organic papers

2-(4-Chlorophenacyloxy)-4-methyl-6,7,8,9-tetrahydro-5H-cyclohepta[b]pyridine

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In the known reaction of *N*-phenacylation of 2-methoxypyridine, the *O*-phenacyl derivative was occasionally obtained. The title compound, $C_{19}H_{20}ClNO_2$, was studied by ^{1}H NMR and X-ray diffraction techniques.

Comment

In the course of our systematic study of the effect of size of cycloalkane fragments on the reactivity of pyridine-based heterocycles (Albov *et al.*, 2004*a*), we have described earlier the crystal structure of 2-methoxy-4-methyl-6,7,8,9-tetrahydro-5*H*-cyclohepta[*b*]pyridine, (1) (Albov, Rybakov, Babaev, Fedyanin & Aslanov, 2004). In the reaction of (1) with 4-chlorophenacyl bromide we obtained 1-(4-chlorophenacyl)-4-methyl-6,7,8,9-tetrahydro-5*H*-cyclohepta[*b*]pyridin-2(1*H*)-one (Albov *et al.*, 2004*b*). Our attempt to improve the yield in that reaction occasionally led us to the title compound, (2) (Fig. 1).
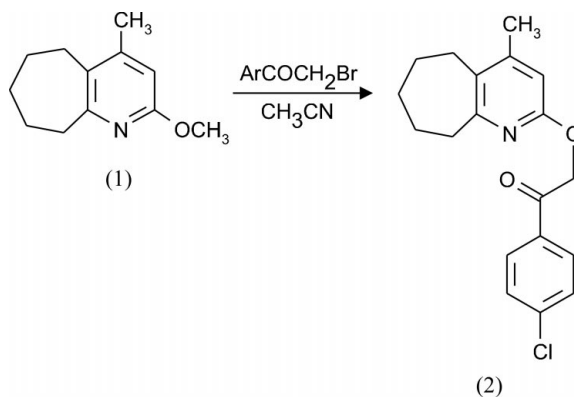
We can speculatively propose two reasons for this unusual substitution. First, self-condensation of phenacyl bromide releases HBr, which removes methyl as methyl bromide. The consequent treatment of the resultant pyridone with phenacyl bromide yields compound (2). Second, the phenacyl cation may perform electrophilic substitution of the methyl cation.

In general, the structures of the bicyclic ring systems in (1) and (2) are very much alike. In both of them cycloheptene rings are in a chair conformation and bond lengths are closely similar. In (2), the torsion angle C20—C15—C14—O14 is 174.32 (19)°, indicating conjugation in the benzoyl fragment.

Experimental

Compound (1) (1.70 g) and 4-chlorophenacyl bromide (1.95 g) were boiled in acetonitrile (15 ml) for 6 h. When thin-layer chromatography showed only traces of the starting materials in the solution, the solvent was evaporated and the product was washed with acetone

(yield 1.79 g, 61%). The product was recrystallized from acetone (m.p. 465–467 K). ^{1}H NMR (DMSO-d_6, 400 MHz, p.p.m.): 1.55 (m, 4H, 7-CH$_2$ + 8-CH$_2$), 1.80 (m, 2H, 9-CH$_2$), 2.65–2.75 (m, 4H, 6-CH$_2$ + 10-CH$_2$), 2.25 (s, 3H, 12-CH$_3$), 5.45 (s, 2H, 13-CH$_2$), 6.45 (s, 1H, 3-CH), 7.49, 7.95 (dd, 4H, Ar).

Crystal data

C$_{19}$H$_{20}$ClNO$_2$	$Z = 2$
$M_r = 329.81$	$D_x = 1.288$ Mg m^{-3}
Triclinic, $P\bar{1}$	Cu $K\alpha$ radiation
$a = 6.2691$ (16) Å	Cell parameters from 25
$b = 9.2424$ (10) Å	reflections
$c = 14.926$ (3) Å	$\theta = 32–35°$
$\alpha = 94.390$ (10)°	$\mu = 2.06$ mm^{-1}
$\beta = 98.02$ (2)°	$T = 293$ (2) K
$\gamma = 94.56$ (2)°	Prism, colourless
$V = 850.3$ (3) Å^3	$0.25 \times 0.23 \times 0.21$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{max} = 74.9°$
Non-profiled ω scans	$h = -7 \rightarrow 7$
Absorption correction: none	$k = -11 \rightarrow 11$
3409 measured reflections	$l = 0 \rightarrow 18$
3409 independent reflections	1 standard reflection
2390 reflections with $I > 2\sigma(I)$	every 200 reflections
$R_{int} = 0.000$	intensity decay: 2%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.050$	$w = 1/[\sigma^2(F_o^2) + (0.1026P)^2]$
$wR(F^2) = 0.144$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.95$	$(\Delta/\sigma)_{max} = 0.001$
3409 reflections	$\Delta\rho_{max} = 0.16$ e Å^{-3}
209 parameters	$\Delta\rho_{min} = -0.15$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—C18	1.737 (2)	C8—C9	1.509 (2)
N1—C2	1.301 (2)	C9—C10	1.553 (2)
N1—C11	1.3671 (19)	C10—C11	1.5094 (19)
C2—O2	1.362 (2)	C13—C14	1.512 (3)
O2—C13	1.425 (2)	C14—O14	1.222 (2)
C3—C4	1.350 (2)	C14—C15	1.494 (2)
C4—C5	1.406 (2)	C15—C20	1.376 (3)
C4—C12	1.520 (2)	C15—C16	1.395 (3)
C5—C11	1.3948 (19)	C16—C17	1.379 (3)
C5—C6	1.539 (2)	C17—C18	1.357 (4)
C6—C7	1.563 (2)	C18—C19	1.397 (4)
C7—C8	1.536 (2)	C19—C20	1.385 (3)
C2—N1—C11	116.25 (14)	C5—C6—C7	113.56 (12)
N1—C2—O2	118.48 (15)	C8—C7—C6	115.37 (14)
N1—C2—C3	124.24 (16)	C9—C8—C7	116.06 (14)
O2—C2—C3	117.28 (14)	C8—C9—C10	114.70 (14)
C2—O2—C13	116.07 (13)	C11—C10—C9	115.80 (13)
C4—C3—C2	119.13 (15)	N1—C11—C5	120.78 (13)
C3—C4—C5	117.02 (15)	N1—C11—C10	115.02 (12)
C3—C4—C12	120.04 (16)	C5—C11—C10	123.12 (13)
C5—C4—C12	121.64 (16)	O2—C13—C14	112.46 (15)
C11—C5—C4	119.09 (14)	O14—C14—C15	121.64 (17)
C11—C5—C6	119.80 (13)	O14—C14—C13	121.29 (16)
C4—C5—C6	121.06 (13)	C15—C14—C13	117.06 (15)

All H atoms were positioned geometrically (C—H = 0.93–0.97 Å) and refined as riding, with U_{iso}(H) = 1.2 or 1.5 U_{eq} of the parent C atom.
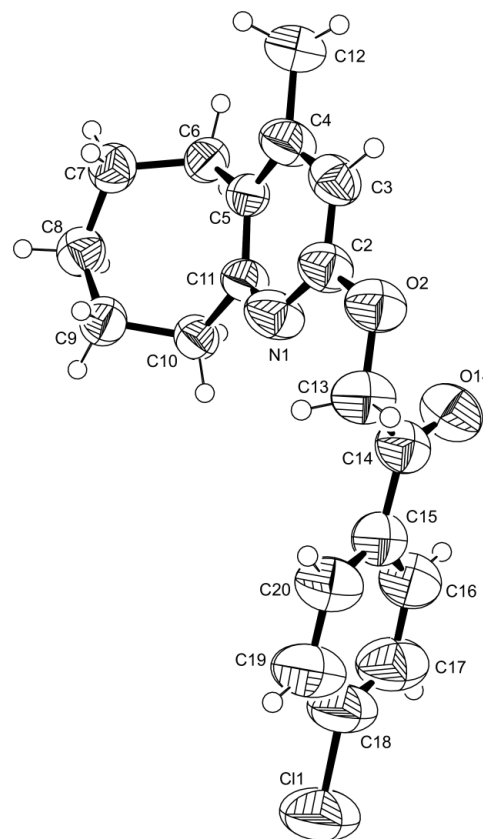

Figure 1
ORTEP-3 view (Farrugia, 1997) of (2), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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