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HALOGENATION OF 2,7-DI-TERT-BUTYL-TRANS-10b,10c-DIALKYL-10b,10c-DIHYDROPYRENES[1,2]

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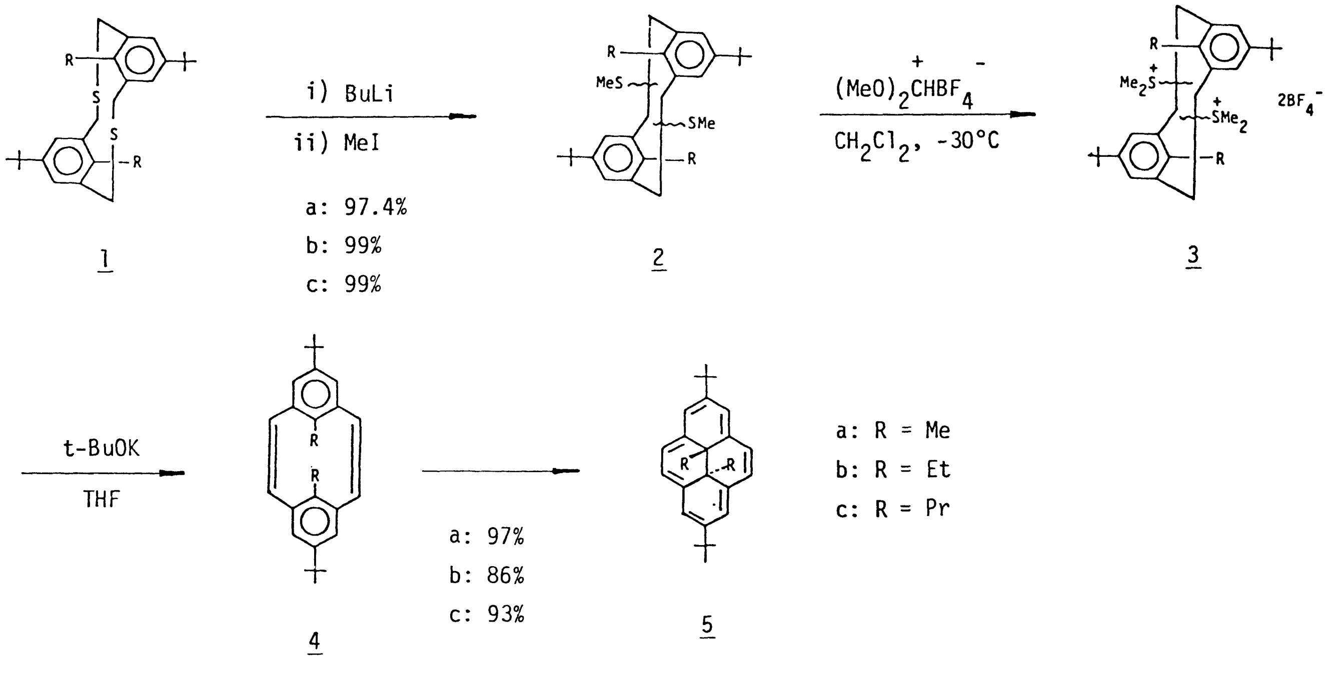
Treatment of 2,7-di-tert-butyl-trans-10b,10c-dialkyl-10b,10c-dihydropyrenes 5a-5c with bromine afforded the corresponding tetrabromides 7a-7c in good yields, respectively. The tetrachloro derivative of 5a was also obtained in 40% yield by the treatment of 5a with SO_2Cl_2. The bromination of 5a-5c with bromine in the presence of Fe powder gave the dealkylated compound 2,7-di-tert-4,5,9,10-tetrabromopyrene 8 in good yields, respectively. When 5a-5c were treated with I_2, 2,7-di-tert-butylpyrene 9 was obtained in good yields, in all cases.

Although trans-10b,10c-dialkyl-10b,10c-dihydropyrenes have been prepared by Boekelheide and his co-workers,[3-9] their preparative routes from easily available compounds seem to bo too long for practical purposes. So the chemistry of 10b,10c-disubstituted 10b,10c-dihydropyrenes are very poor.

In this communication, we wish to report the halogenations such as iodination, bromination, and chlorination of 2,7-di-tert-butyl-trans-10b,10c-dialkyl-10b,10c-dihydropyrenes (5).

The compounds 4, 8,16-dialkyl-anti-3,5-di-tert-butyl[2.2]metacyclophane-1,9-dienes, were easily prepared from anti-dithia[3.3]metacyclophanes 1 which[10] were obtained from the corresponding 1-alkyl-4-tert-butylbenzenes in three steps according to the reported methods.[8,9]

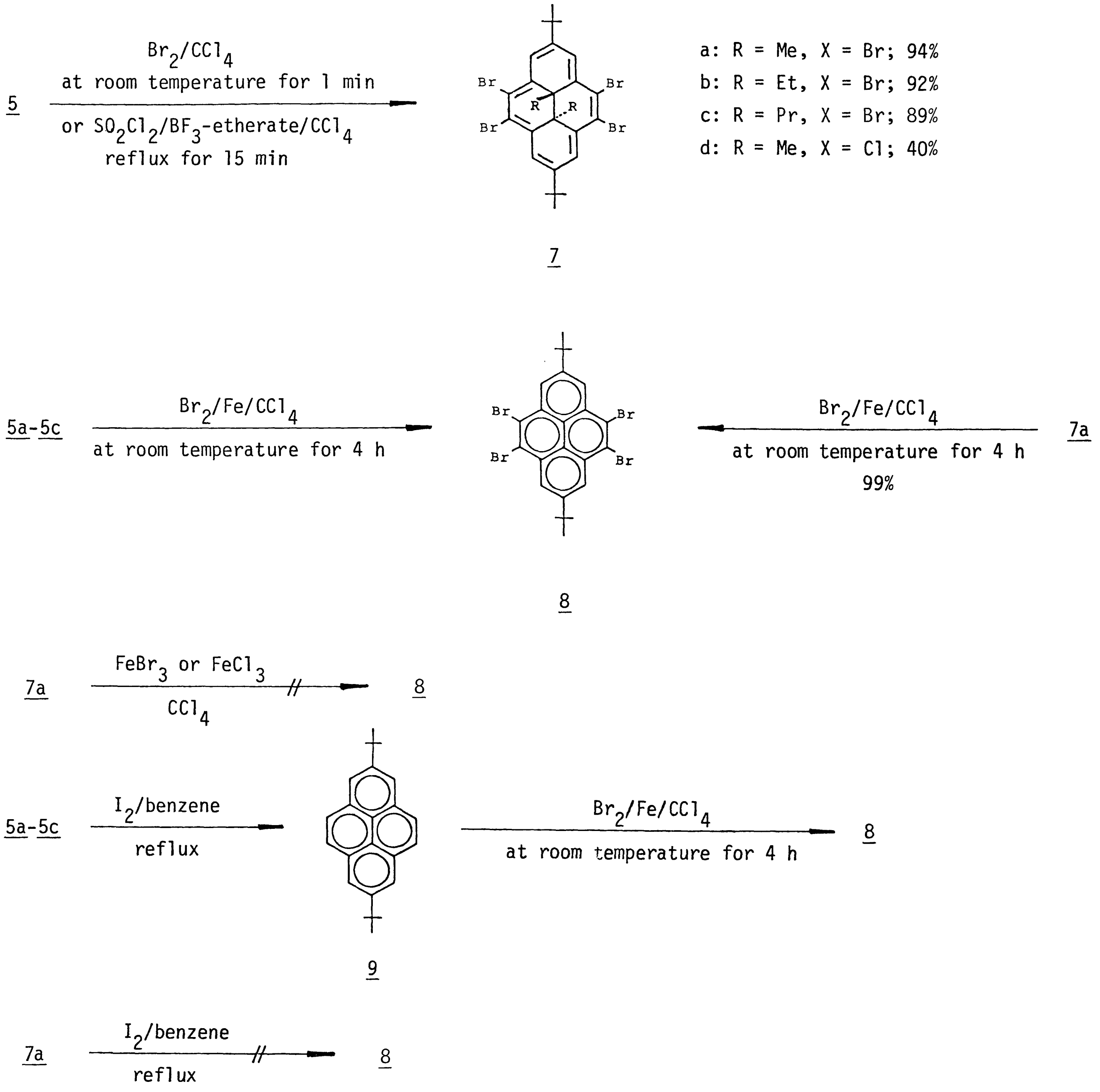


Scheme 1

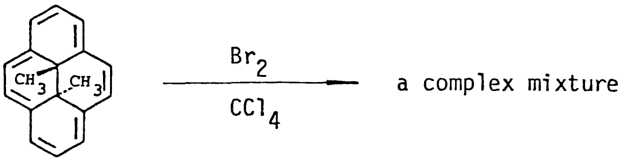
These compounds 4a-4c are very labile and change spontaneously to the corresponding 5a-5c. Although the compound 5a could be recrystallized from hexane, the compounds 5b-5c were labile in boiling hexane and purified by only column chromatography on silica gel.

Boekelheide and his co-workers[5] reported that the bromination of trans-10b,10c-dimethyl-10b,10c-dihydropyrene (6) in a carbon tetrachloride solution afforded only a complex mixture of polybromo derivatives. Recently, Mitchell and his co-workers[11] reinvestigated this reaction and obtained also the same result even at -78°C.

The treatment of 5a-5c with bromine in a carbon tetrachloride solution according to the method reported by Boekelheide and his co-workers[5] caused immediate decolorization of the bromine solution



Scheme 2



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with evolution of hydrogen bromide, and there was an uptake of 4 moles of bromine before the bromine color persisted. After the reaction mixture was washed with water, the organic layer was extracted with dichloromethane. The dichloromethane solution was washed with water, dried over sodium sulfate and evaporated in vacuo to leave the residue, which was purified by column chromatography on silica gel to give the corresponding tetrabromides 7a-7c. The compound 7a was recrystallized from hexane, and the compounds 7b-7c as well as 5b-5c were purified by column chromatography on silica gel, because these compounds were labile in boiling hexane.

Also, the chlorination of 5a with sulfuryl chloride in the presence of BF_3-etherate in a carbon tetrachloride solution afforded the corresponding tetrachloride 7d. The bromination of 5a-5c in the presence of Fe powder gave surprisingly the dealkylated compound, 2,7-di-tert-butyl-4,5,9,10-tetrabromopyrene (8) in good yields, respectively. This compound 8 was also obtained by the treatment of 7a with Br_2/Fe, but not with $FeBr_3$ nor $FeCl_3$ in a carbon tetrachloride solution.

These findings mean that $FeBr_3$ which might be produced from the bromine and Fe presented in the bromination of 5 did not catalyze the dealkylation mentioned above and that the combination of bromine and $FeBr_3$ should be necessary for the dealkylation.

Such dealkylation reaction was observed in the iodination of 5a-5c. That is, when 5a-5c were treated with I_2 (5 molar ratio to 5) in boiling benzene for 48 h, 2,7-di-tert-butylpyrene (9) was obtained in good yields, in all cases. In the iodination of 5c, propyl iodide could be detected.

Table 1. Melting points, appearances, and NMR of 5 and its halogenation products[a)]

Compound	Melting point (°C)	Appearances (Solvent)	NMR Spectra ($CDCl_3$) δ
5a	203~204	dark green needles (Hexane)	-4.06 (6H, s), 1.70 (18H, s), 8.52 (4H, s), 8.60 (4H, s).
5b	155~157	dark brown prisms	-3.66 (4H, q, J = 7.5 Hz), -1.74 (6H, t, J = 7.5 Hz), 1.66 (19H, s), 8.39 (4H, s), 8.52 (4H, s)
5c	155~157	dark brown prisms	-3.81~-3.64 (4H, m), -1.74~-1.34 (4H, m), -0.56 (6H, t, J = 7.5 Hz), 1.66 (18H, s), 8.36 (4H, s), 8.50 (4H, s).
7a	228~230	green prisms (Hexane)	-3.50 (6H, s), 1.71 (18H, s), 8.96 (4H, s).
7b	165~166	dark brown prisms	-3.08 (4H, q, J = 7.5 Hz), -1.53 (6H, t, J = 7.5 Hz), 1.66 (18H, s), 8.96 (4H, s).
7c	188~189	dark brown prisms	-2.26~-3.08 (4H, m), -1.55~-1.16 (4H, m), -0.40 (6H, t, J = 7.5 Hz), 1.67 (18H, s), 8.96 (4H, s).
7d	235~237	deep green plates (Hexane)	-3.44 (6H, s), 1.71 (18H, s), 5.88 (4H, s)
8	287~288	colorless plates (Hexane)	1.61 (18H, s), 8.90 (4H, s).
9	210~212	pale yellow prisms (Hexane)	1.48 (18H, s), 8.97 (4H, s), 8.14 (4H, s).

a) All compounds gave the satisfactory elemental analyses.

On the other hand, similar treatment of 7a with I_2 in boiling benzene did not give any product, but 7a was recovered in almost quantitatively. These results suggest that I_2 might be more active than Br_2 for the dialkylation of electron-rich 5a-5c but less active than Br_2-$FeBr_3$ for the dealkylation of electron-poor 7a-7c.

The dealkylations described above are the first examples in the field of 10b,10c-dialkyl-10b,10c-dihydropyrenes and seem to be of interest aspect of the reaction mechanisms.

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