

Synthesis of 1*H*-Cyclobuta[*de*]naphthalene by Organometallic Methodology

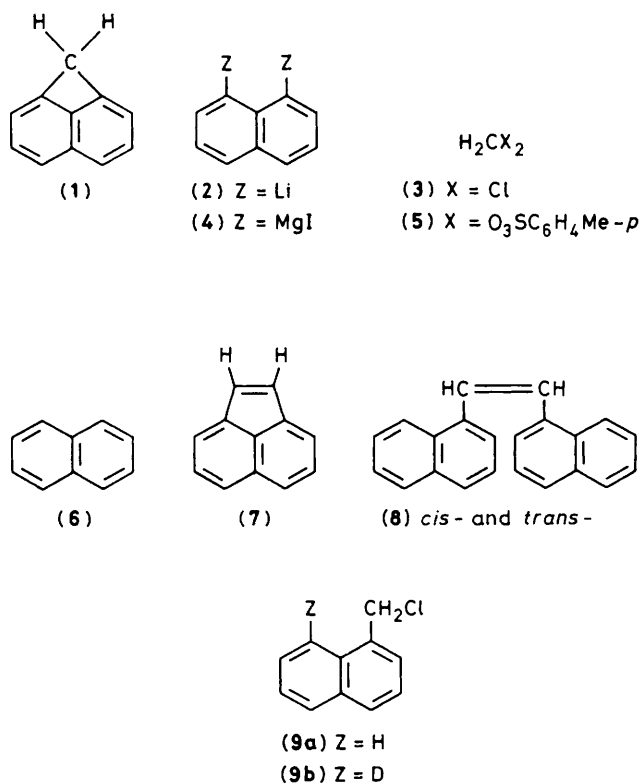
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1*H*-Cyclobuta[*de*]naphthalene is preparable by reactions of 1,8-dilithionaphthalene with dichloromethane and 1,8-bis(iodomagnesium)naphthalene with methylene bis(toluene-*p*-sulphonate).

1*H*-Cyclobuta[*de*]naphthalene (**1**) and its derivatives are of considerable interest,¹⁻⁵ and it has been synthesised by: reduction (LiAlH₄ or Mg, HCl) of 1-bromo-1*H*-cyclobuta[*de*]naphthalene prepared by photolysis of sodium 8-bromo-

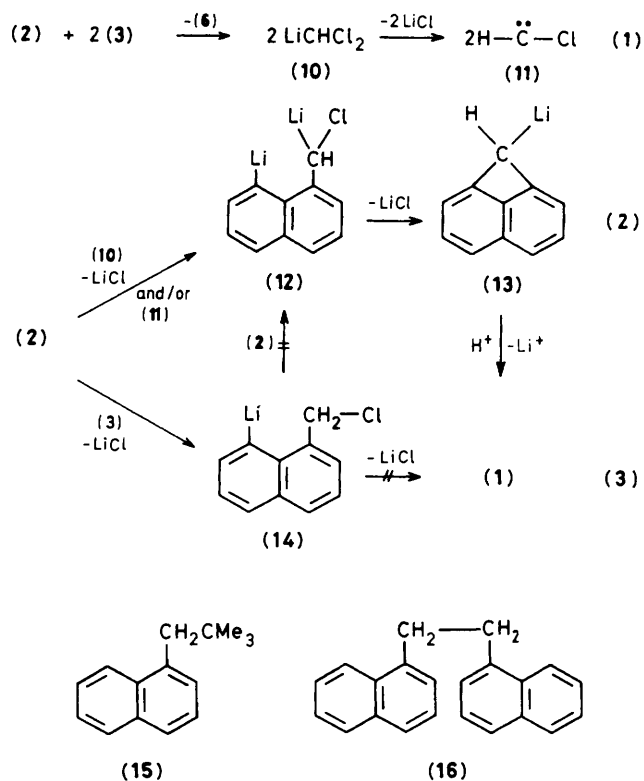
1-naphthaldehyde *p*-tosylhydrazonate;¹ flash-pyrolysis (400—800 °C, 10⁻²—10⁻⁴ Torr) of 1- or 2-naphthyldiazomethanes;⁴ flow-thermolysis (525—650 °C, 0.05—0.1 Torr) of [methoxy-(1- or 2-naphthyl)methyl]trimethylsilanes.⁵ The routes to



compound (1) suffer the disadvantages that preparation of the precursors is inefficient and laborious and/or high-temperature, low-pressure gas-phase technology is required. We now report synthesis of (1) from 1,8-dilithionaphthalene⁶ (2) and dichloromethane (3) and from 1,8-bis(iodomagnesio)naphthalene (4)⁷ and methylene bis(toluene-*p*-sulphonate) (5).⁸ The present organometallic reactions, though also of low yield, are practical for synthesis of (1) because of the convenience of the reagents, equipment, and experimental techniques. The methodology may also be advantageous for preparation of naphthyl-substituted-1*H*-cyclobuta[*de*]naphthalenes and other *peri*-methanoarenes.

Reaction of (2) and (3) at -78 to 25°C yields (1) (3–4%) along with naphthalene (6) (30–37%), acenaphthylene (7) (13–22%), *cis*- and *trans*-1,2-bis(1-naphthyl)ethylenes (8), and more complex products. The use of tetramethylethylenediamine (TMEDA) in diethyl ether at lower temperatures leads to an improvement; thus, (2) and (3) (2.0–20.0 equiv.) in TMEDA (2.0–2.3 equiv.)–diethyl ether at -100 to -60°C give (1) (18–21%) along with (6) (31–42%), (7), (8), and 1-chloromethylnaphthalene (9a). Arene (1) is separable by vacuum distillation or by gas or column chromatography.

The mechanism by which (2) and (3) yield (1) is also of interest, of relevance to which is the formation of (6), a major product apparently produced by diprotonation of (2). Further, no deuteriated (6) is obtained when the reaction mixture from (2) and (3) in diethyl ether is quenched with deuterium oxide, thus indicating that (2) is totally consumed before work-up. More direct insight comes from reactions of (2) with dideuteriodichloromethane (1.2 equiv.) in TMEDA (2.1 equiv.)–diethyl ether at -60°C to give highly deuteriated (6) (38–42% yield, 60–63% ²H₂ at C-1 and C-8 and 27–29% ²H at C-1) and 1,1-dideuteriocyclobuta[*de*]naphthalene (1) (15–19% yield, 90% ²H₂ at C-1). The experiments thus indicate that deprotonation of (3) by (2) to give (6) and



presumably dichlorolithiomethane (10) is a major reaction (equation 1) and suggest that (12) is formed (equations 1 and 2) by reaction of (10) with (2) or/and by collapse of (10) to monochlorocarbene (11) which is then captured by (2). Loss of lithium chloride and ring-closure of (12) would give (13) and then (1) by proton-transfer from the remaining (3). Generation of the carbenoid (10)⁹ (4.1 equiv.) from (3) and *t*-butyl-lithium in diethyl ether at -100°C followed by slow addition of (2) (1.0 equiv.) in TMEDA (2.2 equiv.)–diethyl ether at -100°C and warming the mixture does give (1) (18%) along with (6) (25–35%) in agreement with equations (1) and (2). It has not yet been possible, however, to control the reaction of discrete (10) and/or (11) with (2) to improve the conversion into (1).[†]

Alternative routes to (1) might involve 1-chloromethyl-8-lithionaphthalene (14), derived from reaction of (3) and (2) in equation (3). The behaviour of discrete (14) was determined under the conditions for the conversion of (2) by (3) into (1). Addition of *t*-butyl-lithium (2 equiv.) to 8-bromo-1-chloromethylnaphthalene in diethyl ether at -100°C gives (14) as shown by its conversion (>55%) by MeOD into 1-chloromethylnaphthalene (9b) containing >85% deuterium at C-8. Warming the mixture from 8-bromo-1-chloromethylnaphthalene and *t*-butyl-lithium to 25°C however does not yield (1); only 1-neopentyl-naphthalene (15) (6%), 1,2-di(1-naphthyl)ethane (16) (46%), and more complex coupling products are formed. Similar results are obtained from (14) and TMEDA–diethyl ether, and thus (14) is not involved in the present route to (1) from (2) and (3).

The utility of organometallic analogues of (2) for synthesis of (1) is also being investigated. Addition of alkynylcopper

[†] A major reaction of (10) under these conditions is conversion into *cis*- and *trans*-1,2-dichloroethylenes (ref. 10). Further study of the generation of (10) and (11) from (2) and (3) is in progress.

reagents, copper-(i) or -(ii) halides, or iron(III) chloride to (2) and then reaction with dichloro, dibromo- or di-iodomethane, respectively, in diethyl ether, tetrahydrofuran, or hexamethylphosphoric triamide at -78 to 25 °C fail to give (1). Similarly, the dihalogenomethanes and (4), as prepared from 1,8-di-iodonaphthalene and magnesium (4–8 equiv.) in tetrahydrofuran, do not yield (1). Of interest however is that (4) and (5) give (1) (20%), (6), (30%), and coupling products in refluxing tetrahydrofuran (48 h). The efficiency of this method for preparing (1) is comparable with that based on (2) and (3) in TMEDA–diethyl ether. The mechanism by which (5) is converted into (1) by (4) is not yet known however.

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