

Note

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## A Convenient Preparation of *N*-Acyl-1-aza-1,3-diene from $\beta$ -Formylenamide and Its Utility in Inverse Electron Demand Diels–Alder Reactions

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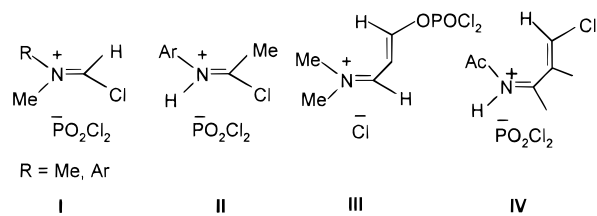
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### Introduction

The Diels–Alder reaction of 1-azadienes is a valuable methodology for synthesis of nitrogen heterocycles<sup>1</sup> bearing endocyclic enamine moieties that are key intermediates in the preparation of complicated heterocycles<sup>2a</sup> and natural products.<sup>2b</sup> The  $4\pi$  participation of simple 1-azadienes is rarely observed in normal [4 + 2] cycloaddition reactions; however, this problem could be circumvented by introducing either electron-withdrawing<sup>1,3</sup> or electron-donating<sup>4</sup> substituents onto the nitrogen. Fowler<sup>2</sup> and Boger<sup>5</sup> have shown that substitution of the azadiene nitrogen by a strongly electron-withdrawing *N*-acyl or *N*-sulfonyl group favors considerably the inverse electron demand Diels–Alder (IEDDA) reactivity of the desired azadienes. Nevertheless, enormous efforts have been made toward production of electron-deficient 1-aza-1,3-butadienes that enable  $4\pi$  participation of  $\alpha,\beta$ -unsaturated imines in [4 + 2] cycloaddition reactions. These have included intramolecular [4 + 2] cycloaddition of in situ generated *N*-acyl-1-aza-1,3-butadienes by vacuum pyrolysis<sup>6</sup> and under thermal condition,<sup>7</sup> in situ generated *o*-quinomethide monoimines,<sup>8</sup> the HOMO<sub>diene</sub> controlled Diels–Alder reaction of 1-(dimethylamino)-1-aza-1,3-butadienes,<sup>9</sup> the Lewis acid catalyzed intramolecular [4

Scheme 1



+ 2] cycloaddition reaction of in situ generated 2[(*tert*-butyldimethylsilyloxy)-1-aza-1,3-butadienes,<sup>10</sup> and intermolecular [4 + 2] cycloaddition of *N*-sulfonyl-1-aza-1,3-butadienes.<sup>11</sup> Recently significant attention has been drawn<sup>12</sup> to the influence of a cyano group at C-2, together with different nitrogen substituents (COR, Ph, alkyl, OMe, SO<sub>2</sub>Ph), on the Diels–Alder reactivity of azadiene systems. Interestingly, literature reveals that C-2-alkyl substituted *N*-acyl-1-azadienes are rare compounds, although corresponding 2-alkyl-*N*-sulfonyl-1-azadienes have provided well-behaved dienophiles for [4 + 2] cycloaddition studies.<sup>13</sup>

The Vilsmeier reagent, which is derived from *N,N*-dimethylformamide and phosphorus oxychloride, corresponds to a chloromethyleneiminium salt structure (I, R=Me, Scheme 1). The potential of carbon–carbon bond-forming reactions of halomethylene iminium salts involving aromatic and acyclic or alicyclic nuclei has been extensively studied.<sup>14</sup> The Vilsmeier reactions of enamides were found to proceed by cyclization of intermediate II to give fused pyridoderivatives.<sup>15</sup> The ring closure of *N*-aryl-*N*-methylformamides to quinolines can also be effected by treatment of electrophilic iminium salt (I, R = Ar) with enamine via “reverse Vilsmeier approach”.<sup>16</sup> All of these examples include amine precursors in which an enolizable formyl or acyl group is directly linked to the nitrogen atom. Nevertheless, Ulrich et al.<sup>17</sup> reported that 3-(dimethylamino)acrolein is a prototype vinyl homologue of dimethylformamide, which could be employed for preparation of  $\alpha,\beta$ -unsaturated imine III to incorporate an acrolein moiety to a suitable nucleophile. These results suggested that if properly substituted

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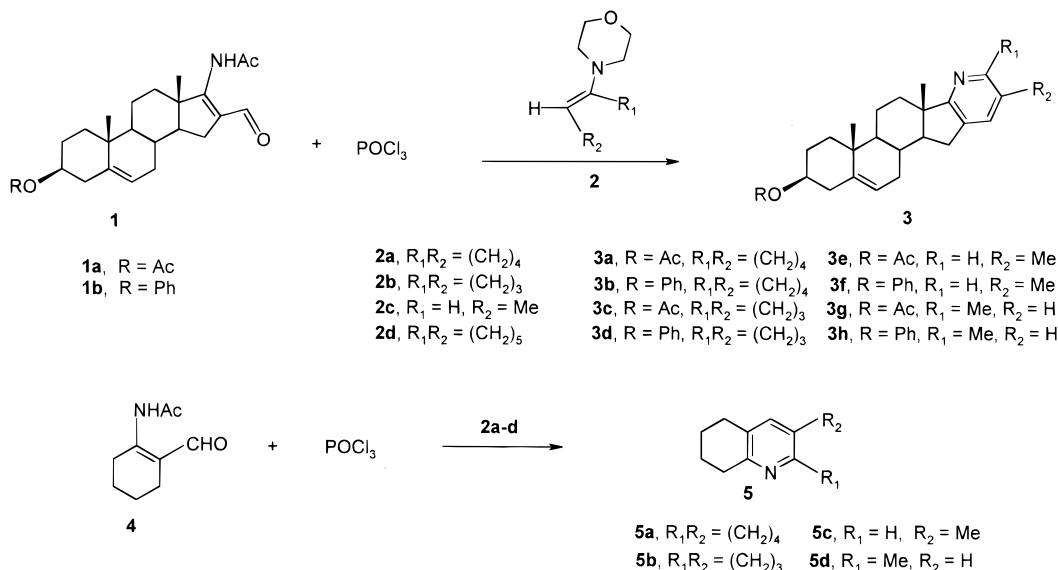
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## Scheme 2



enamines or enamides were chosen, a similar enolization sequence would yield a 1-aza-1,3-diene system.

With this in mind, we elected to synthesize a novel class of  $\alpha, \beta$ -unsaturated imines of the type **IV** from 1-acetamido-2-formyl-1-alkenes. It was anticipated that reaction of this  $\beta$ -formyl enamide and  $\text{POCl}_3$  would generate a highly reactive and electrophilic substrate that could behave as an electron-deficient 1-aza-1,3-diene in a [4 + 2] cycloaddition reaction. Recently we have reported the preparation of a novel class of steroidal  $\beta$ -formyl enamide<sup>18</sup> and conveniently employed it as potential intermediate for synthesis of 17,17-dichloro-16-(*E*)-chloromethyleneandrost-5-enes<sup>19a</sup> and steroidal des-D diynes.<sup>19b</sup> We foresee enormous scope for this functionality as a new substrate in the emerging field of enamides.<sup>20</sup> Herein, we report a facile  $\text{POCl}_3$ -mediated conversion of  $\beta$ -formyl enamides to *N*-acyl-1-aza-1,3-diene systems and their convenient application in an IEDDA reaction with enamines<sup>21</sup> to construct ring-D annelated pyrido(17,16-b)- and tetrahydroquinolino(17,16-b)steroids.<sup>22</sup>

## Results and Discussion

Steroidal  $\beta$ -formyl enamides (**1a,b**) were prepared from 16-dehydropregnenolone oxime under the influence of Vilsmeier reagent in good yields.<sup>18</sup> Conversion of cyclohexanone to 1-acetamido-1-cyclohexene<sup>23</sup> followed by

Vilsmeier formylation under mild condition afforded 1-acetamido-2-formyl-1-cyclohexene (**4**) in 69% yield. Treatment of **1a** with 3 molar equiv of  $\text{POCl}_3$  at 0–10 °C for 1 h and subsequent reaction with freshly prepared *N*-morpholino-1-cyclohexene (**2a**) in refluxing dichloroethane gave **3a** in 51% yield (Scheme 2). In addition, from the reaction mixture the compound 3- $\beta$ -acetoxy-17-oxo-16(*E*)-chloromethyleneandrost-5-ene<sup>19a</sup> was isolated in 30% yield. Similarly, steroidal formyl enamides (**1a,b**) in combination with  $\text{POCl}_3$  reacted with morpholino-enamines (**2a–c**) to afford products **3a–f** in 51–57% yields. However, the reaction of *N*-morpholino-1-propene (**2c**) with **1a** resulted 3- $\beta$ -acetoxy-5',6'-dihydro-5'-methyl-6'-morpholino-pyrido(17,16-b)androst-5-ene (**D**,  $R_1 = \text{H}$ ,  $R_2 = \text{Me}$ ),<sup>24</sup> which required additional acid treatment to give product **3e**. Similarly, the alicyclic formyl enamide (**4**) reacted with enamines (**2a–c**) to afford **5a–c** in 47–52% yields. All of the products were characterized by spectroscopical and elemental analysis.

The reaction is proposed to proceed by an IEDDA reaction mechanism involving a transient *N*-acyl-1-aza-1,3-butadiene intermediate (**A**). The  $\text{POCl}_3$ -promoted azadiene intermediate might form as a result of enolization and chlorination of  $\beta$ -formyl enamides (**1a**), followed by abstraction of the proton from quaternary nitrogen by  $^-\text{OPOCl}_2$  species. The *N*-acyl-1-azadiene moiety acts as an electron-deficient diene and is involved in an IEDDA reaction<sup>21</sup> with an electron-rich enamine (**2a**) to afford an endocyclic piperidine enamine intermediate (**B**,  $R_1, R_2 = (\text{CH}_2)_4$ ), which facilitates loss of  $\text{Cl}^-$  ion to form iminium intermediate **C**. The nucleophilic attack on the *N*-carbonyl group leads to loss of  $\text{AcNu}$ , which is followed by elimination of morpholine to afford aromatic product **3a** (Scheme 3). The  $^1\text{H}$ NMR spectra of intermediate **A** exhibited a singlet signal at  $\delta$  7.18 for conjugated C-16 imine proton, thus favoring an azadiene structure. All

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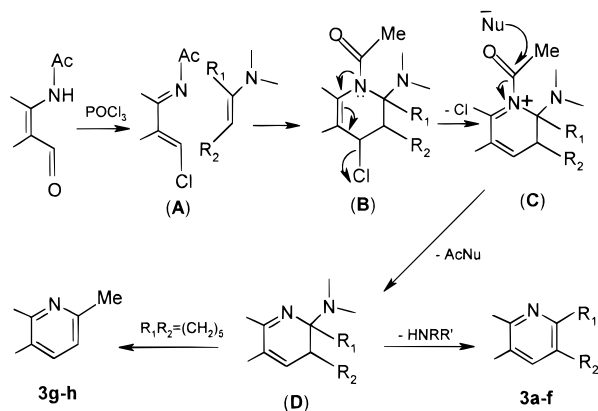
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(24) The intermediate **D** exhibited a doublet at  $\delta$  5.58 ( $J = 10.2$  Hz) for methine proton of dihydropyridine and characteristic methylene proton signals for morpholine protons appeared at  $\delta$  3.56 (t,  $J = 5$  Hz) and 2.52, respectively. When it was treated with methanolic HCl, all of these signals disappeared completely, and two new meta coupled signals at  $\delta$  7.90 and 7.15 ( $J = 2.0$  Hz) were observed.

Scheme 3



attempts to isolate intermediate **A** failed; rather we obtained 3- $\beta$ -acetoxy-17-oxo-16(*E*)-chloromethylene-androst-5-ene as the sole product, which further supported the existence of a 1-azadiene intermediate.<sup>19a</sup> The isolation of stable intermediate **D** ( $R_1 = \text{H}$ ,  $R_2 = \text{Me}$ ) from reaction between **1a** and aliphatic enamine (**2c**) indicated that conformationally less strained cycloadduct **D** disfavored the loss of morpholine to aromatize under reaction conditions.

In contrast, the reaction of *N*-morpholino-1-cyclohepten (**2d**) with *N*-acyl-1-azadiene of **1a,b** afforded **3g,h** instead of the expected cycloheptane-fused pyridosteroid [**3**,  $R = \text{Ac}$  or  $\text{PhCO}$ ,  $R_1R_2 = (\text{CH}_2)_5$ ]. The <sup>1</sup>H NMR of **3g** showed two characteristic ortho-coupled signals at  $\delta$  7.42 and 6.19 ( $J = 7$  Hz) for the pyridine ring. Obviously, the formation of **3g** resulted from the cleavage of the cycloheptane ring in the cycloadduct (**D**). The formation of the unexpected reaction product **3g**, therefore, may be accounted for by an unusual type of bond breakage and rearrangement under thermal condition leading to aromatization of dihydropyridine intermediate **D** [ $R_1R_2 = (\text{CH}_2)_5$ ] with concomittal loss of morpholine and butadiene. The generation of butadiene was ascertained by GLC analysis of the gaseous product. Similarly, formyl enamide **4** reacted with **2d** to afford **5d** in 45% yield.

To increase the electron-deficient character<sup>25</sup> of *N*-acyl conjugated imines, the catalytic effect of a Lewis acid<sup>26</sup> on the course of the IEDDA reaction was studied. The  $\text{TiCl}_4$ -catalyzed reaction of **1a** with enamine **2a** showed enhancement of the electrophilicity of 1-azadiene and gave **3a** as a single regioisomer (82%). Similarly,  $\text{BF}_3 \cdot \text{OEt}_2$  was found to stabilize intermediate **A** and catalyzed the [4 + 2] cycloaddition reaction, minimizing side products (Table 1). The mechanism of the reaction is not clear; however, it may be assumed that the Lewis acid probably forms a complex with the oxygen atom of the acetyl group, enhancing the electron-deficient character of *N*-acyl-1-azadiene and accelerating the rate of [4 + 2] cycloaddition reaction.

The work represents our first attempt to use  $\beta$ -formyl-enamides as useful precursors of 1-aza-1,3-butadiene in carbocycles. The route presented here should be useful in the synthesis of a variety of other pyridine and

Table 1. Influence of Lewis Acid on Inverse Electron Demand Diels–Alder Reactions

entry	$\beta$ -formyl enamide <sup>a</sup>	enamine	Lewis acid <sup>b</sup>	reaction time/temp	prod. <sup>c</sup>	yield (%) <sup>d</sup>
1	<b>1a</b>	<b>2a</b>		4 h, 80 °C	<b>3a</b>	51
2			$\text{TiCl}_4$	1 h, 20 °C	<b>3a</b>	82
3	<b>1b</b>	<b>2a</b>		4 h, 80 °C	<b>3b</b>	55
4			$\text{TiCl}_4$	1 h, 20 °C	<b>3b</b>	85
5	<b>1a</b>	<b>2b</b>		4 h, 80 °C	<b>3c</b>	57
6			$\text{TiCl}_4$	1 h, 20 °C	<b>3c</b>	88
7	<b>1b</b>	<b>2b</b>		4 h, 80 °C	<b>3d</b>	52
8			$\text{TiCl}_4$	1 h, 20 °C	<b>3d</b>	80
9	<b>1a</b>	<b>2c</b>		5 h, 80 °C	<b>3e</b>	57
10			$\text{BF}_3 \cdot \text{OEt}_2$	2 h, 20 °C	<b>3e</b>	74
11	<b>1b</b>	<b>2c</b>		5 h, 80 °C	<b>3f</b>	51
12			$\text{BF}_3 \cdot \text{OEt}_2$	2 h, 20 °C	<b>3f</b>	72
13	<b>1a</b>	<b>2d</b>		4.5 h, 80 °C	<b>3g</b>	55
14			$\text{BF}_3 \cdot \text{OEt}_2$	1.5 h, 20 °C	<b>3g</b>	75
15	<b>1b</b>	<b>2d</b>		5.5 h, 80 °C	<b>3h</b>	53
16			$\text{BF}_3 \cdot \text{OEt}_2$	2 h, 20 °C	<b>3h</b>	69

<sup>a</sup> Three molar equivalents of  $\text{POCl}_3$  was employed. <sup>b</sup> One-half molar equivalent of Lewis acid was used. <sup>c</sup> All reactions were carried under nitrogen atmosphere. <sup>d</sup> Isolated yields.

quinoline derivatives. From our study it is evident that Lewis acid catalyses the intermolecular IEDDA reaction of *N*-acyl-1-azadiene and enamine. From the standpoints of yield and experimental simplicity, the  $\text{POCl}_3$ -mediated process represents an attractive strategy to hitherto inaccessible 2-alkyl substituted *N*-acyl-1-aza-1,3-butadienes. Currently we are studying the scope of this reaction in regard to other electron-rich dienophiles.

### Experimental Section

All anhydrous reactions were performed under a nitrogen atmosphere using flame-dried glassware. DMF was dried over  $\text{CaH}_2$ , and  $\text{POCl}_3$  was freshly distilled. Compounds **1a,b** were prepared from 16-DPA oxime following our earlier procedure.<sup>18</sup>

**1-Acetamido-2-formyl-1-cyclohexene (4).** A mixture of acetamide (300 mg, 5 mmol), cyclohexanone (980 mg, 10 mmol), and *p*-toluenesulfonic acid (50 mg) was placed in a 250 mL round-bottom flask containing 100 mL of dry toluene and refluxed under Dean stark conditions for 24 h. After removal of a calculated amount of water, the reaction was stopped and the solvent was distilled under reduced pressure to obtain a thick solid mass. It was extracted with hexane/ $\text{CH}_2\text{Cl}_2$  and dried over  $\text{Na}_2\text{SO}_4$ , and solvent was removed to afford 1-acetamido-1-cyclohexene, yield 514 mg (74%), mp 59–61 °C (lit.<sup>23</sup> 62–64 °C). The solid product was dissolved in  $\text{CH}_2\text{Cl}_2$  (50 mL), cooled, and added to a Vilsmeier reagent freshly prepared from  $\text{POCl}_3$  (5.84 mL) and DMF (5.60 mL). The reaction was stirred at 0–15 °C for 3 h and worked up by quenching in ice-cold water. The organic layer was separated after neutralization with  $\text{NaHCO}_3$ , and the aqueous portion was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic portions were combined, washed with water, and dried over  $\text{Na}_2\text{SO}_4$ . Removal of the solvent and column chromatography separation (toluene/acetone 90:10) gave **4** as a white solid; yield 426 mg (69%), mp 115–16 °C (ethyl acetate),  $R_f = 0.15$  ( $\text{CHCl}_3$ ); IR  $\nu_{\text{max}}$  (KBr) 3250, 1720  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  12.06 (bs, 1H, –NH), 9.28 (s, 1H, CHO), 3.07 (s, 2H), 2.42 (s, 2H), 2.13 (s, 3H), 1.93 (bs, 4H); MS  $m/z$  167 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_9\text{H}_{13}\text{NO}_2$ : C, 64.64; H, 7.83; N, 8.37. Found: C, 64.69; H, 7.73; N, 8.52.

**3 $\beta$ -Acetoxy-(5',6',7',8'-tetrahydro)-quinolino(17,16-b)androst-5-ene (3a).** Powdered 16-formyl-17-acetamido-androst-5,16-diene (**1a**, 399 mg, 1 mmol) was added to  $\text{POCl}_3$  (459 mg, 3 mmol) under a nitrogen atmosphere at 0 °C in a 250 mL round-bottom flask. The reaction mixture was stirred magnetically at 0 °C for 15 min, during which time it turned from colorless to red. It was diluted with dry  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (100 mL), and to this cold mixture was added the morpholine enamine of cyclohexanone (**2a**, 451 mg, 3 mmol). The reaction mixture was allowed to stir for 30 min at room temperature to increase the reaction temperature to 25 °C, and then it was further refluxed for 4 h

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under a nitrogen atmosphere. The reaction was monitored by TLC, and on completion of reaction it was quenched in ice-cold water. After neutralization with solid  $\text{NaHCO}_3$  to pH  $\sim$ 7.5, the organic layer was separated, and the aqueous layer was extracted with  $\text{ClCH}_2\text{CH}_2\text{Cl}$ . The organic extracts were combined, washed with water, and dried over  $\text{Na}_2\text{SO}_4$ . Removal of the solvent gave a red gummy product that was purified by preparative TLC on silica gel (EtOAc/hexane 20:80) to afford product **3a** as white solid: yield 215 mg (51%), mp 173 °C (methanol),  $[\alpha]_D^{25} -33^\circ$  (*c*, 0.7,  $\text{CHCl}_3$ ),  $R_f = 0.6$  (hexane/EtOAc 80:20); IR  $\nu_{\text{max}}$  (KBr) 1736  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.16 (s, 1H), 5.41 (bs, 1H), 4.61 (m, 1H), 2.89 (bs, 2H), 2.70–2.61 (m, 3H), 2.43–2.29 (m, 6H), 2.03 (s, 3H), 1.10 (s, 3H), 0.97 (s, 3H), 1.91–1.13 (m, 14H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  171.55, 170.85, 162.52, 140.66, 134.54, 134.13, 131.04, 119.66, 74.73, 56.03, 50.68, 44.80, 38.74, 36.92, 36.92, 34.31, 31.14, 30.86, 30.20, 29.92, 28.60, 23.50, 22.12, 21.56, 20.17, 19.74, 19.26, 17.17; MS  $m/z$  359 ( $\text{M}^+ - \text{CH}_3\text{COOH}$ ), 344. Anal. Calcd for  $\text{C}_{28}\text{H}_{37}\text{NO}_2$ : C, 80.14; H, 8.88; N, 3.33. Found: C, 79.98; H, 8.76; N, 3.52.

**3 $\beta$ -Benzoyloxy-(5',6',7',8'-tetrahydro)-quinolino(17,16-b)-androst-5-ene (3b)**: 265 mg (55%), mp 170 °C (Et<sub>2</sub>O/*n*-hexane 50:50)  $[\alpha]_D^{25} -9.5^\circ$  (*c*, 0.70,  $\text{CHCl}_3$ ),  $R_f = 0.7$  (*n*-hexane/EtOAc 90:10). Anal. Calcd for  $\text{C}_{33}\text{H}_{39}\text{NO}_2$ : C, 82.29; H, 8.16; N, 2.91. Found: C, 82.15; H, 8.22; N, 3.01.

**3 $\beta$ -Acetoxy-(5',6',7',8'-trimethylene)-pyrido(17,16-b)androst-5-ene (3c)**: 230 mg (57%), mp 176 °C (methanol),  $[\alpha]_D^{25} -34.2^\circ$  (*c*, 1.95,  $\text{CHCl}_3$ ),  $R_f = 0.6$  ( $\text{CHCl}_3/\text{EtOAc}$  94:6). Anal. Calcd for  $\text{C}_{27}\text{H}_{35}\text{NO}_2$ : C, 79.96; H, 8.69; N, 3.45. Found: C, 80.10; H, 8.85; N, 3.56.

**3 $\beta$ -Benzoyloxy-(5',6'-trimethylene)-pyrido(17,16-b)-androst-5-ene (3d)**: 244 mg (52%), mp 177 °C (Et<sub>2</sub>O/*n*-hexane 50:50),  $[\alpha]_D^{25} -8^\circ$  (*c*, 1.05,  $\text{CHCl}_3$ ),  $R_f = 0.65$  (*n*-hexane/EtOAc 75:25). Anal. Calcd for  $\text{C}_{32}\text{H}_{37}\text{NO}_2$ : C, 82.19; H, 7.98; N, 2.99. Found: C, 82.25; H, 7.72; N, 3.08.

**3 $\beta$ -Acetoxy-(5'-methyl)-pyrido(17,16-b)androst-5-ene (3e)**: 215 mg (57%), mp 186 °C (methanol)  $[\alpha]_D^{25} -50^\circ$  (*c*, 0.25,  $\text{CHCl}_3$ ),  $R_f = 0.6$  (*n*-hexane/EtOAc 80:20). Anal. Calcd for  $\text{C}_{25}\text{H}_{33}\text{NO}_2$ : C, 79.11; H, 8.76; N, 3.69. Found: C, 79.28; H, 8.56; N, 3.50.

**3 $\beta$ -Benzoyloxy-5'-methyl-pyrido(17,16-b)androst-5-ene (3f)**: 226 mg (51%), mp 190 °C (methanol),  $[\alpha]_D^{25} -15^\circ$  (*c*, 0.90,  $\text{CHCl}_3$ ),  $R_f = 0.70$  (*n*-hexane/EtOAc 80:20). Anal. Calcd for  $\text{C}_{30}\text{H}_{35}\text{NO}_2$ : C, 81.59; H, 7.99; N, 3.17. Found: C, 81.45; H, 7.89; N, 3.11.

**3 $\beta$ -Acetoxy-(6'-methyl)-pyrido(17,16-b)androst-5-ene (3g)**: 210 mg (55%), mp 210 °C (*n*-hexane/ $\text{CH}_2\text{Cl}_2$  80:20)  $[\alpha]_D^{25} -45.2^\circ$

(*c*, 0.75,  $\text{CHCl}_3$ ),  $R_f = 0.6$  (*n*-hexane/EtOAc 80:20). Anal. Calcd for  $\text{C}_{25}\text{H}_{33}\text{NO}_2$ : C, 79.11; H, 8.76; N, 3.69. Found: C, 79.58; H, 8.36; N, 3.59.

**3 $\beta$ -Benzoyloxy-6'-methyl-pyrido(17,16-b)androst-5-ene (3h)**: 235 mg (53%), mp 215 °C (methanol),  $[\alpha]_D^{25} -12^\circ$  (*c*, 1,  $\text{CHCl}_3$ ),  $R_f = 0.70$  (*n*-hexane/EtOAc 80:20). Anal. Calcd for  $\text{C}_{30}\text{H}_{35}\text{NO}_2$ : C, 81.59; H, 7.99; N, 3.17. Found: C, 81.50; H, 7.88; N, 3.10.

**1,2,3,4,5,6,7,8-Octahydroacridine (5a)**: yield 95 mg (51%), mp 69 °C (lit.<sup>27</sup> 70–71 °C),  $R_f = 0.8$  (toluene/ $\text{CH}_2\text{Cl}_2$  80:20); IR  $\nu_{\text{max}}$  (KBr) 2950, 1520  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.09 (s, 1H), 3.10–2.65 (m, 8H), 1.80–1.52 (m, 8H); MS  $m/z$  187 ( $\text{M}^+$ ).

**2',3'-Trimethylene-5,6,7,8-tetrahydroquinoline (5b)**: 82 mg (47%), bp<sub>18 mmHg</sub> 160–61 °C (lit.<sup>28</sup> bp<sub>12 mmHg</sub> 140–42 °C),  $R_f = 0.8$  (toluene); IR  $\nu_{\text{max}}$  (KBr) 2930, 1525,  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  6.90 (s, 1H), 3.15–2.60 (m, 8H), 2.05–1.85 (m, 6H); MS  $m/z$  173 ( $\text{M}^+$ ).

**3-Methyl-5,6,7,8-tetrahydroquinoline (5c)**: 76 mg (52%), bp<sub>20 mmHg</sub> 135–36 °C (lit.<sup>27</sup> bp<sub>17 mmHg</sub> 126–27 °C),  $R_f = 0.75$  (toluene), IR  $\nu_{\text{max}}$  (KBr) 2900, 1610  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  8.31 (d, 1H,  $J = 2.5$ ), 7.25 (d, 1H,  $J = 2.5$ ), 2.90–2.75 (m, 4H), 2.30 (s, 3H), 1.95–1.72 (m, 4H); MS  $m/z$  147 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{10}\text{H}_{13}\text{N}$ : C, 81.59; H, 8.90; N, 9.51. Found: C, 81.50; H, 8.90; N, 9.45.

**2-Methyl-5,6,7,8-tetrahydroquinoline (5d)**: 66 mg (45%), bp<sub>20 mmHg</sub> 128–30 °C (lit.<sup>27</sup> bp<sub>12 mmHg</sub> 101–104 °C),  $R_f = 0.75$  (toluene); IR  $\nu_{\text{max}}$  (KBr) 2910, 1615  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.72 (d, 1H,  $J = 9$  Hz), 7.30 (d, 1H,  $J = 9.0$  Hz), 2.80–2.65 (m, 4H), 2.13 (s, 3H), 1.90–1.65 (m, 4H); MS  $m/z$  147 ( $\text{M}^+$ ).

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**Supporting Information Available:** The IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and mass spectral data for compounds **3b–h**. The material is available free of charge via the Internet at <http://pubs.acs.org>.

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