CHEMISTRY LETTERS, pp. 405-408, 1978. Published by the Chemical Society of Japan

INTRAMOLECULAR CYCLOADDITION PRODUCTS OF TETRAETHYL [3.3](1,4)-NAPHTHALENO(9,10)ANTHRACENOPHANE-2,2,15,15-TETRACARBOXYLATE AND TETRAETHYL [3.3]PARACYCLO(9,10)ANTHRACENOPHANE-2,2,11,11-TETRACARBOXYLATE

Teruo SHINMYOZU, Takahiko INAZU, and Tamotsu YOSHINO
Department of Chemistry, Faculty of Science, Kyushu University 33,
Hakozaki 6-10-1, Higashi-ku, Fukuoka 812

[3.3](1,4)Naphthaleno(9,10)anthracenophane derivative(3) was converted into the photoisomer(4) on exposure to light. The similar photochemical isomerization(7→8) was observed in the case of [3.3]-paracyclo(9,10)anthracenophane derivative(7). Besides this, the isomer(6) due to the intramolecular Diels-Alder reaction was also formed by heating 7 at ca. 100°.

In cyclophane system containing anthracene nucleus, only [2.2](9,10)anthracenophane[1)], syn-[2.2](1,4)anthracenophane[2)] and [10](9,10)anthracenopha-4,6-diyne[3)] have been known to give photoisomers. Recently S. Misumi et al. have reported the thermal Diels-Alder reaction in the triple-layered anthracenophane.[4)] In the course of our studies on the syntheses of [3.3]cyclophanes containing anthracene nucleus, we found that [3.3](1,4)naphthaleno(9,10)anthracenophane derivative(3) and [3.3]paracyclo(9,10)anthracenophane derivative(7) gave cycloaddition products.

9,10-Bis(chloromethyl)anthracene(1) and the tetraester(2) were coupled in the presence of sodium hydride in refluxing dioxane under high dilution conditions. Products were separated by chromatography on silica-gel with benzene-chloroform(2:1) to give greenish-yellow crystals(3) and colorless crystals(4) in 48.1 and 8.4% yields, respectively. Compound 4 is considered to be formed on exposure to scattering light during isolation and purification, because it was not found in the initial crude products.

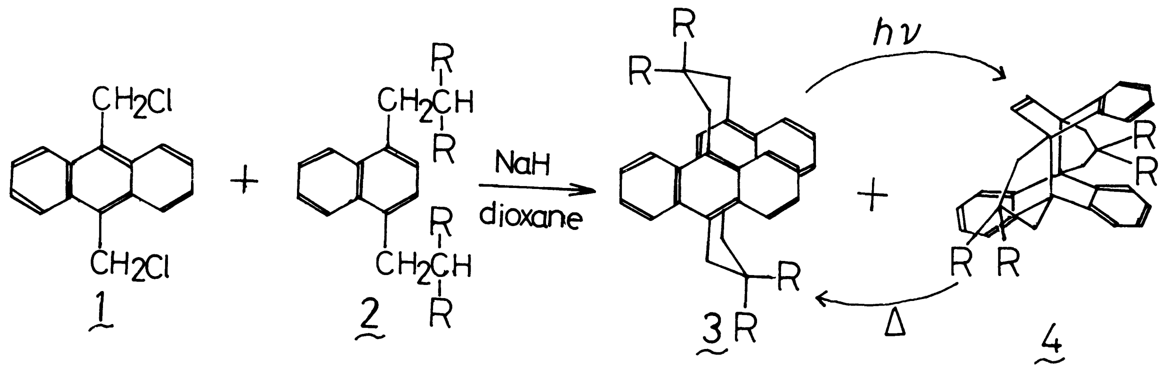


Fig.1 R = $COOCH_2CH_3$

When a chloroform solution of 3 was left stand, the colorless photoisomer 4 was actually produced by $[\pi 4s+\pi 4s]$ cycloaddition reaction. The more smooth conversion was attained by irradiating the solution with a high-pressure mercury lamp. On the contrary, when 4 was heated above its melting point, it was rapidly reconverted to the original greenish-yellow compound(3), which is stable to heat. 3: greenish-yellow prisms from benzene-ligroin, mp 243.0-244.0°. Found: C, 74.84; H, 6.26%; mol wt (MS,M^+) 674. 4: colorless crystals from ether-petroleum benzin, mp 154.0-154.5°. Found: C, 74.68; H, 6.28%; mol wt(MS,M^+) 674. Calcd for $C_{42}H_{42}O_8$: C, 74.76; H, 6.27%; mol wt 674.

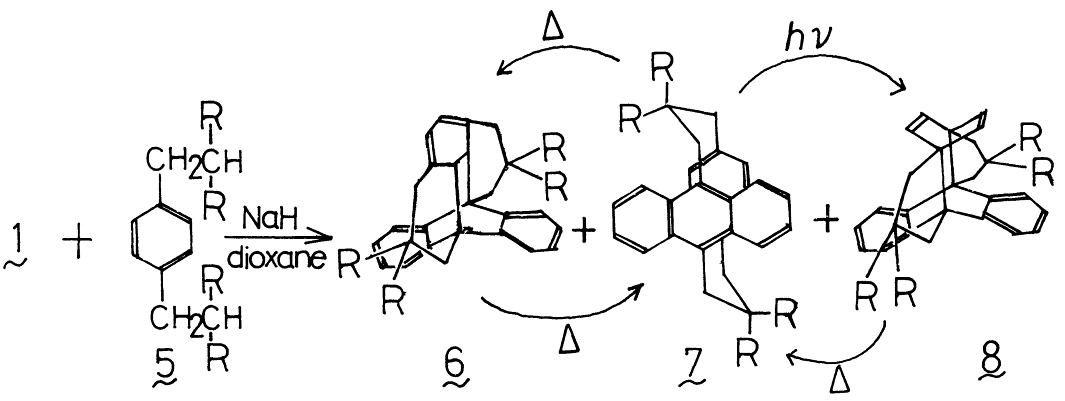
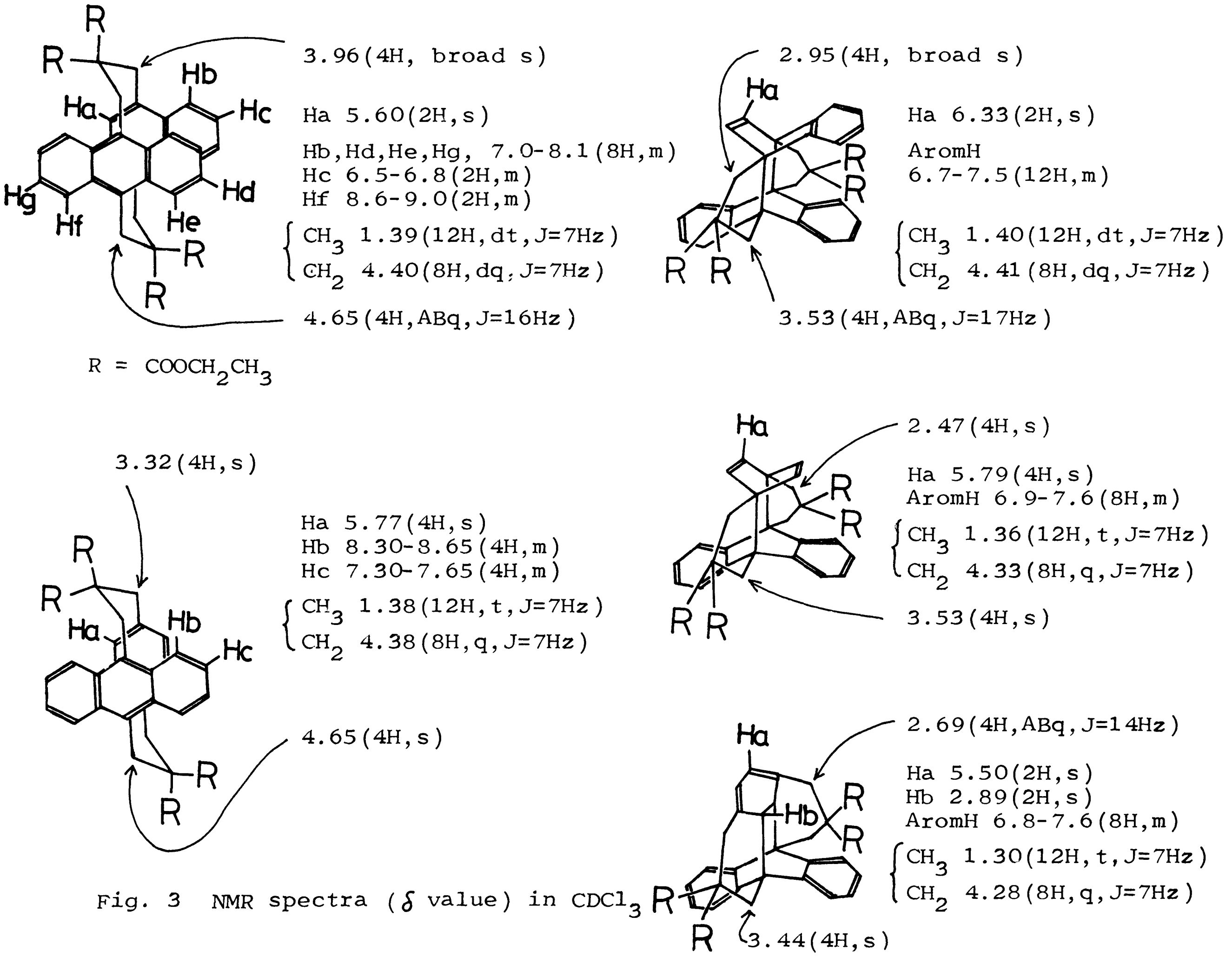


Fig. 2

In the coupling reaction of the dichloride(1) and tetraester(5), the yellowish-green compound melting at 163.5-164.5° and two kinds of the colorless compounds melting at 183.5-184.5° and 160.5-162.0°, respectively, were obtained in 20.1% total yield. These compounds exibited the same molecular ion peak at 624. The colorless compound melting at higher temperature was the main product and identified as 6 on a basis of its NMR spectrum. Another colorless compound was found to be the photoisomer(8). The yellowish-green compound was identified as 7 by the spectroscopic data. It was assumed that 6 was formed thermally, because it was found in the crude product. But 8 was assumed to be formed photochemically during the separation in a similar way that 4 was obtained along with 3. Photochemical isomerization of 7 afforded the corresponding photoisomer 8. When 8 was heated at 170° for 1 min, a 1:1 mixture of 6 and 7 was produced. When 7 was heated at ca. 100°, it was slowly converted into 6 by the intramolecular Diels-Alder reaction. When 6 was heated at 190° for 1 min, a 3:2 mixture of 6 and 7 was obtained, but prolonged heating resulted in partial decomposition. This suggests that retro-Diels-Alder reaction occurred on heating. 7: yellowish-green crystals from ether, mp 163.5-164.5°. Found: C, 72.98; H, 6.49%; mol wt(MS,M^+) 624. 6: colorless needles from ether, mp 183.5-184.5°. Found: C, 72.89; H, 6.42%; mol wt(MS,M^+) 624. 8: colorless plates from ether, mp 160.5-162.0°. Found: C, 73.08; H, 6.36%; mol wt(MS,M^+) 624. Calcd for $C_{38}H_{40}O_8$: C, 73.06; H, 6.45%; mol wt 624.



3.96(4H, broad s)
Ha 5.60(2H,s)
Hb,Hd,He,Hg, 7.0-8.1(8H,m)
Hc 6.5-6.8(2H,m)
Hf 8.6-9.0(2H,m)
CH_3 1.39(12H,dt,J=7Hz)
CH_2 4.40(8H,dq,J=7Hz)
4.65(4H,ABq,J=16Hz)

R = $COOCH_2CH_3$

2.95(4H, broad s)
Ha 6.33(2H,s)
AromH 6.7-7.5(12H,m)
CH_3 1.40(12H,dt,J=7Hz)
CH_2 4.41(8H,dq,J=7Hz)
3.53(4H,ABq,J=17Hz)

3.32(4H,s)
Ha 5.77(4H,s)
Hb 8.30-8.65(4H,m)
Hc 7.30-7.65(4H,m)
CH_3 1.38(12H,t,J=7Hz)
CH_2 4.38(8H,q,J=7Hz)
4.65(4H,s)

2.47(4H,s)
Ha 5.79(4H,s)
AromH 6.9-7.6(8H,m)
CH_3 1.36(12H,t,J=7Hz)
CH_2 4.33(8H,q,J=7Hz)
3.53(4H,s)

2.69(4H,ABq,J=14Hz)
Ha 5.50(2H,s)
Hb 2.89(2H,s)
AromH 6.8-7.6(8H,m)
CH_3 1.30(12H,t,J=7Hz)
CH_2 4.28(8H,q,J=7Hz)
3.44(4H,s)

Fig. 3 NMR spectra (δ value) in $CDCl_3$

As described above, the remarkable feature that the cycloaddition reaction takes place more easily in [3.3]cyclophane than in [2.2]cyclophane is attributable to the following reasons. (1) In [4+4]cycloaddition reaction, the product from [2.2]cyclophane contains two extremely strained cyclobutane rings, whereas the product from [3.3]cyclophane gives merely almost strain-free cyclopentane rings. (2) Steric interference between the bulky ethoxycarbonyl groups and the aromatic protons also may favor the cycloaddition. Synthetic studies of other [3.3]cyclophanes containing anthracene nucleus are now under investigation. The data of NMR spectra are shown in Fig. 3.

References

1) J. H. Golden, J. Chem. Soc., 3741 (1961).

2) T. Toyoda, I. Otsubo, T. Otsubo, Y. Sakata, and S. Misumi, Tetrahedron Lett., 1731 (1972).

3) T. Inoue, T. Kaneda and S. Misumi, Tetrahedron Lett., 2969 (1974).

4) T. Toyoda, A. Iwama, Y. Sakata, and S. Misumi, Tetrahedron Lett., 3203 (1975).
T. Toyoda, A. Iwama, T. Otsubo, and S. Misumi, Bull. Chem. Soc. Jpn., 49, 3300 (1976).

(Received February 10, 1978)