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LAYERED COMPOUNDS. XXIV.[1] THE SYNTHESIS OF METACYCLOPOLYNUCLEAR CARBOPHANES[2] VIA TRANSANNULAR REACTION OF MULTILAYERED METACYCLOPHANES

Teruo Umemoto, Toshihide Kawashima, Yoshiteru Sakata, and Soichi Misumi
The Institute of Scientific and Industrial Research, Osaka University
Suita, Osaka, Japan

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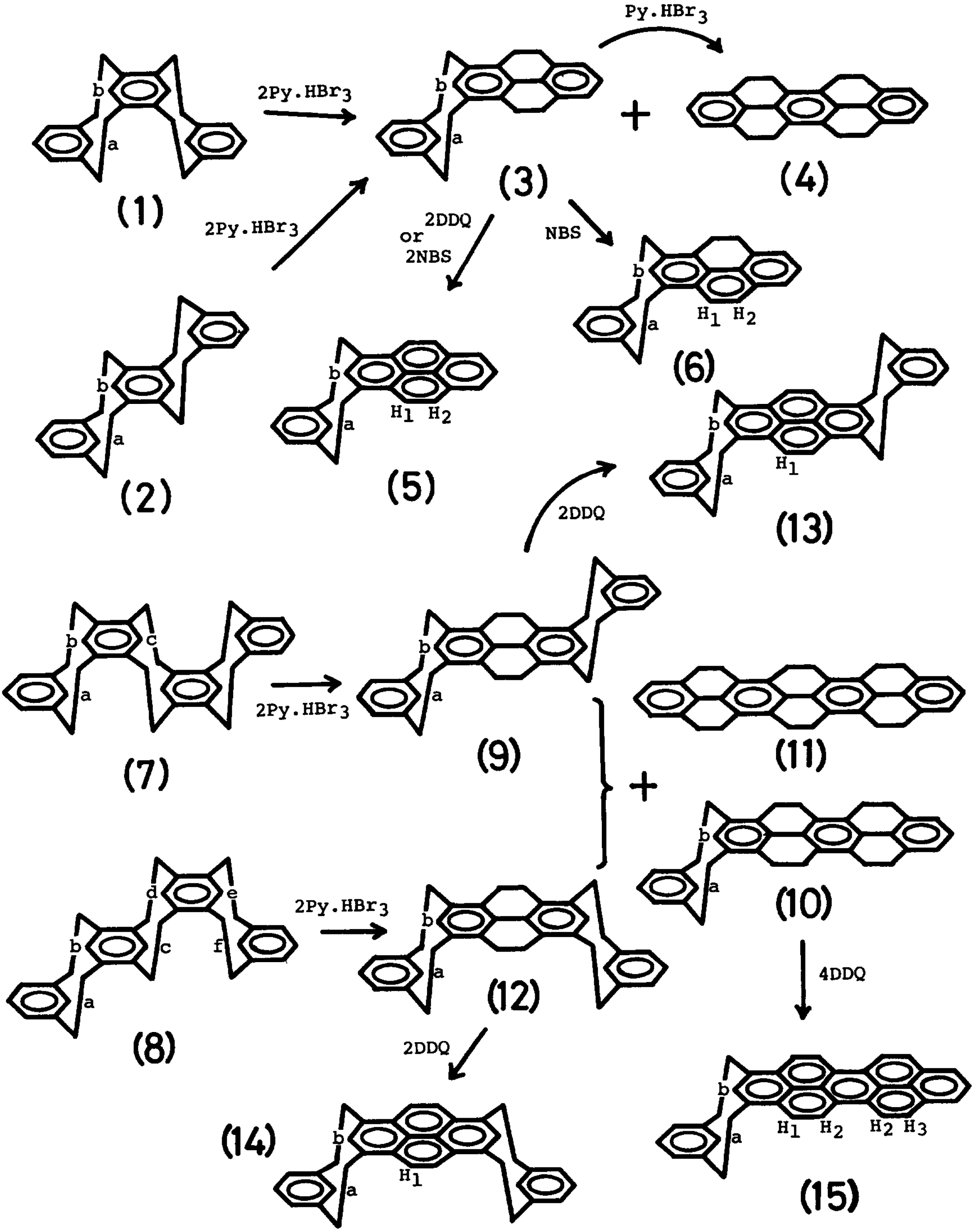
We have previously described the synthesis of multilayered metacyclophanes and their thermal isomerization.[3] Since [2.2]metacyclophane reacts with electrophiles to give tetrahydropyrene,[4] it is expected that a new series of metacyclophanes is available from the multilayered metacyclophanes. We now report the synthesis of unique metacyclophanes containing polynuclear aromatic hydrocarbons from isomeric multilayered metacyclophanes by the transannular reaction-dehydrogenation sequence which has been accomplished in excellent yields with pyridinium hydrobromide perbromide (Py.HBr$_3$) and then DDQ or NBS.

(1) was reacted with two molar equiv. of Py.HBr$_3$ in CH$_2$Cl$_2$ at 0°C for 90 mins. to give, with vigorous evolution of HBr, a mixture of (3)(62%, colorless plates from EtOH, m.p. 169.5-171°C) and (4)(24%, colorless scales from n-hexane, 258-259°C decomp.), which were separated by column chromatography on silica gel. Under the same conditions (2) gave (3)(54%) and (4)(41%). (3) was refluxed with 2DDQ in benzene for 1 hr. or 2NBS in CCl$_4$ for 30 mins. to afford a quantitative yield of (5)(colorless needles from EtOH, m.p. 187-188°C) after purification by column chromatography on alumina. On the other hand, when (3) was treated with 1NBS, it gave (6)(33%, colorless plates from n-pentane, m.p. 149-150°C) besides (5)(29%) and the starting compound (26%), which were readily separated by column chromatography on silica gel coated with trinitrobenzene.

Treatment of (7) with 2Py.HBr$_3$ in a similar manner to that described for (1) afforded (9)(30%, colorless columns from benzene-pentane, m.p. 263-264°C), (10)(51%, colorless plates from benzene-hexane, m.p. 264-266°C), and (11)(14%,


(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)
(9)
(10)
(11)
(12)
(13)
(14)
(15)
2Py.HBr$_3$
Py.HBr$_3$
2DDQ or 2NBS
NBS
2DDQ
4DDQ
a
b
c
d
e
f
H_1
H_2
H_3
+

colorless prisms from toluene, 300°C decomp.). Similarly, (8) gave (12)(48%, colorless fine needles from CH_2Cl_2-EtOH, m.p. 261-263°C), (10)(34%), and (11) (19%). (9) was stirred with excess DDQ in benzene at room temperature for 36 hrs. and then at 60°C for 1.5 hrs. to give (13)(colorless fine needles from CH_2Cl_2-EtOH, m.p. 318-318.5°C with decomp.) quantitatively. (12) was treated with excess DDQ at 60°C for 30 mins. to afford a quantitative yield of (14) (colorless plates from benzene-hexane, m.p. 323-324°C with decomp.). Dehydrogenation of (10) with excess DDQ in boiling benzene gave quantitatively (15) (reddish orange scales from toluene, m.p. 341-342°C in sealed tube). All of new compounds showed satisfactory nmr, ir, mass, and uv spectra and elemental analysis.

The fact that (4) is obtained also by treatment of (3) with $Py.HBr_3$ indicates that the transannular reactions[4] proceed stepwise in all cases of the multilayered metacyclophanes.

Nmr data are shown in the table. The inner aromatic proton Ha of (5) appears at high field whereas Hb at low field as compared with those of (3). These differences can be explained by larger anisotropy effect of pyrene system than that of benzene ring. This is supported by the intermediary protons of (6) having phenanthrene system. H_1 protons appear at lower field than H_2's of (5) and (6) by ca. 0.3 ppm, which is well understandable as steric compression with the equatorial protons of ethylene bridges. A similar steric relationship is observed between H_1 and H_3 in (15).

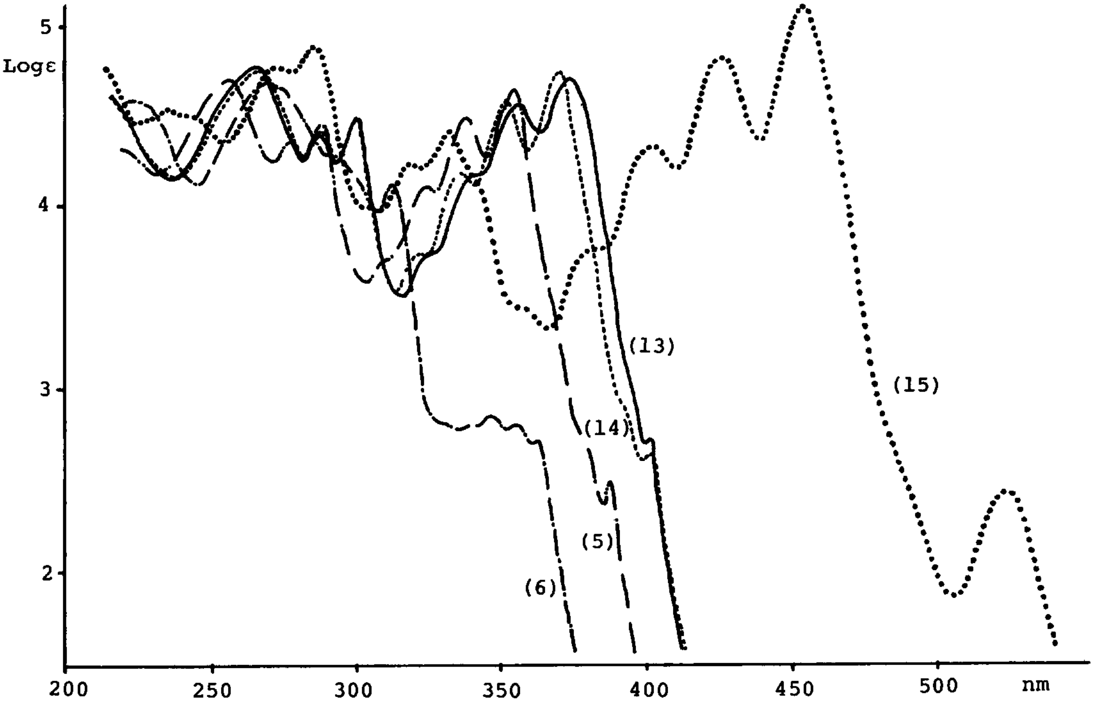
Electronic spectra of metacyclo-pyrenophanes (5, 13, and 14) and -pero-

NMR data of aromatic protons τ values in $CDCl_3$

	(3)	(5)	(6)	(9)	(10)	(12)	(13)	(14)	(15)
Ha	5.54	6.42	6.02	5.54	5.54	5.44	6.32	6.24	6.34
Hb	5.70	4.88	5.25	5.70	5.68	5.68	4.93	4.85	4.73
H_1		1.61 (d,J=8.9Hz)	1.96 (d,9.0)				1.60	1.62	1.25 (d,9.5)
H_2		1.93 (d,J=8.9Hz)	2.25 (d,9.0)						0.61 (d,9.5)
H_3									1.59 (d,9.5)

pyrenophane (15) are shown in the figure. The absorption curves are substantially attributed to the containing polynuclear aromatic hydrocarbons with a minor effect of metacyclophane moieties.

In contrast to the ready thermal isomerizations of (2) and (8) to (1) and (7) respectively, it is interesting that (13) showed no isomerization to (14) under the same conditions.



Electronic spectra of metacyclo-polynuclear carbophanes in tetrahydrofuran.

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