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Medium-sized cyclophanes. Part 58.[1] Photochemical introduction of acetoxy groups to the bridged methylenes of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]metacyclophane

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The photoreaction of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]metacyclophane **1b** in acetic acid at room temperature using a high pressure Hg lamp led to the first successful introduction of acetoxy groups into the methylene groups.

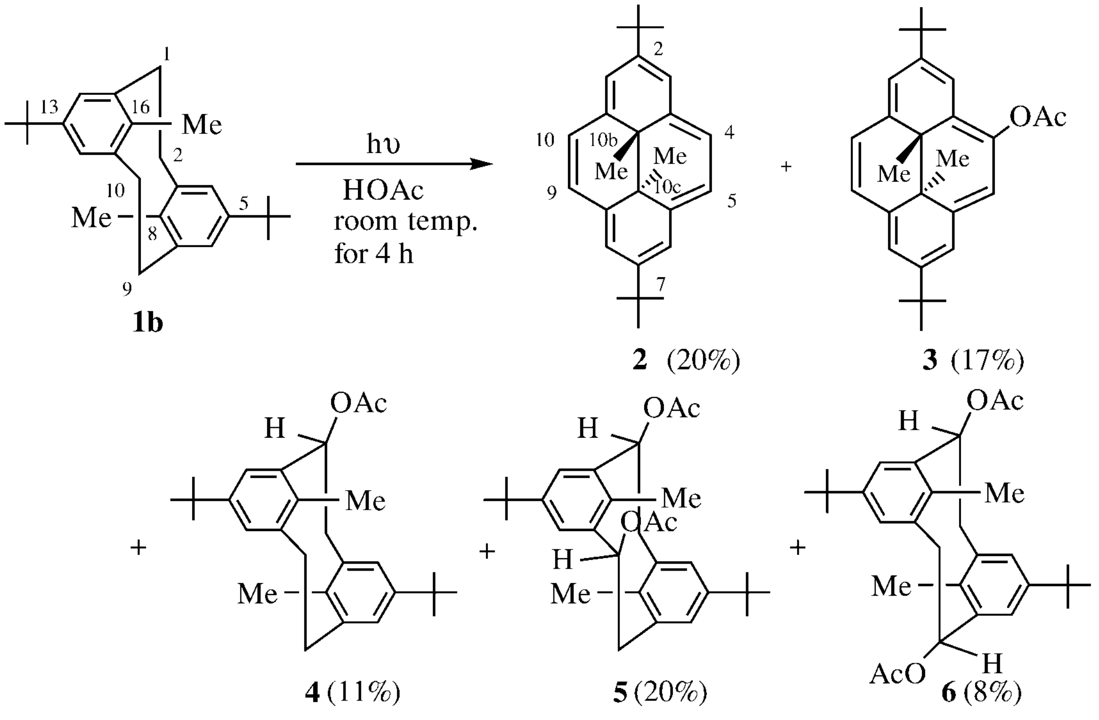
Keywords: cyclophanes, photoreaction

For many years various research groups have been attracted by the chemistry and spectral properties of the [2.2]MCP ([2.2]MCP = [2.2]metacyclophane) skeleton.[2] Its conformation, which was elucidated by X-ray measurements,[3] is frozen into a chair-like non-planar form. Many attempts have been made directly to introduce the functional groups into the methylene groups of [2.2]MCPs, but these have failed because of the deviation of the benzyl carbon atom from the plane of the benzene ring.[2] We previously reported[4] the first success in the introduction of chloro group into the methylene groups of 8,16-dimethyl[2.2]MCP **1a** including the reaction of 8,16-dimethyl[2.2]MCP with iodine monochloride.

However, we have not yet succeeded in introducing substituents into the methylene groups of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP **1b** due to the novel transannular reaction arising from the electronic interaction between two benzene rings, the proximity of the 8,16-positions and the release of the considerable strain energy to form the more stable annulene π-electron system, 10b,10c-dihydropyrene. Thus, the reaction of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]-MCP **1b** with iodine monochloride only affords 4,5,9,10-tetrachloro-2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene in good yield.[5] No formation of the substitution product at the methylene groups of 8,16-dimethyl[2.2]MCP was observed under the reaction conditions used. We undertook the present work in order to extend the novel reaction mentioned above. In this paper we report the first success of the photochemical introduction of acetoxy groups to the bridged methylenes of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP **1b**.

Results and discussion

When a solution of **1b** in $CHCl_3$ was exposed to sunlight, the initially colourless solution of **1b** gradually became dark green,



Scheme 1

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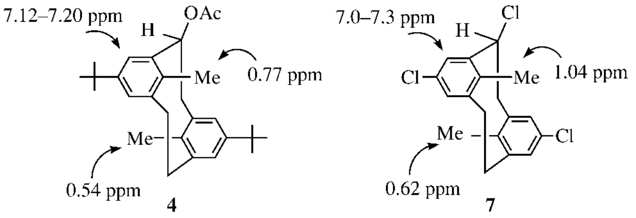
which colour change strongly suggests the formation of *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene **2**.[6] The progress of the photoreaction was monitored by the ^{1}H NMR and after 24 h, *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene **2** was obtained as deep green prisms in 60% yield along with a recovery of the starting compound **1b**. A similar result was obtained in $CHCl_3$ with a low pressure murcury lamp to afford **2** in 50% yield. A similar colour change was also observed during the irradiation of **1b** in acetic acid solution with a high-pressure murcury lamp (400W). After colum chromatography of the reaction mixture with hexane and benzene as eluent *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene **2** and 4-acetoxy derivative **3** were obtained in 20 and 17% yields, respectively. Interestingly, monoacetoxy compounds 1-acetoxy-5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP **4** and diacetoxy compounds **5**, **6** were also isolated in 11, 20 and 8% yields, respectively. Although the yields of **4**, **5** and **6** are low, this result is the first introduction of a functional group such as the acetoxy group into the methylene groups of [2.2]MCP. In contrast, similar treatment of 8,16-dimethyl[2.2]MCP **1a** afforded a mixture of intractable products and a colour change like that from the *tert*-butyl derivative **1b** was not observed under the reaction conditions used. This result strongly suggests that the *tert*-butyl group might play an important role in stabilising the intermediates generated during the irradiation.

The structures of products **2** and **3** were determined on the basis of their elemental analyses and spectral data. The assignment of **2** was carried out by the comparison with an authentic sample.[5b] The ^{1}H-NMR spectrum of **3** shows internal methyl protons as singlets at δ –3.87, –3.82 and acetoxy methyl protons as a singlet at δ 2.62 (relative intensity 2:1). Three aromatic protons are observed as a singlet at δ 8.41 and doublets at δ 8.44, 8.45 (J = 12.7 Hz), which are clearly associated with the protons at C-5, C-9 and C-10, respectively. Structure **3** can also be determined by the fact that the nonequivalent methyl and *tert*-butyl groups in **3** give rise to detectably different resonances as a result of the effect of the acetoxy group.

The structures of products **4**, **5** and **6** were also determined on the basis of their elemental analyses and spectral data. We previously assigned[4] the ^{1}H-NMR signals of 1-*exo*-5,13-trichloro-8,16-dimethyl[2.2]MCP **7** as indicated in Fig. 1, and we have assigned the ^{1}H-NMR signals of **4** in a similar fashion. Thus, the ^{1}H-NMR spectrum of **4** shows two internal methyl resonances as singlets at δ 0.54, 0.77 and a bridge methine signal as a multiplet around δ 6.20–6.22. One of the two methyl protons is in a strongly deshielding region of oxygen atoms of *exo*-OAc on the ethylene bridge resulting in a much larger downfield shift (δ 0.77) than that of the other one (δ 0.54). In contrast, the aromatic protons were observed as a multiplet around δ 7.12–7.20, which is almost same as that for the *exo*-Cl arrangement of **7** (δ 7.0–7.3). A deshielded aromatic proton due to the *endo*-OAc oxygen atom on the ethylene bridge was not observed. On the basis of the spectral data, compound **4** is assigned the structure, 1-*exo*-acetoxy-5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP.

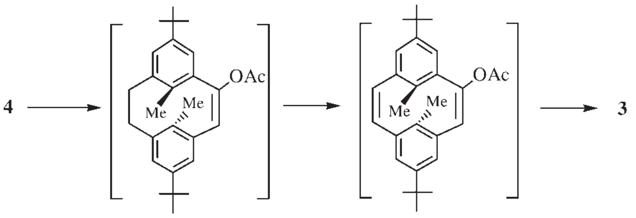
The ^{1}H-NMR spectrum of **5** shows two internal methyl resonances as singlets at δ 0.50, 0.97, a bridge methine signal as a multiplet around δ 6.20–6.22, and two aromatic protons as a singlet at δ 7.22. One of the methyl protons was also observed to be deshielded by the two acetoxy groups on the ethylene bridges resulting in a much larger downfield shift (δ 0.97) than that of **4**. These data are strongly supported that the two OAc groups are *exo*- and *exo*-arrangement and located at the same side to the ethylene bridges in the cyclophane ring. Therefore, compound **5** is found to be 1,10-di-*exo*-acetoxy-5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP. We have assigned the ^{1}H-NMR signals of **6** in a similar fashion. Thus, one internal methyl resonance and the aromatic protons were observed as a singlet at δ 0.74 and a pair of doublets at δ 7.18, 7.22 (J = 1.98 Hz), respectively, attributable to the C_2-symmetrical structure. The ^{13}C-NMR spectrum also supports this structure. On the basis of the spectral data, compound **6** is assigned the structure, 1,9-di-*exo*-acetoxy-5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP.[7]



4 **7**

Fig. 1

It was also found that the irradiation of **2** in acetic acid under the same reaction conditions did not afford acetoxy substitution product **3**. Only the recovery of the starting compound **2** resulted. This finding suggests that the intermediate for the formation of **3** should be **4**. Oxidation of acetate **4** to form the corresponding 1-acetoxy[2.2]MCP-1-ene **8**, from which **3** might be produced via intermediate 1-acetoxy[2.2]MCP-1,9-diene **9** is expected on the basis of earlier reported observations that [2.2]MCP-1,9-diene gave tautomerisation product 10b,10c-dihydropyrene.[8]



8 **9**

Scheme 2

Although the detailed mechanism of formation of **4** is not clear at present, it is concluded that the present novel photoreaction leads to the first direct introduction of an acetoxy group into the both methylene groups of [2.2]MCP **1b**. The preparation of 4-acetoxy-2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene **3** from **1b** through **4** appears to be a useful route to *trans*-10b,10c-dihydropyrene derivatives, and studies of the scope and limitation of the route are in progress.

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