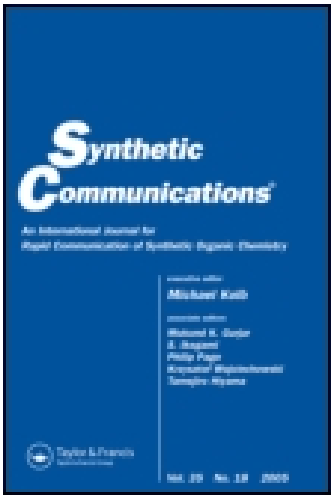

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Studies on Sequential Claisen Rearrangement: Charge-Accelerated [3,3]-Sigmatropic Rearrangement Leading to Polyheterocycles

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Studies on Sequential Claisen Rearrangement: Charge-Accelerated [3,3]-Sigmatropic Rearrangement Leading to Polyheterocycles

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Abstract: A number of quinolone-annulated pentacycles have been regioselectively synthesized in 90–95% yields by sequential Claisen rearrangements. The second synthesis is anhydrous $AlCl_3$-catalyzed charge-accelerated aromatic Claisen rearrangement of 1-aryloxymethyl-6-alkyl-3*H*-pyrano[2,3-c]quinolin-5(6*H*)-ones in dichloromethane at rt for 5–10 min. The precursors were synthesized by the thermal [3,3]-sigmatropic rearrangement of the corresponding ethers.

Keywords: anhydrous aluminium chloride, Lewis acid–catalyzed Claisen rearrangement, polyheterocycles, quinolone derivatives

INTRODUCTION

Several pyranoquinolones such as flindersine and its derivatives are widely distributed in nature[1] and are very important because of their pronounced biological properties.[2] According to recent reports,[2] quinolone derivatives show significant antibacterial activity, DNA-gyrase inhibition, and marked cytotoxicity against animal and plant tumors. Because of their biological and medicinal importance, several methods for their synthesis have been developed. Claisen rearrangement[3] is a preeminent methodology for the construction of the C-C bond in organic synthesis with a high degree of regioselectivity. In the course of our studies, we previously reported the synthesis of

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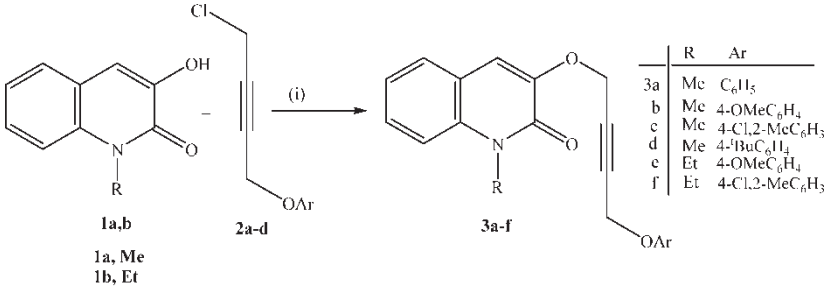
several polyheterocycles by the application of sigmatropic rearrangement.[4] Earlier we reported,[5] the regioselective synthesis of 3,4-fused furo- and pyrano quinolones by [3,3]-sigmatropic rearrangement of the ethers of 3- and 4-hydroxy quinolones. Thermal rearrangement[6] required high temperature and long time, so we attempted Lewis acid–catalyzed Claisen rearrangement.[7] Among the different catalysts reported in the literature,[8] $AlCl_3$ and its derivatives are known to be efficient for Claisen rearrangement. We therefore became interested in trying the reaction in the presence of anhydrous aluminium chloride under mild conditions. Here we report the results.

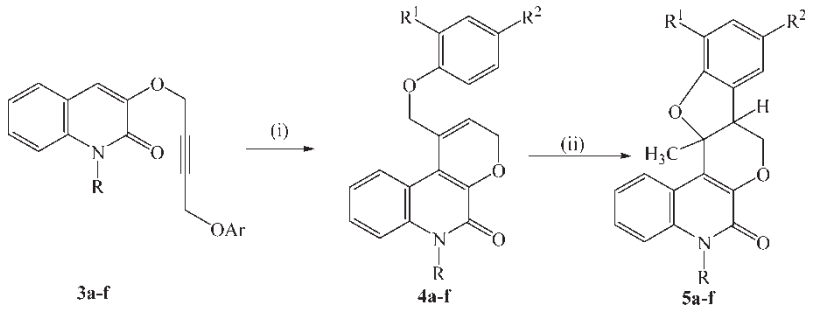
RESULTS AND DISCUSSION

The requisite starting materials, 3-(4′-aryloxybut-2′-ynyloxy)-1-alkylquinolin-2(1*H*)-ones **3a**–**f**, were synthesized in 75–88% yields by the classical alkylation of 3-hydroxy-1-alkylquinolin-2(1*H*)-ones **1a**,**b** with different 1-aryloxy-4-chlorobut-2-ynes **2a**–**d** in refluxing dry acetone in the presence of anhydrous potassium carbonate and a small amount of sodium iodide (Finkelstein's[9] condition) for 8–10 h (Scheme 1). The compounds **1a**,**b** in turn were prepared from 1-alkyl isatin and diazomethane by a slight modification[10] of the published procedure.[11]

A thermal [3,3]-sigmatropic rearrangement of **3a**–**f** was utilized for the synthesis of 3*H*-pyranoquinolones **4a**–**f**. Therefore, ethers **3a**–**f** were refluxed in chlorobenzene[5a] for 10–12 h to give 1-aryloxymethyl-5-alkyl-3*H*-pyrano[2,3-*c*]quinolin-5(6*H*)-ones **4a**–**f** in 90–95% yield (Scheme 2). Compounds **4c**–**f** were characterized from their elemental analyses and spectroscopic data. Compounds **4a**–**f** contained an allyl aryl ether moiety favorable for further [3,3]-sigmatropic rearrangement. This prompted us to undertake a study on the Claisen rearrangement of compounds **4** for the synthesis of polyheterocyclic compounds. Claisen rearrangement catalyzed by Lewis acids[8] has been known to occur under mild conditions, giving



Scheme 1. Regards and conditions: (i) dry acetone, anhy. K_2CO_3, NaI, reflux, 8–10 h.



Scheme 2. Regents and conditions: (i) chlorobenzene, reflux, 10–12 h; (ii) anhydrous $AlCl_3$, dry DCM, rt, 5–10 min.

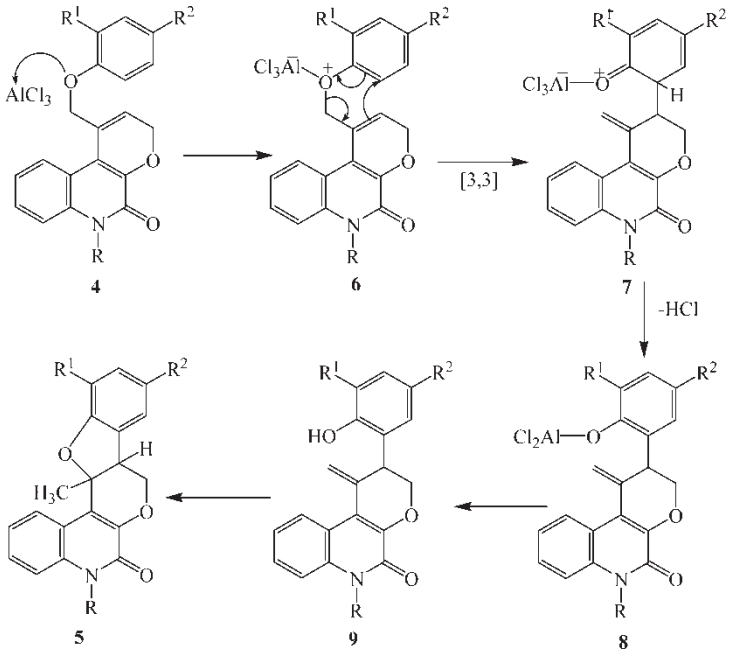
excellent yields of products. When substrate **4a** in dichloromethane was stirred with anhydrous $AlCl_3$ at room temperature for 8 min, we found that the reaction was complete and afforded a white solid, mp 182°C in 92% yield. This was characterized from its elemental analyses and spectroscopic data. ^{1}H NMR (500 MHz) spectra of **5a** revealed $\delta_H = 1.94$ (s, 3H), 3.76 (s, 3H), 3.85 (dd, 1H, $J = 2$ Hz, 12.9 Hz), 4.67 (dd, 1H, $J = 4.5$ Hz, 13.1 Hz), 4.84 (dd, 1H, $J = 2$ Hz, 4.5 Hz), 6.73–8.31 (m, 8H). Mass spectrum of **5a** showed a molecular ion peak at m/z 319 (M^+). Compounds **4b–f** were similarly treated to give the products **5b–f** in 90–95% yields (Scheme 2).

The mechanistic rationalization for the formation of products **5a–f** can be explained by a series of steps involving an initial charge-accelerated [3,3]-sigmatropic rearrangement. Substrates **4** can form an ether–$AlCl_3$ complex **6** that may undergo [3,3]-sigmatropic rearrangement through a charge delocalized transition state to give the intermediate **7** followed by rapid tautomerization and proton exchange to give intermediates **9**. These intermediates **9** undergo a 5-*exo*-cyclization to give the polyheterocyclic products **5** (Scheme 3).

In conclusion, we have demonstrated one oxy-Claisen rearrangement of propynyl vinyl ether followed by a second oxy-Claisen rearrangement of allyl aryl ether, which is run under mild conditions using Lewis acid–catalyzed charge acceleration. This methodology is simple and straightforward for the construction of the polyheterocyclic compounds in excellent yields.

EXPERIMENTAL

The melting points were recorded in open capillaries and are uncorrected. UV absorption spectra were recorded in ethanol on a Shimadzv model no. UV-2401PC spectrometer. IR spectra were run on KBr disks for solid samples and neat for liquid samples on a Fourier transform infrared (FTIR) spectrophotometer, Perkin-Elmer model no. L 120-000A. ^{1}H NMR spectra were determined for solutions in deuteriochloroform with TMS as internal standard on



Scheme 3.

Brucker-DPX-300 (300 MHz) at Indian Institute of Chemical Biology (IICB) (Kolkata) and Brucker-DRS-600 (500 MHz) spectrometers at Bose Institute (Kolkata). Silica gel [(60–120 mesh), Spectrochem, India] was used for chromatographic separation. Silica gel G [E Merck. (India)] was used. Petroleum ether refers to the fraction boiling between 60 and 80°C.

General Procedure for the Preparation of 3-(4-Arylbut-2-ynyloxy)-1-alkylquinolin-2-ones 3a–f

The compounds 3-(4-arylbut-2-ynyloxy)-1-alkylquinolin-2-ones **3a–f** were prepared according to the earlier published[5a] procedure. Compounds **3a** and **3b** were reported[5a] earlier.

Data

Compound **3c**

Yield 88%; white solid, mp 102°C; UV (EtOH): $\lambda_{max} = 224, 280, 333$ nm; IR (KBr): $\nu_{max} = 2920, 1715, 1590\ cm^{-1}$; ^1H NMR ($CDCl_3$, 300 MHz):

$\delta_H = 2.14$ (s, 3H), 3.69 (s, 3H), 4.70 (t, 2H, $J = 1.5$ Hz), 4.90 (t, 2H, $J = 1.5$ Hz), 6.92–7.34 (m, 8H); MS: m/z = 367, 369 (M^+). Anal. calcd. for $C_{21}H_{18}NO_3Cl$: C, 68.57; H, 4.93; N, 3.81%. Found: C, 68.81; H, 5.05; N, 3.70%.

Compound **3d**

Yield 88%; gummy mass, UV (EtOH): $\lambda_{max} = 223, 282, 328$ nm; IR (neat): $\nu_{max} = 2922, 1720, 1596\ cm^{-1}$; ^1H NMR ($CDCl_3$, 300 MHz): $\delta_H = 1.01$ (s, 9H), 3.68 (s, 3H), 4.68 (t, 2H, $J = 1.5$ Hz), 4.89 (t, 2H, $J = 1.5$ Hz), 6.90–7.32 (m, 9H); MS: m/z = 375 (M^+). Anal. calcd. for $C_{24}H_{25}NO_3$: C, 76.77; H, 6.71; N, 3.73%. Found: C, 77.02; H, 6.81; N, 3.83%.

Compound **3e**

Yield 85%; white solid, mp 68°C; UV (EtOH): $\lambda_{max} = 222, 281, 330$ nm; IR (KBr): $\nu_{max} = 2922, 1710, 1600\ cm^{-1}$; ^1H NMR ($CDCl_3$, 300 MHz): $\delta_H = 1.39$ (t, 3H, $J = 7$ Hz), 3.79 (s, 3H), 4.46 (q, 2H, $J = 7$ Hz), 4.67 (t, 2H, $J = 1.5$ Hz), 4.88 (t, 2H, $J = 1.5$ Hz), 6.92–7.28 (m, 9H); MS: m/z = 363, (M^+). Anal. calcd. for $C_{22}H_{21}NO_4$: C, 72.71; H, 5.82; N, 3.85%. Found: C, 72.83; H, 5.74; N, 3.79%.

Compound **3f**

Yield 82%; white solid, mp 76°C; UV (EtOH): $\lambda_{max} = 223, 281, 332$ nm; IR (KBr): $\nu_{max} = 2922, 1715, 1620\ cm^{-1}$; ^1H NMR ($CDCl_3$, 300 MHz): $\delta_H = 1.38$ (t, 3H, $J = 7$ Hz), 2.21 (s, 3H), 4.44 (q, 2H, $J = 7.1$ Hz), 4.66 (t, 2H, $J = 1.5$ Hz), 4.88 (t, 2H, $J = 1.5$ Hz), 6.95–7.30 (m, 8H); MS: m/z = 381, 383 (M^+). Anal. calcd. for $C_{22}H_{20}NO_3Cl$: C, 69.20, H, 5.28, N, 3.67%. Found: C, 69.08; H, 5.39; N, 3.61%.

General Procedure for the Rearrangement of Compounds 3a–f

The rearrangement of compounds **3a–f** were carried out according to the earlier published[5a] procedure. Compounds **4a** and **4b** were reported[5a] earlier.

Compound **4c**

Yield 95%; white solid, mp 186°C; UV (EtOH): $\lambda_{max} = 224, 320$ nm; IR (KBr): $\nu_{max} = 2920, 1680, 1590\ cm^{-1}$; ^1H NMR ($CDCl_3$, 300 MHz): $\delta_H = 2.16$ (s, 3H), 3.75 (s, 3H), 4.76 (d, 2H, $J = 4$ Hz), 4.92 (s, 2H), 6.25 (t, 1H, $J = 4$ Hz), 6.87–7.38 (m, 7H); MS: m/z = 367, 369 (M^+). Anal.

calcd. for $C_{21}H_{18}NO_3Cl$: C, 68.57; H, 4.93; N, 3.81%. Found: C, 68.80; H, 5.04; N, 3.88%.

Compound **4d**

Yield 90%; gummy mass; UV (EtOH): $\lambda_{max} = 225$, 320 nm; IR (neat): $\nu_{max} = 2920$, 1665, 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): $\delta_H = 1.05$ (s, 9H), 3.79 (s, 3H), 4.77 (d, 2H, $J = 4$ Hz), 4.91 (s, 2H), 6.21 (t, 1H, $J = 4$ Hz), 6.90–7.25 (m, 8H); MS: $m/z = 375$, (M^+). Anal. calcd. for $C_{24}H_{25}NO_3$: C, 76.77; H, 6.71; N, 3.73%. Found: C, 76.62; H, 6.84; N, 3.65%.

Compound **4e**

Yield 92%; white solid, mp 156°C; UV (EtOH): $\lambda_{max} = 224$, 330 nm; IR (KBr): $\nu_{max} = 2920$, 1670, 1585 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): $\delta_H = 1.39$ (t, 3H, $J = 7$ Hz), 3.76 (s, 3H), 4.47 (q, 2H, $J = 7$ Hz), 4.78 (d, 2H, $J = 4$ Hz), 4.90 (s, 2H), 6.27 (t, 1H, $J = 4$ Hz), 6.92–7.53 (m, 8H); MS: $m/z = 363$, (M^+). Anal. calcd. for $C_{22}H_{21}NO_4$: C, 72.71; H, 5.82; N, 3.85%. Found: C, 72.88; H, 5.92; N, 3.74%.

Compound **4f**

Yield 92%; white solid, mp 130°C; UV (EtOH): $\lambda_{max} = 223$, 333 nm; IR (KBr): $\nu_{max} = 2920$, 1665, 1580 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): $\delta_H = 1.40$ (t, 3H, $J = 6.9$ Hz), 2.05 (s, 3H), 4.46 (q, 2H, $J = 7$ Hz), 4.76 (d, 2H, $J = 4$ Hz), 4.91 (s, 2H), 6.24 (t, 1H, $J = 4$ Hz), 6.68–7.75 (m, 7H); MS: $m/z = 381$, 383 (M^+). Anal. calcd. for $C_{22}H_{20}NO_3Cl$: C, 69.20; H, 5.28; N, 3.67%. Found: C, 69.34; H, 5.19; N, 3.73%.

General Procedure for the Preparation of Compounds 5(a–f)

The compounds **4a–f** (0.1 g) were dissolved in dry dichloromethane and stirred at room temperature for 5–10 min in the presence of a catalytic amount of anhydrous aluminium chloride. Then the reaction was decomposed with ice water and extracted with dichloromethane (3 × 15 mL). Then the dichloromethane layer was washed with water (3 × 10 mL) and brine (1 × 10 mL) and then dried (Na_2SO_4). Dichloromethane was removed, and the residual mass was chromatographed over silica gel. The products were obtained in 90–95% yields when the column was eluted with pet ether–ethyl acetate (4:1).

Data

Compound **5a**

Yield 92%; white solid, mp 182°C; UV (EtOH): $\lambda_{max} = 230, 252, 260$ nm; IR (KBr): $\nu_{max} = 2920, 1700, 1610\ cm^{-1}$; ^1H NMR ($CDCl_3$, 500 MHz): $\delta_H = 1.94$ (s, 3H), 3.76 (s, 3H), 3.85 (dd, 1H, $J = 2$ Hz, 12.9 Hz), 4.67 (dd, 1H, $J = 4.5$ Hz, 13.1 Hz), 4.84 (dd, 1H, $J = 2$ Hz, 4.5 Hz), 6.73–8.31 (m, 8H); MS: $m/z = 319$ (M^+). Anal. calcd. for $C_{20}H_{17}NO_3$: C, 75.22; H, 5.37; N, 4.39%. Found: C, 75.43; H, 5.30; N, 4.48%.

Compound **5b**

Yield 93%; white solid, mp 192°C; UV (EtOH): $\lambda_{max} = 229, 252, 265$ nm; IR (KBr): $\nu_{max} = 2920, 1705, 1600\ cm^{-1}$; ^1H NMR ($CDCl_3$, 500 MHz): $\delta_H = 1.91$ (s, 3H), 3.75 (s, 3H), 3.81 (s, 3H), 3.89 (dd, 1H, $J = 2$ Hz, 13 Hz), 4.66 (dd, 1H, $J = 4.5$ Hz, 13 Hz), 4.84 (dd, 1H, $J = 2$ Hz, 4.5 Hz), 6.75–8.24 (m, 7H); MS: $m/z = 349$, (M^+). Anal. calcd. for $C_{21}H_{19}NO_4$: C, 72.19; H, 5.48; N, 4.01%. Found: C, 72.35; H, 5.59; N, 4.09%.

Compound **5c**

Yield 95%; white solid, mp 202°C; UV (EtOH): $\lambda_{max} = 228, 250, 262$ nm; IR (KBr): $\nu_{max} = 2920, 1700, 1620\ cm^{-1}$; ^1H NMR ($CDCl_3$, 500 MHz): $\delta_H = 1.92$ (s, 3H), 2.16 (s, 3H), 3.76 (s, 3H), 3.85 (dd, 1H, $J = 2$ Hz, 13 Hz), 4.69 (dd, 1H, $J = 4.5$ Hz, 13 Hz), 4.86 (dd, 1H, $J = 2$ Hz, 4.5 Hz), 6.75–8.16 (m, 6H); MS: $m/z = 367$, 369 (M^+). Anal. calcd. for $C_{21}H_{18}NO_3Cl$: C, 68.57; H, 4.93; N, 3.81%. Found: C, 68.43; H, 5.05; N, 3.88%.

Compound **5d**

Yield 90%; white solid, mp 170°C; UV (EtOH): $\lambda_{max} = 229, 251, 265$ nm; IR (KBr): $\nu_{max} = 2920, 1725, 1630\ cm^{-1}$; ^1H NMR ($CDCl_3$, 500 MHz): $\delta_H = 1.08$ (s, 9H), 1.88 (s, 3H), 3.77 (s, 3H), 3.81 (dd, 1H, $J = 2$ Hz, 13 Hz), 4.67 (dd, 1H, $J = 4.5$ Hz, 13 Hz), 4.85 (dd, 1H, $J = 2$ Hz, 4.5 Hz), 6.79–8.32 (m, 7H); MS: $m/z = 375$, (M^+). Anal. calcd. for $C_{24}H_{25}NO_3$: C, 76.77; H, 6.71; N, 3.73%. Found: C, 76.99; H, 6.78; N, 3.81%.

Compound **5e**

Yield 92%; white solid, mp 198°C; UV (EtOH): $\lambda_{max} = 230, 251, 260$ nm; IR (KBr): $\nu_{max} = 2920, 1720, 1625\ cm^{-1}$; ^1H NMR ($CDCl_3$, 500 MHz): $\delta_H = 1.38$ (t, 3H, $J = 7$ Hz), 1.91 (s, 3H), 3.80 (s, 3H), 3.89 (dd, 1H, $J = 2$ Hz, 13 Hz), 4.45 (q, 2H, $J = 7$ Hz), 4.65 (dd, 1H, $J = 4.5$ Hz, 13 Hz),

4.82 (dd, 1H, $J = 2$ Hz, 4.5 Hz), 6.80–8.01 (m, 7H); MS: m/z = 363, (M^+). Anal. calcd. for $C_{22}H_{21}NO_4$: C, 72.71; H, 5.82; N, 3.85%. Found: C, 72.89; H, 5.87; N, 3.78%.

Compound **5f**

Yield 95%; white solid, mp 206°C; UV (EtOH): $\lambda_{max} = 228, 252, 260$ nm; IR (KBr): $\nu_{max} = 2920, 1715, 1610\ cm^{-1}$; ^1H NMR ($CDCl_3$, 500 MHz): $\delta_H = 1.39$ (t, 3H, $J = 7$ Hz), 1.91 (s, 3H), 2.12 (s, 3H), 3.84 (dd, 1H, $J = 2$ Hz, 13 Hz), 4.45 (q, 2H, $J = 7$ Hz), 4.68 (dd, 1H, $J = 4.5$ Hz, 13 Hz), 4.85 (dd, 1H, $J = 2.1$ Hz, 4.5 Hz), 6.85–8.24 (m, 6H); MS: m/z = 381, 383 (M^+). Anal. calcd. for $C_{22}H_{20}NO_3Cl$: C, 69.20; H, 5.28; N, 3.67%. Found: C, 69.46; H, 5.40; N, 3.75%.

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