Synthesis and Photochemical Behaviour of 3-(Estran-16-yl)acrylates and 2-(Estran-16-yl)vinyl Ketones†

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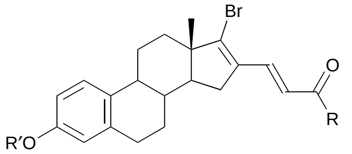
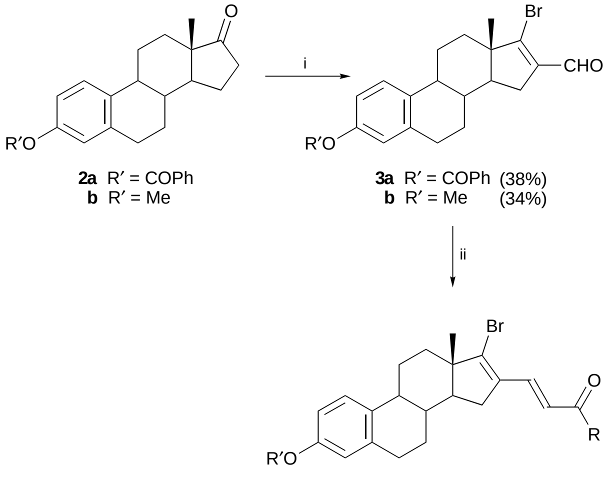
C-16-substituted steroids having an unsaturation in the side chain have been synthesized by sequential Arnold–Vilsmeier and Wittig reactions, subsequent photochemical studies showing the formation of either a dimeric structure or the occurrence of *E*/*Z*-isomerization; for one example, treatment with H_2 over Pd–C led to full reduction of the side-chain and ring D.

Steroids play an important role in biological membranes.[2] In close relationship to this role is their ability to show liquid crystalline (LC) behaviour.C-17-alkyl-substituted steroids, *e.g.* cholesterol, have found numerous applications in LC studies.[4] However, C-16-alkyl-substituted analogues have not been as widely studied.

In the course of our interest in the potential liquid crystalline behaviour of C-16-substituted steroids, we have prepared a number of estrone compounds **1a–d** as precursors, containing an unsaturated side-chain at C-16.



1a R = Ph, R′ = COPh
b R = Me, R′ = COPh
c R = OEt, R′ = COPh
d R = OEt, R′ = Me



2a R′ = COPh
b R′ = Me

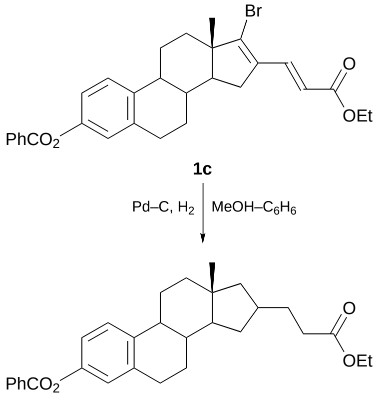
3a R′ = COPh (38%)
b R′ = Me (34%)

(55–78%)

Scheme 1 *Reagents:* i, PBr_3, DMF, $CHCl_3$; ii, $Ph_3P{=}C(CO)R$ (**4**), $PhCO_2H$, C_6H_6, 80 °C

Introduction of the side chain at C-16 was achieved in a straightforward two-step preparation. Arnold–Vilsmeier reaction[6] of **2** furnished the 17-bromo-16-formylestrone **3**, Wittig reaction of which with stabilized phosphoranes **4** gave **1a–d**. Benzoic acid was used as catalyst (Scheme 1). In an exemplary reduction, the 17-bromo-16,19-diene **1c** was fully hydrogenated to **5** (Scheme 2).

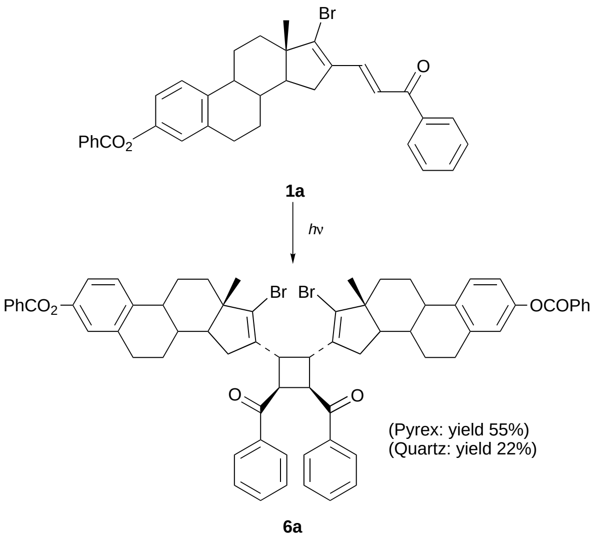
In the photoirradiation of **1a** the dimeric compound **6a** is formed (Scheme 3).



1c

5 (62%)

Scheme 2



1a

(Pyrex: yield 55%)
(Quartz: yield 22%)

6a

Scheme 3

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*To receive any correspondence.
†Dedicated to Professor Dr. André Campos Neves on the occasion of his 70th birthday.
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Techniques used: ^{1}H, ^{13}C, IR and UV spectroscopy

References: 22

Schemes: 4

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