A synthesis of 10-aryl-2,7-dimethyl-4,5-dioxo-3,6,9- trioxa-3,4,5,6,9, 10-hexahydroanthracene catalysed by KF-alumina

Youjian Feng[a], Yuan Gao[b], Songlei Zhu[a], Tuanjie Li[a], Xiaojing Zhang[a], Shujiang Tu[a]* and Daqing Shi[a]

[a]Department of Chemistry, Xuzhou Normal University, Key laboratory of Biotechnology on Medical Plant, Jiangsu, Xuzhou, Jiangsu 221009, P. R. China

[b]Department of Chemistry, Shenzhen University, Guangdong; Shenzhen, 518060, P. R. China

A series of 10-aryl-2,7-dimethyl-4,5-dioxo-3,6,9- trioxa-3,4,5,6,9,10-hexaanthracenes were prepared by the reaction of aromatic aldehydes with triacetic acid lactone in ethylene glycol catalysed by KF-alumina.

Keywords: 10-aryl-2,7-dimethyl-4,5-dioxo-3,6,9- trioxa-3,4,5,6,9,10-hexahydroanthracene, KF-alumina

The utility of fluoride salts as potential bases in a variety of synthetic reactions has been recognised in recent years.[1,2] However, the low solubility of fluoride salts in ordinary solvents hampers their wide application in organic synthesis. On the other hand, there has been increasing use of inorganic solid supports as catalysts resulting in higher selectivity, milder reaction conditions and easier work-up for many reactions.[3,4] Condensation reactions of carbonyl compounds with active methylene compounds are one of the most important synthetic methods for substituted alkenes. The reactions are generally catalysed by bases or Lewis acids.[5] Moreno-Manas and coworkers have reported that the condensation reaction of an aromatic aldehyde with triacetic acid lactone using piperidine as catalyst in acetic acid forms arylbis(4-hydroxy-6-methyl-oxo-2*H*-pyran-3-yl)methanes.[6] However, on treatment of an aromatic aldehyde with triacetic acid lactone in ethylene glycol as solvent using KF-alumina as catalyst, Knoevenagel condensation, Michael addition and cyclodehydration have taken place and 10-aryl-2,7-dimethyl-4,5-dioxo-3,6,9-trioxa-3,4,5,6,9,10-hexahydroanthracenes were obtained. In our previous papers,[7,8,9] we have reported that alumina coated with potassium fluoride (KF-alumina) is a versatile reagent for Knoevenagel reactions and Michael addition condensations. In this paper, we report the preparation of 10-aryl-2,7-dimethyl-4,5-dioxo-3,6,9-trioxa-3,4,5,6,9,10-hexahydroanthracenes by the reaction of aromatic aldehydes with triacetic acid lactone in ethylene glycol catalysed by KF-alumina.

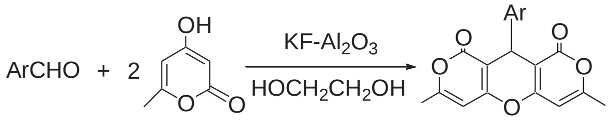
By treating two molar equivalents of triacetic acid lactone with an aromatic aldehyde in ethylene glycol at 85°C for 3–5 h catalysed by KF-alumina the desired 10-aryl-2,7-dimethyl-4,5-dioxo-3,6,9-trioxa-3,4,5,6,9,10-hexahydroanthracenes were obtained in moderate yields (50.0–89.3%). The results obtained are shown in Table 1.

All the compounds obtained gave analysis for C, H, N in good agreement with calculated values, and the structures were established on the basis of spectroscopic data and confirmed by X-ray diffraction studies on a monocrystal of **3h**.

The synthetic route is shown in Scheme 1.

Table 1 Yields of the products

Entry	Ar	Isolated yield/%
3a	C_6H_5	78
3b	$4\text{-}CH_3C_6H_4$	74
3c	$2\text{-}ClC_6H_4$	80
3d	$2\text{-}BrC_6H_4$	66
3e	$4\text{-}BrC_6H_4$	64
3f	$4\text{-}OHC_6H_4$	89
3g	$4\text{-}OH\text{-}3\text{-}OCH_3C_6H_3$	70
3h	$4\text{-}NO_2C_6H_4$	50



1 **2** **3**

Scheme 1

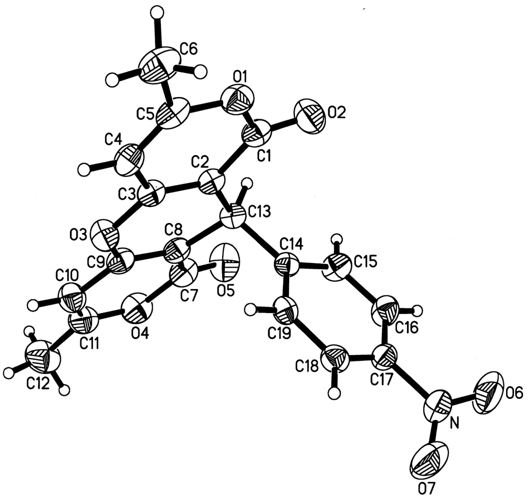


Fig. 1 X-ray crystal structure of **3h**.

Experimental

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a FT IR-8101 spectrometer in KBr. ^1H NMR spectra were measured on a DPX 400 MHz spectrometer using TMS as internal standard and $CDCl_3$ as solvent. X-ray diffraction was measured on a Siemens P4 diffractometer.

General procedure for synthesis of 10-aryl-2,7-dimethyl-4,5-dioxo-3,6,9-trioxa-3,4,5,6,9,10-hexahydroanthracenes 3: A dry 50 ml flask was charged with aromatic aldehyde 2 (2 mmol), triacetic acid lactone (4 mmol), KF-alumina (250 mg) and ethylene glycol (10 ml). The mixture was stirred at 85°C for 3–5 h (TLC). Then the solid material was filtered off and was washed with a little ethanol. The filtrate was poured into 200 ml water. The white solid was filtered off, then washed with water. The crude solid was purified by recrystallisation from 95% EtOH to give (3).

Below for AA'xx' systems: $J^* = J_{23} + J_{25}$

10-phenyl-2,7-dimethyl-4,5-dioxo-3,6,9-trioxa-3,4,5,6,9,10-hexahydroanthracene, **3a**: m.p. 295–297°C(Lit. 297–298)[11], IR (KBr, ν): 3091, 1724, 1705, 1637, 1604, 1438, 1240, 1182, 1136, 1034, 974, 829, 752, 707, 599 cm^{-1}; ^1H NMR ($CDCl_3$, δ): 2.24(s, 6H, CH_3), 4.83(s, 1H, CH), 5.99(s, 2H, C=CH), 7.17–7.35 (m, 5H, ArH); (Found: C, 70.92; H, 4.28. $C_{19}H_{14}O_5$ requires: C, 70.80; H, 4.38%).

10-(4-methylphenyl)-2,7-dimethyl-4,5-dioxo-3,6,9-trioxa-3,4,5,6,9,10-hexa-hydroanthracene, **3b**: m.p. 282–284°C, IR(KBr, ν):

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* Correspondence. E-mail: laotu2001@263.net

3091, 1720, 1611, 1518, 1442, 1377, 1349, 1247, 1180, 1138, 1043, 973, 835, 790, 738, 689, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 2.23 (s, 6H, CH_3), 2.27(s, 3H, CH_3), 4.79(s, 1H, CH), 5.98(s, 2H, C=CH), 7.08(m, *J*=8.4 Hz, 2H, ArH), 7.23(m, *J*=8.4 Hz, 2H, ArH); (Found: C, 71.30; H, 4.64. $C_{20}H_{16}O_5$ requires C, 71.42; H, 4.78%).

10-(2-chlorophenyl)-2,7-dimethyl-4,5-dioxo-3,6,9-trioxa-3,4,5,6,9,10-hexa-hydroanthracene, **3c**: m.p. 271–273°C, IR(KBr, ν): 3091, 1732, 1705, 1647, 1610, 1479, 1442, 1379, 1247, 1186, 1142, 1037, 972, 810, 756, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 2.24(s, 6H, CH_3), 5.07(s, 1H, CH), 5.96(s, 2H, C=CH), 7.14–7.53(m, 4H, ArH); (Found: C, 64.06; H, 3.60. $C_{19}H_{13}ClO_5$ requires C, 63.97; H, 3.67%).

10-(2-bromophenyl)-2,7-dimethyl-4,5-dioxo-3,6,9-trioxa-3,4,5,6,9,10-hexahydroanthracene, **3d**: m.p. 273–275°C, IR(KBr, ν): 3085, 1729, 1641, 1610, 1525, 1444, 1380, 1243, 1240, 1137, 1039, 968, 840, 794, 748 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 2.25(s, 6H, CH_3), 5.11(s, 1H, CH), 5.96(s, 2H, C=CH), 7.05–7.47(m, 4H, ArH); (Found: C, 56.98; H, 3.21. $C_{19}H_{13}BrO_5$ requires C, 56.88; H, 3.27%).

10-(4-bromophenyl)-2,7-dimethyl-4,5-dioxo-3,6,9-trioxa-3,4,5,6,9,10-hexahydroanthracene, **3e**: m.p. 293–295°C, IR(KBr, ν): 3085, 1749, 1718, 1639, 1604, 1490, 1375, 1242, 1186, 1132, 1075, 966, 815, 706, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 2.25(s, 6H, CH_3), 4.79(s, 1H, CH), 5.99(s, 2H, C=CH), 7.23(m, *J**=6.5 Hz, 2H, ArH), 7.39(m, *J**=6.5 Hz, 2H, ArH); (Found: C, 56.96; H, 3.34. $C_{19}H_{13}BrO_5$ requires C, 56.88; H, 3.27%).

10-(4-hydroxyphenyl)-2,7-dimethyl-4,5-dioxo-3,6,9-trioxa-3,4,5,6,9,10-hexa- hydroanthracene, **3f**: m.p. 242–244°C, IR(KBr, ν): 3433, 3091, 1760, 1730, 1703, 1611, 1600, 150, 1438, 1377, 1242, 1201, 1186, 964, 916, 804, 742, 692, 670 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 2.25(s, 6H, CH_3), 4.85(s, 1H, CH), 5.99(s, 2H, C=CH), 7.6.99 (m, *J**=8.5 Hz, 2H, ArH), 7.35(m, *J**=8.5 Hz, 2H, ArH); (Found: C, 67.58; H, 4.09. $C_{19}H_{14}O_6$ requires C, 67.45; H, 4.17%).

10-(4-hydroxy-3-methoxyphenyl)-2,7-dimethyl-4,5-dioxo-3,6, 9-trioxa-3,4,5,6,9,10-hexa-hydroanthracene, **3g**: m.p. 281–283°C, IR(KBr, ν): 3415, 3097, 1768, 1728, 1640, 1602, 1500, 1442, 1377, 1241, 1137, 1029, 962, 900, 842 794, 702, 640, cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 2.25(s, 6H, CH_3), 3.85(s, 3H, OCH_3), 4.86(s, 1H, CH), 5.99(s, 2H, C=CH), 6.86-7.20(m, 3H, ArH); (Found: C, 65.32; H, 4.45. $C_{20}H_{16}O_7$ requires C, 65.22; H, 4.38%).

10-(4-nitrophenyl)-2,7-dimethyl-4,5-dioxo-3,6,9-trioxa-3,4,5,6,9,10-hexa-hydroanthracene, **3h**: m.p. 289–291°C, IR(KBr, ν): 3085, 1722, 1639, 1608, 1515, 1440, 141378, 1348, 1245, 1188, 1136, 1035, 974, 839, 744, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 2.27 (s, 6H, CH_3), 4.92(s, 1H, CH), 6.04(s, 2H, C=CH), 7.23(m, *J**=9.4 Hz, 2H, ArH), 7.53(m, *J**=9.4 Hz, 2H, ArH); (Found: C, 62.30; H, 3.46; N, 3.74. $C_{19}H_{13}NO_7$ requires C, 62.13; H, 3.57; N, 3.81%).

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10 X-ray crystallography for **3**h: Empirical formula $C_{19}H_{13}NO_7$, F_W =367.30, *T*=297(2)K, monoclinic, space group P2(1)/*c*, *a*=10.669(1)Å, *b*=11.544(1)Å, *c*=14.045(2)Å, β=105.98(1)°, *V*=1663.0(3)Å^3, *Z*=4, *Dc*=1.467 Mg/m^3, λ*(MoKα)*= 0.71073Å, μ= 0.114 mm^{-1}, *F(000)*=760. 1.99°<θ<24.99°, *R*=0.0380, *wR*=0.0944. *S*=1.018, Largest diff. Peak and hole: 0.188 and –0.168e. Å^{-3}. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-226174.
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