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Formylation of an indolenine: 2-(diformylmethylidene)-3,3-dimethyl-2,3-dihydro-1*H*-indole

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.095
Data-to-parameter ratio = 14.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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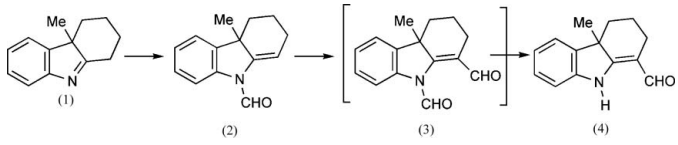
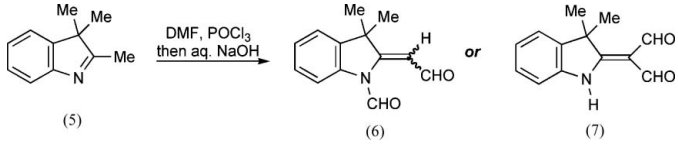
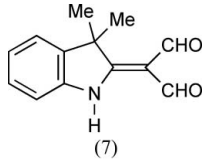
Reaction of 2,3,3-trimethyl-3*H*-indole with dimethylformamide/$POCl_3$ and then aqueous NaOH produces 2-(diformylmethylidene)-2,3-dihydro-3,3-dimethylindole, $C_{13}H_{13}NO_2$. The crystal structure shows the molecule to be planar, with the exception of the two methyl groups, which lie above and below the plane.

Comment

Reaction of the 3,3-disubstituted 3*H*-indole, (1), with the Vilsmeier reagent (dimethylformamide and $POCl_3$) (Cheng *et al.*, 1999, 2002; Fischer *et al.*, 1925; Jutz, 1976; Vilsmeier & Haack, 1927) gave compound (2), the product of *N*-formylation (Fritz, 1959). Further reaction of (2) with the Vilsmeier reagent and subsequent alkaline hydrolysis produced compound (4) (Fritz, 1959). Formation of this product presumably involves the intermediate *N*,*C*-diformyl derivative (3), from which the *N*-formyl group is then hydrolytically removed.







According to this previous work, we expected that the 2,3,3-trimethylindolenine, (5) (2,3,3-trimethyl-3*H*-indole), would react with the Vilsmeier reagent to form an *N*-formylated product. However, when (5) was subjected to the Vilsmeier conditions, at 323 K, followed by aqueous alkaline hydrolysis, a diformyl product was obtained in 56% yield. On the basis of the earlier work (Fritz, 1959), it appeared that (5) had been converted into (6). However, ^{1}H NMR analysis of the diformyl product showed the presence of an NH H atom, inconsistent with structure (6). In order to define the structure, crystals

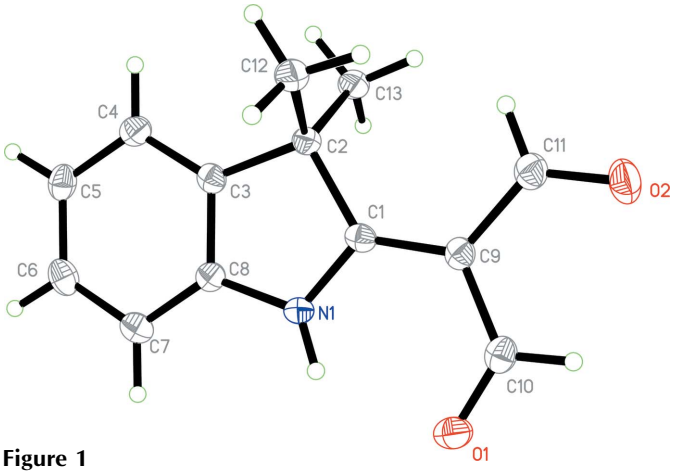


Figure 1
A plot of (7), with displacement ellipsoids drawn at the 50% probability level.

were grown and subjected to X-ray analysis, which showed the product to be the title compound, (7) (Fig. 1).

In the solid state, the molecule of (7) is planar, with the exception of the two methyl groups, which lie above and below the plane. The greatest deviation from the least-squares plane through atoms C1–C11/N1/O1/O2 is 0.052 (1) Å for C2.

Further examples of this interesting conversion, together with the utilization of such diformyl compounds for heterocyclic ring synthesis, will be described in a forthcoming paper.

Experimental

To dimethylformamide (10 ml) cooled in an ice bath, phosphorus oxychloride (6 ml, 66 mmol) was added dropwise with stirring over a period of 2 h at below 298 K. After the addition was complete, a solution of trimethylindolenine, (5) (12.6 mmol), in dimethylformamide (10 ml) was added dropwise. The cooling bath was removed and the reaction mixture was stirred at 323 K for 2 h. The resulting solution was added to ice-cooled water, the pH was adjusted to 8.0 by the addition of aqueous NaOH (35%) and the mixture was extracted with ethyl acetate (3 × 30 ml). The organic layer was washed with hot water and dried over Na_2SO_4. The solvent was evaporated and the resulting crude product was purified by column chromatography on silica gel, eluting with ethyl acetate–toluene (1:5 *v*/*v*), to give the pure diformyl compound, (7), as yellow crystals.

Crystal data

$C_{13}H_{13}NO_2$
M_r = 215.24
Monoclinic, $P2_1/c$
a = 12.1488 (13) Å
b = 12.2273 (13) Å
c = 7.3404 (8) Å
β = 99.329 (2)°
V = 1076.0 (2) Å^3
Z = 4
D_x = 1.329 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1781 reflections
θ = 2.4–26.3°
μ = 0.09 mm^{-1}
T = 100 (2) K
Prism, yellow
0.65 × 0.50 × 0.50 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
4520 measured reflections
2177 independent reflections
1729 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 26.4°
$h = -14 \rightarrow 14$
$k = -15 \rightarrow 10$
$l = -6 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.095
S = 0.99
2177 reflections
151 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···O1	0.858 (16)	2.075 (16)	2.7021 (15)	129.3 (13)
N1—H1*N*···O2^{i}	0.858 (16)	2.157 (16)	2.8254 (15)	134.4 (14)

Symmetry code: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$.

The H atom bonded to atom N1 was found by difference Fourier methods and refined isotropically. H atoms bonded to C atoms were included in calculated positions, using the riding method, with C—H distances of 0.95–0.98 Å and U_{iso}(H) = 1.2U_{eq}(C), or 1.5U_{eq}(C) for methyl groups. The methyl groups were allowed to rotate but not to tip.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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