

# Reactions of an Indeno[1,2-*b*]indole and Novel Rearrangements of a Dioxodibenz[*b,f*]azocine to Derivatives of 5,12-Diaza- and 5-Oxa-12-aza-chrysene

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Oxidation of 10-benzylidene-5-methyl-5,10-dihydroindeno[1,2-*b*]indole (**2**) gives the dioxodibenz[*b,f*]azocine (**3**), which reacts (probably *via* a transannular interaction) with hydroxylamine and with ethylamine to give oxa-aza- and diaza-chrysene derivatives (**5**) and (**6**); the X-ray crystal structure of (**5**) is reported.

Although the synthesis of the indenoindole (**1**) was published<sup>1</sup> over 60 years ago, no further details of its chemistry have appeared, apart from its recently reported<sup>2</sup> reactions with dimethyl acetylenedicarboxylate.

We have found that (**1**) reacts quantitatively with aromatic aldehydes in the presence of base to give benzylidene derivatives, *e.g.* (**2**) (m.p. 167–168 °C)<sup>†</sup> (from 4-tolualdehyde). With hydrogen peroxide, the product (**2**) ring opens to give the dioxodibenz[*b,f*]azocine (**3**) (m.p. 218–219 °C) in 60% yield. Phenylhydrazine adds to (**3**), and ring closure then affords, in 60% yield, the novel pyrazolodibenzazocine derivative (**4**) (m.p. 223–225 °C). The product (**4**) exhibits in its <sup>1</sup>H n.m.r. spectrum a diagnostic low-field aliphatic AB double-doublet (2H). Treatment of (**3**) with hydroxylamine in pyridine however, failed to yield either an oxime or an oxazole; instead, an intensely fluorescent product was obtained, m.p. 174–175 °C, in 20% yield. Its spectra showed the presence of an ester carbonyl, but no olefinic proton, which suggested the 5-oxa-12-azachrysene structure

(**5**). This was confirmed by a single-crystal X-ray structure analysis;‡ a perspective view of the structure is shown in Figure 1. The remaining product consisted of polymeric material. Refluxing (**3**) with ethylamine in absolute ethanol gave the 5,12-diazachrysene (**6**) (m.p. 222–223 °C), which is also fluorescent, in 50% yield. Other primary amines reacted similarly to give analogous products. The formation of both (**5**) and (**6**), involving the novel transformation of an azocine benzylidene derivative into two fused six-membered heterocyclic rings, may be considered to occur *via* a transannular interaction between a substituent at C-12 (which is formed after attack by the reagent) and the amide carbonyl group, resulting in cleavage of the amide, and followed immediately by a favoured 6-*endo-trig* ring closure involving attack of the resulting amine on the β-carbon atom of the former α,β-unsaturated ketone. A Drieding model of (**3**) shows the close proximity between C-12 (ketone) and C-6 (amide carbonyl) in several of the likely conformations.

Only a few reports of the synthesis of the ring systems present in (**5**) and (**6**) have appeared. Earlier<sup>3</sup> attempts to synthesise 5-oxa-12-azachrysenes failed, but recently amide derivatives have been synthesised from 4-hydroxyquinoline and diphenyl carbonate.<sup>4</sup> 5,12-Diazachrysenes have now also been prepared *via* similar routes involving 4-hydroxy-<sup>5</sup> and 4-amino-quinolines,<sup>6</sup> and also from a benzyne intermediate of

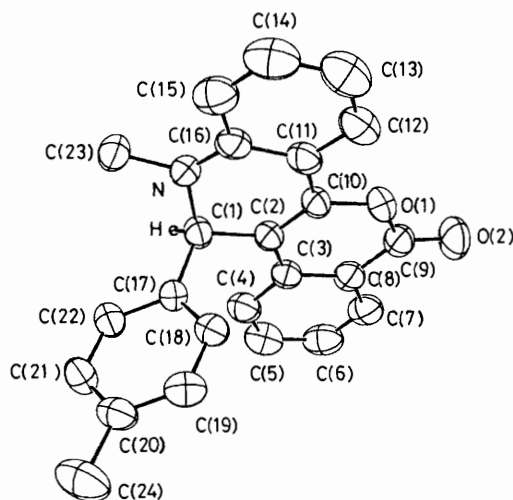
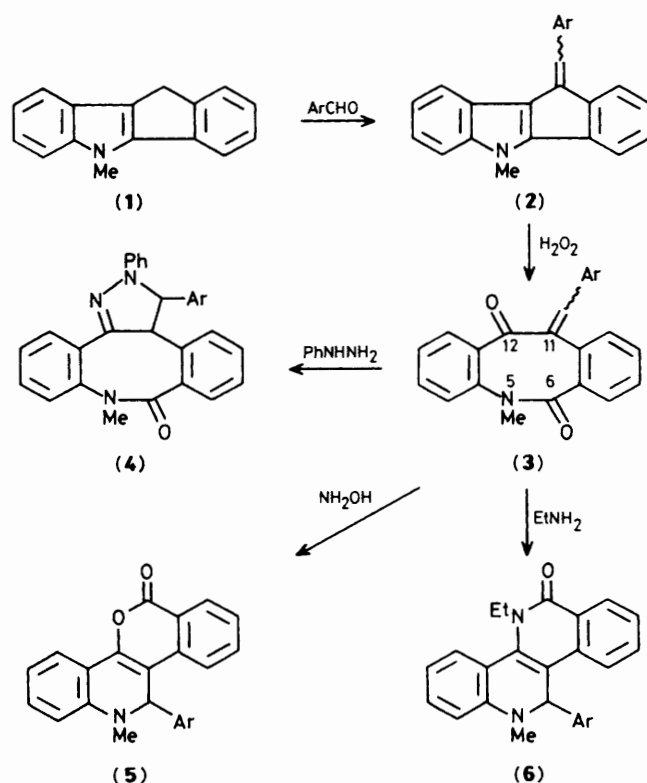


Figure 1. ORTEP drawing of the molecule (**5**).

‡ Crystal data: C<sub>24</sub>H<sub>29</sub>NO<sub>2</sub>, triclinic, space group *P* $\bar{1}$ , *a* = 8.527(1), *b* = 9.503(1), *c* = 11.962(2) Å, α = 110.98(1), β = 91.18(1), γ = 96.24(1)°, *U* = 987.7(4) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.307 g cm<sup>-3</sup>, *R* = 0.042, *R<sub>w</sub>* = 0.066. Enraf-Nonius CAD-4 diffractometer; 3538 reflections measured, 2270 with *I* ≥ 2σ(*I*) used in the refinement. Programs: B. A. Frenz and Assoc., and Enraf-Nonius SDP-1985. Atomic co-ordinates, bond lengths and angles, and thermal parameters, have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

† All new compounds synthesised gave satisfactory spectroscopic and elemental analytical data.

a Schiff's base.<sup>7</sup> The present paper describes a viable and novel route to these ring systems from a readily available indole. The generality of these rearrangements is being studied.

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