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

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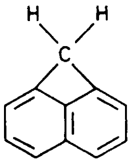
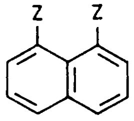
1*H*-Cyclobuta[*de*]naphthalene is preparable by reactions of 1,8-dilithionaphthalene with dichloromethane and 1,8-bis(iodomagnesio)naphthalene with methylene bis(toluene-*p*-sulphonate).

1*H*-Cyclobuta[*de*]naphthalene (**1**) and its derivatives are of considerable interest,[1–5] and it has been synthesised by: reduction ($LiAlH_4$ 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



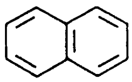
(1)



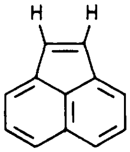
(2) Z = Li
(4) Z = MgI

H_2CX_2

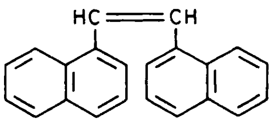
(3) X = Cl
(5) X = $O_3SC_6H_4Me$-*p*



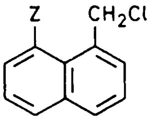
(6)



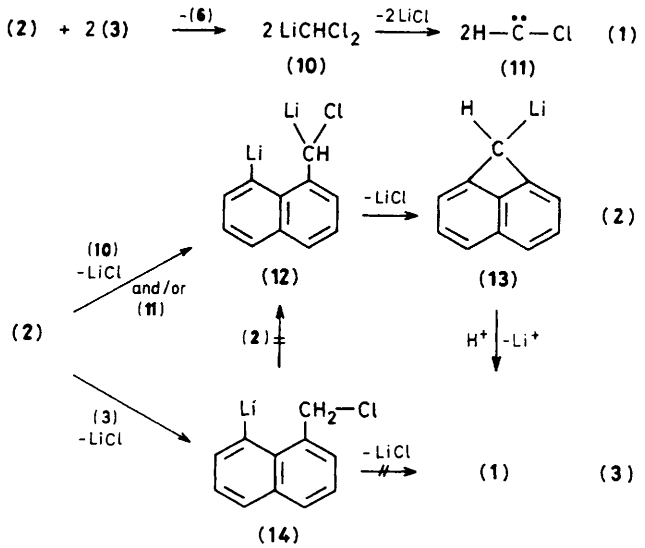
(7)

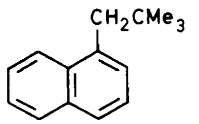


(8) *cis*- and *trans*-

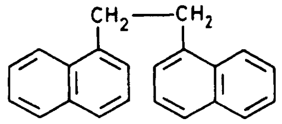


(9a) Z = H
(9b) Z = D





(15)



(16)

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-dilithionaphthalene[6] (**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% $^2H_2$ at C-1 and C-8 and 27—29% ^2H at C-1) and 1,1-dideuteriocyclobuta[*de*]naphthalene (**1**) (15–19% yield, 90% $^2H_2$ 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-neopentylnaphthalene (**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

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† 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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