Stereochemistry of the Reductive Alkylation of Anthracene

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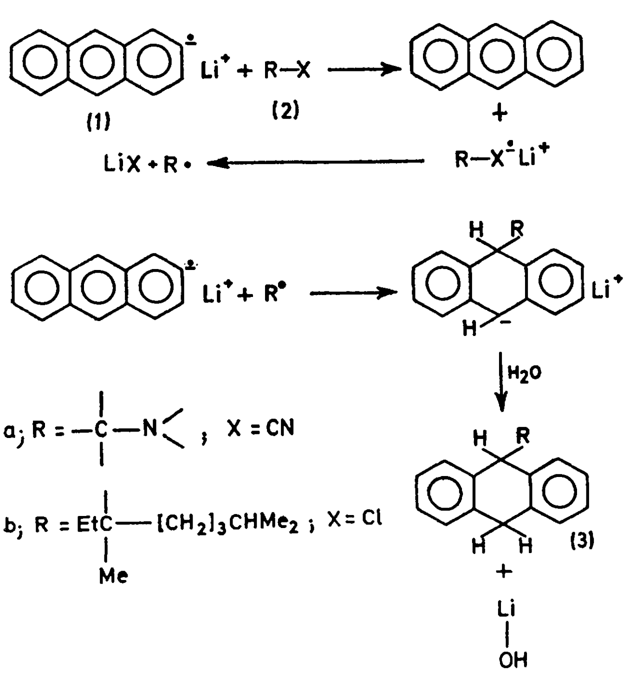
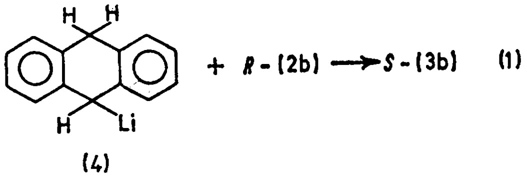
Summary Alkylation of lithium dihydroanthracenylide by (−)*R*-6-chloro-2,6-dimethyloctane occurs with racemization and only a small degree of inversion of configuration, in agreement with the main pathway involving the previously proposed radical–radical anion combination.

Retention of configuration has been reported in substitution reactions of cyclopropyl halides with alkylsodium,[1] and retention of configuration has also been observed in the substitution of the cyano-group of α-aminonitriles (**2a**) by anthracenyl-lithium (**1**).[2] However, for other substitution reactions, such as the Wurtz reaction, which may involve anionic[3] or radical[4] intermediates, inversion of configuration occurs.[3]



Scheme

In view of these opposing results, we have investigated the stereochemistry of the substitution of a chiral halide (**2b**) by (**1**), a reaction which may also occur *via* a similar intermediate.



(4)

The known (−)-*R*-6-chloro-2,6-dimethyloctane (**2b**) (α_D^{25} −0·02°†), easily prepared from linalool,[5] was used, and the expected dihydroanthracene (**3b**) was formed (50% overall).‡ A pure sample of the chiral (**3b**) has a rotation $[\alpha]_D^{25}$ (*c* 6·3, EtOH) −0·22°. The configuration of (**3b**) as well as the optical yield of the overall reaction in the Scheme was determined by treatment of (**2b**) with reagent (**4**) [reaction (1)]. Reagent (**4**) was prepared by reaction of butyllithium with 9,10-dihydroanthracene.[6] Since it is known that substitution of alkyl halides by allylic and benzylic organolithium reagents occurs with complete inversion of configuration[7] and (**4**) is a similar type of reagent, we may assume that reaction (1) involves complete inversion of figuration.

The main products of the reaction of (**4**) with (**2b**) are alkenes formed by elimination but (**3b**) is also formed in low yield (7% isolated pure product). The rotation of (**3b**) is of the same sign, but is much higher than that of the compound obtained as in the Scheme {$[\alpha]_D^{25}$ (*c* 11·3, EtOH) −3·92°}, which shows that the absolute configuration of

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† With the known experimental procedure, presumably some racemization occurred, so the chirality of our halide is lower than that previously reported.[5] We thank Dr. Teisseire (Roure-Bertrand Sons and Dupont Co) for a gift of linalool.

‡ Satisfactory analytical and spectral data were obtained.

(**3b**) obtained in both reactions is *S* but that substitution of the alkyl halide (**2b**) by (**1**) Scheme involves an important racemization, and partial inversion.

The high degree of racemization agrees with the radical–radical anion combination mechanism already proposed[2] and demonstrates that the previously observed retention of configuration is exceptional and not typical of anthracenyl-lithium reagents. The low degree of inversion is being investigated further.§

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§ The observed inversion of configuration may be explained by the formation of a small amount of (**4**) by the known hydrogen abstraction from ethereal solvents by reagent (**1**).[8] We have no direct evidence that this process occurs here.

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