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FORMATION OF 10b,10c-DIHYDRO-10b,10c-DIMETHYLPYRENES IN REACTION OF 8,16-DIMETHYL[2.2]METACYCLOPHAN-1-ENES WITH PROTONIC ACIDS

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Reaction of 8,16-dimethyl[2.2]metacyclophan-1-enes with protonic acids such as 57% hydroiodic acid and trifluoroacetic acid afforded the corresponding 10b,10c-dihydro-10b,10c-dimethylpyrenes. Similar reaction with 47% hydrobromic acid and 36% hydrochloric acid gave surprisingly halogenated 10b,10c-dihydro-10b,10c-dimethylpyrenes.

Although some [2.2]metacyclophan-1-enes were prepared,[1,2)] there is a few information on their chemical behavior.[2,3)] Reaction of 5,13-di-tert-butyl-8,16-dimethyl[2.2]metacyclophan-1-ene with bromine has been reported[2)] to afford 4,5,9,10-tetrabromo-2,7-di-tert-butyl-10b,10c-dihydro-10b,10c-dimethylpyrene, while reaction of [2.2]paracyclophan-1-ene with deuterium bromide and bromine[4)] afforded exclusively cis adduct, respectively. We report here on the reaction of 8,16-dimethyl[2.2]metacyclophan-1-ene (**1a**)[5)] and its 5,13-di-tert-butyl derivative **1b**[2)] with protonic acids.

Reaction of **1a** and **1b** with various protonic acids was carried out in dioxane at room temperature with stirring. Usual work up gave, after SiO_2 chromatography, 10b,10c-dihydro-10b,10c-dimethylpyrenes **2a-2e**, as is summarized in Table 1.

The structures of **2a**, **2b**, and **2c** were identified by their spectral data and comparison of their melting points with those of authentic samples.[2,7,8)] The structures of **2d** and **2e** were assumed by their spectral data.[6)]

Table 1 clearly indicates the occurence of trans annular reaction in **1a** and **1b** for the first time in all acids employed and introduction of Br or Cl atom with HBr or HCl into dihydropyrene system.

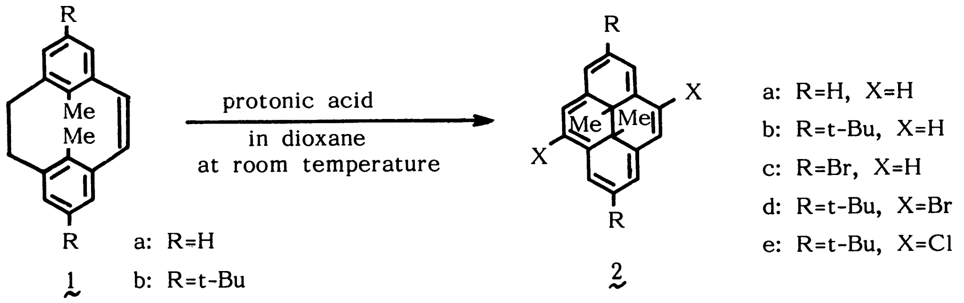


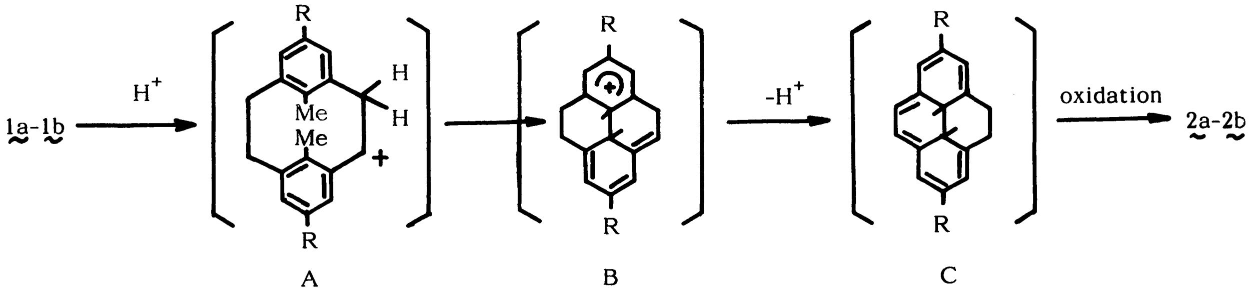
Table 1. Reaction of 8,16-Dimethyl[2.2]metacyclophan-1-enes with Protonic Acids

Run	Cyclophanene	Protonic acid	Time/h	Product[6] (yield/%)	Recovery of stating material (%)
1	**1a**	57% HI	3	**2a**[7](22)[a]	18
2	**1a**	47% HBr	2	**2c**[8](6)[a]	68
3	**1b**	57% HI	2	**2b**[2](41)[a]	10
4	**1b**	47% HBr	2	**2d**(34)[a]	25
5	**1b**	36% HCl	2	**2e**(7)[b]	88
6	**1b**	36% HCl	4	**2e**(11)[b]	79
7	**1b**	CF_3COOH	5	**2b**(27)[b]	73

a) Isolated yields. b) Relative yields obtained by NMR.

Compound **2b** seems to a possible intermediate for formation of **2d** in the reaction of **1b** with 47% HBr. Indeed, when **2b** was treated with 47% HBr under similar conditions, **2d** was formed in 85% yield. However, when **2a** was treated with 47% HBr under similar conditions, starting material was recovered almost quantitatively.

Although detailed mechanisms of formation of **2a**-**2b** from **1a**-**1b** are not clear, a possible reaction pathway might be proposed as follows:



Oxidation of the intermediate C with oxygen in air might afford **2a**-**2b**. Indeed, when reaction of **1b** with 47% HBr was carried out under nitrogen atmosphere, **1b** was recovered in 86% yield and **2b** was obtained in only 11% yield.

References

1) H. Blaschke, C. E. Ramey, I. Calder, and V. Boekelhide, J. Am. Chem. Soc., 92, 3675 (1970).
2) M. Tashiro and T. Yamato, J. Am. Chem. Soc., 104, 3701 (1982).
3) C. E. Ramey and V. Boekelheide, J. Am. Chem. Soc., 92, 3681 (1970).
4) R. E. Singler and D. J. Cram, J. Am. Chem. Soc., 94, 3512 (1972).
5) M. Tashiro, T. Yamato, and K. Kobayashi submitted for publication.
6) The melting points and spectral data of new compounds in Table 1 summarized follow.
2d: deep green prisms (hexane); mp 213-214 °C (decomp.); IR (KBr) 3040, 2960, 1580, 1460, 1375, 1330, 1215, 1180, 1115, 945, 880, 770, 665 cm^{-1}; ^1H-NMR ($CDCl_3$) δ -3.80 (6H, s), 1.69 (18H, s), 8.41 (2H, d, J = 2 Hz), 8.60 (2H, s), 8.76 (2H, d, J = 2 Hz); MS (m/e) 500, 502, 504 (M^+).
2e: deep green prisms (hexane); mp 218-222 °C (decomp.); IR (KBr) 3040, 2960, 1585, 1440, 1360, 1335, 1235, 1205, 1180, 1115, 1090, 970, 950, 910, 885, 800, 780, 665 cm^{-1}; ^1H-NMR ($CDCl_3$) δ -3.75 (6H, s), 1.68 (18H, s), 8.42 (4H, s), 8.80 (2H, s); MS (m/e) 412, 414, 416 (M^+).
7) V. Boekelheide and J. B. Phillips, J. Am. Chem. Soc., 89, 1695 (1967).
8) J. B. Phillips, R. J. Molyneux, E. Sturm, and V. Boekelheide, J. Am. Chem. Soc., 89, 1704 (1967).

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