Tetrahedron Letters No. 36, pp 3159 - 3162, 1975. Pergamon Press. Printed in Great Britain.

LAYERED COMPOUNDS. XXIX.[1] [2.2](2,7)PYRENOPHANE AND ITS 1,13-DIENE

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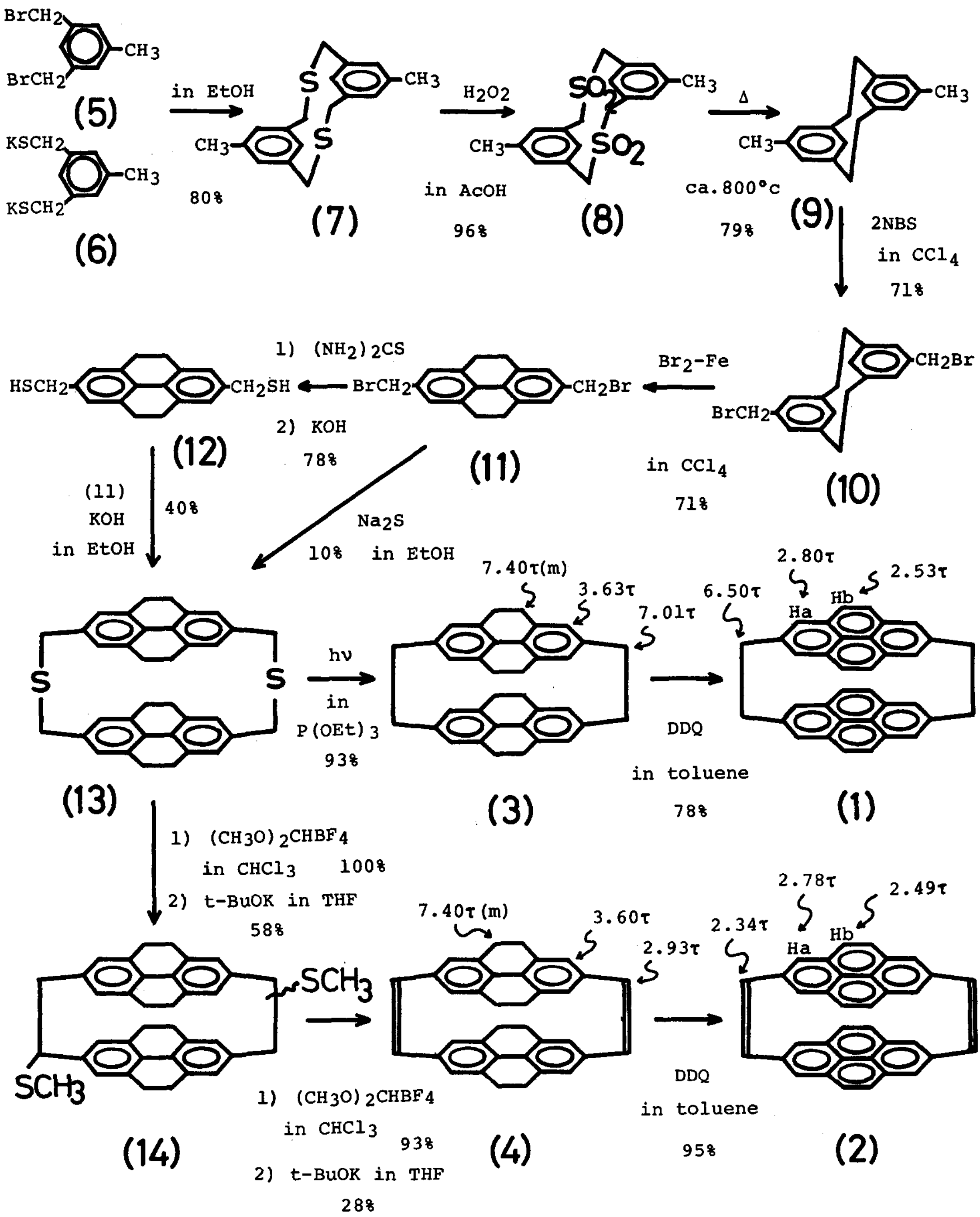
(Received in Japan 28 June 1975; received in UK for publication 24 July 1975)

Recently the studies of a wide variety of condensed aromatic [2.2]carbophanes[2] have been extensively undertaken from the view point of transannular interaction, while no [2.2]pyrenophane, especially a typical model for excimer fluorescence studies,[3] has been thus far reported. In order to synthesize [2.2]pyrenophanes we chose [2.2]metacyclophane rather than pyrene derivatives as a precursor because the former could be easily converted to the desired pyrene framework by characteristic transannular reaction[4] without troublesome insolubility of the intermediates. We now report the synthesis of [2.2](2,7)pyrenophane(1) and its 1,13-diene(2), which was accomplished successfully by contriving the transannular reaction of 5,13-bisbromomethyl[2.2]metacyclophane with bromine-iron as a key step followed by dimerization and finally by dehydrogenation.

Coupling of (5) with (6) under dilute condition gave disulfide(7)(needles from hexane, mp 102-102.5°C). Treatment of (7) with hydrogen peroxide in acetic acid at 70°C, followed by pyrolysis under atmospheric pressure gave 5,13-dimethyl[2.2]metacyclophane(9)(colorless plates from alcohol, mp 145-146°C). The conversion of (9) to its dibromide(10) was readily achieved using NBS ((10): colorless prisms from carbon tetrachloride, mp 205-206°C). Into the cold solution of (10) in carbon tetrachloride were added 1.8 molar equivalent amount of bromine and a small amount of iron powder. The transannular reaction was complete in ca. 10 min. under vigorous stirring at room temperature and gave tetrahydropyrene derivative(11)(colorless scales from carbon tetrachloride, mp 227-229°C with decomp.). Dibromide(11) was converted by the usual way to dimercaptan(12)(colorless leaflets from carbon tetrachloride, mp 190-192°C). Equivalent molar mixture of (11) and (12) in tetrahydrofuran was added dropwise to a large


BrCH2
CH3
BrCH2
(5)
KSCH2
CH3
KSCH2
(6)
in EtOH
80%
S
CH3
S
CH3
(7)
H2O2
in AcOH
96%
SO2
CH3
SO2
CH3
(8)
Δ
ca.800°c
79%
CH3
CH3
(9)
2NBS
in CCl4
71%
CH2Br
BrCH2
(10)
Br2-Fe
in CCl4
71%
BrCH2
CH2Br
(11)
1) (NH2)2CS
2) KOH
78%
HSCH2
CH2SH
(12)
(11)
KOH
in EtOH
40%
Na2S
10%
in EtOH
S
S
(13)
hν
in
P(OEt)3
93%
7.40τ(m)
3.63τ
7.01τ
(3)
DDQ
in toluene
78%
6.50τ
2.80τ
2.53τ
Ha
Hb
(1)
1) (CH3O)2CHBF4
in CHCl3 100%
2) t-BuOK in THF
58%
SCH3
SCH3
(14)
1) (CH3O)2CHBF4
in CHCl3
93%
2) t-BuOK in THF
28%
7.40τ(m)
3.60τ
2.93τ
(4)
DDQ
in toluene
95%
2.34τ
2.78τ
2.49τ
Ha
Hb
(2)

amount of boiling alcohol containing alkali for 17.5 hr to give (13)(colorless plates from toluene, ca. 270°C decomp.). An alternative synthesis of (13) was carried out by the reaction of (11) with sodium sulfide. Irradiation of (13) in triethylphosphite with high pressure mercury lamp under nitrogen bubbling for 5 hr gave (3)(colorless plates from benzene, ca. 315°C decomp.). It was refluxed with DDQ in toluene for 15 hr and the reaction mixture was chromatographed through a short column of alumina to afford the desired pyrenophane (1)(yellow leaflets from toluene, 310°C decomp., Mass 456(M^+), 228($M^+/2$)).

On the other hand, (13) was methylated with the Borch reagent, followed by the Stevens rearrangement[5] with excess potassium t-butoxide for 11 hr to give an isomeric mixture of (14). Without further separation (14) was treated again with the Borch reagent under the same condition as in the case of (13) and then the salt was stirred with excess potassium t-butoxide in tetrahydrofuran at room temperature for 13 hr to give octahydro[2.2](2,7)pyrenophane(4)(colorless prisms from benzene, mp 303-305°C with decomp., Mass 460(M^+)). Finally, (4) was refluxed with DDQ in toluene for 12.5 hr to yield [2.2](2,7)pyrenophane-1,13-diene(2)(yellow plates from toluene, ca. 340°C decomp., Mass 452(M^+)).

NMR data(in deuteriochloroform) are shown in the reaction scheme. One may find there is a difference between the chemical shifts of Ha and Hb protons in (1) contrary to the same position of the corresponding protons in pyrene. It is assumed that Ha's lie closer to the opposed pyrene ring than Hb's by considering the X-ray structure analysis[6] of [2.2]paracyclophane and related compounds. Accordingly the difference of chemical shifts may be due to the difference in ring current effect of the opposed pyrene ring on the two protons of (1). With the similar consideration the corresponding protons of (2) are assigned. It is noteworthy that the vinyl protons of (2) and (4), which can be easily assigned by relative intensities, appear at lower field than the aromatic protons similarly to the case of [2.2.2](1,3,5)cyclophane-1,9,17-triene[7].

As seen in the Figure the electronic spectra of (1) and (2) show remarkable red shift of the longest wavelength bands and small blue shift of the bands in a range 320-340 nm, compared with that of pyrene. It may be due to transannular π-electron interaction between chromophores. Very similar spectra of (1) and

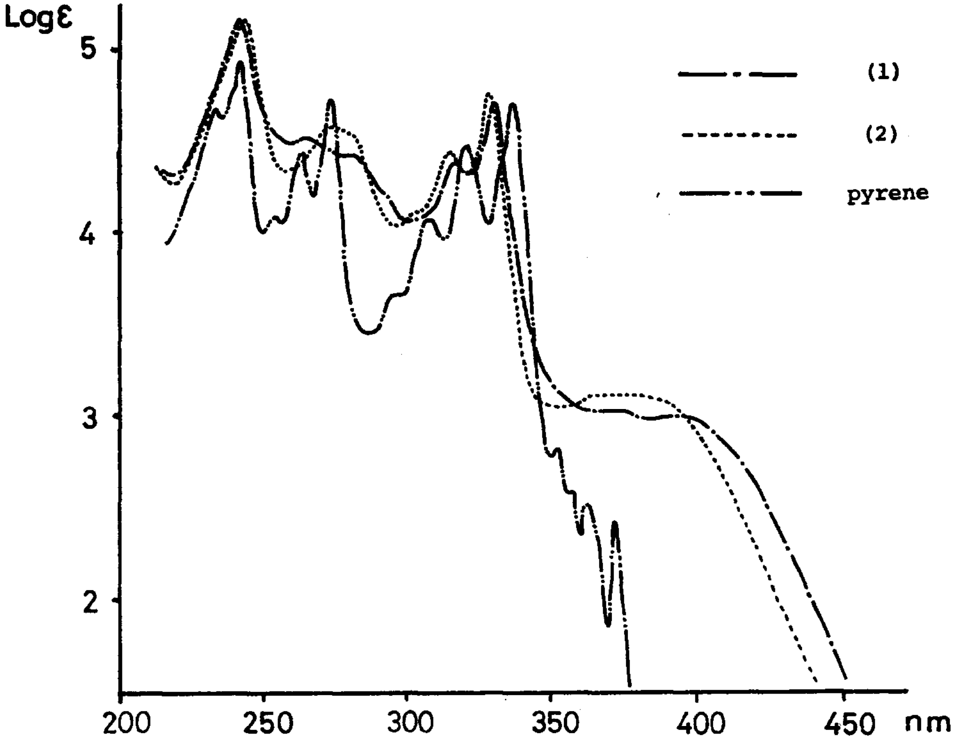


Figure Electronic spectra in tetrahydrofuran

(2) indicate minor electronic effect of additional double bonds in (2). The compounds (1) and (2) exhibited excimer emission bands at longer wavelength (540 and 510 nm, respectively) than that of pyrene(ca. 470 nm). It will be discussed elsewhere.

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