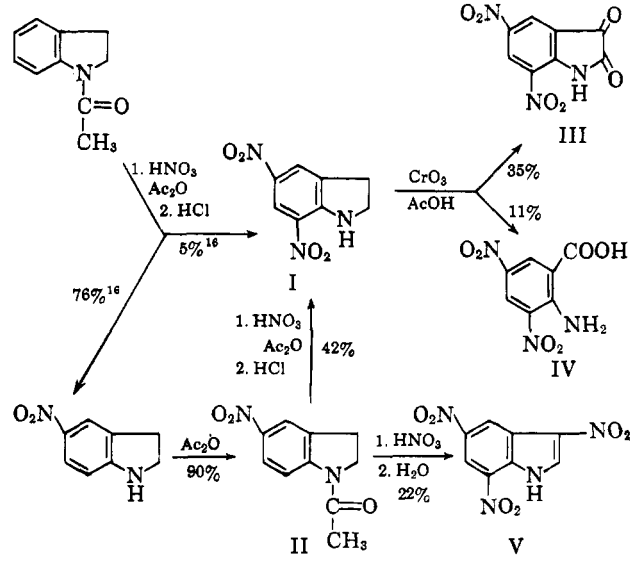
As indoles do not nitrate in the 7-position,[2] synthetic approaches to 7-nitroindoles have depended largely on ring closure to a benzene ring in which a nitro group has been prelocated in the potential 7-position.[3-14] The recently described[15,16] general method for preparation of indoles containing a nitro group in the benzene ring, by nitration of the corresponding indolines following by dehydrogenation, has only been applied to the synthesis of 5- and 6-nitroindoles. An adaptation of the indoline method, involving nitration of the indole–sodium bisulfite adduct and subsequent alkaline hydrolysis, recently has been used, however, for the synthesis of both 5- and 7-nitroindole.[17] Evidence for 5,7-dinitration of an acylindoline is available from an earlier example: Strychnine[18] is degraded by 20% nitric acid[19] (in a reaction which involves nitration, oxidation, and hydrolysis) to 5,7-dinitroindole-2,3-dicarboxylic acid (dinitrostrycholcarboxylic acid),[20] which undergoes decarboxylation to what was proved to be 5,7-dinitroindole-2-carboxylic acid (dinitrostrychol),[4,20,21] or further nitration in fuming nitric acid to 3,5,7-trinitroindole-2-carboxylic acid (trinitrostrychol).[4,20]

Nitration of 1-acetylindoline is reported to give 5-nitroindoline (64[22]–74[16]%), and a dinitroindoline (5%) of melting point 243–244°, which was assumed to be 5,7-dinitroindoline (I).[16] In this paper we report proof that dinitration of 1-acetylindoline and mononitration of the presumed intermediate, 1-acetyl-5-nitroindoline (II), gives 5,7-dinitroindoline (I). Chromic acid oxidation of the dinitroindoline gave as degradation products the known compounds, 5,7-dinitroisatin (III) and 3,5-dinitroanthranilic acid (IV). Attempts to dehydrogenate I to the still unknown 5,7-dinitroindole were unsuccessful, either with palladium on carbon (also tried on the acetyl derivative of I) or with tetrachloro-1,2-benzoquinone, compound I being recovered unchanged in moderate yields.

Addition of 1-acetyl-5-nitroindoline to fuming nitric acid gave a trinitro derivative, which, as indicated by its low hydrogen content, is an indole. The compound is colorless in the solid state, but appears to dissociate as an acid in ethanol solution, with the longest wavelength absorption as a broad band at 413 mμ. The compound is tentatively assigned the structure 3,5,7-trinitroindole (V), and is believed to be formed by dehydrogenation of a probable intermediate, 1-acetyl-



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5,7-dinitroindoline, followed by nitration of the resulting indole at the now available 3-position,[2] and subsequent deacetylation. The compound was resistant to chromic acid oxidation.

Experimental

Melting points were determined on a calibrated Fisher-Johns hot stage.

1-Acetyl-5-nitroindoline (II).—A solution of 5-nitroindoline[16] (8.63 g., 0.0525 mole) in acetic anhydride (100 cc.) was refluxed for 1 hr., then cooled, and the resulting mixture poured into an excess of water. The mixture was stirred until all of the acetic anhydride dissolved. The precipitate was recrystallized from acetone–methanol, yielding pale yellow needles (9.74 g., 90%), m.p. 177–179°; lit.[22] m.p. 173.5–175.5°; $\lambda_{max}^{95\%\ EtOH}$ mμ (log ε): 231 (4.01), 340 (4.12); ν_{NH}^{Nujol} none, $\nu_{C=O}^{Nujol}$ 1667 (s), $\nu_{NO_2}^{Nujol}$ 1513 (s), 1319 (s) cm.$^{-1}$.

1-Acetyl-5,7-dinitroindoline.—Fuming nitric acid (*d* 1.5, 6 cc.) was added dropwise, with stirring, at a temperature maintained below 16°, to a mixture of 1-acetyl-5-nitroindoline (3.00 g., 0.0145 mole) and acetic anhydride (70 cc.) cooled initially to 10° in an ice bath. The resulting solution was then removed from the ice bath and stirred until the temperature reached 40°, at which point it was poured into ice–water and the mixture stirred until all of the acetic anhydride dissolved. The resulting precipitate was recrystallized from acetone–methanol, giving yellow needles (1.87 g., 51%), m.p. 207–212°. Sublimation at 200° (1 mm.) and recrystallization of the sublimate from acetone–methanol yielded the analytical sample, m.p. 210–212°; $\lambda_{max}^{95\%\ EtOH}$ mμ (log ε): 226 (4.23), 265 infl. (3.75), 345 (4.02); $\nu_{C=O}^{Nujol}$ 1695 (s), ν_{NO}^{Nujol} 1546 (s), 1520 (s), 1344 (s), 1299 (vs) cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_9N_3O_5$ (251.20): C, 47.81; H, 3.61; N, 16.73. Found: C, 48.05; H, 3.73; N, 16.45.

5,7-Dinitroindoline (I). A. From 1-Acetylindoline.—The compound was prepared,[16] along with 5-nitroindoline, by nitration of 1-acetylindoline, except that the procedure for purification of the dinitro product was changed. The crude dinitro product was not recrystallized from xylene but was dissolved in benzene–ethyl acetate (4:1 by volume) and placed on a column of neutral alumina (25 g.) which had been packed wet with petroleum ether (b.p. 60–68°). Elution with 4:1 benzene–ethyl acetate gave in 2% yield orange needles, m.p. 244–245°; lit.[16] 5%, yellow crystals, m.p. 243–244°; $\lambda_{max}^{95\%\ EtOH}$ mμ (log ε): 218 (4.03), 263 (4.00), 364 (4.15), 404 infl. (3.90); ν_{NH}^{Nujol} 3290 (m), $\nu_{NO_2}^{Nujol}$ 1534 (ms), 1497 (ms), 1335 (ms), 1312 (s) cm.$^{-1}$.

Anal. Calcd. for $C_8H_7N_3O_4$ (209.16): C, 45.94; H, 3.37; N, 20.09. Found: C, 46.06; H, 3.42; N, 19.86.

B. From 1-Acetyl-5-nitroindoline.—Fuming nitric acid (*d* 1.5, 4 cc.) was added dropwise, with stirring, to a solution of 1-acetyl-5-nitroindoline (2.00 g., 0.00970 mole) in acetic anhydride (50 cc.) kept at 15°. The yellow solution was then stirred at room temperature for 0.75 hr., during which time it warmed up to a maximum temperature of 35°. The solution was poured into water and stirred until all of the acetic anhydride had dissolved. The resulting yellow precipitate was refluxed in concentrated hydrochloric acid (50 cc.) for 1 hr. and the mixture cooled. The precipitate was recrystallized from acetone–ethanol, with charcoal, yielding light orange needles (0.85 g., 42%), m.p. 244–245°. There was no depression in m.m.p. 244–245° with the sample prepared from 1-acetylindoline, and the infrared spectra in Nujol were identical.

Oxidative Degradation of 5,7-Dinitroindoline.—A solution of chromium(VI) oxide (1.50 g., 0.0150 mole) in water (5 cc.) was added to a suspension of 5,7-dinitroindoline (0.66 g., 0.00316 mole) in acetic acid (100 cc.). The resulting black solution was stirred at room temperature for 40 hr., and then poured into an excess of water. The green aqueous solution was extracted with ethyl acetate. The ethyl acetate solution was extracted with aqueous saturated sodium bicarbonate until carbon dioxide was no longer evolved. The ethyl acetate solution was then concentrated to a small volume, and petroleum ether (b.p. 60–68°) was added. The resulting orange precipitate was recrystallized from ethyl acetate–benzene, with charcoal, yielding **5,7-dinitroisatin (III)** as orange-yellow crystals (0.26 g., 35%), m.p. 209–210°; lit.[23,24] m.p. 209–210°; $\lambda_{max}^{95\%\ EtOH}$ mμ (log ε): 239 (4.07), 257 infl. (4.02), 323 (4.06), 393 (3.42); ν_{NH}^{Nujol} 3290 (m), $\nu_{C=O}^{Nujol}$ 1773 (s), 1754 (ms), 1631 (s), $\nu_{NO_2}^{Nujol}$ 1558 (s), 1541 (ms), 1337 (vs), 1289 (s) cm.$^{-1}$. There was no depression in m.m.p. 209–210° with a sample of m.p. 209–210° prepared[23] by nitration of isatin, and the infrared spectra in Nujol were identical.

The sodium bicarbonate extracts were acidified to pH 2 with aqueous hydrochloric acid, and the resulting solution was extracted with ethyl acetate. The ethyl acetate extracts were dried over magnesium sulfate and concentrated until only acetic acid remained as a solvent, and then water was added. The brown precipitate was recrystallized from methanol–water, yielding **3,5-dinitroanthranilic acid (IV)** as golden yellow needles (0.08 g., 11%), m.p. 256°; lit.[25,26] m.p. 256°, lit.[27] 265°, lit.[28] 268°; $\lambda_{max}^{95\%\ EtOH}$ mμ (log ε): 237 (4.09), 336 (4.11), 392 (3.87); ν_{NH}^{Nujol} 3370 (m), 3250 (m), $\nu_{C=O}^{Nujol}$ 1672 (s), $\nu_{NO_2}^{Nujol}$ 1515 (ms), 1328 (vs) cm.$^{-1}$.

3,5,7-Trinitroindole (V).—1-Acetyl-5-nitroindoline (6.09 g., 0.0295 mole) was added slowly to fuming nitric acid (*d* 1.5, 24 cc.) at 5° and then the solution was poured into an excess of water. The resulting precipitate was recrystallized twice from acetone–methanol, once with charcoal, yielding white needles (1.67 g., 22%), m.p. 232–233°; $\lambda_{max}^{95\%\ EtOH}$ mμ (log ε): 216 (4.30), 286 (4.11); does not obey Beer's law in the long wave-length region, λ_{max} 413 very broad: $c = 1.444 \times 10^{-4}$ mole/l. (3.03), $c = 6.19 \times 10^{-5}$ mole/l. (3.26), $c = 4.12 \times 10^{-5}$ mole/l. (3.37); ν_{NH}^{Nujol} 3360 (m), $\nu_{NO_2}^{Nujol}$ 1531 (s), 1379 (s), 1344 (s) or 1307 (s), cm.$^{-1}$. The compound is soluble in aqueous 1% sodium hydroxide but not in saturated sodium bicarbonate solution.

Anal. Calcd. for $C_8H_4N_4O_6$ (252.14): C, 38.11; H, 1.60; N, 22.22. Found: C, 38.25; H, 1.70; N, 21.76.

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The Free-Radical-Induced Reaction of Ethylene with 1,1,2,2-Tetrabromoethane

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Attempts to telomerize ethylene with 1,1,2,2-tetrabromoethane (TBE) to obtain compounds of the type $CHBr_2CHBr(C_2H_4)_nBr$ did not give rise to these materials but produced α,ω-dibromo *n*-alkanes. These appear to be products of the indirect telomerization of ethylene with bromine. Thus, when ethylene and TBE reacted under pressure in the presence of benzoyl peroxide at 100° the reaction product contained 1,2-dibromoethylene, 1,2-dibromoethane, 1,4-dibromobutane, 1,6-dibromohexane (putative), and bromobenzene. The latter undoubtedly originated from the initiator. Because of its low concentration, that component of the product assumed to be 1,6-dibromohexane could not be positively identified.

The relatively high concentration of 1,2-dibromoethylene and the fact that no other high-boiling materials were shown by gas chromatography clearly indictates that the expected telomerization between TBE and ethylene did not occur. Similar results were obtained in reactions between TBE and ethylene with thermal initiation at 200°.

The presence of both 1,2-dibromoethylene and 1,2-dibromoethane can be explained by the decomposition