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LAYERED COMPOUNDS. XXXI.1) UNUSUAL REACTION OF METHYL SUBSTITUTED [2.2]PARACYCLOPHANES WITH CUPRIC NITRATE IN ACETIC ANHYDRIDE

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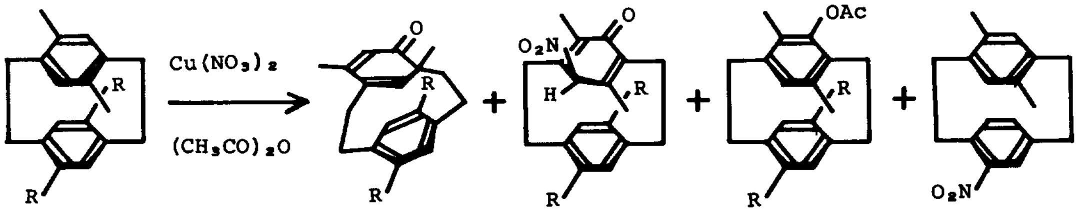
It was much reported that transannular π-electronic interaction and molecular strain function as motive force in electrophilic substitutions and skeletal rearrangements of layered paracyclophanes.2) In this paper, we wish to report further examples which were observed in nitration of methyl substituted [2.2]paracyclophanes with cupric nitrate-acetic anhydride. Normal substitutions have been found for non-benzenoid aromatic hydrocarbons with the same reagent3) and few layered cyclophanes with nitric acid-acetic anhydride.4)

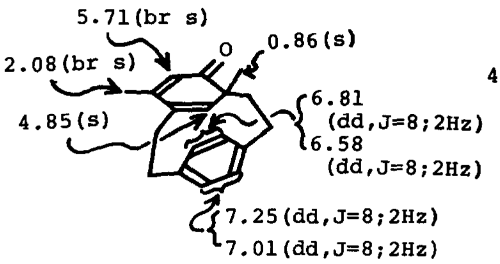
Treatment of 4,7-dimethyl[2.2]paracyclophane (Ia) with cupric nitrate-acetic anhydride at -20~-18°C afforded a mixture of skeletally rearranged dienone (IIa, 30% yield, faintly yellow plates from alcohol, m.p. 134°C), nitrodienone (IIIa, 5%, faintly yellow needles from benzene:alcohol(1:1), m.p. 164~165°C with decomp.), acetoxy derivative (IVa, <0.5%), and nitro derivative (Va, 1%, pale yellow prisms from n-hexane:benzene(2:1), m.p. 125.5~126.5°C).



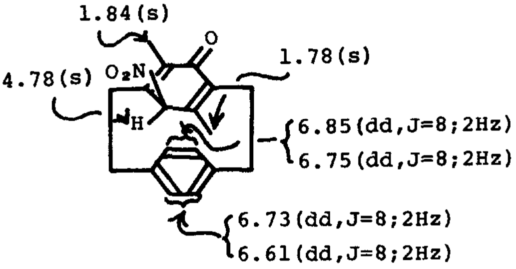
$\mathrm{I}_{a,b}$ a:R=H b:R=CH_3 $\mathrm{II}_{a,b}$ $\mathrm{III}_{a,b}$ $\mathrm{IV}_{a,b}$ V_{a}

Table 1. Spectral data of compounds II_a and III_a

	II_a	III_a
IR (KBr disk) cm^{-1}	1638, 1624 ($\upsilon_{C=O}$ and $\upsilon_{C=C}$)	1627 ($\upsilon_{C=O}$), 1538 and 1354 (υ_{NO_2})
Mass (m/e)	252 (M^+, 32), 135 (34), 104 (100)	297 (M^+,7), 252 (38), 148 (100), 104 (50)
UV (THF) λ_{max} nm(ε)	230 sh (6300), 276 sh (1190), 320 (4290), 380 sh (330), 400 sh (190)	239 (10200), 290 sh (1450) 320 sh (590), 380 sh (55)



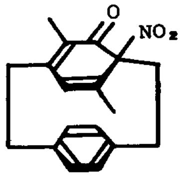
II_a



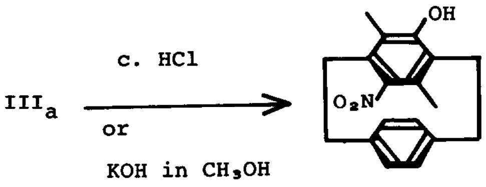
III_a

Fig. 1. ^{1}H-nmr spectra of compounds II_a and III_a (in $CDCl_3$, δ ppm from TMS)

Similarly, 4,7,12,15-tetramethyl[2.2]paracyclophane (Ib) gave a mixture of the corresponding products (IIb, 54%, faintly yellow plates from alcohol, m.p.132.5°C; IIIb, 5%, colorless long plates from alcohol, m.p. 172~173.5°C; IVb, 7%, colorless prisms from n-hexane, m.p. 85~86°C). All the products were separated by column chromatography on silica gel and liquid chromatography.[5] The structures of the paracyclophane-dienones (IIa and IIIa) were determined on the basis of elemental analysis and spectral data shown in Table 1 and Fig. 1. The corresponding dienones (IIb and IIIb) show spectral data similar to those of IIa and IIIa, respectively. Another structure VI, presumed for the nitrodienone derived from Ia, is excluded from the fact that the signal at 91.4 ppm on its noise decoupled ^{13}C-nmr spectrum (TMS standard) shows a large coupling constant of 148 Hz in its off-resonance spectrum and gives rise to a sharp singlet in the selective decoupling of the methine proton at 4.78 ppm. Moreover, the structure



(VI)



(VII)

IIIa was clearly confirmed by additional evidence that the nitrodienone was quantitatively transformed to isomeric nitrophenol (VII) by either acidic or alkaline catalysis (VII, yellow prisms from benzene:n-hexane, m.p. 130~131.5°C). In spite of easily enolizable structure, the isolation of this intriguing dienone compound is mainly attributable to that the concerning proton of III is protected from the attack of nucleophile under mild conditions and π-electronic repulsion between the nitrodienone moiety and its transannular benzene ring is less than that between the nitrophenol moiety and the benzene ring in VII.

A number of acetoxynitro adducts like XI have been isolated in the reactions with nitric acid-acetic anhydride instead of cupric nitrate-acetic anhydride in the present case, and the adduct has been thought to be formed by way of the two-steps mechanism initiated by the attack of nitronium ion.$^{6)}$ Of three

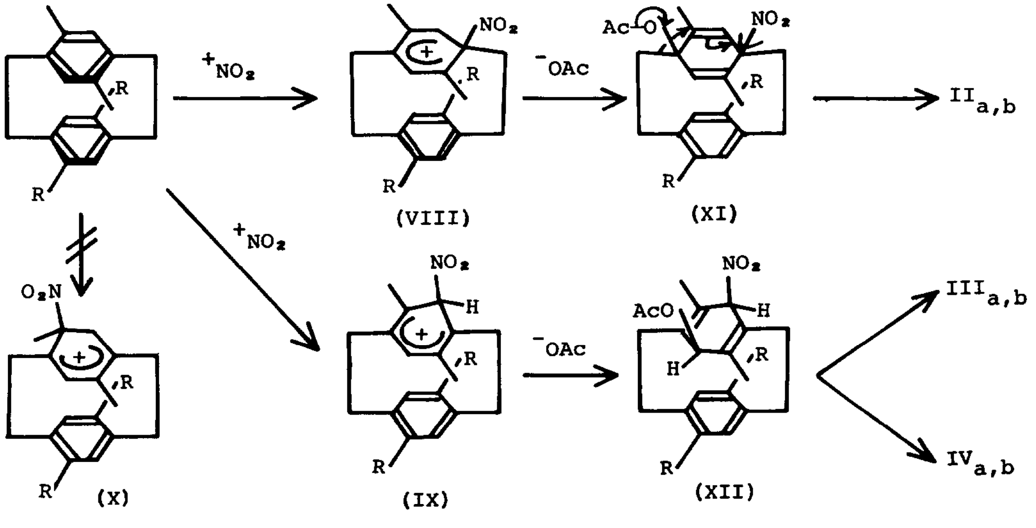


Fig. 2. A reaction mechanism of $I_{a,b}$ to $II_{a,b}$, $III_{a,b}$ and $IV_{a,b}$

formally possible σ-complexes in the present study (VIII ~ X). VIII is probably the most stable one because its σ-complex moiety may be more planar and less strained than the others (IX and X) on the basis of molecular model examination. Major products IIa,b would be yielded by the addition of acetoxy anion to this σ-complex followed by skeletal rearrangement-elimination under strain releasing as shown in Fig. 2. Thus, the transformation of the adduct XI to II is ascribed into more severe strain which is responsible for significant π-electronic repulsion between the diene moiety and its transannular benzene ring in XI. On the other hand, the minor products, IIIa,b and IVa,b, would be afforded through a common adduct XII derived from less stable σ-complex IX.

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