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# A NOVEL APPROACH TO 5,5'-DIISOPROPYL-3,3'-BI-2*H*-CYCLOHEPTA[*b*]FURAN-2-ONE †

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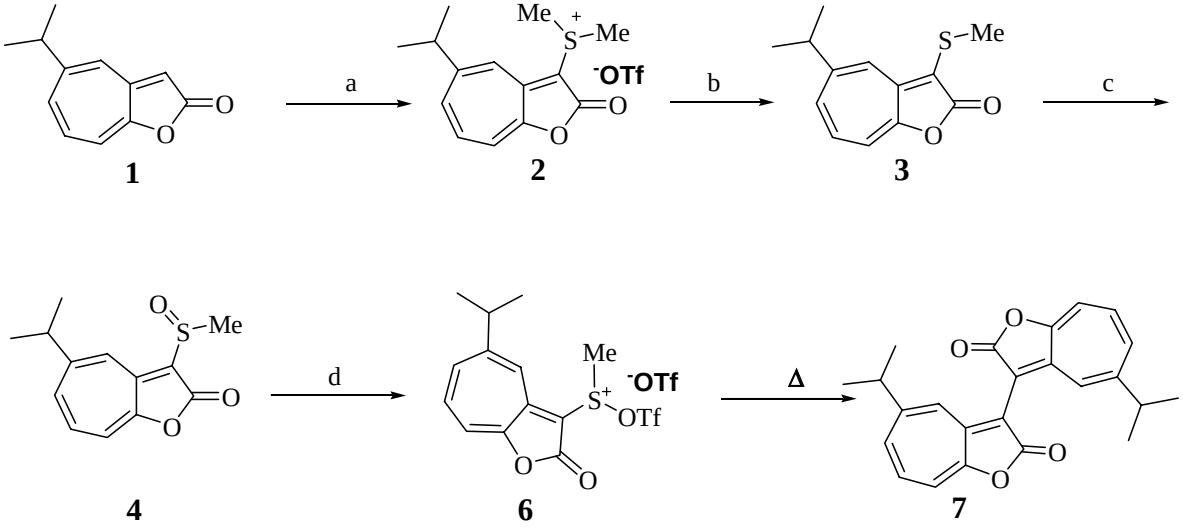
**Abstract**− 5-Isopropyl-2*H*-cyclohepta[*b*]furan-2-one (**1**) reacted with DMSD to give dimethyl(5-isopropyl-2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)sulfonium trifluoromethane-sulfonate (**2**), which was treated with $Et_3N$ to give 5-isopropyl-3-methylthio-2*H*-cyclohepta[*b*]furan-2-one (**3**). Sulfide **3** was oxidized with *m*CPBA to give sulfoxide **4** and sulfone **5**. The salt **6** which comes from the treatment of **4** with $Tf_2O$ converted to an unexpected product, 5,5'-diisopropyl-3,3'-bi-2*H*-cyclohepta[*b*]furan-2-one (**7**), thermally.

2*H*-Cyclohepta[*b*]furan-2-ones[1] were known as one of the heteroazulenes. Although there are several reports of electrophilic substitution in azulenes,[2] reports[3] of electrophilic substitution of 2*H*-cyclohepta[*b*]furan-2-ones are a very few. 2*H*-Cyclohepta[*b*]furan-2-ones were used as precursors of azulenes from long time ago.[4] Recently, they became to be used as tools for extended π-electronic conjugated systems. New stabilized carbocations and redox systems have been synthesized.[3] On account of the synthesis

† Dedicate to late Professor Dr. Ivar Ugi.

of new extended π-electronic conjugated systems using 2-oxo-2*H*-cyclohepta[*b*]furan-3-yl group, further research for the reactivity of 2*H*-cyclohepta[*b*]furan-2-one and its derivatives is very important. Previously we reported 2*H*-cyclohepta[*b*]furan-2-one reacted with trifluoromethanesulfonylpyridinium trifluoromethanesulfonate, electrophilically to give 3-dihydropyridinyl-2*H*-cyclohepta[*b*]furan-2-one and subsequent treatment with sodium hydroxide in ethanol gave 3-(4-pyridinyl)-2*H*-cyclohepta[*b*]furan-2-one in excellent yields.[5] There is not a sulfur derivative of 2*H*-cyclohepta[*b*]furan-2-one as far as I know. Now we will report here another electrophilic substitution reaction of 5-isopropyl-2*H*-cyclohepta[*b*]furan-2-one[6] (**1**) with dimethyl(trifluoromethanesulfonyloxy)sulfonium trifluoromethanesulfonate, "dimethyl sulfide ditriflate" (DMSD) which can act as a highly reactive S-electrophile[7] and conversion to 5,5'-diisopropyl-3,3'-bi-2*H*-cyclohepta[*b*]furan-2-one from this product.




a: **DMSD** b: **$Et_3N$** c:***m*CPBA** d:**$Tf_2O$**

Compound **1** reacted with DMSD which was prepared *in situ* by the reaction of DMSO with $Tf_2O$ to give crude dimethyl(5-isopropyl-2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)sulfonium trifluoromethansulfonate (**2**). Purification of **2** is very difficult owing to oil. Crude **2**[9] reacted with triethylamine to give 5-isopropyl-3-methylthio-2*H*-cyclohepta[*b*]furan-2-one (**3**)[10] as orange oil in 96% yield from **1**. Compound **3** was oxidized with *m*CPBA to give sulfoxide **4**[11] (yellow cryst., mp 88.5-90˚C) and sulfone **5**[12] (yellow cryst., mp 111-112˚C) in 35% and 58% yields, respectively. A solution of $Tf_2O$ in $CH_2Cl_2$ was added to a solution of **4** in $CH_2Cl_2$ at 0˚C to give a solution of (5-isopropyl-2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)-methyl(trifluoromethanesulfonyloxy)sulfonium trifluoromethanesulfonate (**6**). After stirring for 30 min at room temperature, the solvent was removed by evaporation to give 5,5'-diisopropyl-3,3'-bi-2*H*-cyclohepta[*b*]furan-2-one (**7**)[13] as reddish brown plate crystals (mp 218-219˚C, crystallized from 2-propanol) in 68% yield from **4**. When compound **1** was added to the solution of **6**,

expected product, bis(5-isopropyl-2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methylsulfonium trifluoromethanesulfonate could not be observed until now. We could get only homocoupling product **7**. It suggests that C3-S bond of sulfonium ion **6** easily cleavages homolytically to give 5-isopropyl-2-oxo-2*H*-cyclohepta[*b*]furan-3-yl radical, followed by dimerization.

Comparing with chemical shifts of seven-member ring protons without at 4-positon in compounds **1**-**7** (see **REFERENCE & NOTES** 8-13), magnitude of low field shifts increases in following order, **1**<**3**<**7**<**4**<**5**<**2**. Sulfur groups work as electron-withdrawing groups in this order. Further optimization of each steps and the research for their reactivity of these products are going on.

In conclusion, although some problems of yields and reaction control still remain, the following dimerizing procedure for compound **1**, electrophilic substitution of **1** with DMSD, demethylation of **2** with $Et_3N$, oxidation of **3**, activation of **4** with $Tf_2O$, and radical homocoupling, is accomplished. This process will become a convenient protocol for dimerization 2*H*-cyclohepta[*b*]furan-2-ones without a substituent at 3-position.

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8. **1**; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.13 (bs, 1H, H-4), 6.89 (dd, *J*=9.2 11.2 Hz, 1H, H-7), 6.79 (d, *J*=9.2 Hz, 1H, H-8), 6.69 (d, *J*=11.2 Hz, 1H, H-6), 5.62 (d, *J*=1.2 Hz, 1H, H-3), 2.73 (sept, *J*=6.8 Hz, 1H, -C$\underline{H}$$(CH_3)_2$), 1.17 (d, *J*=6.8 Hz, 6H, -CH(C$\underline{H}_3$$)_2$).
9. **2**; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J*=1.2 Hz, 1H, H-4), 7.71 (t, *J*=9.6 Hz, 1H, H-7), 7.66 (dd, *J*=9.6, 1.2 Hz, 1H, H-8), 7.57 (dt, *J*=9.6, 1.2 Hz, 1H, H-6), 3.35 (s, 6H, -$S^+(CH_3)_2$), 3.25 (sept, *J*=6.8 Hz, 1H, -C$\underline{H}$$(CH_3)_2$), 1.39 (d, *J*=6.8 Hz, 6H, -CH(C$\underline{H}_3$$)_2$).
10. **3**;$^1$H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J*=1.2Hz , 1H, H-4), 6.99 (dd, *J*=11.2, 9.2 Hz, 1H, H-7), 6.87 (d, *J*=9.2 Hz, 1H, H-8), 6.79 (dd, *J*=11.2, 1.2 Hz, 1H, H-6), 2.89 (sept, *J*=6.8 Hz, 1H, -C$\underline{H}$$(CH_3)_2$), 2.41 (s, 3H, -SC$\underline{H}_3$), 1.29 (d, *J*=6.8 Hz, 6H, -CH(C$\underline{H}_3$$)_2$).
11. **4**; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H, H-4), 7.37 (dd, *J*=11.2, 9.2 Hz, 1H, H-7), 7.30 (dd, *J*=9.2, 1.2 Hz, 1H, H-8), 7.20 (d, *J*=11.2 Hz, 1H, H-6), 3.16 (s, 3H, -SOC$\underline{H}_3$), 3.02 (sept, *J*=6.8 Hz, 1H, -C$\underline{H}$$(CH_3)_2$), 1.32 (d, *J*=6.8 Hz, 6H, -CH(C$\underline{H}_3$$)_2$).
12. **5**; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J*=1.2 Hz, 1H, H-4), 7.65 (d, *J*=10.8, 9.6 Hz, 1H, H-7), 7.58 (dd, *J*=9.6, 1.2 Hz 1H, H-8), 7.47 (dt, *J*=10.8, 1.2 Hz, 1H, H-6), 3.30 (s, 3H, -$SO_2$C$\underline{H}_3$), 3.12 (sept, *J*=6.5 Hz, 1H, -C$\underline{H}$$(CH_3)_2$), 1.36 (d, *J*=6.5 Hz, 6H, -CH(C$\underline{H}_3$$)_2$).
13. **7**; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J*=1.2 Hz, 2H, H-4, 4'), 7.05 (dd, *J*=10.4, 9.2 Hz, 2H, H-7, 7'), 7.01 (dd, *J*=9.2, 1.2 Hz, 2H, H-8, 8'), 6.88 (dt, *J*=10.4, 1.2 Hz, 2H, H-6, 6'), 2.85 (sept, *J*=6.8 Hz, 2H, -C$\underline{H}$$(CH_3)_2$), 1.26 (d, *J*=6.8 Hz, 12H, -CH(C$\underline{H}_3$$)_2$).