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Carbanion induced synthesis of dibenzo[*a*,*c*]cycloheptenes through ring transformation reactions of 2*H*-pyran-2-one†

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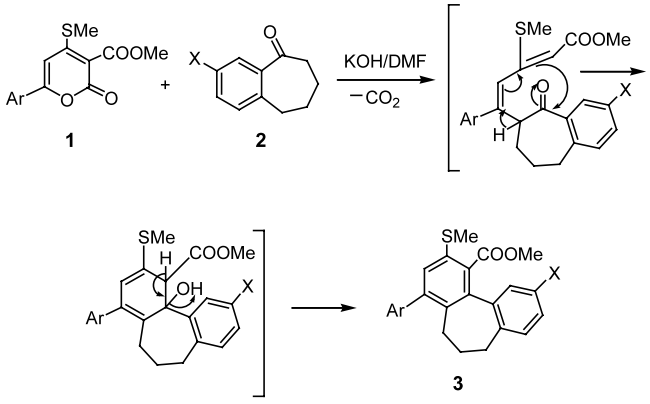
Abstract—An efficient and convenient one-pot synthesis of 4-aryl-2-methylsulfanyl-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene-1-carboxylate **3a**–**n** has been delineated and illustrated through carbanion induced ring transformation of 6-aryl-3-carbomethoxy-4-methylsulfanyl-2*H*-pyran-2-ones **1** with benzosuberone **2**.

The efficient synthesis and the properties of *ortho–ortho′* bridged biphenyls continue to be of interest in many areas of chemistry.[1,2] The synthesis of such biaryls has been a challenging and fascinating undertaking in natural product chemistry as numerous natural products such as polyketides, terpenes, lignans, coumarins, flavanoids, tannins and many alkaloids possess this ring system.[3] Annulated arenes with electron donor and acceptor substituents are recognized as molecular subunits for the expression of non-linear optical properties by acquiring high polarisability.[4] Because of their interesting properties, not only as bioactive natural products, but also as chiral reagents in asymmetric reactions,[5] natural and unnatural biaryls are considered attractive synthetic targets. Here we report an efficient one-pot synthesis of highly functionalized *ortho–ortho′* bridged biaryls.

There are only a limited number of procedures reported in the literature for the construction of *ortho–ortho′* bridged biphenyls which suffer from limitations of low yields and multistep syntheses. Earlier, dibenzo-[*a*,*c*]cycloheptenes have been prepared[1a] following a sequence of reactions starting from phenanthrene and dichlorodibenzobicyclo[4.1.0]heptatriene. They have also been synthesized via the pyrolysis of 1,2:3,4 dibenzotropilidine,[6] in poor yields. Attempts were made to prepare dibenzo[*a*,*c*]-cycloheptene from biphenyl-5-propionic acid[7] but the results were not satisfactory. However, dehydration of colchinol[8] led to the formation of the desired compound. Recently, ring-substituted systems such as 6-methyl- and 6-phenyl-5*H*-dibenzo-



3	Ar	X	Yield (%)
a	4-FC_6H_4	H	39
b	4-ClC_6H_4	H	35
c	4-BrC_6H_4	H	33
d	4-$CH_3C_6H_4$	H	37
e	3-ClC_6H_4	H	31
f	2-pyridyl	H	33
g	2-thienyl	H	32
h	4-FC_6H_4	F	35
i	4-ClC_6H_4	F	39
j	4-BrC_6H_4	F	41
k	3-ClC_6H_4	F	31
l	2-thienyl	F	33
m	4-(imidazol-1-yl)phenyl	F	31
n	4-(*s*-triazol-1-yl)phenyl	F	30

Scheme 1.

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[*a*,*c*]cycloheptenes have been obtained from the reaction of MeLi and PhLi with dibenzotropolone.[9]

Our approach to the synthesis of 4-aryl-2-methylsulfanyl-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene-1-carboxylate **3** is based on the carbanion induced ring transformation of 6-aryl-3-carbomethoxy-4-methylsulfanyl-2*H*-pyran-2-one **1** with 1-benzosuberone **2**. The lactone **1** may be considered as a cyclic ketene-hemimethylthio acetal with three electrophilic centers namely C-2, C-4 and C-6 in its molecular makeup, in which C-6 is highly susceptible to attack by nucleophiles due to extended conjugation and the presence of an electron withdrawing substituent at position 3 of the lactone ring. The benzosuberone **2** has been used as a source of carbanions which can be generated in situ using powdered KOH in DMF. The reaction is possibly initiated by attack of the carbanion at C-6 with ring opening, followed by decarboxylation and condensation–cyclization involving keto and methylene groups. This is a one-pot reaction in which a mixture of pyran-2-one **1**, benzosuberone **2** and powdered KOH in DMF was stirred at ambient temperature for 40–50 h under an inert atmosphere. After this time, the reaction mixture was poured into ice-water and the solution was neutralized with 10% HCl. The crude product was purified by column chromatography to afford the corresponding methyl 4-aryl-2-methylsulfanyl-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene-1-carboxylates **3a**–**n** in moderate yields (Scheme 1). This procedure is highly versatile and provided a genuine and convenient one-pot synthesis of highly functionalized dibenzo[*a*,*c*]cycloheptenes.

All the compounds were characterized by spectroscopic analysis.[10]

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10. Typical procedure for **3a**: A mixture of 3-carbomethoxy-6-(4-fluorophenyl)-4-methylthio-2*H*-pyran-2-one (0.29 g, 1 mmol) and 1-benzosuberone (0.16 g, 1 mmol) and powdered KOH (0.085 g, 1.5 mmol) in dry DMF (10 ml) was stirred at room temperature for 40 h. After completion of the reaction, the mixture was poured into ice water with vigorous stirring and neutralized with 10% HCl. The crude product obtained was filtered, washed with water and finally purified on a silica gel column using $CHCl_3$:hexane (1:1) as eluent. The viscous liquid obtained was characterized spectroscopically, yield 39%; NMR ($CDCl_3$) δ 1.18–1.56 (m, 2H, CH_2), 1.98 (t, $J=6.2$ Hz, 2H, CH_2), 2.51 (s, 3H, SCH_3), 2.62 (t, $J=6.2$ Hz, 2H, CH_2), 3.97 (s, 3H, OCH_3), 6.88 (s, 1H, CH), 7.11–7.24 (m, 4H, ArH), 7.29–7.41 (m, 4H, ArH); IR (neat) ν 1723 cm^{-1} (CO); MS m/z 392 (M^+). **3b**: mp 172°C; δ 1.25–1.58 (m, 2H, CH_2), 2.05 (t, $J=6.2$ Hz, 2H, CH_2), 2.53 (s, 3H, SCH_3), 2.60 (t, $J=6.2$ Hz, 2H, CH_2), 3.96 (s, 3H, OCH_3), 6.91 (s, 1H, CH), 7.21 (d, $J=8.0$ Hz, 2H, ArH), 7.27–7.39 (m, 4H, ArH), 7.49 (d, $J=8.0$ Hz, 2H, ArH). **3c**: mp 188°C; δ 1.18–1.50 (m, 2H, CH_2), 2.03 (t, $J=6.2$ Hz, 2H, CH_2), 2.53 (s, 3H, SCH_3), 2.65 (t, $J=6.2$ Hz, 2H, CH_2), 3.94 (s, 3H, OCH_3), 6.92 (s, 1H, CH), 7.01–7.18 (m, 4H, ArH), 7.21–7.39 (m, 4H, ArH). **3d**: oil; δ 1.15–1.46 (m, 2H, CH_2), 2.03 (t, $J=6.2$ Hz, 2H, CH_2), 2.39 (s, 3H, CH_3), 2.51 (s, 3H, SCH_3), 2.55 (t, $J=6.2$ Hz, 2H, CH_2), 3.93 (s, 3H, OCH_3), 6.92 (s, 1H, CH), 7.01–7.18 (m, 4H, ArH), 7.21–7.34 (m, 4H, ArH). **3e**: 128°C; δ 1.18–1.49 (m, 2H, CH_2), 1.97 (t, $J=6.2$ Hz, 2H, CH_2), 2.50 (s, 3H, SCH_3), 2.58 (t, $J=6.2$ Hz, 2H, CH_2), 3.96 (s, 3H, OCH_3), 6.98 (s, 1H, CH), 7.02–7.20 (m, 4H, ArH), 7.29–7.38 (m, 4H, ArH). **3f**: oil; δ 1.28–1.60 (m, 2H, CH_2), 2.09 (t, $J=6.0$ Hz, 2H, CH_2), 2.51 (s, 3H, SCH_3), 2.59 (t, $J=6.0$ Hz, 2H, CH_2), 3.93 (s, 3H, OCH_3), 6.90 (s, 1H, CH), 7.01–7.15 (m, 4H, ArH), 7.20–7.31 (m, 4H, pyridyl). **3g**: mp 162°C; δ 1.25–1.56 (m, 2H, CH_2), 2.06 (t, $J=6.4$ Hz, 2H, CH_2), 2.50 (s, 3H, SCH_3), 2.62 (t, $J=6.4$ Hz, 2H, CH_2), 3.96 (s, 3H, OCH_3), 7.01 (s, 1H, CH), 7.08–7.13 (m, 3H, thienyl), 7.20–7.31 (m, 4H, ArH). **3h**: oil; δ 1.25–1.52 (m, 2H, CH_2), 1.97 (t, $J=6.2$ Hz, 2H, CH_2), 2.50 (s, 3H, SCH_3), 2.58 (t, $J=6.2$ Hz, 2H, CH_2), 3.92 (s, 3H, OCH_3), 6.96 (s, 1H, CH), 7.05–7.16 (m, 4H, ArH), 7.22–7.36 (m, 3H, ArH). **3i**: 162°C; δ 1.26–1.58 (m, 2H, CH_2), 2.17 (t, $J=6.2$ Hz, 2H, CH_2), 2.56 (s, 3H, SCH_3), 2.68 (t, $J=6.2$ Hz, 2H, CH_2), 3.77 (s, 3H, OCH_3), 6.96 (s, 1H, CH), 7.16 (d, $J=8.0$ Hz, 2H, ArH), 7.28 (d, $J=8.0$ Hz, 2H, ArH), 7.35–7.54 (m, 3H, ArH). **3j**: 184°C; δ 1.25–1.48 (m, 2H, CH_2), 2.06 (t, $J=6.0$ Hz, 2H, CH_2), 2.50 (s, 3H, SCH_3), 2.59 (t, $J=6.1$ Hz, 2H, CH_2), 3.92 (s, 3H, OCH_3), 6.85 (s, 1H, CH), 7.13–7.22 (m, 4H, ArH),

7.26–7.39 (m, 3H, ArH). **3k**: oil; δ 1.23–1.49 (m, 2H, CH_2), 2.10 (t, $J=6.2$ Hz, 2H, CH_2), 2.51 (s, 3H, SCH_3), 2.59 (t, $J=6.2$ Hz, 2H, CH_2), 3.91 (s, 3H, OCH_3), 6.98 (s, 1H, CH), 7.09–7.27 (m, 4H, ArH), 7.32–7.44 (m, 3H, ArH). **3l**: oil; δ 1.18–1.39 (m, 2H, CH_2), 2.01 (t, $J=6.2$ Hz, 2H, CH_2), 2.51 (s, 3H, SCH_3), 2.57 (t, $J=6.2$ Hz, 2H, CH_2), 3.90 (s, 3H, OCH_3), 6.95 (s, 1H, CH), 7.04–7.11 (m, 3H, thienyl), 7.19–7.47 (m, 3H, ArH). **3m**: oil; δ 1.15–1.36 (m, 2H, CH_2), 2.08 (t, $J=6.2$ Hz, 2H, CH_2), 2.48 (s, 3H, SCH_3), 2.55 (t, $J=6.2$ Hz, 2H, CH_2), 3.68 (s, 3H, OCH_3), 6.96 (s, 1H, CH), 7.14–7.25 (m, 4H, ArH), 7.35–7.49 (m, 3H, ArH), 7.53–7.63 (m, 2H, imidazolyl), 7.91 (s, 1H, imidazolyl). **3n**: oil; δ 1.25–1.49 (m, 2H, CH_2), 2.07 (t, $J=6.2$ Hz, 2H, CH_2), 2.45 (s, 3H, SCH_3), 2.53 (t, $J=6.2$ Hz, 2H, CH_2), 3.92 (s, 3H, OCH_3), 6.95 (s, 1H, CH), 7.16–7.28 (m, 3H, ArH), 7.42–7.56 (m, 3H, ArH), 7.99 (s, 1H, triazolyl).