Synthesis of aceotoxy- and thioaceotoxy-substituted oxa[9]helicene derivatives from benzofuzed-2,2'-diphenoquinone

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Keywords: Oxa helicene; Acetoxylation; Thioacetoxylation; Spiro-lactone; Enantiopurity.

When benzofused-2,2'-biphenoquinone 1 reacted with acetic acid (it acted as both nucleophile and solvent) at room temperature for 24 hours, it produced an inseparable 1:1 mixture of aceotoxy-oxa[9]helicene 2 and spiro-lactone 3, where 3 is a rearranged product of 1. When the mixture of 2 and 3 was further refluxed in acetic acid for 8 hours, the spiro-lactone 3 rearranged to another rearrangement product pyranone 4. Finally, 2 were well separated from 4 by using column chromatography. On the other hand, when benzofused-2,2'-biphenoquinone 1 reacted with thioacetic acid at room temperature for 24 hours, it produced a mixture of thioaceotoxy-oxa[9]helicene 5 and oxa[9]helicene 6. When enantiomerically pure benzofused-2,2'-diphenoquinone (P)/(M)-1a was used as the starting substrate, both aceotoxy- and thioaceotoxy-substituted oxa[9]helicene derivatives ((P)/(M)-2a and (P)/(M)-5a) were obtained with retention of their enantiopurities.