CHEMISTRY LETTERS, pp. 1347-1350, 1977. Published by the Chemical Society of Japan

SYNTHESIS OF [3.3]PARACYCLOPHANE-5,8-QUINONE

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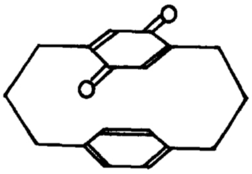
[3.3]Paracyclophane-5,8-quinone I was synthesized. Its charge-transfer absorption maximum at 406 nm (ε 407) showed a marked red shift as compared with that of [2.2]- and [4.4]paracyclophanequinones.

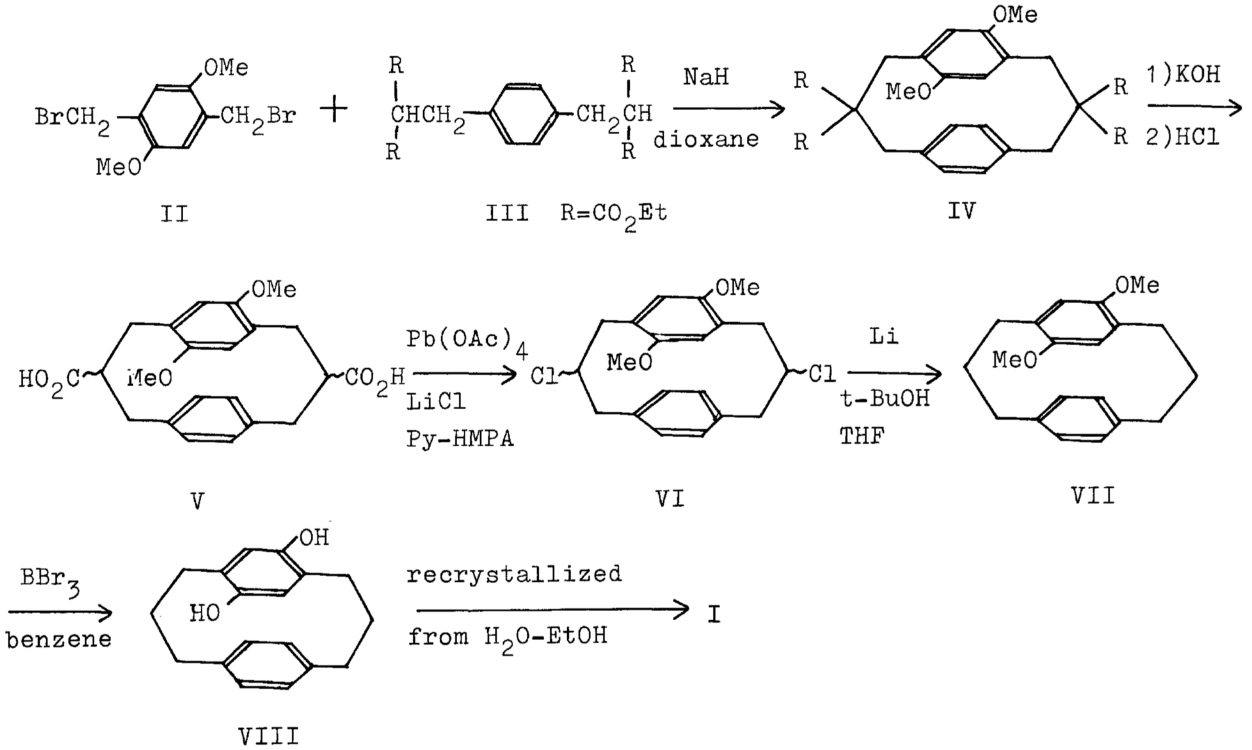


I

D. J. Cram et al. prepared [2.2]- and [4.4]paracyclophanequinone,$^{1,2)}$ and reported that their charge-transfer bands appeared at 340 (ε 597) and 288 nm (ε 1290), respectively. Recently S. Misumi et al. synthesized triple-layered [2.2]paracyclophanequinones.$^{3)}$ In connection with the stabilities of [m.n]paracyclophane-tetracyanoethylene complexes,$^{4)}$ it is interesting to investigate [3.3]paracyclophanequinone, since it is expected to be the most stable intramolecular complex in a series of [m.n]paracyclophanequinones. In this sense, we wish to report the synthesis of [3.3]paracyclophane-5,8-quinone I by use of a similar procedure for the synthesis of [3.3]metacyclophane.$^{5)}$

1,4-Bis(bromomethyl)-2,5-dimethoxybenzene II and tetraethyl p-diethylbenzene-$\omega,\omega,\omega',\omega'$-tetracarboxylate III were coupled in the presence of sodium hydride in refluxing dioxane to give the cyclic tetraester IV in 12 % yield. In this coupling reaction dioxane seems to be a more suitable solvent than xylene. IV: colorless prisms from ether-petroleum ether, mp 145-146°. Found: C, 65.60; H, 6.95 %; mol wt (MS, M^+) 584. Calcd for $C_{32}H_{40}O_{10}$: C, 65.74; H, 6.90 %; mol wt 584.7. The cyclic tetraester IV was hydrolyzed into the diacid V under an alkaline condition in 90 % yield. V: colorless prisms from chloroform-DMSO, mp 283-284°(decomp.). The diacid V was treated with lead tetraacetate and lithium chloride in pyridine-HMPA at 70-90° for 1 hr to give the dichloride VI in 85 % yield. VI: colorless prisms from ethanol, mp 202.5-205.0°. Found: C, 65.63; H, 5.99 %; mol wt (MS, M^+) 364. Calcd for $C_{20}H_{22}Cl_2O_2$: C, 65.76; H, 6.07 %; mol wt 365.3. The dichloride VI was reduced with lithium and tert-butanol in refluxing THF to give 5,8-dimethoxy[3.3]paracyclophane VII in 80 % yield. VII: colorless leaflets from methanol, mp 131.5-132.0°. Found: C, 80.75; H, 8.19 %; mol wt (MS, M^+) 296. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16 %; mol wt 296.4. VII was treated with boron tribromide in benzene and the resulting crude product was sublimed at 180-190° under reduced pressure to give [3.3]paracyclophene-5,8-diol VIII in 86 % yield. VIII: colorless needles, mp over 200° (decomp.). Found: C, 80.40; H, 7.52 %; mol wt (MS, M^+) 268. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51 %; mol wt 268.4; IR(KBr): ν_{OH} 3375, 3460 cm^{-1}. When crude 5,8-diol VIII was recrystallized from water-ethanol in air, the desired [3.3]paracyclophane-5,8-quinone I was obtained as brownish-yellow crystals in 75 % yield from VII. I: brownish-yellow needles by sublimation, mp 166.5-167.5°. Found: C, 80.84; H, 6.80 %; mol wt (MS, M^+) 266. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81; mol wt 266.3. IR(KBr): $\nu_{C=O}$ 1640 cm^{-1}.

The electronic spectra of I, VIII, 2,5-dimethylbenzene-1,4-diol IX and 2,5-dimethyl-1,4-benzoquinone X are shown in Fig. 1, and the pmr spectra of I, VII and VIII in Fig. 2. I shows three absorption maxima at 261.5(ε 13700), 312(ε 2240) and



Scheme I

406 nm(ε 407). A characteristic broad absorption band at the longest wave length seems to be the charge-transfer band. The position of λ_{max} of this band was dependent on the polarity of solvent. For example, λ_{max} in cyclohexane occurred at a position 12 nm shorter than that in acetonitrile. It is known that the charge-transfer absorption maximum of a complex between an aromatic hydrocarbon such as [m.n]paracyclophane and tetracyanoethylene gives information on π-basisity of the donor molecule.[6)] The charge-transfer band of I appeared in a region of markedly longer wave length compared with those of [2.2]- and [4.4]paracyclophanequinones, which occurred at 340 and 288 nm, respectively. Because of less strain and more flexibility in I than those in [2.2]paracyclophanequinone and also because of closer proximity between the benzene and quinone moieties in I than that in [4.4]paracyclophanequinone and higher homologs, [3.3]paracyclophane-5,8-quinone I of all the [m.n]paracyclophanequinones may be the most stable intramolecular charge-transfer complex.

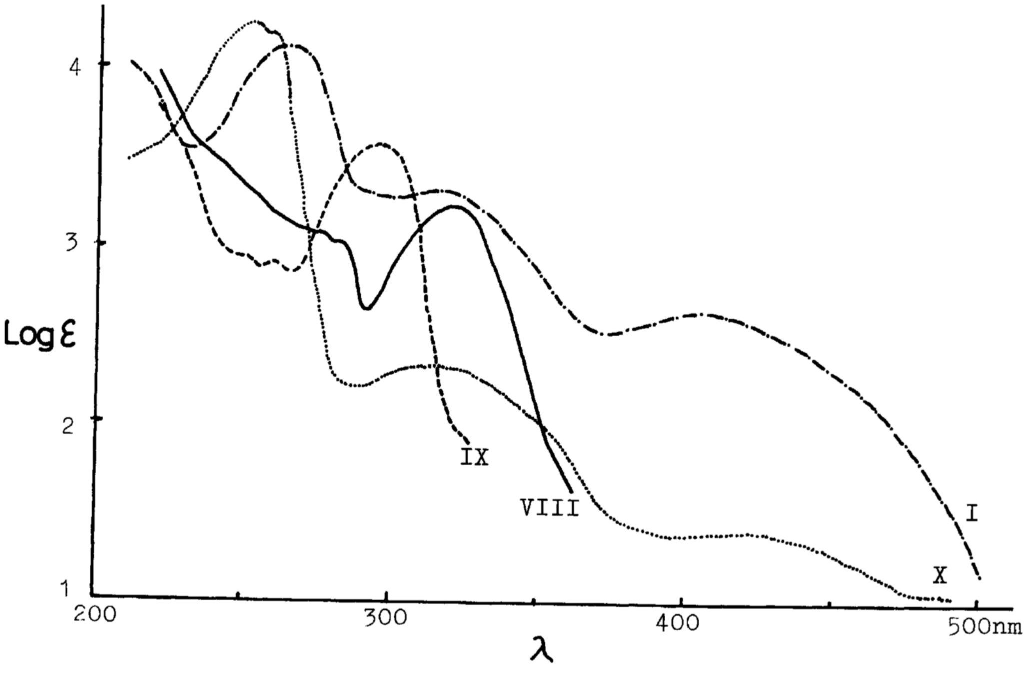
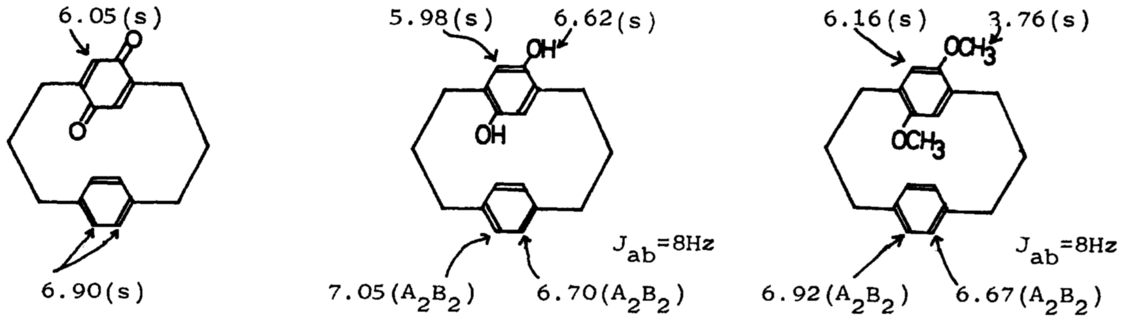


Fig. 1. The electronic spectra of I, VIII, IX, and X in acetonitrile.



($CDCl_3$) I

($CDCl_3$: DMSO=3:1) VIII

($CDCl_3$) VII

Fig. 2. NMR spectra of I, VII, and VIII.

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(Received August 22, 1977)