

Formation of 10b-Bromomethyl-10c-methyl-10b,10c-dihdropyrenes from the Corresponding [2.2]Metacyclophanes[†]

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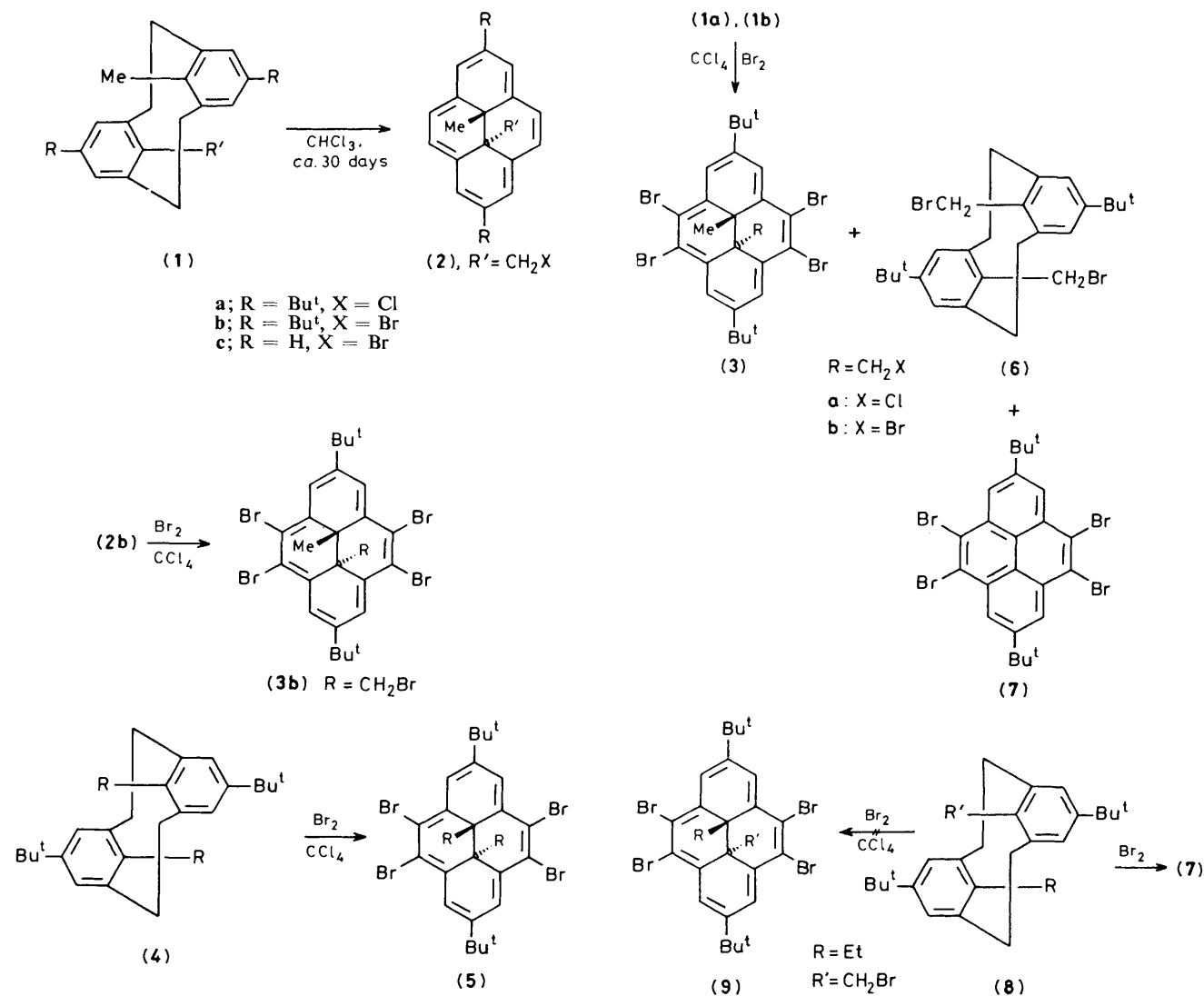
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2,7-Di-*t*-butyl-10b-halogenomethyl-10c-methyl-10b,10c-dihdropyrenes (**2a**) and (**2b**) were spontaneously formed when solutions of the corresponding 5,13-di-*t*-butyl-8-halogenomethyl-16-methyl[2.2]metacyclophanes (**1a**) and (**1b**) in CHCl₃ were left for a long time at room temperature; treatment of the [2.2]metacyclophanes (**1a**) and (**1b**) with bromine afforded the corresponding tetrabromo-10b,10c-dihdropyrenes (**3a**) and (**3b**).

Although 10b- and 10c-substituents in 10b,10c-dihdropyrenes are expected to have interesting chemical properties

since they are surrounded by annulene π -electrons, 10b,10c-dihdropyrenes having 10b- and 10c-substituents other than alkyl¹ have not been prepared. We report here formation of the title compounds from the corresponding [2.2]metacyclophanes by spontaneous oxidation in CHCl₃ solution or by treatment with bromine.

[†] For Part 9 of the series Metacyclophanes and Related Compounds, see M. Tashiro, T. Arimura, and T. Yamato, to be published.



Initially colourless solutions of the [2.2]metacyclophanes (1a) or (1b) in CHCl₃, prepared for the measurement of their ¹H n.m.r. spectra,² gradually became dark green. Their ¹H n.m.r. spectra after about 30 days showed new methyl and methylene signals at δ ca. -3.9 and ca. -1.5 for (1a) and (1b), together with the original methyl (δ 0.58) and methylene (δ 3.07) signals.

These results suggested that the corresponding 10b,10c-dihydropyrenes (2a) and (2b) might have been formed in each case, and indeed, small amounts of compounds (2a) and (2b)† were isolated by silica gel chromatography. When the solution of (1b) was exposed to daylight for 4 h, the conversion into (2b) was more rapid, and (2b) was obtained in 51% yield.

When a solution of (1c) in CHCl₃ was left for some time, (1c) was recovered almost quantitatively; (2c) was not obtained, although the colour of the solution changed gradually, as with (1a) and (1b), but in this case to dark purple.

Bromination³ of (2b) with bromine in CCl₄ solution afforded the pentabromo-compound (3b).

Since it has been reported that⁴ similar bromination of the [2.2]metacyclophanes (4) afforded the corresponding tetrabromodihydropyrenes (5) in good yields, we thought that bromination of (1b) might give (3b) directly.

Indeed, treatment of (1a) or (1b) with bromine in CCl₄ solution gave a mixture of the corresponding dihydropyrene derivatives (3a) or (3b),§ the [2.2]metacyclophane (6),⁴ and the tetrabromopyrene (7).³ Compound (3b) could be isolated in ca. 26% yield by silica gel chromatography from the reaction of (1b), but, in the reaction of (1a), halogen exchange occurred and a small amount of (3b) was formed, together with (6) and (7), in addition to (3a). Purification of (3a) was thus difficult.

In contrast, bromination of (8) under similar conditions

† (2a): green prisms (from hexane); m.p. 175–177 °C (decomp.); ¹H n.m.r. (CDCl₃) δ -3.88 (3H, s), -1.50 (2H, s), 1.65 (18H, s), and 8.30–8.64 (8H, m); m/z 378, 380 (M^+); (2b): green prisms (from hexane); m.p. 162–164 °C (decomp.).

§ (3a): dark brown prisms (from hexane), m.p. 168–170 °C; ¹H n.m.r. (CDCl₃) δ -3.40 (3H, s), -1.08 (2H, s), 1.66 (18H, s), 8.91 (2H, s), and 9.12 (2H, s); m/z 689, 691, 693, 695, 697, 699 (M^+); (3b): dark brown prisms (from hexane), m.p. 175–177 °C.

afforded only compound (7) in good yield but not compound (9).

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