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LAYERED COMPOUNDS. XXV.[1] PEROPYRENE AND TEROPYRENE

-A NEW SYNTHETIC ROUTE OF PYRENE-LIKE POLYNUCLEAR AROMATIC HYDROCARBONS-

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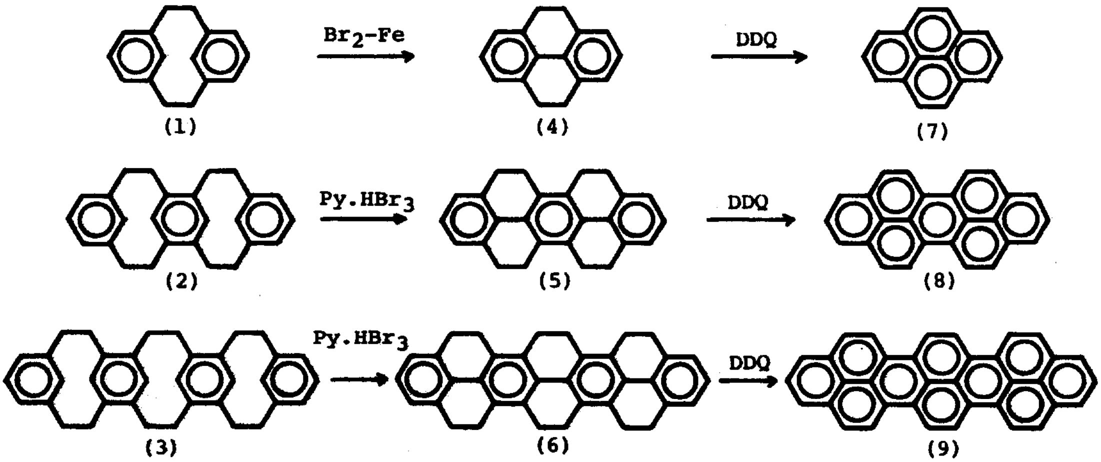
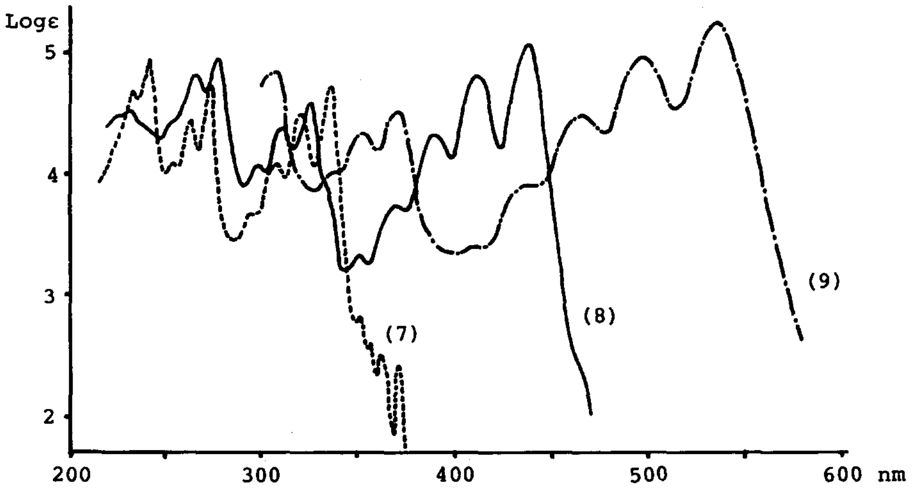
We wish to report the synthesis of polynuclear aromatic hydrocarbons, peropyrene[2] and teropyrene[3] from multilayered metacyclophanes by transannular reaction-dehydrogenation sequence[1] which has been accomplished in excellent yields with pyridinium hydrobromide perbromide(Py.HBr$_3$) and then DDQ under mild conditions. Thus this synthetic route was found to be useful for preparation of pyrene-like polynuclear aromatic hydrocarbons.

Each conformer of triple-layered metacyclophane(2) was treated with 2 mol equiv. of Py.HBr$_3$ in CH$_2$Cl$_2$ at 0°C for ca. 2 hrs. to give (5) in ca. 40% yield. When (5) was refluxed with excess DDQ in benzene for 22 hrs., followed by filtration through alumina, peropyrene(8) was afforded in a quantitative yield (golden leaflets from toluene, m.p. 378-379°C in sealed tube). A conformer (with no center-of-symmetry) of quadruple-layered metacyclophane(3)[4] was treated with 3Py.HBr$_3$ in CH$_2$Cl$_2$ at 0°C for 1 hr. to give (6) in 55% yield.





Electronic spectra of (7) and (8) in THF and (9) in 1,2,4-trichlorobenzene

(6) was dehydrogenated with excess of DDQ in boiling xylene under vigorous stirring, followed by sufficient washing of dark purple precipitate with benzene, alcohol, hot water, and acetone successively, to afford a new polynuclear hydrocarbon, teropyrene(9) in a quantitative yield. For analyses, a portion of the precipitate was recrystallized from a large amount of xylene after filtration of its hot 1,2,4-trichlorobenzene solution through a short column of alumina (dark reddish purple powder, m.p. >500°C, mass m/e M^+450.1375. Calcd. for $C_{36}H_{18}$ 450.1407). Pyrene(7) was also obtained quantitatively by dehydrogenation of tetrahydropyrene(4) with DDQ in boiling benzene, which was derived from [2.2]metacyclophane(1) by Fe-Br_2 treatment in a quantitative yield.[5]

Electronic spectra of (7)~(9) are shown in the figure. The p-bands at the longest wavelength (λmax 337 nm for (7), 438 for (8), and 537 for (9)) showed the same extent of red shift (ca. 100 nm) with increasing chromophores.

References

1) Part XXIV: T. Umemoto, T. Kawashima, Y. Sakata and S. Misumi, *Tetrahedron Letters* (1975) in press.

2) E. Clar, G. S. Fell, C. T. Ironside and A. Balsillie, *Tetrahedron*, 10, 26 (1960).

3) We will call the new compound(9) "teropyrene", since it is seen as a ring system containing three pyrene units and as a mixed system of terrylene and pyrene like peropyrene originated from perylene and pyrene.

4) T. Umemoto, T. Otsubo and S. Misumi, *Tetrahedron Letters*, 1573 (1974).

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