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LAYERED COMPOUNDS. XXVIII.[1] [2.2](1,3)PYRENOPHANE AND ANOTHER TRIPLE-LAYERED METACYCLO-PYRENOPHANE

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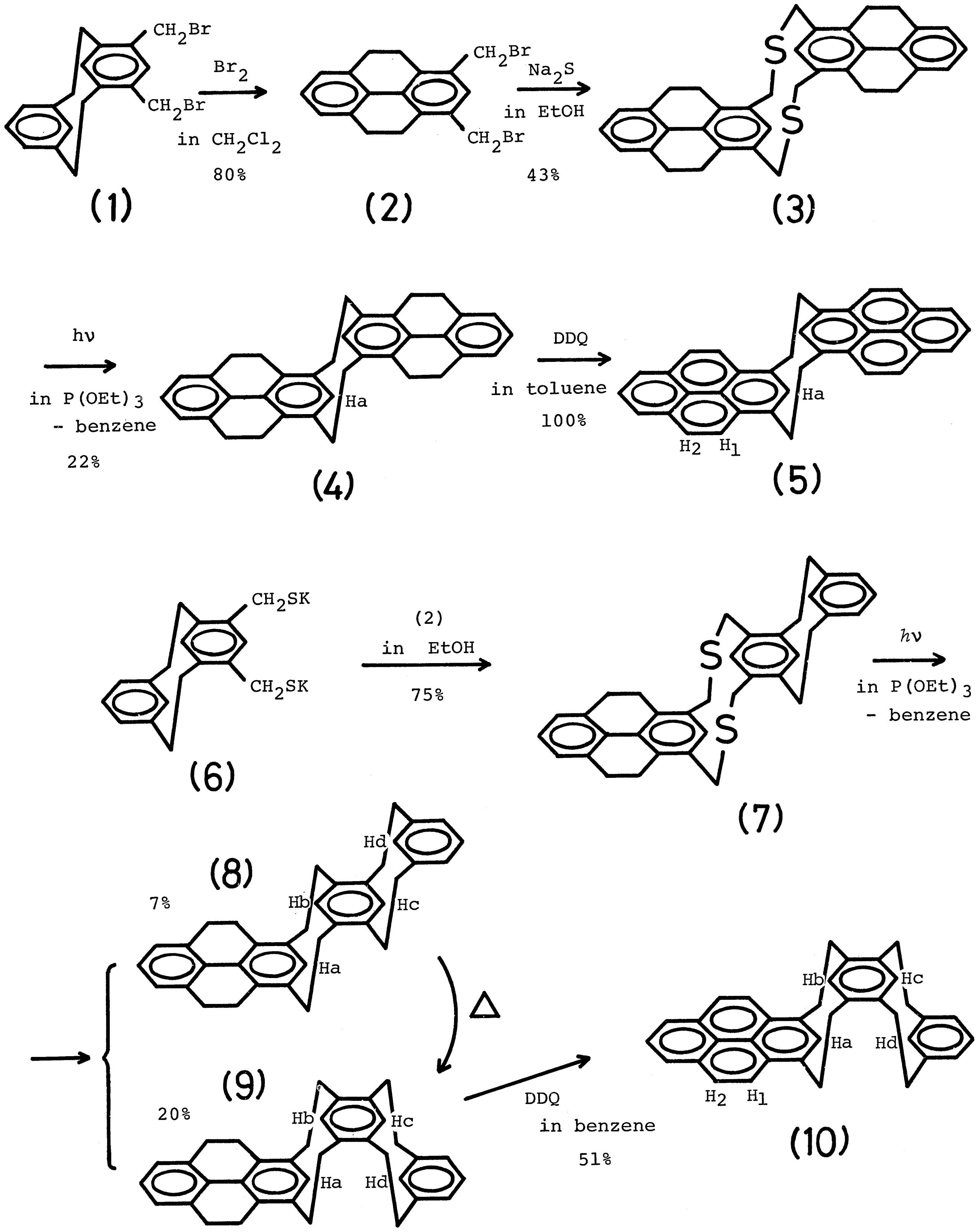
[2.2](1,3)Pyrenophane (5) and a triple-layered metacyclopyrenophane (10) were synthesized successfully via transannular reaction of 4,6-bisbromomethyl[2.2]metacyclophane with bromine as a key step and finally by dehydrogenation with DDQ.

We have previously described the synthesis of a series of metacyclo-polynuclear carbophanes[2] by the transannular reaction of multilayered metacyclophanes[3] with Py·HBr$_3$, followed by dehydrogenation. By this reaction sequence, however, it was difficult to synthesize [2.2](1,3)pyrenophane (5) because quadruple-layered metacyclophanes were unable to give an important precursor (4) owing to its greater ease of transannular reaction at the center of the molecule[2]. We now report the synthesis of [2.2](1,3)pyrenophane (5) and another triple-layered metacyclo-pyrenophane (10), which are important as model compounds of transannular π-electronic interaction or excimer fluorescence. It was reached with success by contriving the transannular reaction[4] of 4,6-bisbromomethyl-[2.2]metacyclophane with bromine as an important step.

Dibromide (1) was treated with 2.3 molar equivalent amount of bromine in methylene chloride under ice-salt cooling to give (2) (80%, colorless scales from benzene, mp 234-236°C with decomp.). Coupling of (2) with sodium sulfide in alcohol under dilute condition afforded disulfide (3)(43%, colorless plates from benzene, mp 259-262°C). (3) was irradiated in triethyl phosphite-benzene (8:1) with high-pressure mercury lamp at room temperature for 12 hr. under nitrogen bubbling. During irradiation octahydro[2.2](1,3)pyrenophane (4) appeared as white precipitates(22%, colorless leaflets from toluene, ca. 320°C


(1)
CH2Br
CH2Br
Br2
in CH2Cl2
80%
(2)
CH2Br
CH2Br
Na2S
in EtOH
43%
(3)
S
S
hν
in P(OEt)3
- benzene
22%
(4)
Ha
DDQ
in toluene
100%
(5)
Ha
H2 H1
(6)
CH2SK
CH2SK
(2)
in EtOH
75%
(7)
S
S
hν
in P(OEt)3
- benzene
(8)
7%
Hd
Hb
Hc
Ha
Δ
(9)
20%
Hb
Hc
Ha
Hd
DDQ
in benzene
51%
(10)
Hb
Hc
Ha
Hd
H2 H1

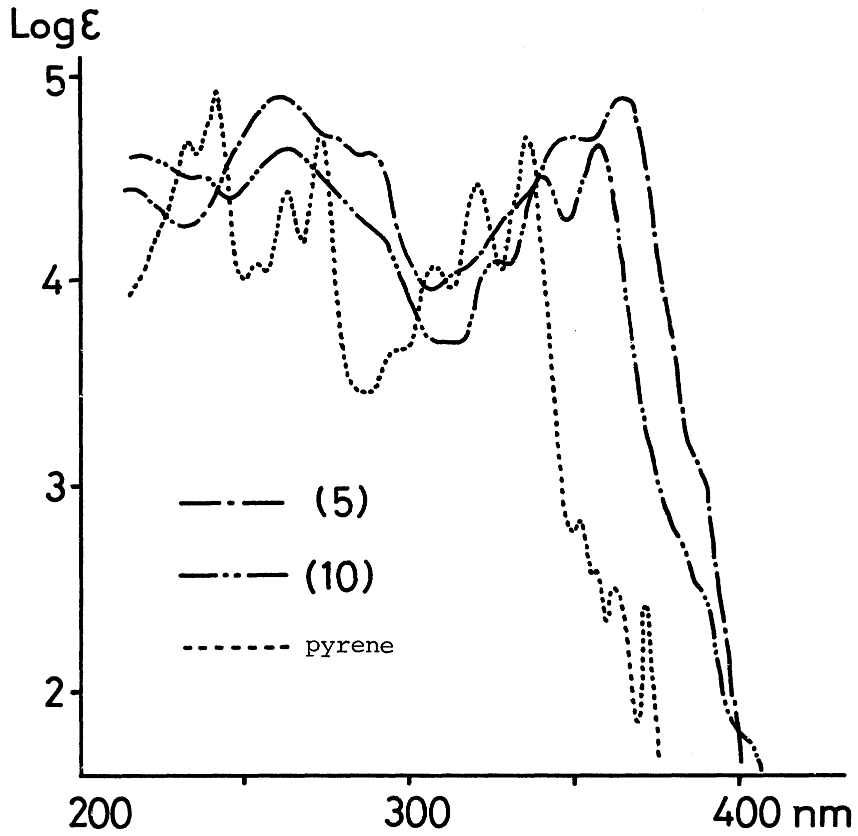
decomp.). A toluene solution of (4) was heated to reflux with a slight excess of DDQ for 17 hr. After evaporation of the solvent the residue was taken up in methylene chloride and chromatographed through a short column of alumina (activity III) to afford (5) in a quantitative yield. For analysis it was rechromatographed on alumina (activity I) and recrystallized from toluene (colorless granulars, 322°C decomp., Mass 456 (M^+), 428 (M^+-28)).

Coupling of (2) with (6) in alcohol under dilute condition afforded (7)(75%, colorless granulars from methylene chloride-hexane, mp 207-208°C). When (7) was irradiated in triethylphosphite-benzene (40:1) for 9 hr., there formed two isomeric products. After separation by chromatography over silica gel, u,d-isomer[5] (9) (colorless leaflets from ethyl acetate, mp 281-283°C with decomp.) and u,u-isomer (8)(colorless fine needles from methylene chloride-ethyl acetate, mp 275-277°C with decomp.) were isolated in 20% and 7% yields, respectively. Their structures were assigned by nmr analysis. (9) was refluxed with DDQ in benzene for 21 hr. and the reaction mixture was chromatographed over alumina to afford u,d-isomer (10) of triple-layered metacyclo-pyrenophane (51%, colorless needles from ethyl acetate, mp 302-303°C, Mass 462 (M^+), 434 (M^+-28)). It was found that (8) was readily isomerized to (9) under the same thermal condition as in the case of (9)→(10) for ca. 1 hr., and therefore dehydrogenation of (8) was not carried out.

NMR data are shown in the Table. On going from (9) to (10), Ha proton is shifted to downfield whereas Hb shifted to upfield both by ca. 0.9 ppm. In addition Hd appears at low field by 0.19 ppm. These changes can be explained by larger anisotropy effect of pyrene ring than that of benzene ring. On the other hand, there is no change between Ha's of (4) and (5). It is probably attributed

NMR data of aromatic protons τ values in $CDCl_3$

	(4)	(5)	(8)	(9)	(10)
Ha	5.57	5.50	5.57	5.01	4.19
Hb			5.76	5.67	6.57
Hc			5.94	5.82	5.76
Hd			5.61	5.01	4.82
H_1		1.46 (d,J=10 Hz)			1.54 (d,J=9 Hz)
H_2		1.84 (d,J=10 Hz)			1.92 (d,J=9 Hz)



Electronic spectra of pyrenophanes in THF.

to that both increased shielding and deshielding effects on Ha's, caused by the conversion of two tetrahydropyrenes into two pyrenes, are compensated each other. A downfield shift of H_1's of (5) by 0.38 ppm as compared with H_2's can be ascribed to the steric compression between H_1's and the equatorial protons of ethylene bridges. The same steric compression is observed in (10).

The electronic spectra of (5) and (10) are shown in the Figure. There are observed bathochromic shift and disappearance of fine structure in the spectra of (5) and (10), compared with that of pyrene as a reference. It is probably due to some transannular interaction between chromophores as well as ring strain. Emission spectra of (5) and other pyrenophanes will be presented elsewhere.

References

1) Part XXVII: H. Tatemitsu, T. Otsubo, Y. Sakata, and S. Misumi, to be submitted.

2) T. Umemoto, T. Kawashima, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 1975, 463.

3) T. Umemoto, T. Otsubo, and S. Misumi, *ibid.*, 1974, 1573.

4) T. Sato, M. Wakabayashi, Y. Okamura, T. Amada, and K. Hata, *Bull. Chem. Soc. Japan*, 40, 2363 (1967).

5) A stair-like conformer is given the symbol u,u and a zigzag conformer the symbol u,d (u=up; d=down) for conformational isomers like (8) and (9).

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