Rh$_2$(OAc)$_4$-Catalysed Cycloaddition of Ethyl Diazoacetate to 1,2-Dialkoxybenzenes: a New Type of Stable Norcaradiene

Masakatsu Matsumoto,*[a] Tamaki Shiono,[a] Hiroshi Mutoh,[b] Masaaki Amano[b] and Satoshi Arimitsu[b]

[a] *Department of Materials Science, Kanagawa University, Tsuchiya, Hiratsuka, Kanagawa 259-12, Japan*
[b] *Tokyo Research Laboratory, Yuki Gosei Kogyo, Sakashita, Itabashi, Tokyo 174, Japan*

Rh$_2$(OAc)$_4$-catalysed cycloaddition of ethyl diazoacetate (EDA) to 1,2-methylenedioxybenzene **1** gives the corresponding cycloheptatrienes **6** and **7**, whereas the reaction of 1,2-dimethoxybenzene **3** affords a new type of stable norcaradiene **9**.

The cycloaddition of carbenes (carbenoids) to aromatics is an important entry route to the construction of 7-membered rings,[1] and its application to 1,2-dialkoxybenzenes should become a facile synthon of tropolones. However, the reaction of 1,2-methylenedioxybenzene **1** with ethyl diazoacetate (EDA) has been reported[2] to give a C–O bond insertion product **2** instead of cycloaddition products. 1,2-Dimethoxybenzene **3** has been reported to undergo the cycloaddition affording cycloheptatrienes **4**[3] or **5** (Scheme 1).[4]We have examined the metal-catalysed reaction of 1,2-dialkoxybenzenes **1** and **3** with EDA and found results significantly different from those reported; Rh$_2$(OAc)$_4$ catalyses effectively the cycloaddition of carbene (carbenoid) derived from EDA to **1** to afford cycloheptatrienes (CHT) **6** and **7**, whereas **3** gives a new type of stable norcaradiene (NCD) **9**.

A solution of EDA (1.1 g, 10 mmol) in **1** (1.2 g, 10 mmol) was added dropwise over 2 h into a stirred solution of Rh$_2$(OAc)$_4$ (0.03 g, 0.7 mol% based on EDA) in **1** (4.9 g, 40 mmol) at room temp. After the evolution of N$_2$ ceased, the reaction mixture was chromatographed on silica gel and eluted with hexane–ethyl acetate (5 : 1) to afford CHT **6** (42% yield based on EDA) and **7** (9%) with no detectable amount of the product **2**. The reaction was also examined by the use of other catalysts; Rh$_2$(OCOCF$_3$)$_4$, Pd(OAc)$_2$ and Cu[(CF$_3$CO)$_2$CH$_2$]$_2$ gave low yields of the adducts **6** and **7**, and Cu(OAc)$_2$, Cu(OCOCF$_3$)$_2$ and Cu(acac)$_2$ scarcely effected the desired reaction. The reaction temperature (0–50 °C) had little influence upon the selectivity (**6** : **7**) and the yields.

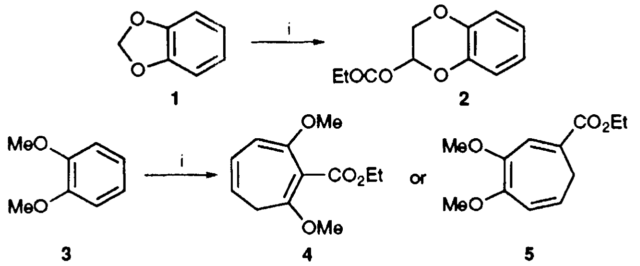
The Rh-catalysed cycloaddition of EDA to **3** occurred similarly at the 3,4-carbons and the 4,5-carbons of **3** to yield **8** (8%) and **9** (26%), which was a norcaradiene (colourless crystals from hexane. mp 79–80 °C)† in place of the expected CHT **10**. Treatment of **9** with tetracyanoethylene (TCNE) in benzene at room temp. gave exclusively the Diels–Alder adduct **11** [mp 138 °C (decomp.)].

Although the CHT structure is in general more stable than the NCD structure, a variety of compounds have been known to prefer the NCD structure.[5] An important electronic factor to stabilize the NCD has been proposed[6] to be the placement of a π-acceptor, such as a cyano group, at the 7-position; the interaction between the ligand π-system at the 7-position and the Walsh orbital of the cyclopropane ring weakens the 1–6 antibonding and in consequence strengthens the 1–6 bond.[7] The π-donors at the 3- and 4-positions are also expected to stabilize the NCD structure by strengthening the 1–6 bonding.‡ Compound **9** is probably the first example of NCD stabilized by methoxy groups as the π-donors at the 3- and 4-positions. Even at 80 °C, evidence for the existence of the tautomeric CHT **10** in NCD **9** was not observed by NMR analysis. Heating the NCD **9** at 130 °C for 3 h gave an isomeric CHT **12** in 47% yield. These facts reveal the remarkable stability of NCD **9**, though further analysis by NMR at higher temperatures is required to discuss in detail the valence tautomerism of NCD **9** and CHT **10**.

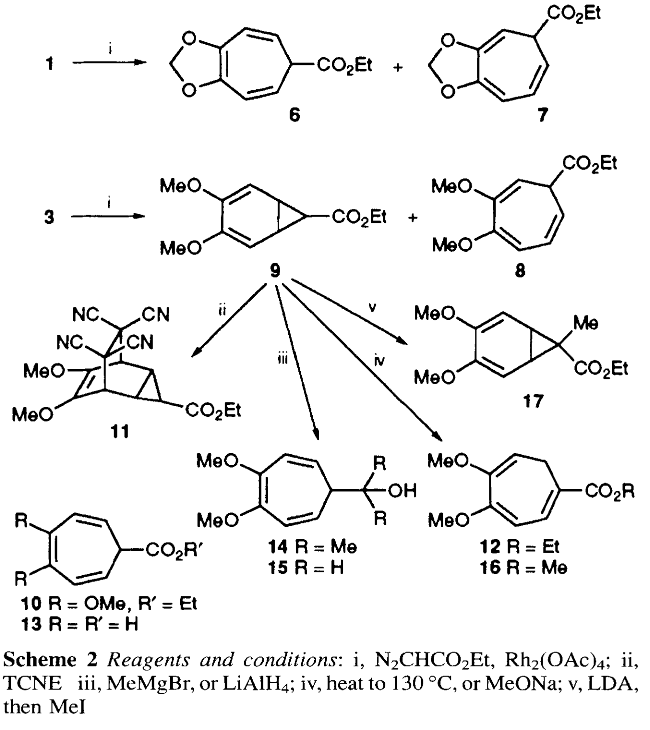
The facts that Buchner's acid **13** exists predominantly as the CHT structure[8] suggests that the ethoxycarbonyl group at the 7-position is not a strong enough π-acceptor to prefer the NCD structure. When NCD **9** was treated with MeMgBr to make the ethoxycarbonyl group ineffective as the π-acceptor, a CHT **14** was produced in 88% yield. The reduction of **9** with LiAlH$_4$ also gave a CHT **15** in 95% yield. These results demonstrated that the methoxy groups alone are insufficient to maintain the NCD structure and the ethoxycarbonyl group and the methoxy groups act together to stabilize NCD **9**.

The transesterification of **9** with MeONa in MeOH caused the ring-opening of the cyclopropane and the double bond isomerization to afford CHT **16** in 77% yield, though the hydrolysis of **9** by NaOH gave a complex mixture. The hydrogen at the 7-position of **9** was easily substituted with a methyl group by MeI and LDA at −78 °C in THF to give the stable NCD **17** (89% yield), which was hydrolysed without any alteration of its skeleton.

The significant difference between the cases of **6** and **9** may be due to the degree of conjugation between the lone pairs of oxygens and the π-system of NCD. For CHT **6**, the lone pairs of



Scheme 1 *Reagents and conditions*: i, N$_2$CHCO$_2$Et, heat



Scheme 2 *Reagents and conditions*: i, N$_2$CHCO$_2$Et, Rh$_2$(OAc)$_4$; ii, TCNE iii, MeMgBr, or LiAlH$_4$; iv, heat to 130 °C, or MeONa; v, LDA, then MeI

oxygens in the methylenedioxy may not overlap the π-system enough to prefer the NCD structure.§[9]

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Footnotes

† **9** was assigned as an *exo*-isomer by NMR spectral analysis: ^{1}H NMR (400 MHz, $CDCl_3$ at 30 °C) δ 0.78 (t, *J* 3.9 Hz, 1H), 1.28 (t, *J* 7.3 Hz, 3H), 2.82 (ddd, *J* 4.4, 3.9 and 2.4 Hz, 2H), 3.64 (s, 6H), 4.17 (q, *J* 7.3 Hz, 2H), 5.38 (dd, *J* 4.4 and 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$ at 30 °C) δ14.2, 24.8, 38.6, 55.4, 60.6, 100.2, 148.5, 175.5; IR(KBr) ν/cm^{-1} 2981, 2938, 2837, 1734, 1517, 1265, 1155, 1146, 1030; MS (*m*/*z*, %) 224(M$^+$, 15), 195(15), 151(100).

‡ An MO calculation (extended Hückel) suggested that, both for norcaradiene and its 7-carboethoxy analogue, the introduction of 3- and 4-methoxy groups strengthens the bond order of C(1)–C(6).

§ In the parent 1,2-dialkoxybenzenes, the bond order of C_{Ar-O} has been reported to be **3** ≫ **1**.[9] A similar tendency may be expected for CHT/NCD.

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