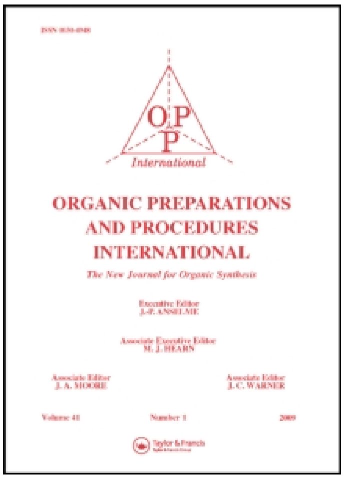

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CHLORINATION OF 5,13-DI-*t*-BUTYL-8,16-DIMETHYL[2.2]METACYCLOPHANE

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oil, n_D^{25} 1.5343. GC analysis showed the product to be >98% pure **2**. The IR and NMR spectra of this material and of authentic **2** (see above) were identical.

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CHLORINATION OF 5,13-DI-*t*-BUTYL-8,16-DIMETHYL[2.2]METACYCLOPHANE[†]

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(02/27/84)

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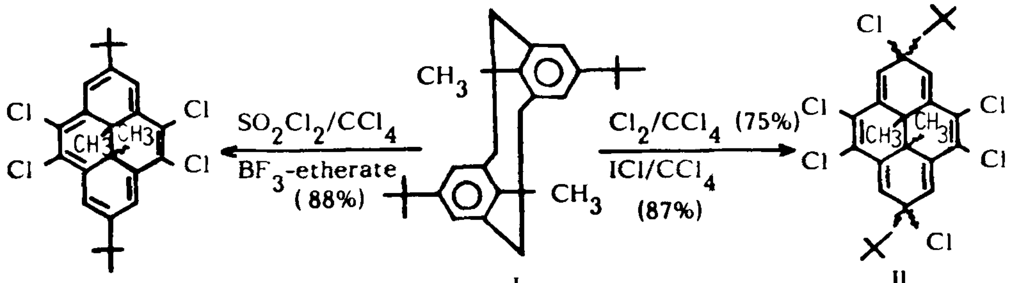
It was previously reported that bromination of 5,13-di-*t*-butyl-8,16-dimethyl[2.2]metacyclophane (I) afforded a novel product, 2,7-di-*t*-butyl-4,5,9,10-tetrabromo-10b,10c-dimethyl-10b,10c-dihydropyrene.[1] We now describe the chlorination of I with chlorine, iodine monochloride, and sulfuryl chloride (Scheme I).

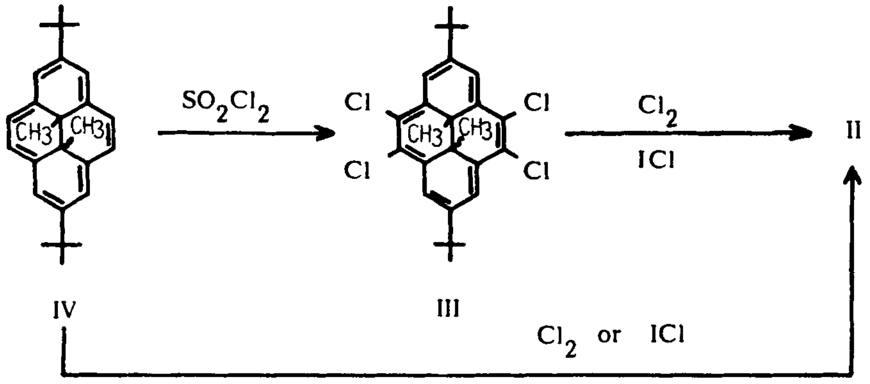


III I II

Scheme I

Treatment of I with chlorine and iodine monochloride in carbon tetrachloride, did not yield 2,7-di-*t*-butyl-4,5,9,10-tetrachloro-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (III), the product expected from the result of bromination of I with bromine, but instead afforded 2,7-di-*t*-butyl-2,4,5,7,9,10-hexachloro-*trans*-10b,10c-dihydropyrene (II);[2] II was also obtained in good yields from chlorination of 2,7-di-*t*-butyl-10b,10c-dimethyl-10b,10c-hydropyrene (IV) by treatment with the same chlorinating reagents. Reaction of I with sulfuryl chloride in the presence of BF_3 etherate afforded III in good yield; this reaction did not occur in the absence of the catalyst. It had been previously reported that compound IV reacted with SO_2Cl_2 to give III which was converted to II by treatment with chlorine and iodine monochloride.[2]

Treatment of II with 10% $Na_2S_2O_3$ solution or Zn powder in acetic acid afforded III in good yields. Unfortunately, the stereochemistry of II is still obscure. The above results suggest that the formation of II from the chlorination of I with chlorine and iodine monochloride proceed through the formation of III.



Scheme II

EXPERIMENTAL SECTION

Chlorination of 5,13-Di-t-butyl-8,16-dimethyl[2.2]metacyclophane (I) with Sulfuryl Chloride.- To a solution of 403 mg (1.16 mmol) of I and 4 ml of sulfuryl chloride in 120 ml of carbon tetrachloride was added 1 ml of boron trifluoride etherate at room temperature. The reaction mixture was refluxed for 12 hrs, and it was poured into a large amount of ice-water. The organic layer was extracted with dichloromethane. The dichloromethane solution was dried over sodium sulfate and evaporated *in vacuo* to leave the residue which was chromatographed on silica gel using hexane as an eluent to give 424 mg (88%) of III as deep green plates (hexane), mp. 235-237°, lit.[2] mp. 235-237°.

Chlorination of I with Chlorine.- Through a solution of 200 mg (0.58 mmol) of I in 80 ml of carbon tetrachloride was passed chlorine gas with stirring at room temperature for 15 min. The reaction mixture was evaporated *in vacuo* to leave the residue which was treated with small amounts of hexane to give 252.4 mg (75%) of II as colorless needles (benzene), mp. 222-226° (dec.), lit.[2] mp. 222-226° (dec.).

Chlorination of I with Iodine Chloride.- To a solution of 200 mg (0.58 mmol) of I in 80 ml of carbon tetrachloride was added a solution of 1.41 g (8.7 mmol) of iodine monochloride in 20 ml of carbon tetrachloride with stirring at room temperature. After the reaction mixture was stirred for 2 hrs, it was evaporated *in vacuo* to leave the residue which was treated with a small amount of hexane to give 275 mg (87%) of II, mp. 222-226° (dec.).

Reduction of II with an Aqueous Sodium Thiosulfate.- A solution of 200 mg (0.343 mmol) of II in 80 ml of carbon tetrachloride was shaken with 100 ml of aqueous 10% sodium thiosulfate solution in a separatory funnel. The organic layer was washed with water, dried over Na_2SO_4 and evaporated *in vacuo* to leave the residue which was chromatographed on silica gel with hexane as an eluent to give 147.1 mg (89%) of III, mp. 225-237° (dec.).

Reduction of II with Zinc Powder.- To a solution of 200 mg (0.343 mmol) of II in 80 ml of AcOH was added 200 mg (3.05 mmol) of zinc powder, and the solution was heated on the water bath for 30 min. The reaction mixture was filtered and concentrated to leave the residue, which was extracted with dichloromethane. The dichloromethane extract was washed with water, dried over Na_2SO_4 and evaporated in vacuo to leave the residue which was chromatographed on silica gel with hexane as an eluent give 149 mg (90%) of III.

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PREPARATION OF BROMOBENZOIC ACIDS FROM THE CORRESPONDING BROMOTOLUENES VIA THE KROEHNKE METHOD

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Although oxidation of bromotoluenes (I), which have one or two bromo groups in the ortho positions, was carried out according to the reported methods[1,2] in order to obtain the corresponding bromobenzoic acids, their yields were very poor (a few percent).