Aromatization and Hydrogen-Shift of 7-Substituted 1,3,5-Cycloheptatrienes in the Presence of Palladium(II) Acetate

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Reaction of 7-ethoxycarbonyl-1,3,5-cycloheptatriene with palladium(II) acetate afforded 2- and 4-formylbenzoic acid ethyl ester and diethyl maleate *via* aromatization, and a mixture of position isomers of the cycloheptatriene through hydrogen-shift. The reaction with 7-cyano-1,3,5-cycloheptatriene was also investigated. The reactions are considered to proceed through palladium complexes of the cycloheptatrienes and their norcaradiene isomers.

Keywords cycloheptatriene; palladium(II) acetate; aromatization; hydrogen-shift

Much work has been done on the synthesis and the structures of transition metal complexes of conjugated seven-membered cyclic compounds such as cycloheptatrienes or azepines.[1] However, there are few reports dealing with the reactivities of these cyclic compounds in the presence of transition metal complexes.[2,3] Since these compounds are able to undergo reaction *via* several pathways such as intramolecular cyclization, ring cleavage, aromatization, addition or substitution, it is of interest to investigate what kind of reaction becomes predominant in these compounds in the presence of transition metal complexes.

Previously, we reported that the reaction of 1,3,5-cycloheptatriene with benzene in the presence of palladium(II) acetate afforded a substituted product, 1-phenyl-1,3,5-cycloheptatriene.[3] As part of a series of studies on the reactions of seven-membered cyclic compounds with transition metal complexes, we report here the reactions of 7-substituted-1,3,5-cycloheptatrienes with palladium(II) acetate.

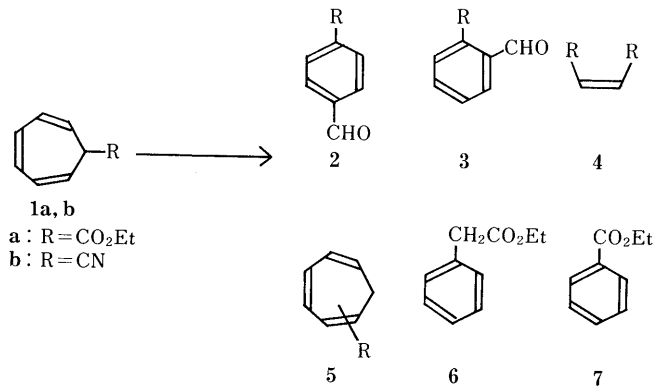

Fig. 1

Results and Discussion

7-Ethoxycarbonyl-1,3,5-cycloheptatriene (**1a**) was allowed to react with an equimolecular amount of palladium(II) acetate in the presence of 5 molar eq of sodium acetate in acetonitrile at 80 °C for 4 h. After treatment with water, the reaction mixture was separated by thin-layer chromatography on silica gel to give 4-formylbenzoic acid ethyl ester (**2a**), 2-formylbenzoic acid ethyl ester (**3a**),[4] diethyl maleate (**4a**), and a mixture of positional isomers of **1a** (**5a**)[5] in 8, 8, 14, and 24% yields, respectively. The change of the solvent from acetonitrile to acetic acid resulted in the formation of **2a** (9%), **3a** (11%), and **4a** (4%), **6** (3%),[6] and **7** (8%).[6]

Analogous reactions proceeded with 7-cyano-1,3,5-cycloheptatriene (**1b**). The reaction of **1b** in acetonitrile under the same conditions as above afforded 4-cyanobenzaldehyde (**2b**),[7] 2-cyanobenzaldehyde (**3b**),[6] and a mixture of positional isomers of **1b** (**5b**)[5] in 2, 1, and 6% yields, respectively.[6] The reaction at a lower temperature (at room temperature, for 24 h) gave an analogous result (**2b**, 4%; **5b**, 12%). The reaction in acetic acid at 80 °C provided **2b** and **5b** in 9 and 4% yields, respectively.

The formation of each product is considered to proceed

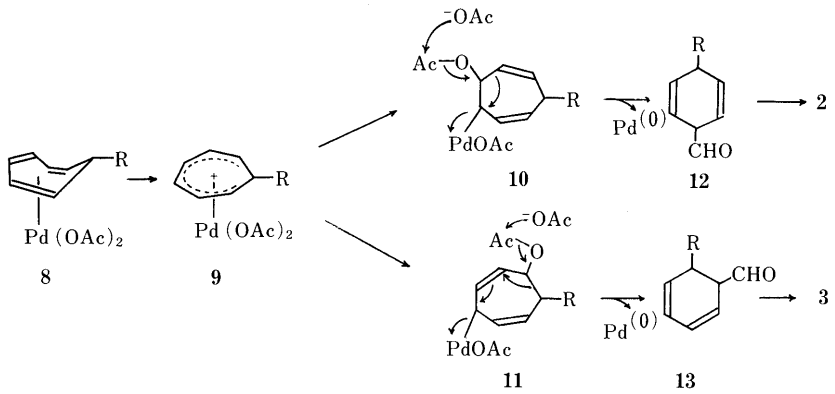

Fig. 2

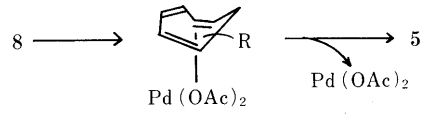

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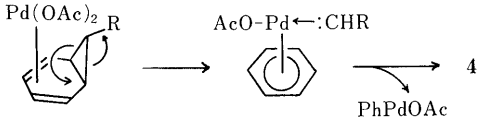
Fig. 3



15 16

Fig. 4

as follows. One electron oxidation of a complex (**8**) by palladium gives a palladium(I)–tropylium ion complex (**9**), which reacts with acetate ion to form **10** and **11**. In both **10** and **11**, the carbonyl carbon atoms can be attacked by acetate ions. The simultaneous one electron oxidation by palladium releases palladium metal and acetic anhydride, to afford cyclohexadiene-type intermediates (**12** and **13**, respectively). Further oxidations by palladium or oxygen in air give **2** and **3**, respectively.

Hydrogen transfer in the complex (**8**) generates **14**, which produces **5** with release of palladium(II) acetate. Coordination of palladium is considered to be advantageous for this hydrogen transfer process because **5** was not formed in the absence of palladium(II) acetate.

Cycloheptatrienes are known to have norcaradiene forms as valence isomers, in which the cyclopropane rings can be cleaved to give aromatization products such as **6**.[8] The formation of **4** is thought to proceed *via* this type of cyclopropane ring cleavage mechanism. The interaction between the palladium metal and the carbon atom of the cyclopropane ring is considered to yield a carbenoid complex (**16**),[9] which then dimerizes to form **4**.

Experimental

Wako gel C-200 and Wako gel B-5F were used for column and thin-layer chromatography, respectively. Palladium(II) acetate was a product of N. E. Chemical Co. Ltd.

Reaction of 7-Ethoxycarbonyl-1,3,5-cycloheptatriene (1a) with Palladium(II) Acetate in Acetonitrile A mixture of **1a** (490 mg, 3 mmol), palladium(II) acetate (670 mg, 3 mmol) and sodium acetate (1230 mg, 15 mmol) was stirred for 4 h at 80 °C in acetonitrile (32 ml). After filtration, the solvent was evaporated. The resulting residue was poured into water and extracted with ether. The extract was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was separated by thin-layer chromatography on silica gel using hexane–ethyl acetate (8 : 2) as a developing solvent to give **5a** as an oil (120 mg, 24%, Rf=0.76), a yellow oil (74 mg, Rf=0.58) and **4a** as an oil (36 mg, 14%, Rf=0.48). The yellow oil was found to be a 1 : 1 mixtue of **2a** and **3a** by ^{1}H- and ^{13}C-NMR spectral analysis. Thus, the yields of **2a** and **3a** were both 8%.

Reaction of 1a with Palladium(II) Acetate in Acetic Acid A mixture of **1a** (490 mg, 3 mmol), palladium(II) acetate (670 mg, 3 mmol) and sodium acetate (1230 mg, 15 mmol) in acetic acid (32 ml) was stirred at 80 °C for 4 h. After the usual treatment, the reaction mixture was subjected to thin-layer chromatography on silica gel using hexane–ethyl acetate (8 : 2) as a developing solvent to give a yellow oil (120 mg, Rf=0.85), **6** (15 mg, 3%, Rf=0.70), **7** (36 mg, 8%, Rf=0.65), and **4a** as an oil (16 mg, 4%, Rf=0.65). The yellow oil was found to be a 9 : 11 mixture of **2a** and **3a** by ^{1}H- and ^{13}C-NMR spectral analysis. Thus, the yields of **2a** and **3a** were 9 and 11%, respectively.

Reaction of 7-Cyano-1,3,5-cycloheptatriene (1b) with Palladium(II) Acetate in Acetonitrile A mixture of **1b** (350 mg, 3 mmol), palladium(II) acetate (670 mg, 3 mmol) and sodium acetate (1230 mg, 15 mmol) was stirred for 4 h at 80 °C in acetonitrile (32 ml). After the usual treatment the reaction mixture was separated by thin-layer chromatography on silica gel using hexane–ethyl acetate (8 : 2) as a developing solvent to give **5b** as an oil (22 mg, 6%, Rf=0.60), a yellow oil (Rf=0.34), and a brown oil (Rf=0.25). The yellow oil was further separated by thin-layer chromatography on silica gel using benzene–ether (9 : 1) as a developing solvent to give **17** as a yellow oil (41 mg, 23%, Rf=0.82)[7] and **2b** as crystals (12 mg, 2%, Rf=0.72). The brown oil was also further separated by thin-layer chromatography on silica gel using benzene–ether (8 : 2) to give **17** as an oil (43 mg, 25%, Rf=0.73)[7] and **3b** as crystals (7 mg, 1%, Rf=0.59).

Reaction of 1b with Palladium(II) Acetate in Acetonitrile at Room Tempeature A mixture of **1b** (350 mg, 3 mmol), palladium(II) acetate (670 mg, 3 mmol) and sodium acetate (1230 mg, 15 mmol) in acetonitrile (32 ml) was stirred at room temperature for 24 h. The reaction mixture was treated in the same way as described above to give **5b** (42 mg, 12%), **17** (45 mg, 26%),[7] and **2b** (15 mg, 4%).

Reaction of 1b with Palladium(II) Acetate in Acetic Acid A mixture of **1b** (350 mg, 3 mmol), palladium(II) acetate (670 mg, 3 mmol) and sodium acetate (1230 mg) in acetic acid (32 ml) was stirred at 80 °C for 4 h. After the usual treatment the reaction mixture was separated by thin-layer chromatography on silica gel using hexane–ethyl acetate (8 : 2) as a developing solvent to give **5b** as an oil (13 mg, 4%, Rf=0.69) and **2b** as crystals (36 mg, 9%, Rf=0.59).

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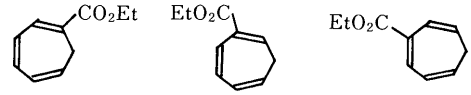
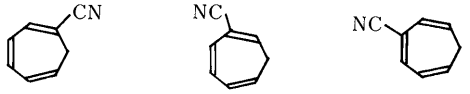
References and Notes

1) S. D. Reynolds, T. A. Albright, *Organometallics*, **4**, 980 (1985); L. B. Kool, M. D. Rausch, R. D. Rogers, *J. Organomet. Chem.*, **297**, 289 (1985); D. G. Bourner, L. Brammer, M. Green, G. Moran, A. G. Orpen, C. Reeve, C. J. Schaverien, *J. Chem. Soc., Chem. Commun.*, **1985**, 1409.
2) K. Saito, *Heterocycles*, **24**, 1831 (1986); K. Saito, Y. Horie, K. Takahashi, *J. Organomet. Chem.*, **363**, 231 (1989); K. Saito, M. Kozaki, K. Takahashi, *Heterocycles*, **31**, 1491 (1990).
3) K. Saito, *J. Organomet. Chem.*, **338**, 265 (1988).
4) The complete separation of the mixture of **2a** and **3a** was not accomplished but sufficient amounts of **2a** and **3a** for spectral analyses were isolated. R. J. Spangler, L. G. Henscheid, K. T. Buck, *J. Org. Chem.*, **42**, 1693 (1977); J. Bromilow, R. T. C. Brownlee, D. J. Craik, M. Sedek, R. W. Taft, *ibid.*, **45**, 2429 (1980).
5) The oils **5a** and **5b** were still mixtures. It was presumed from their spectral properties that **5a** and **5b** consist of positional isomers (**1a**, **17**, **18**, **19**, and **1b**, **20**, **21**, **22**, respectively). The ratios of positional isomers were **1a** : **17** : **18** : **19** = 1.0 : 5.6 : 1.9 : 6.1, and **1b** : **20** : **21** : **22** = 9.3 : 2.1 : 1.0 : 4.0, respectively. These values were evaluated from the integral values of the proton linked to the sp^3 carbon atom at the 7-position of the cycloheptatriene ring in the ^{1}H-NMR spectra. The ^{1}H-NMR spectrum of **5a** showed well separated signals, so that all signals were assigned as follows using the proton double resonance method. The signals corresponding to **1a** and **19** were assigned by means of comparison with those of authentic samples. On the other hand, in the ^{1}H-NMR spectrum of **5b**, some signals overlapped each other so that not all the peaks could be assigned.



17 18 19



20 21 22

Fig. 5

5a: MS (rel. intensity) m/z: 164 (M^+, 9), 135 (23), 119 (17), 105 (17), 91 ($-CO_2Et$, 100). ^{1}H-NMR ($CDCl_3$) δ: **1a**: 1.31 (t, J=7.2Hz), 2.54 (dd, J=1.3, 5.5 Hz), 4.26 (q, J=7.2 Hz), 5.44 (dd, J=5.5, 8.9 Hz),

6.26 (bd, $J=8.9$ Hz), 6.66 (dd, $J=2.9$, 3.5 Hz). **17**: 1.40 (t, $J=7.2$ Hz), 2.64 (d, $J=7.1$ Hz), 4.38 (q, $J=7.2$ Hz), 5.57 (td, $J=7.1$, 9.2 Hz), 6.26 (dd, $J=5.7$, 9.2 Hz), 6.81 (dd, $J=5.7$, 11.1 Hz), 6.66 (dd, $J=5.9$, 11.1 Hz), 7.24 (d, $J=5.8$ Hz). **18**: 1.25 (t, $J=7.2$ Hz), 2.35 (t, $J=7.2$ Hz), 4.15 (q, $J=7.2$ Hz), 5.45,[a] 6.23 (dd, $J=5.5$, 6.2 Hz), 6.49 (t, $J=7.2$ Hz), 6.71,[a] 7.15 (d, $J=11.6$ Hz). **19**: 1.35 (t, $J=7.2$ Hz), 2.30 (t, $J=6.9$ Hz), 4.29 (q, $J=7.2$ Hz), 5.45,[a] 5.68 (td, $J=6.9$, 9.4 Hz), 6.34 (dd, $J=5.9$, 9.4 Hz), 6.73 (d, $J=9.6$ Hz), 7.69 (d, $J=5.9$ Hz).

5b: MS (rel. intensity) m/z: 117 (M^+, 13), 116 (M^+-1, 100), 103 (20), 89 (30). ^{1}H-NMR ($CDCl_3$) δ: **1b**: 3.00 (t, $J=6.1$ Hz), 5.40 (dd, $J=6.1$, 8.9 Hz), 6.34 (ddd, $J=2.9$, 2.9, 8.9 Hz), 6.75 (dd, $J=2.9$, 2.9 Hz). **20**: 2.53 (d, $J=7.0$ Hz), 5.57 (td, $J=7.0$, 9.5 Hz), 6.34,[a] 6.61 (dd, $J=6.1$, 11.3 Hz), 6.83 (d, $J=6.1$ Hz), 6.85 (dd, $J=5.8$, 11.3 Hz). **21**: 2.40 (t, $J=7.0$ Hz), 5.45,[a] 6.10 (t, $J=7.0$ Hz). The other three signals were not found due to overlapping with other strong signals. **22**: 2.37 (t, $J=7.0$ Hz), 5.52 (td, $J=7.0$, 9.5 Hz), 5.71 (td, $J=7.0$, 9.5 Hz), 6.27 (d, $J=9.5$ Hz), 6.30,[a] 7.24 (d, $J=5.8$ Hz). *a*) Since these signals overlapped with each other or other strong signals, the coupling constants of these signals could not be determined.

6) C. J. Pouchert, J. R. Campball, "The Aldrich Library of NMR Spectra," 2nd ed., Vol. 8, Aldrich Chem. Co., Milwaukee, 1975.

7) *a*) In addition to the products described in the text a yellow oil (**23**) was obtained in the reaction of **1b** in acetonitrile at 80 °C (48% yield) and at room temperature (26% yield). This oil was deduced to be a mixrure of positional isomers of dicyanobitropil from the following spectral properties. **23**: MS (rel. intensity) m/z: 232 (M^+, 2), 231 (M^+-1, 8), 116 ($C_7H_6CN^+$, 100), 103 (14). ^{1}H-NMR ($CDCl_3$) δ: 1.60 (m, 7H[7b]), 2.11 (m, 12H), 2.31 (m, 2H), 2.52 (m, 1H), 5.30 (m, 9H), 5.38 (m, 4H), 5.46 (m, 3H), 5.57 (m, 5H), 5.93 (m, 9H), 6.42 (m, 22H), 6.76 (m, 9H), 6.82 (m, 2H), 6.93 (m, 10H), 7.02 (m, 5H), 7.35 (d, $J=5.8$ Hz, 5H); *b*) These numbers of protons refer only to the relative intensities of the signals. *c*) K. Okamoto, K. Komatsu,

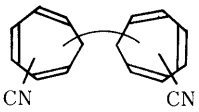


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Fig. 6

O. Murai, O. Sakaguchi, Y. Matsui, *Bull. Chem. Soc. Jpn.*, **46**, 1785 (1973); W. Bauer, J. Daub, A. Hasnhundl, K. M. Rapp, P. Schmidt, *Tetrahedron Lett.*, **22**, 2977 (1981); R. Mynott, R. Neidlein, H. Schwager, G. Wilk, *Angew. Chem. Int. Ed. Engl.*, **25**, 367 (1986).

8) G. Maier, *Angew. Chem. Int. Ed. Engl.*, **6**, 402 (1967).

9) R. W. Hoffman, J. Schneider, *Tetrahedron Lett.*, **1967**, 4347.