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Synthesis of functionalized polycyclic compounds via a novel aromatic oxy-Cope rearrangement

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Abstract—Polycyclic compounds have been prepared by aromatic dianionic oxy-Cope rearrangements involving the π bonds of two phenyl rings in a [3,3] sigmatropic rearrangement.

Ever since the first report[1] that 1,2-divinyl-1,2-diols undergo dianionic oxy-Cope rearrangement for the synthesis of benzotropones, there have been several reports[2] of this route being employed for the synthesis of polycyclic structures. Aromatic oxy-Cope rearrangement involving aromatic rings such as 1- and 2-naphthyl, 2-furanyl and 2-benzofuranyl as one of the substituents have also been reported.[3] Helicenes have been prepared[4] via aromatic oxy-Cope rearrangement involving the π bond of a phenanthrene ring. Uyehara and co-workers have reported[5] participation of the π bonds of a phenyl and *o*- and *p*-methoxyphenyl rings in the sigmatropic oxy-Cope rearrangement. Previously we reported[6] the first instance of an aromatic dianionic oxy-Cope rearrangement involving the π bonds of both naphthyl rings of 1,2-dinaphthyl-1,2-diols derived from cyclic α-diketones. In continuation of this work we herein report the base catalysed rearrangements of the 9,10-diphenyl-9,10-diol of phenanthrene-9,10-dione, 1,2-di(*p*-methoxyphenyl)-1,2-diol and the 1,2-diphenyl-1,2-diol of acenaphthene-1,2-dione. This is the first instance where a diphenyl diol and a di(*p*-methoxyphenyl) diol have been observed to undergo aromatic dianionic oxy-Cope rearrangement were the π bonds of two phenyl rings form the 1,5-hexadiene system necessary for [3,3] sigmatropic rearrangement.

1,2-Diphenylacenaphthene-1,2-diol **1**[7] was prepared by the addition of 4 equiv of phenylmagnesium bromide to 1,2-acenaphthaquinone in dry THF. The rearrangement of diol **1** was studied under different conditions using *t*-BuOK in dry THF, *t*-BuOK in dry *t*-BuOH and NaH in dry THF. The products with yields are reported in Table 1. The diol **1** on treatment with 10 equiv of the base gave compound **2** as a white solid and compound **3** as a pale yellow solid. The ^{1}H NMR spectrum of **2** showed a D_2O exchangeable signal at δ 1.57 (2H, s) for the OH protons and a signal at δ 6.6 (2H, s) for the methine protons. The ^{1}H coupled ^{13}C NMR spectrum showed a doublet at δ 73.87 for the C–OH carbons. The mass spectrum showed a molecular ion peak at m/z 338.402. The IR spectrum of compound **3** showed a very strong peak at 1654 cm^{-1} for the carbonyl stretching and a peak at 3532 for the OH stretch. The ^{1}H NMR spectrum showed a signal at δ 3.32 (1H, d, $^3J = 4.10$ Hz) for the ring methine proton and at δ 3.30 (1H, s, D_2O exchangeable) for the OH proton. The ^{1}H coupled ^{13}C NMR showed a doublet at δ 74.14 for the ring CH and singlets at δ 98.97 for C–OH and at δ 198.12 for the carbonyl carbon. The mass spectrum showed a molecular ion peak at m/z 336.3872.

The structures of compounds **2** and **3** were assigned based on spectral data supported[8] by elemental analysis. Formation of **2** involves a dianionic oxy-Cope rearrangement of **1**, when treated with the base followed by isomerisation. Formation of **3** occurs by tandem dianionic oxy-Cope/transannular ring closure in the presence of a base followed by air oxidation. A similar air oxidation has previously been reported[6] by us.

Keywords: Dianionic oxy-Cope rearrangement; Polycyclic compounds; Transannular reaction.

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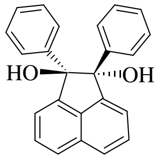
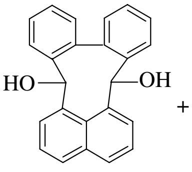
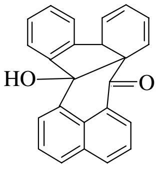
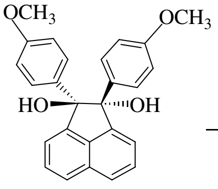
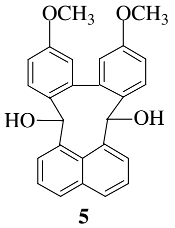
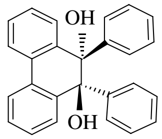
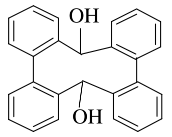
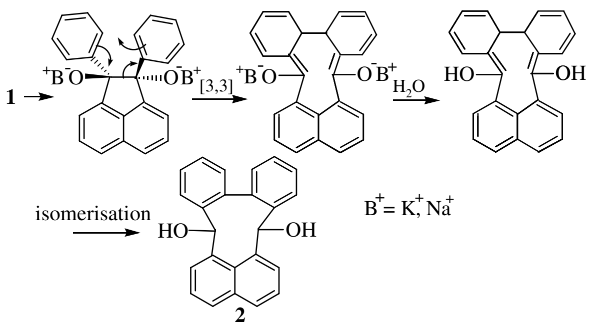
Table 1. Rearrangement under different basic conditions

Entry	Oxy-Cope system	Conditions	Products	Yield
1	 **1**	a. Method A, rt, 3 h	 **2** +  **3**	**2a** (30%), **3a** (60%)
2		b. Method B, rt, 4 h		**2b** (25%), **3b** (65%)
3		c. Method C, reflux, 1 h		**2c** (40%), **3c** (0%)
4	 **4**	a. Method A, reflux, 2 h	 **5**	**5a** (60%)
5		b. Method B, reflux, 4 h		**5b** (62%)
6		c. Method C, reflux, 2 h		**5c** (45%)
7	 **6**	a. Method A, reflux, 3 h	 **7**	**7a** (60%)
8		b. Method B, rt, 5 h		**7b** (65%)
9		c. Method C, reflux, 4 h		**7c** (40%)

Methods: A: *t*-BuOK/THF, B: *t*-BuOK/*t*-BuOH and C: NaH/THF.

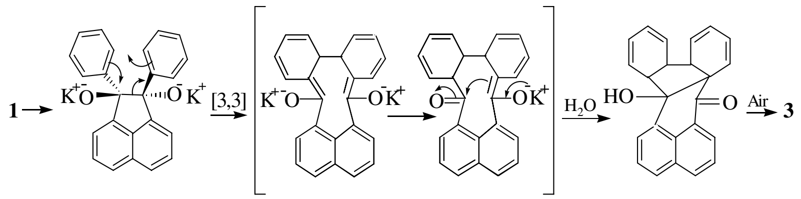
Similar tandem oxy-Cope/transannular mechanisms have also been reported[9] (Schemes 1 and 2).

1,2-Di(*p*-methoxyphenyl)acenaphthene-1,2-diol **4** was prepared by the addition of 4 equiv of *p*-methoxyphenylmagnesium bromide to 1,2-acenaphthaquinone in dry THF, giving a white solid (mp 159–160 °C, 70%).The IR spectrum showed OH stretching at 3535 and 3516 cm^{-1} and the absence of carbonyl stretching. The ^{1}H NMR spectrum showed a D_2O exchangeable signal at δ 2.2 (2H, s), a resonance at δ 3.8 (6H, s) for the OCH_3 protons and signals at δ 6.8–7.9 (14H, m) for the aromatic protons. The mass spectrum showed a molecular ion peak at *m*/*z* 398.4531. The rearrangement of diol **4** was studied under different conditions using *t*-BuOK in dry THF, *t*-BuOK in dry *t*-BuOH and NaH in dry THF. The products with yields are given in Table 1. The diol **4** on treatment with 10 equiv of the base gave compound **5** as a white solid. The IR spectrum showed a broad peak at 3436 cm^{-1} for the OH and the absence of carbonyl stretching. The ^{1}H NMR showed a D_2O exchangeable signal at δ 1.61 (2H, br s) for both OH groups. The ^{1}H coupled ^{13}C NMR spectrum showed a doublet at δ 73.0 for the C–OH carbon and two quartets at δ 55.32 and δ 55.29 for the OCH_3 carbons. The mass spectrum showed a molecular ion peak at *m*/*z* 398.4539. The structures of compounds **4** and **5** were assigned[10] based on the spectral data and elemental analysis. The mechanism of formation of compound **5** is as in Scheme 1.



Scheme 1. Mechanism of the formation of **2**.

9,10-Diphenylphenanthrene-9,10-diol **6**[11] was prepared by the addition of 4 equiv of phenylmagnesium bromide to 9,10-phenanthraquinone in dry THF. The rearrange-



Scheme 2. Mechanism of the formation of **3**.

ment of diol **6** was studied as before giving compound **7** as a white solid.[12] The IR spectrum showed a broad peak at 3390 cm^{-1} for the OH and absence of carbonyl stretching. The ^1H NMR showed a D_2O exchangeable signal at δ 6.0 (2H, s) for the OH and at δ 7.25 (2H, s) for the methine protons. The ^1H coupled ^{13}C NMR spectrum showed a doublet at δ 115.4 for both C–OH carbons. The mass spectrum showed a molecular ion peak at m/z 364.49.

We observed formation of a transannular product in addition to the usual oxy-Cope product, only in the case of 1,2-diphenylacenaphthene-1,2-diol **2**. The polycyclic compounds **2**, **5** and **7** were isolated as diastereomers. The best yields of the products were obtained with *t*-BuOK as the base and *t*-BuOH as solvent (method B). We presume that the higher polarity of the solvent is the reason for the greater yield of the products via this method. Further work is being carried out in our laboratory on these lines.

In conclusion our work reports an easy route to the synthesis of functionalized polycyclic compounds from simple starting materials via a novel diaromatic dianionic oxy-Cope rearrangement.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.11.177.

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8. Tandem dianionic oxy-Cope rearrangement/transannular reaction of **1** (Table 1, entry 1): A solution of **1** (0.169 g, 0.0005 mol) in dry THF (5 ml) was added to a suspension of *t*-BuOK (0.560 g, 0.005 mol) in dry THF (5 ml). The mixture was stirred under N_2 at rt for 3 h and quenched with a satd solution of NH_4Cl (10 ml). The product was extracted into diethyl ether (3 × 10 ml) and the combined organic phases were washed with water, dried over anhyd Na_2SO_4 and evaporated. Purification of the residue by column chromatography on silica gel, with ethyl acetate/hexane (0.5:10) as eluent afforded the diol **2** as a white solid (mp 119–120 °C), (0.005 g), 30% yield. Further elution with ethyl acetate/hexane (2:10) gave a pale yellow solid **3** (mp 113–114 °C), (0.010 g) 60% yield. Compound **2**: IR (KBr, cm^{-1}) 3501, 1596, 1494, 1446, 1024, 714; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm) 1.57 (2H, s, D_2O exchangeable), 6.6 (2H, s), 6.8–8.0 (14H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 134.21, 132.95, 130.70, 129.23, 128.95, 128.59, 128.42, 128.16, 126.39, 125.61, 123.02, 73.87. HRMS: calcd for $C_{24}H_{18}O_2$, (M^+): 338.4024. Found: 338.4020. Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.14; H, 5.41. Compound **3**: IR (KBr, cm^{-1}) 3532, 1654, 1577, 1449, 1271, 771, 715; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm) 3.30 (1H, s, D_2O exchangeable), 3.32 (1H, d, $^3J = 4.10$ Hz), 6.6–8.02 (14H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm), 198.12, 144.22, 140.78, 137.95, 137.27, 135.66, 135.22, 133.14, 132.82, 132.26, 130.73, 130.33, 129.26, 128.88, 128.62, 128.42, 127.51, 127.09, 126.71, 125.92, 125.20, 123.32, 98.97, 74.14. HRMS: calcd for $C_{24}H_{16}O_2$, (M^+): 336.3868. Found: 336.3872 (10%). Anal. Calcd for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79. Found: C, 85.61; H, 4.82.
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10. Dianionic oxy-Cope rearrangement of **4** (Table 1, entry 5): A solution of **4** (0.200 g, 0.0005 mol) in dry *t*-BuOH (10 ml) was added to a suspension of *t*-BuOK (0.560 g, 0.005 mol) in dry *t*-BuOH (10 ml).The mixture was refluxed under N_2 for 4 h and then quenched with a satd solution of NH_4Cl (10 ml). The product was extracted into diethyl ether (3 × 10). The ether layer was washed with water, dried over anhyd Na_2SO_4 and evaporated. Purification of the residue by column chromatography on silica gel, with ethyl acetate/hexane (1:10) as eluent afforded the diol **5** as a white solid (mp 118–120 °C), (0.074 g) 62% yield. IR (KBr, cm^{-1}) 3435 (br), 2958, 1607, 1251, 824; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm) 1.61 (2H, br s, D_2O exchangeable), 3.82 (3H, s), 3.84 (3H, s), 6.55 (2H, s) 6.85–7.8 (12H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 132.1, 132.0, 130.20, 127.70, 127.66, 126.71, 125.58, 124.0, 122.0, 113.96, 113.41, 73.0, 55.29, 55.32. HRMS: calcd for $C_{26}H_{22}O_4$, (M^+): 398.4536. Found: 398.4539. Anal. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.56. Found: C, 78.31; H, 5.60.
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12. Dianionic oxy-Cope rearrangement of **6** (Table 1, entry 9): A solution of **6** (0.182 g, 0.0005 mol) in dry THF (10 ml) was added to a suspension of NaH (0.240 g, 0.005 mol, 50% dispersion in mineral oil washed with petrol 60–80 °C, 3 × 10 ml) in dry THF (5 ml). The mixture was refluxed under N_2 for 4 h, cooled and then quenched with a satd solution of NH_4Cl (10 ml). The product was extracted into diethyl ether (3 × 10 ml) and

the combined organic phases were washed with brine and water, then dried over anhyd Na_2SO_4 and evaporated. Purification of the residue by column chromatography on silica gel, with ethyl acetate/hexane (0.3:10) as eluent, afforded **7** as a white solid, (mp 128–130 °C), (0.073 g) 40% yield. IR (KBr, cm^{-1}) 3390, 1634, 1597, 1493, 1293, 1209, 751; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm) 6.0 (2H, s, D_2O exchangeable), 7.25 (2H, s), 7.4–8.7 (16H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 158.05, 141.87, 130.24, 129.62, 127.72, 127.44, 127.18, 127.06, 125.69, 124.95, 123.15, 122.99, 121.79, 115.49. HRMS: calcd for $C_{26}H_{20}O_2$, (M^+): 364.44. Found: 364.49. Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.68; H, 5.53. Found: C, 85.72; H, 5.59.