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LAYERED COMPOUNDS. XXII.[1] ISOMERIC MULTILAYERED [2.2]METACYCLOPHANES AND THEIR THERMAL ISOMERIZATIONS

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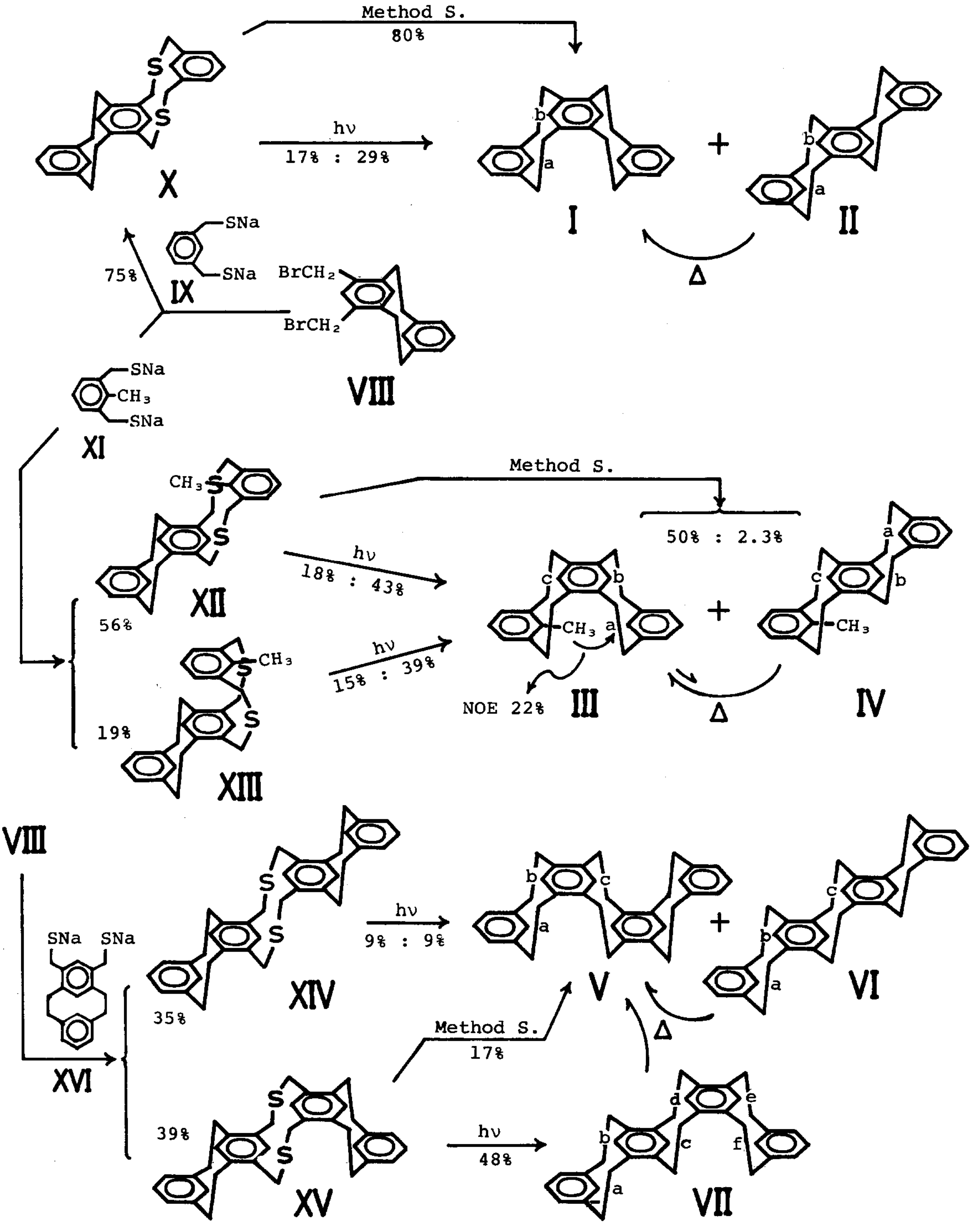
We have previously described the synthesis of multilayered [2.2]metacyclophanes by way of the Stevens rearrangement as a key step.[2] Under such conditions other intriguing conformational isomers could not be detected. Recently photochemical extrusion of sulfur in trivalent organophosphorus solvents was developed for a convenient synthesis of cyclophanes.[3,4] The photo-desulfurization was extended to s series of multilayered [2.2]metacyclophanes with success. We now report on preparation and assignment of several conformational isomers, I~VII, which were found to undergo a prompt thermal isomerization of interest. The photoreaction was carried out under nitrogen at room temperature using a quartz tube, a 400W high-pressure mercury lamp, and triethylphosphite as a solvent.

Coupling of dibromide VIII with IX in boiling alcohol under dilute condition afforded disulfide X (75%, colorless columns from ligroin, m.p. 194~195°C). The 12-membered ring containing sulfurs as in X is, in general, conformationally free from variable-temperature NMR analysis. Irradiation of X for 19 hrs. gave I (17%, colorless scales from alcohol, m.p. 208~209°C) and II (29%, colorless needles from ethyl acetate, m.p. 148~151°C). As an alternative route, methylation of X with the Borch reagent followed by the Stevens rearrangement with potassium t-butoxide in boiling tetrahydrofuran and subsequent desulfurization with Raney nickel in boiling alcohol resulted in the formation of I alone (80% over-all yield) (Method S).

Similarly, coupling of VIII with XI gave XII (56%, colorless columns from benzene, m.p. 197~198°C) and XIII (19%, colorless granular crystals from benzene, m.p. 197~198°C). The structures of these isomers were assigned by NMR


Method S.
80%
S
S
X
hν
17% : 29%
b
a
I
+
b
a
II
Δ
SNa
SNa
75%
IX
BrCH₂
BrCH₂
VIII
SNa
CH₃
SNa
XI
Method S.
CH₃
S
S
XII
50% : 2.3%
hν
18% : 43%
c
b
CH₃
a
+
a
c
b
CH₃
56%
CH₃
S
S
hν
15% : 39%
NOE 22%
III
Δ
IV
19%
XIII
VIII
S
S
XIV
hν
9% : 9%
b
c
a
+
c
b
a
SNa
SNa
35%
V
VI
XVI
Method S.
17%
Δ
S
39%
S
XV
hν
48%
d
e
b
c
f
a
VII

analysis. Irradiation of XII for 19 hrs. gave III (18%, colorless leaflets from alcohol, m.p. 186.5~187.5°C) and IV (43%, colorless columns from ethyl acetate-methanol, m.p. 152~154°C). XIII was irradiated for 19 hrs. to afford III (15%) and IV (39%) at the almost same ratio. XII was treated according to Method S to give III (50%) and IV (2.3%).

Coupling of VIII with XVI, which was derived from VIII, afforded XIV (35%, colorless plates from toluene, m.p. 256~258°C with decomp.) and XV (39%, colorless columns from benzene, m.p. 233~235°C). During irradiation of XIV for 7 hrs., VI appeared as a precipitate because of its extreme insolubility and it was obtained by filtration followed by washing with methylene chloride (9%, fine crystals, 252°C decomp. in sealed tube). Treatment of the filtrate gave V (9%, colorless needles from toluene, 330°C decomp. in sealed tube). Recrystallization of VI was impossible because of insolubility and thermal instability. Irradiation of XV for 5 hrs. afforded only VII (48%, colorless needles from methylene chloride-methanol, m.p. >320°C in sealed tube), whereas by Method S XV gave V alone (17%). The results of the photoreactions above-stated suggest that the extrusion of sulfurs stepwise proceeds through biradical intermediates.[5] All of the new compounds were separated by silica gel and/or alumina chromatography and showed satisfactory NMR, IR, MASS, and UV spectra and elemental analysis.

In contrast to difficult conformational flapping of [2.2]metacyclophanes,[6] it is particularly surprising that a thermal isomerization between conformers of multilayered [2.2]metacyclophanes is quite easy to take place. II in toluene-d_8 at 100°C afforded a 1:1 mixture of II and I after 3~4 minutes and completely transformed to I after 16~18 mins. Both VII and VI likewise altered to V. Under the same condition IV gave a 1:1 mixture of III and IV after ca. 10 mins. and finally reached a equilibrium mixture of a 17:1 ratio which was also attained on treatment of III. Incomplete transformation of IV into III can be accounted for by destabilization due to steric repulsion between Ha and methyl group in III as expected from molecular model examination. In fact, nuclear Overhauser effect between them was observed as 22% area enhancement of the Ha signal with irradiation on the methyl signal for III, but not observed for IV. The thermal isomerization elucidates that I and V are obtained as the sole product by the use of

Method S from X and XV, respectively.

NMR data offer further information concerning isomeric structures as shown in the table. Downfield shift of Ha's (τ 4.97) in I compared to the corresponding ones (τ 5.59) in II is explained by deshielding effect of the third benzene rings closely situated, and a marked downfield shift of Ha signal (τ 4.36) in III can be accounted for by an additional deshielding effect due to steric compression between Ha and the methyl group besides magnetic anisotropy of the third benzene ring. Downfield shift of the methyl groups (τ 8.93) in III compared to that (τ 9.42) in IV can be explained as a sum of the anisotropy and the steric compression effects. The aromatic protons of V ~ VII also are satisfactorily assigned on the basis of the data above. We will report on these assignments in details in the near future.

NMR data of aromatic inner protons τ values in $CDCl_3$

	Ha	Hb	Hc	Hd	He	Hf
I	4.97	5.88				
II	5.59	5.96				
III	4.36	6.33	6.43	8.93 (CH_3)		
IV	5.79	6.15	6.41	9.42 (CH_3)		
V	4.90	5.80	5.05			
VI	5.55	5.93	5.79			
VII	5.52	5.86	5.16	5.65	5.86	4.90

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