Inhibition of the Bromine-catalysed Isomerisation of α,β-Dibromostyrene by Graphite

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Phenylacetylene is stereoselectively brominated by molecular bromine adsorbed on graphite in carbon tetrachloride, to produce *E*-α-β-dibromostyrene; isomerisation of the *E*-isomer to the *Z*-isomer, usually catalysed by bromine, is inhibited by graphite.

Recently, solid adsorbents have been used for selective reactions in organic synthesis.[1] Significant improvements of regioselectivity have been achieved in a wide variety of organic reactions by use of supported reagents formed by adsorption of reagent molecules onto the surface of solid adsorbents. However, only a few studies on the stereoselective control by use of supported reagents have been reported.[2] It is well known that dihalogenoalkenes can be isomerised using bromine as a catalyst.[3] Although the addition of the bromine to phenylacetylene give *E*-α-β-dibromostyrene *E*-(**1**), exclusively, the resulting *E*-isomer is readily isomerised by excess bromine. Therefore, the adducts always consist of a mixture of *E*- and *Z*-isomers.[4]

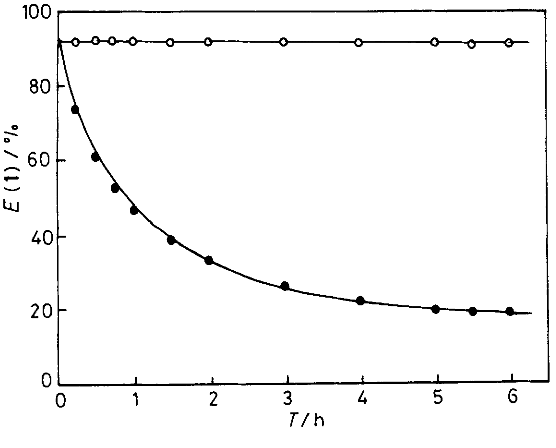
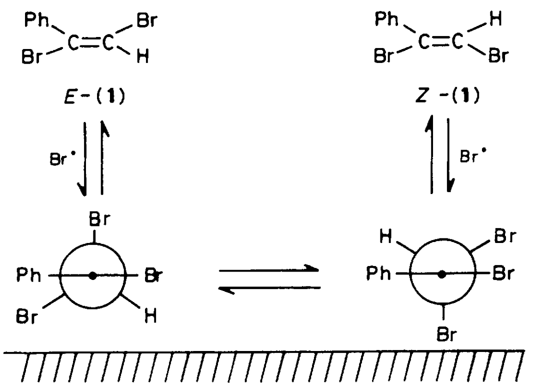


Figure 1. Isomerisation of *E*-α-β-dibromostyrene, (○) in presence of graphite and (●) without graphite.

We have found that graphite inhibits the isomerisation of *E*-(**1**) to *Z*-(**1**) by bromine, and that addition of bromine to phenylacetylene in the presence of graphite in carbon tetrachloride gives *E*-(**1**) in high yield stereoselectively (see Figure 1).

A mixture of *E*-(**1**) (1 mmol) and bromine (0.2 mmol) in carbon tetrachloride was stirred at 20 °C. *E*-(**1**) was readily isomerised to *Z*-(**1**), and an equilibrium mixture consisting mainly of *Z*-(**1**) was obtained after 6 h. In contrast, in the presence of graphite under similar conditions the isomerisation of *E*-(**1**) did not occur, and the recovered yield of *E*-(**1**) was 97%. These results are tentatively explained on the basis of a heterogeneous reaction on the surface of graphite. Thus, the rotation around the C–C bond in the radical intermediate (**2**) adsorbed on the surface of graphite is restricted (see Scheme 1), therefore no appreciable change in isomer ratio is



(**2**)

Scheme 1

observed when the reaction is carried out in the presence of graphite.

A mixture of phenylacetylene (1 mmol) and bromine (2 mmol) in carbon tetrachloride (30 ml) was stirred at 20 °C for 2 h to give the adduct (**1**) quantitatively (*E*: *Z*, 20 : 80). The use of prolonged reaction, higher temperature, and higher ratio of bromine to phenylacetylene generally resulted in *E*→*Z* isomerisation. In the presence of graphite, the ratio of *E*- and *Z*-(**1**) in the product mixture was almost independent of the reaction conditions. Bromination was carried out using a solution of bromine in carbon tetrachloride, adsorbed on graphite, as a brominating reagent. Thus, graphite (5 g) was added to a solution of bromine (2 mmol) in carbon tetrachloride (25 ml), and stirred at 20 °C for 0.5 h. To the resulting mixture was added a solution of phenylacetylene (1 mmol) in carbon tetrachloride (5 ml), and stirring was continued at 20 °C for 2 h. Aqueous sodium thiosulphate was then added, and the mixture was filtered. The organic layer was separated, washed with water and dried. The products were analysed by G.l.c. The yield of (**1**) was 94%, the *E*: *Z* ratio 94 : 6.

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