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9-(1-Acetoxyethylidene)fluorene ('diacetylfluorene'), a by-product from the acetylation of 9-fluorenyllithium

Paul D. Robinson,[a]* Hisham G. Lutfi,[b] Yuqing Hou[b] and Cal Y. Meyers[b]

[a]Department of Geology, Southern Illinois University-4324, Carbondale, IL 62901, USA, and [b]Department of Chemistry and Biochemistry, Southern Illinois University-4409, Carbondale, IL 62901, USA
Correspondence e-mail: robinson@geo.siu.edu

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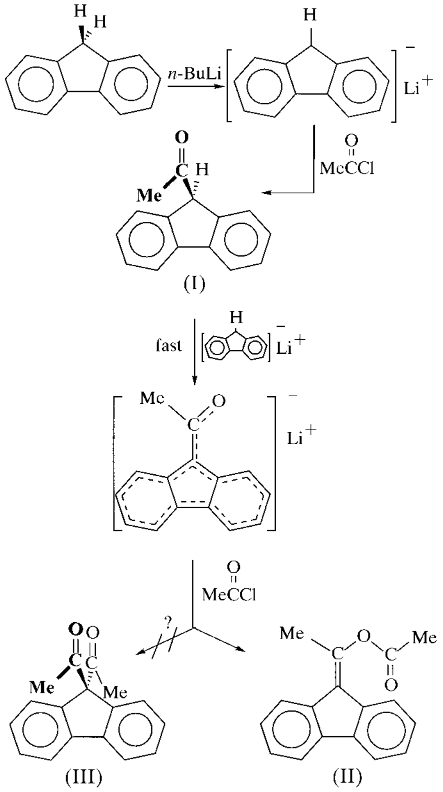
Treatment of 9-fluorenyllithium with acetyl chloride produces 9-acetylfluorene, (I), and several by-products, among which is 'diacetylfluorene', now characterized definitively as 9-(1-acetoxyethylidene)fluorene [IUPAC name: (1-fluoren-9-ylidene)ethyl acetate], (II), $C_{17}H_{14}O_2$, derived from acetylation of initially formed (I). Various parameters disclose substantial structural distortion within (II) emanating from $A^{(1,3)}$ strain associated with the 9-(acetoxyethylidenyl)fluorene system.

Comment

With the objective of preparing 9-acetylfluorene, (I), from the reaction of 9-fluorenyllithium with acetyl chloride, the desired product was obtained (Meyers *et al.*, 2000). Its solution NMR spectrum, which does not definitively convey a configuration, compared favorably with that previously reported by Ohwada & Shudo (1988), who prepared it by an entirely different route. We unequivocally characterized it in crystalline form as the *sp* rotamer. However, thin-layer chromatography of our crude product indicated that our reaction yielded several other products whose precise structures, based on earlier literature reports, were indefinite and controvertial (*cf.* Naik *et al.*, 1988; Rouzaud *et al.*, 1965; Scherf & Brown, 1961; Greenhow *et al.*, 1953; Von & Wagner, 1944; Miller & Bachman, 1935). The question of subsequent reactivity of (I) under the conditions of its formation is pertinent. It is more acidic than 9-fluorenyllithium, which leads to the rapid formation of 9-acetyl-9-fluorenyllithium, which is an enolate and, thus, an ambident nucleophile capable of undergoing C- and/or O-acetylations. Caine (1979) has reviewed C- *versus* O-acylations and -alkylations of metallated ketone enolates. Furthermore, these secondary products could undergo further reaction with the residual nucleophilic 9-fluorenyl anion. The reaction of pivaloyl chloride with 9-fluorenyllithium provided *ap*-9-pivaloylfluorene (Meyers *et al.*, 1991) and, because of significant steric factors, only a small amount of dipivaloylated product, and even this was solely the O-pivaloylated compound (Robinson *et al.*, 2000) from the latter. Steric factors should be only minor in the case of acetylation, allowing diacetylation involving both carbon and oxygen as well as the other reactions suggested above.



Accompanying our preparation of (I) (Meyers *et al.*, 2000), one of the by-products isolated by flash chromatography was suggested by NMR to be 9-(1-acetoxyethylidene)fluorene, (II). As shown in the Scheme above, (II) was produced from subsequent O-acetylation of initially formed (I); there was no indication of the presence of the corresponding C-acetylation product, 9,9-diacetylfluorene, (III). While Greenhow *et al.* (1953) reported the formation and isolation of (II) from acetylations of 9-fluorenylsodium, and directly from acetylation of (I) in pyridine solution, their product characterization was far from definitive and their melting point was substantially different from that of (II) which we obtained. We have now unequivocally confirmed the identity of (II) as 9-(1-acetoxyethylidene)fluorene by its X-ray structure, shown with atom numbering in Fig. 1. Selected bond angles and torsion angles are given in Table 1. Atoms C9, C10, O1 and C13 are coplanar, the greatest deviation from the plane being only 0.012 (2) Å. While C9 is also in the fluorene-ring plane, the angle between the two planes is 8.16 (12)°. This substantial out-of-plane distortion of the C9═C10 double bond is further illustrated by the fact that C13 is out of the fluorene-ring plane by 0.401 (3) Å., C10 by 0.221 (2) Å., and O1 by 0.202 (2) Å. That C10 is symmetrically out of the fluorene plane is also reflected by comparing torsion angles C10—C9—C9a—C4a and C10—C9—C8a—C4b, both of which are non-planar by virtually identical amounts, with angles C8a—C9—C10 and C9a—C9—C10, which are essentially identical. Further distortion is exhibited in the comparison between 'equivalent' angles C9—C10—O1 and C9—C10—C13; the latter is larger by 11.3°. Likewise, while torsion angles C8a—C9—C10—C13 and C8a—C9—C10—O1, respectively, are approximately linear, the corresponding torsion angles C9a—C9—C10—O1 and C9a—C9—C10—C13 exhibit substantial non-linearity. The molecular distortion is apparently associated with the several pertinent non-bonding intramolecular distances that are well within the sum of their respective van der Waals radii: O1···C1 2.926 (3), O1···H1 2.39, C13···H8 2.66 and C8···C13 3.218 (4) Å.

While the distortion in (II) may be regarded as an example of '$A^{(1,3)}$ strain' [*viz*. Malhotra & Johnson (1968); see reviews by Johnson (1968), Lambert (1989) and Eliel & Wilen (1994)], this study may be the first to illustrate this type of strain in a 9-fluorenylidene structure and with the support of definitive X-ray parameters. Out-of-plane $A^{(1,3)}$ distortion was much less apparent in the corresponding dipivaloyl compound (Robinson *et al.*, 2000), although its *tert*-butyl groups might have been expected to impose an even greater distortion than that in (II). It is suggested that a 'normal' out-of-plane $A^{(1,3)}$ distortion in the dipivaloyl compound would enhance the steric strain already engendered by the *tert*-butyl groups. The reduced out-of-plane distortion is the thermodynamic compromise.

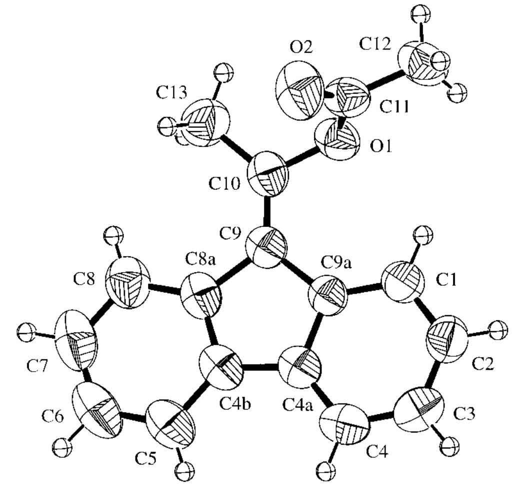


Figure 1
The molecular structure and atom-numbering scheme for (II) with displacement ellipsoids at the 50% probability level.

Experimental

Compound (II) was isolated by flash chromatography as one of the by-products in our preparation of (I) from the reaction of 9-fluorenyllithium with acetyl chloride in tetrahydrofuran under argon (Meyers *et al.*, 2000). Recrystallization from hexane provided colorless crystals, m.p. 353–353.5 K [corrected, no decomposition; literature (Greenhow *et al.*, 1953) m.p. 370–371 K], which were used for the NMR and X-ray diffraction studies. NMR (Varian VXR 300; 300 MHz ^{1}H, 75 MHz ^{13}C; $CDCl_3$; p.p.m.), ^{1}H: δ 2.40 (*s*, 3H), 2.63 (*s*, 3H), 7.31 (*m*, 4H, J = 1.2, 1.5, 6.3 Hz), 7.71 (*m*, 3H, J = 1.5, 6.3 Hz), 7.83 (*dd*, 1H, J = 1.5, 7.5 Hz); ^{13}C: δ 21.21, 21.31, 119.51, 119.81, 124.03, 124.82, 125.19, 126.96, 127.30, 127.46, 127.61, 136.58, 136.67, 139.13, 140.19, 148.57, 168.40.

Crystal data

$C_{17}H_{14}O_2$
$M_r = 250.28$
Orthorhombic, *Pbca*
$a = 9.8818\ (17)$ Å
$b = 27.375\ (6)$ Å
$c = 9.8110\ (12)$ Å
$V = 2654.1\ (8)$ Å^3
$Z = 8$
$D_x = 1.253$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 10.9\text{–}12.9°$
$\mu = 0.081$ mm^{-1}
$T = 296$ K
Ovoid, colorless
0.43 × 0.35 × 0.23 mm

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
4542 measured reflections
2350 independent reflections
1029 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$
$\theta_{\max} = 25.05°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 32$
$l = -11 \rightarrow 11$
3 standard reflections every 100 reflections intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.115$
$S = 0.96$
2350 reflections
174 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.12$ e Å^{-3}
$\Delta\rho_{\min} = -0.13$ e Å^{-3}

Table 1
Selected geometric parameters (°).

C9—C10—O1	117.3 (2)	C9a—C9—C10	126.8 (2)
C9—C10—C13	128.6 (2)	O1—C10—C13	114.0 (2)
C8a—C9—C10	127.0 (2)		
C8a—C9—C10—C13	−1.2 (4)	C8—C8a—C9—C10	7.3 (4)
C8a—C9—C10—O1	−178.79 (19)	C1—C9a—C9—C10	−7.7 (4)
C9a—C9—C10—O1	8.9 (4)	C10—C9—C9a—C4a	171.0 (2)
C9a—C9—C10—C13	−173.6 (2)	C10—C9—C8a—C4b	−171.2 (2)

A redundant data set was collected and averaged during refinement. The rotational orientations of the methyl groups were refined by the circular Fourier method available in *SHELXL*97 (Sheldrick, 1997). All H atoms were riding. The crystal used for data collection was shaped with acetone; the crystals were too soft to be cut by conventional methods.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *LS* in *TEXSAN*, and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* in *TEXSAN* (Johnson, 1965); software used to prepare material for publication: *TEXSAN, SHELXL*97 and *PLATON* (Spek, 2000).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1021). Services for accessing these data are described at the back of the journal.

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