An Optically Stable *o,o*′-Dilithio Biaryl Derivative

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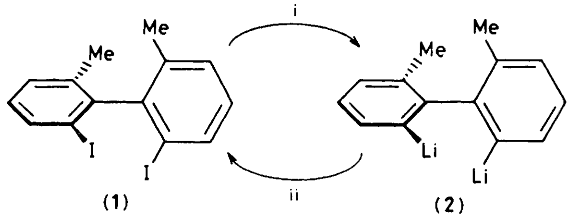
2,2′-dilithio-6,6′-dimethylbiphenyl, prepared from optically pure 2,2′-di-iodo-6,6′-dimethylbiphenyl (**1**) and butyl-lithium in diethyl ether, was found to be stable towards racemisation at −10 °C.

The extremely rapid racemisation of the 4,4′-dibromo and 4,4′-dimethyl derivatives of 2,2′-dilithio-3,3′-bithienyls at −70 °C has been explained as being due to the formation of aggregates with co-planar aromatic rings immediately upon formation from the corresponding bromo derivatives and ethyl-lithium.[1] It was argued that the internal complexation of the lithium atoms allowed a molecular geometry in which the *ortho* substituents (bromo and methyl groups respectively) would not prevent racemisation, which is normally the case.

In a recent report it was demonstrated by *X*-ray diffraction that 2,2′-dilithiobiphenyl formed an aggregate (with tetramethylethylenediamine) in which the aromatic rings were coplanar.[2] The lithium atoms were situated one above and the other below the aromatic plane. This structure is similar to the one suggested by Håkansson in the bithienyl case.[1] Thus, the 2,2′-dilithiated biaryls seemed unsuitable for the preparation of optically active biaryls, even with normally hindering groups such as methyl and bromo groupings.

We now report the first case of an optically stable *o,o*′-dilithiobiaryl, 2,2′-dilithio-6,6′-dimethylbiphenyl (**2**), which is stable towards racemisation for all practical purposes at −10 °C.

A diethyl ether solution of optically pure 2,2′-di-iodo-6,6′-dimethylbiphenyl (**1**) ($[\alpha]^{22}_{D}$ −20.6°; *c* 0.6, EtOH; lit.[3] $[\alpha]^{32}_{D}$ −20.8°; *c* 0.6, EtOH) was treated with 2 equiv. of butyllithium at −10 °C for 20 min. At this point it was checked that no starting material was present by g.c. analysis of a hydrolysed sample. The mixture was then cooled to −60 °C and a solution of iodine (excess) in diethyl ether was added. The mixture was allowed to reach room temperature and, after 20 min, was partitioned between diethyl ether and water; the organic layer was dried and analysed by g.c. The g.c.-yield of (**1**) was 86% and it was isolated in 58% yield, 100% enantiomeric excess ($[\alpha]^{22}_{D}$ −20.7°; *c* 0.6, EtOH) through semipreparative h.p.l.c. (5μ SiO_2, stainless steel column, i.d. 10 mm, length 50 cm, light petroleum, b.p. 60—70 °C, as eluant). 2-Iodo-6,6′-dimethylbiphenyl (9%) and 6,6′-dimethylbiphenyl (5%) were also formed.



i, BuLi, diethyl ether, −10 °C, 20 min; ii, I_2, diethyl ether.

This result shows that, despite previous indications (*vide supra*), suitably substituted 2,2′-dilithiobiphenyls can resist racemisation and can be used for the synthesis of a variety of optically active biaryls; this is now being investigated.

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