benzenesulfonic acid in 125 ml. of ethyl acetate. The precipitate was crystallized from ethyl acetate–ethanol (8:1) to give 19.9 g. (70.3%) of very slightly pink crystals, m.p. 123.5–124.5°.

Anal. Calcd. for $C_{14}H_{21}O_3NS$: C, 59.33; H, 7.47; N, 4.94. Found: C, 59.19, 59.07; H, 7.32, 7.30; N, 4.70, 4.69.

Polymerizations.—The amine and catalyst were weighed into a 23 × 196 mm. test tube under nitrogen. This was chilled to $-80°$, alternately evacuated and flushed with nitrogen, and was finally evacuated and sealed. The ampules were suspended in the vapor of boiling *m*-cresol or methyl salicylate to maintain them at 200° or 222°, respectively. They were shaken after a few minutes to ensure dissolution of the catalyst.

Under these conditions, a mixture of 10.0 g. of 1,4-diazabicyclooctane and 27.8 mg. of its di(hydrobenzenesulfonate) polymerized rather quickly at 200°. A solid white plug was noted after 1 hr., but heating was continued for an additional 9.7 hr. The tough white plug was broken up with a knife and hammer and extracted with ether to give 9.60 g. (96%) of white polymer, η_{inh} (*m*-cresol) 1.90. On a heated bar it blackened at 250° but did not melt below 390°.

Anal. Calcd. for $(C_6H_{12}N_2)_x$: C, 64.24; H, 10.79; N, 25.0. Found: C, 63.75, 63.76, 63.58, 63.48; H, 10.40, 10.47, 10.51, 10.41; N, 24.0, 24.3, 24.7.

A mixture of 10.0 g. of 3-azabicyclo[3.2.2]nonane and 105.1 mg. of its di(hydrobenzenesulfonate) became sirupy when heated for 71 hr. at 222°. Cooling, extraction of the product with ether, and drying gave 3.20 g. (32%) of white polymer, polymer melt temperature 115–130°.

Anal. Calcd. for $(C_8H_{16}N)_x$: C, 77.99; H, 10.63. Found: C, 75.95, 75.72; H, 11.79, 11.77.

The polymer appeared to be hygroscopic.

Polymer Properties.—Poly-1,4-ethylenepiperazine was obtained as an extremely crystalline white solid, insoluble in nonpolar organic solvents. A typical sample had an inherent viscosity of 1.06 in *m*-cresol and 2.11 in 99% formic acid. The end groups were determined by reaction with 2,4-dinitrofluorobenzene. A polymer of inherent viscosity 1.77 had a number average molecular weight of 8800, assuming reaction at only one end of the chain. The infrared spectrum was very similar to that of the model compound, N,N′-dimethylpiperazine. It showed small amounts of NH and NH^+ but no vinyl groups, so that no ring cleavage had occurred. Refluxing the polymer with aqueous alkali did not decrease its inherent viscosity, so that cross-links by quaternary ammonium linkage were not present.

The polyamine from 3-azabicyclo[3.2.2]nonane had inherent viscosities of 0.30 in *m*-cresol, 0.37 in tetrafluoropropanol, and 0.46 in 99% formic acid.

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2,2′-Diindoxyls

ALFRED HASSNER AND MAKHLUF J. HADDADIN[1]

Department of Chemistry, University of Colorado, Boulder, Colorado

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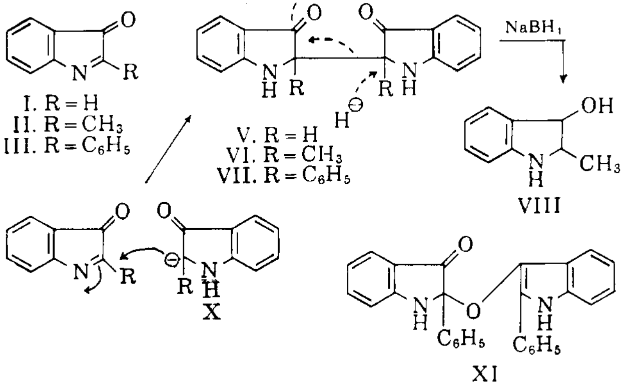
Indoxyl has long been known to be converted to indigo by air in the presence of sodium hydroxide,[2] but the presumed intermediate indoleninone (I) has never been isolated. Recently Neunhoeffer and Lehmann[3] reported the isolation of what they believed to be an indoleninone, namely 2-methylindoleninone (II), as a stable compound. The compound had a molecular weight of 280 in boiling dioxane (calcd. 147) and no spectroscopic data were reported to substantiate the assigned structure. The indoleninone was obtained from ethyl α-(2-carbethoxyanilino)propionate upon Dieckmann condensation, decarbethoxylation and air oxidation of the intermediate 2-methylindoxyl without isolation of intermediates.[2] Our experience with 2-substituted indoxyls[4] suggested that compounds of type II are very unstable and can not be isolated. Furthermore, in 1912, Kalb and Bayer[5] reported 2-phenylindoleninone as a red solid unstable to water or base, while Neunhoeffer[3] claimed the isolation from aqueous sodium hydroxide of both 2-phenyl- and 2-methylindoleninone as yellow stable materials.

The preparation of Neunhoeffer's "2-methylindoleninone," m.p. 174°, was repeated but the product, m.p. 174°, showed strong N–H absorption at 3400 cm.$^{-1}$ and carbonyl absorption at 1680 cm.$^{-1}$. The ultraviolet spectrum of the product displayed peaks at 395, 255, and 235 mμ characteristic of 2,2-disubstituted indoxyls.[6] The n.m.r. spectrum of the product in deuterated dimethylsulfoxide showed a singlet at 8.52 τ (isolated CH_3) and a weak singlet at 6.74 τ (NH) which shifted on addition of acetic acid. Molecular weight determination (289 ± 30; calcd. 292) confirmed a dimeric structure such as 2,2′-dimethyl-2,2′-diindoxyl (VI). Reduction of diindoxyl VI with sodium borohydride yielded 2-methyl-3-hydroxyindoline (VIII) which gave a positive ferric chloride test. Molecular weight determination showed VIII to be a monomer and this fact was confirmed by n.m.r. A possible path for cleavage of VI on hydride reduction is indicated by dotted arrows. Acidification of hydroxyindoline VIII yielded authentic 2-methylindole.

When the preparation of "2-phenylindoleninone" from ethyl α-(2-carbethoxyanilino)-α-phenylacetate (IX) was repeated according to Neunhoeffer and Lehmann,[3] the product obtained was 2,2′-diphenyl-2,2′-diindoxyl (VII), m.p. 180–181°, rather than 2-phenylindoleninone, m.p. 102°. Kalb and Bayer[5] had observed that 2-phenylindoleninone (III) reacts readily with 2-phenylindoxyl (X) in basic solution to yield a dimer, m.p. 180°, for which they favored structure XI over VII. Both VI and VII were prepared by analogous methods and showed similar infrared and ultraviolet absorptions. This and the fact that diindoxyl VII lacked absorption characteristic of an indole chromophore at 280–290 mμ, render structure XI improbable.



The primary product expected from ring closure of diester IX followed by decarboxylation is 2-phenylin-

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[1] Parke, Davis Research Fellow 1961–1962.

[2] *Cf.* P. L. Julian, E. W. Meyer, and H. C. Printy, "Heterocyclic Compounds," Vol. III, R. C. Elderfield, ed., J. Wiley and Sons, New York, N. Y., 1952.

[3] O. Neunhoeffer and G. Lehmann, *Ber.*, **94**, 2960 (1961).

[4] A. Hassner and M. J. Haddadin, *Tetrahedron Letters*, No. **21**, 975 (1962).

[5] L. Kalb and J. Bayer, *Ber.*, **45**, 2150 (1912).

[6] B. Witkop and J. B. Patrick, *J. Am. Chem. Soc.*, **73**, 2188 (1951).

doxyl (X. R = C_6H_5). Partial air oxidation of the latter to 2-phenylindoleninone (III) and immediate addition of the anion of X to indoleninone III in basic solution, as indicated above, can be postulated to explain the formation of 2,2′-diphenyl-2,2′-diindoxyl (VII). A similar path would explain the conversion of indoxyl (X. R=H) to indigo, via leucoindigo V.[7] While leucoindigo (V) is known[8] to air oxidize very readily to indigo, such a process is impossible for the substituted indoxyls VI and VII.

Experimental

All melting points are uncorrected. Analyses were performed by A. Bernhard, Muelheim, Germany. Infrared spectra were run in potassium bromide on a Beckman IR-5 instrument. Ultraviolet spectra were obtained in methanolic solutions. N.m.r. spectra were determined at 60 Mc. in deuteriochloroform, with tetramethylsilane as an internal standard, on a Varian A-60 spectrometer. Molecular weight determinations were obtained in benzene solution on a Mechrolab vapor pressure osmometer Model 301A.

2,2′-Dimethyl-2,2′-diindoxyl (VI).—Ethyl α-(2-carbethoxyanilino)propionate, b.p. 158–164°/3 mm. (lit.,[3] b.p. 196–202°/12 mm.) was prepared by anhydrous esterification of N-(2-carboxyphenyl)alanine (m.p. 209–211° dec.; ν_{max} 3350, 3300–2500, 1725, 1680, 1570 and 1520 cm.$^{-1}$; lit.,[3] m.p. 208–210°) or by esterification of ethyl α-(2-carboxyanilino)propionate, m.p. 95–102°, obtained in 85% yield from anthranilic acid and ethyl α-bromopropionate in neutral solution at 70°.

A solution of ethyl α-(2-carbethoxyanilino)propionate and sodium ethoxide in anhydrous ethanol was heated for 30 min. and poured into water. Aqueous hydrogen peroxide was added and VI was obtained as a yellow precipitate in 88% yield. It was crystallized from methanol–water and melted at 174–176°; reported[3] as II, m.p. 174°. If the reaction solution was poured into dilute hydrochloric acid or into water that was kept in an oxygen-free nitrogen atmosphere the same product (VI) slowly precipitated.

ν_{max} 3280 (NH, sharp and strong), 1675 and 1610 cm.$^{-1}$; $\nu_{max}^{CHCl_3}$ 3400 (NH), 1680, 1610, and 1580 cm.$^{-1}$. λ_{max} 395, 255 (shoulder), and 235 mμ (ϵ 6080, 17000 and 45300 respectively). Mol. wt.: 289 ± 30 (calcd. 292). N.m.r. singlet at 8.52 τ (CH_3) and weak singlet at 6.74 τ (NH) which shifts on addition of two drops of acetic acid.

Anal. Calcd. for $C_{18}H_{16}O_2N_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 73.50; H, 5.63; N, 9.41.

2-Methyl-3-hydroxyindoline (VIII).—To a solution of 1.0 g. of diindoxyl (VI) in 200 ml. of methanol there was added 3 g. of sodium borohydride. The yellow color of the solution disappeared within 3 hr. The solution was evaporated under reduced pressure and the colorless residue was diluted with water and extracted thoroughly with ether. The dried ether extract upon evaporation yielded an oil that solidified on standing (0.92 g.).

Crystallization of the product from ether in the cold or from ether–petroleum ether (b.p. 30–60°) furnished fine white needles of 2-methyl-3-hydroxyindoline (VIII), m.p. 92–94°. The product gave a red coloration with ferric chloride in methanol within 30 min. at room temperature. Mol. wt.: 156 ± 4 (calcd. 147). The n.m.r. spectrum showed two doublets in the methyl region at 8.75 and 8.82 τ (J = 6.5 and 4 c.p.s., respectively) with approximate relative intensities of 1:4. The proton at C-3 was found at 5.35 and 5.46 τ (J = 6.5 and 4 c.p.s. respectively) and in approximate relative intensities of 1:4. This is in accord with a 1:4 ratio of *cis-trans* isomers in VIII.[9] The N—H and O—H absorption appeared as a single concentration-dependent peak in the 7–7.5 τ region. ν_{max} 3200–3000 (NH, OH, broad) and 1610 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{11}ON$: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.23; H, 7.45; N, 9.30.

Conversion of 2-Methyl-3-hydroxyindoline (VIII) **to 2-Methylindole.**—Five drops of 1 *N* hydrochloric acid were added to a solution of 35 mg. of 2-methyl-3-hydroxyindoline (VIII) in 2 ml. of methanol. After 5 min. the solution was made basic with 5% sodium hydroxide and the turbid solution was extracted with ether. The dried ether solution was evaporated on a steambath to leave an oil that solidified on cooling (29 mg.). Crystallization from methanol–water gave needles of 2-methylindole, m.p. 59–59.5°. Admixture with authentic 2-methylindole showed no depression in melting point. The infrared spectrum of the product was superimposable with that of authentic 2-methylindole.

Ethyl α-Bromo-α-phenylacetate.—This ester, b.p. 115° at 3 mm. (lit.,[10] b.p. 150–151° at 10–15 mm.), was prepared by addition of bromine (30 g.) to a solution of 1 g. of phosphorus pentachloride in 20 g. of phenacetyl chloride on the steambath and pouring the reaction mixture after 48 hr. into absolute ethanol.

Ethyl α-(2-Carboxyanilino)-α-phenylacetate.—Anthranilic acid (15.4 g.) was dissolved in a solution containing 1 equivalent of sodium hydroxide and 27 g. of ethyl α-bromo-α-phenylacetate was added. The mixture was stirred and warmed to 45° for 5 min. and the precipitated white solid was collected by filtration (38 g., m.p. 174–176°). The product was soluble in 5% sodium hydroxide and in concd. hydrochloric acid. On recrystallization from methanol–water ethyl α-(2-carboxyanilino)-α-phenylacetate was obtained in shiny white needles that melted at 180–181°. The compounds exhibits blue fluorescence in methanol. ν_{max} 3400 (NH), 2700–2500 (carboxy OH), 1725 (ester C═O) and 1670 cm.$^{-1}$ (carboxy C═O).

Anal. Calcd. for $C_{17}H_{17}O_4N$: C, 68.21; H, 5.73; N, 4.68. Found: C, 68.29; H, 5.71; N, 4.58.

Ethyl α-(2-Carbethoxyanilino)-α-phenylacetate (IX).—Esterification of ethyl α-(2-carbethoxyanilino)-α-phenylacetate with ethanol in the presence of hydrogen chloride led to diester IX as white needles, m.p. 80–81° (lit.,[3] m.p. 72°). ν_{max} 3410, 1725, 1670 and 1600 cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{21}O_4N$: C, 69.70; H, 6.47; N, 4.28. Found: C, 69.08; H, 6.40; N, 4.45.

2,2′-Diphenyl-2,2′-diindoxyl (VII).—To a solution of 1.5 g. of sodium in 30 ml. of absolute ethanol there was added 6 g. of ethyl α-(2-carbethoxyanilino)-α-phenylacetate (IX). The solution was heated under reflux for 40 min. At the beginning the solution developed a deep red color which later turned yellow. The cooled solution was poured into ice–water into which a stream of air was bubbled, and an immediate yellow precipitate appear. After 15 min. of stirring the yellow solid was collected by filtration, washed, and dried to give 2 g. (80%) of crude product m.p. 140–150°. After crystallization from methanol–water and then from benzene 2,2′-diphenyl-2,2′-diindoxyl (VII) melted at 180–182°, with reddening at 175° (lit.,[5] for VII or XI, m.p. 178–180°, with reddening at 178°). ν_{max} 3500 (NH), 1675 (conj. C═O) and 1620 cm.$^{-1}$. Mol. wt. 400 ± 12 (calcd. 406). λ_{max} 400, 260, and 233 mμ (ϵ 5600, 15000, and 61000, respectively).

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(7) In this connection the isolation by E. Giovannini and Th. Lorenz, *Helv. Chim. Acta*, **40**, 1553 (1957), of indigo, presumably *via* leucoindigo, as a minor product in the reduction of isatin with lithium aluminum hydride should be mentioned.

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(9) A. Hassner and M. J. Michelson, *J. Org. Chem.*, **27**, 3974 (1962), have shown that, in five-membered ring *N*-containing heterocycles, $J_{cis} > J_{trans}$ and the protons absorb at higher field in the *trans* isomer than in the *cis* isomer.

(10) N. Zelinsky and L. Buchstab, *Ber.*, **24**, 1877 (1891).

The Synthesis of Organolead–Sulfur Compounds

MALCOLM C. HENRY AND ADOLF W. KREBS[1]

Organic Chemistry Laboratory, Pioneering Research Division,
Quartermaster R & E Command, Natick, Massachusetts

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Although compounds of the type $(Alk)_3PbSR$ have been described,[2] the corresponding $(C_6H_5)_3PbSR$ deriv-

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(1) Research Fellow sponsored by The Lead Industries Association, 292 Madison Ave., New York, N. Y.

(2) (a) H. McCombie and B. C. Saunders, *Nature*, **159**, 491 (1947); (b) B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, 919 (1949); (c) R. Heap and B. C. Saunders, *ibid.*, 2983 (1949); (d) R. Heap, B. C. Saunders, and G. J. Stacey, *ibid.*, 658 (1951).