

1,1- vs. 1,6-Dehalogenation in *gem*-Dibromocyclopropanes. Synthesis of Benzo-*anti*- σ -bishomobenzenet[†]

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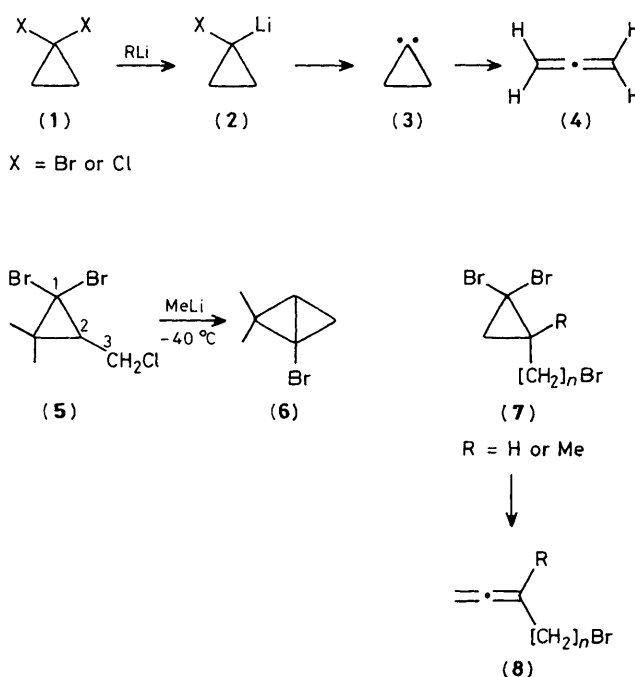
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The bisdibromocarbene adduct (**9a**) on treatment with methyl-lithium at temperatures below *ca.* -50°C undergoes a ring-closure reaction by 1,6-elimination to give after reduction *anti*- σ -bishomobenzene (**11**); above -50°C products derived from 1,1-eliminations and subsequent cyclopropyliden(oid)-allene rearrangements dominate.

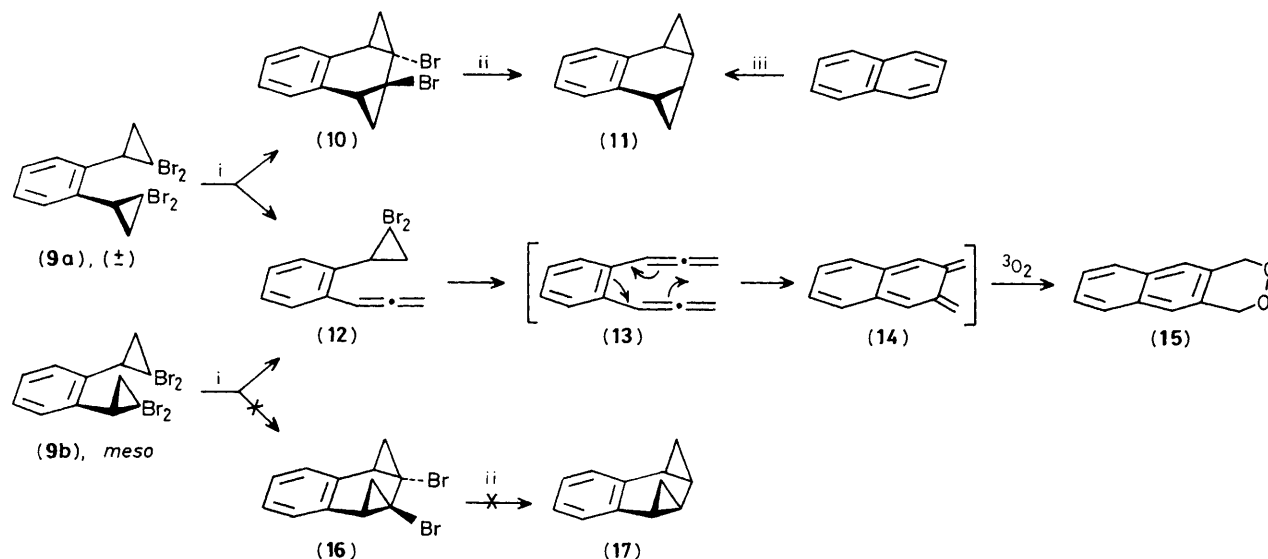
gem-Lithio-halogenocyclopropanes (**2**) are important intermediates in organic synthesis.² They can generally and conveniently be obtained through halogen-lithium exchange^{2f} in reactions of the dihalogenocyclopropanes (**1**) with alkyl-lithium reagents in solution³ or in a 'gas-phase' reaction with methyl-lithium-coated glass turnings at temperatures above $+20^{\circ}\text{C}$.⁴ At *ca.* -100°C the organolithium compounds (**2**) are stable species, undergoing typical organometallic reactions.² Their stability is enhanced by intra- and intermolecular interactions of the metal with heteroatoms.¹ Higher temperatures induce extrusion of lithium halide (α -elimination) from (**2**) and generate the cyclopropylidenoids (**3**)⁵ which undergo similar reactions as those of 'free' cyclopropylidenes, *e.g.* generated from diazocyclopropanes. The typical reaction of (**3**) is their rearrangement to the allenes (**4**).^{2c} The formation of (**3**) from (**1**) results in a net 1,1-dehalogenation (Scheme 1).

Baird⁶ has shown that 1,1,2-trihalogenocyclopropanes upon treatment with methyl-lithium afford halogenocyclopropenes; *i.e.* 1,2- rather than 1,1-dehalogenations take place. Recently Skattebøl and Baird⁷ reported a 1,3-dehalogenation of (**5**) leading to 1-bromobicyclo[1.1.0]butane (**6**). For (**7**; $n = 2$ or 3), however, a 1,4- or 1,5-displacement of Br^- from the corresponding organolithium intermediates with the forma-



[†] Benzo- σ -bishomobenzene = tetrahydrodicyclopropa[*a,c*]naphthalene.

Scheme 1



Scheme 2. Reagents: i, MeLi, -78°C ; ii, Na, NH_3 , MeOH; iii, CH_2N_2 , CuBr.

tion of four- or five-membered rings did not take place. Instead rearrangements to allenes (**8**; $n = 2$ or 3) were observed.⁷ We now disclose the results of our efforts to form six-membered rings via 1,6-eliminations.

The bisdibromocyclopropane adduct (**9**) is a model system for potential 1,6-displacement reactions of bromide ions. Compound (**9**) has been synthesized in our^{8a} and other laboratories,^{8b-d,9} and its reaction with methyl-lithium has been studied. While Sondheimer *et al.*^{8c,d} treated a mixture of the diastereoisomers (**9a**) and (**9b**) at -35°C and observed the formation of (**13**), (**15**), and dimers of 2,3-naphthoquinodimethane (**14**) Höhn and Weyerstahl⁹ reported a quite different result for the reaction of the separated diastereoisomers (**9a**) and (**9b**) with methyl-lithium at -78°C . They reported that the bromine-containing benzo-*anti*- σ -bishomobenzene†(**10**) is formed from (**9a**), while under identical conditions (**9b**) yields the corresponding *syn*-compound (**16**). The mechanisms of these novel ring-fusion reactions, however, are unknown. To gain insight into the mechanism of the formation of the six-membered rings in (**10**) and (**16**) we also have studied the reactions of (**9a**) and (**9b**) with methyl-lithium at -78°C .‡ The purported crystalline (**16**), furthermore, would be an ideal starting material for the preparation of the unknown (**17**), the benzoannellated homologue of the as yet unknown parent *syn*- σ -bishomobenzene. Accordingly, benzo-*anti*- σ -bishomobenzene (**11**) should result e.g. from the reduction of (**10**) (Scheme 2).

The reaction of the higher melting (153 – 154°C ^{8b}) diastereoisomer, assumed⁹ to have the structure (**9b**), with 2.5 equiv. of methyl-lithium (LiBr) in diethyl ether at -78°C followed by reduction, to our surprise, did not afford the expected '*syn*-' hydrocarbon (**17**) but instead benzo-*anti*- σ -bishomobenzene (**11**). However, from the ring closure (**10**) was obtained in ca. 60% yield. The reduction of (**10**) with Na– NH_3 in methanol provided (**11**) in an unoptimized yield of 25%.

‡ Reactions of *gem*-dibromocyclopropanes with methyl-lithium at -78°C sometimes led to the production of substantial amounts of the corresponding mono-bromo- and (or) methylbromo-cyclopropanes which derive from the protonation and (or) methylation, respectively, of the intermediate organolithium compounds.

Compound (**11**) was also synthesized independently by treatment of naphthalene with diazomethane.¹⁰

These results suggested that the diastereoisomers of (**9**) had been assigned⁹ incorrect structures, and this was confirmed by an X-ray structure-analysis (see Figure 1)§ of the higher melting isomer which proved to be the diastereoisomer (**9a**) i.e. (**11**) is formed from (**9a**) via (**10**). The lower melting compound (90 – 91°C ; 78°C ;⁹ 73 – 75°C ^{8c}), correspondingly, has the structure (**9b**). In the reactions of (**9**) with methyl-lithium, the hitherto undetected^{8c,9} monoallene (**12**) was also formed in ca. 10% yield. In the presence of a second equivalent of methyl-lithium, a second cyclopropylidene-allene rearrangement in (**12**) is induced to give (**13**) which after subsequent electrocyclization affords 2,3-naphthoquinodimethane (**14**). In the presence of atmospheric oxygen (work-up procedure) (**14**) is oxidized to the peroxide (**15**) (yield depends on the amount of oxygen present).

In the reaction of (**9b**), under conditions similar to those for (**9a**), the *syn*-compound (**16**) could not be detected.¶ Compared with (**9a**), compound (**9b**) reacts more sluggishly, yielding the monoallene (**12**) and the peroxide (**15**) (ca. 2 : 1)

§ Crystal data for (**9a**): $\text{C}_{12}\text{H}_{10}\text{Br}_4$, $M = 473.8$, monoclinic, space group $\text{C}2/c$, $a = 9.165(3)$, $b = 9.836(3)$, $c = 15.452(3)$ Å, $\beta = 95.66(2)^{\circ}$, $Z = 4$, $D_c = 2.271$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 114.8$ cm^{-1} . Data collection on an Enraf-Nonius CAD4 diffractometer (monochromated Mo- $\text{K}\alpha$ radiation, $2.00 \leq \theta \leq 27.00^{\circ}$, scan width $(1.00 + 0.35 \tan \theta)^{\circ}$, scan speed 1 – $5^{\circ} \text{ min}^{-1}$, 1518 independent reflections); absorption correction by the method of N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158. Full-matrix least-squares refinement, treating heavy atoms anisotropically, hydrogen atoms isotropically (923 reflections having $I > 2.5 \sigma(I)$, final $R = 0.059$, $R_w = 0.054$, weighting scheme $w = k/[\sigma^2(F_o) + (0.0175 F_o)^2]$). The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¶ According to ref. 9, the compound assumed to be (**9a**), which we have shown is in fact (**9b**), and the purported compound (**16**) show identical spectroscopic data.

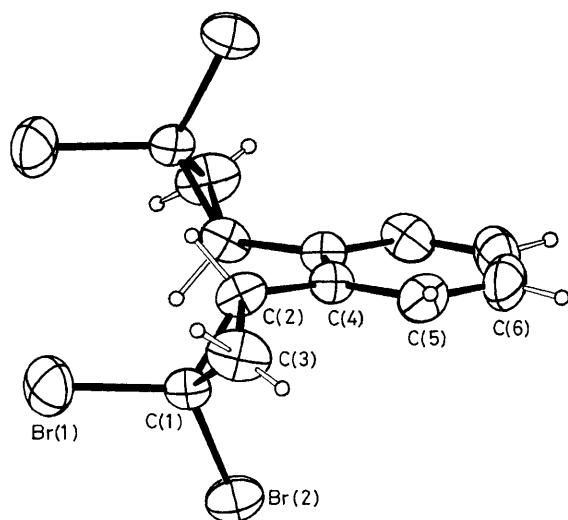


Figure 1. ORTEP plot of the structure of (9a). The molecule has C_2 symmetry. Thermal ellipsoids are at the 50% probability level. Bond lengths (Å): C(1)–C(2) 1.494(12); C(1)–C(3) 1.478(13); C(1)–Br(1) 1.914(8); C(1)–Br(2) 1.906(9); C(2)–C(3) 1.521(12); C(2)–C(4) 1.480(11); bond angles (°): C(2)–C(1)–C(3) 61.6(6); C(2)–C(1)–Br(1) 118.6(6); C(2)–C(1)–Br(2) 120.2(6); C(3)–C(1)–Br(1) 117.0(6); C(3)–C(1)–Br(2) 120.4(6); C(1)–C(2)–C(3) 58.7(6); C(2)–C(3)–C(1) 59.8(6).

as the only main products besides minor amounts of recovered starting material. Steric reasons seem to be responsible for the failure of the cyclization of (9b) to give (16). In order to form the cyclohexane ring in (16) containing vicinal *syn*-cyclopropane rings, the reaction probably has to proceed through a highly sterically hindered transition state. Furthermore, models show that the bromine atoms in *syn*-(16) are eclipsed whereas these atoms in *anti*-(10) have a torsional angle of *ca.* 65°, thereby reducing steric hindrance. In compound (9b) 1,6-dehalogenation to give (16) is obviously prevented, (at higher temperatures?) because 1,1-dehalogenations lead to consecutive cyclopropylidene–allene rearrangements as competing reactions.

In conclusion, we have shown that the reactions of the bisdibromocyclopropane-adduct (9a) with methyl-lithium are temperature dependent.^{4,9} While at temperatures above *ca.* –50 °C the typical cyclopropylidene–allene rearrangements predominate, *i.e.* products are formed derived from (two-fold) 1,1-dehalogenations, at lower temperatures a 1,6-

elimination leading to a bromine-substituted *anti*- σ -bishomobenzene begins to compete. ||

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|| In the reaction of the crystalline bis-adduct,¹¹ resulting from the addition of dibromocyclopropane to *cis*-hexa-1,3,5-triene, with methyl-lithium in the temperature range –65 to –50 °C and subsequent immediate reduction (Li, tetrahydrofuran, BuOH) of the mixture, *anti*- δ -bishomobenzene was formed in very small quantities.¹²