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-8,16dimethyl[2.2]metacyclophan-1-ene with bromine has been reported²⁾ 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 bromine⁴⁾ 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 1b²⁾ 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.



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	сғ _з соон	5	2b(27) ^{b)}	73

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

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

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