

REACTION OF ARYL IODIDE DERIVATIVES WITH HOMO-
CONJUGATED COMPOUNDS IN THE PRESENCE OF PALLADIUM(II)
ACETATE TO FORM HETERO CYCLIC COMPOUNDS

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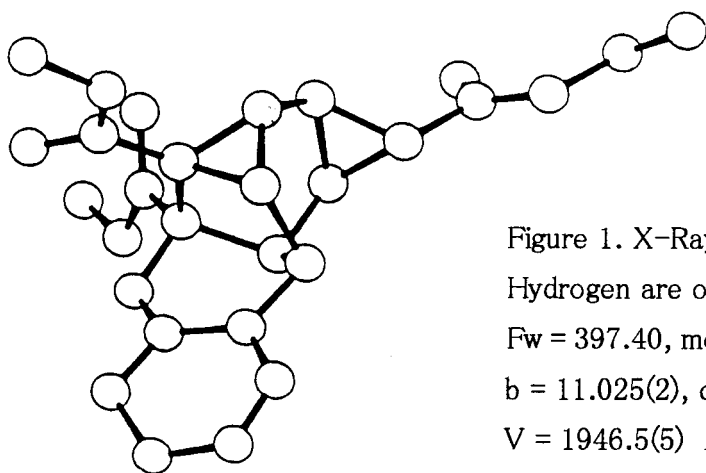
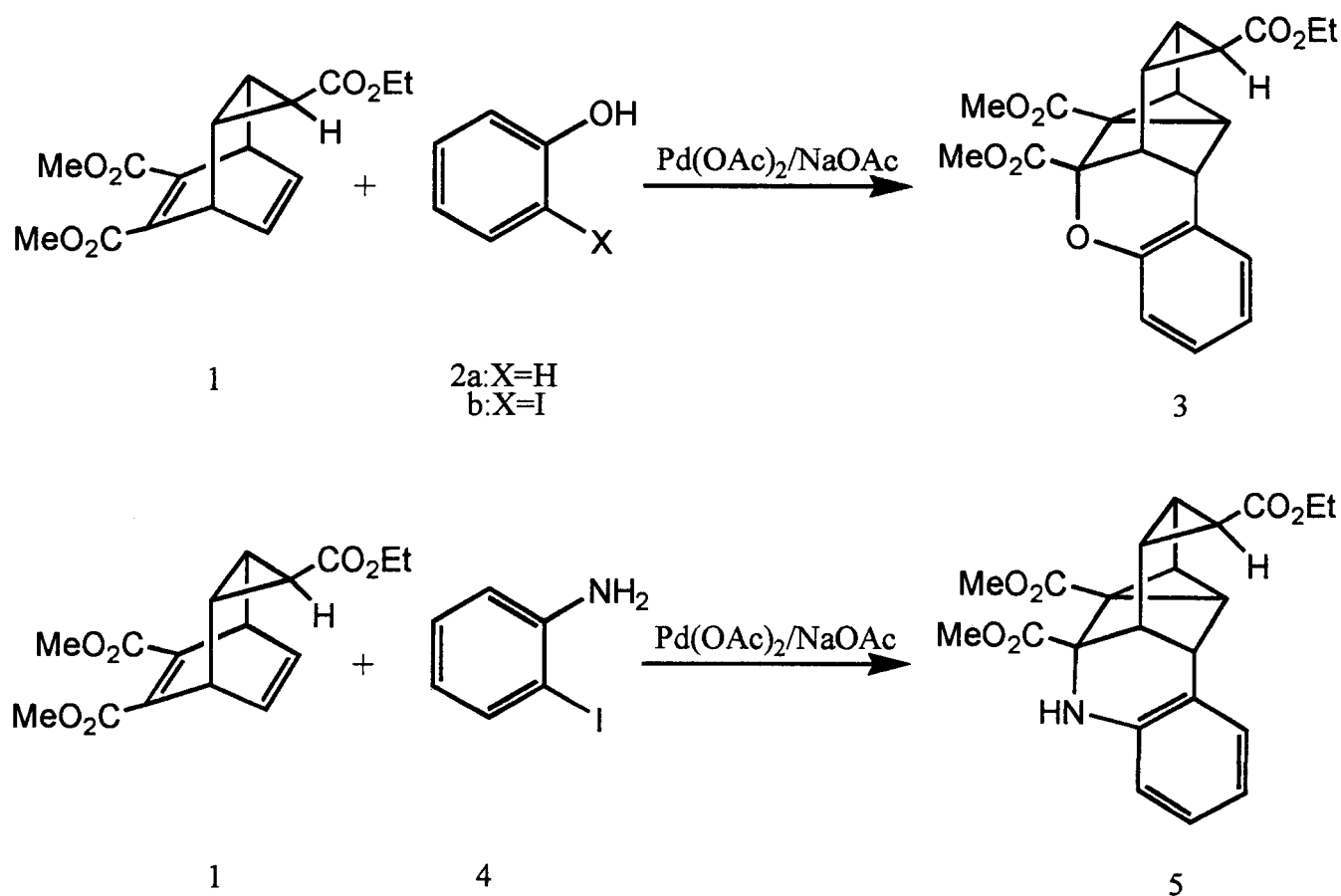
Abstract——Reaction of phenol with a tricyclo[3.2.2.0^{2,4}]nona-6,9-diene derivative in the presence of palladium(II) acetate afforded a cyclic ether compound, which is considered formally derived from the homo Diels-Alder reaction of the tricyclic compound with phenol followed by dehydrogenation reaction. The yield of the cyclic ether compound was improved by a use of 2-iodophenol instead of phenol. The same type of reaction proceeded between the tricyclic compound and 2-iodoaniline to form a cyclic amine derivative.

Homo-conjugated compounds have attracted much attention of chemists not only from a theoretical viewpoint, but also from the synthetic utility through the homo Diels-Alder type cycloaddition reaction.¹ While thermal or photochemical reactions of homo-conjugated compounds have been investigated in detail, the documents concerning their reactions in the presence of any transition metal complexes are scarce in number.²

It is known that palladium complex catalyzed aromatic or vinylic substitutions on several kinds of olefinic compounds.³ Recently, the arylation reaction of norbornadiene in the presence of palladium complex was reported.² We also have reported on a reaction of highly strained homo-conjugated compounds, tricyclo[3.2.2.0^{2,4}]nona-6,9-diene derivative (1), with benzene in the presence of palladium(II) acetate to form a benzo derivative (3), formally *via* homo Diels-Alder type cycloaddition reaction.⁴ Palladium complexes are also known to catalyze reactions of alcohol derivatives with allene derivatives to form ether compounds.⁵ It is of interest to research reactions of alcohol derivatives with homo-conjugated compounds.

As a series of our researches on palladium complex⁶ and strained homo-conjugated compounds,⁷ a reaction of 1 with phenol derivatives in the presence of palladium(II) acetate was investigated. Here the results are reported.

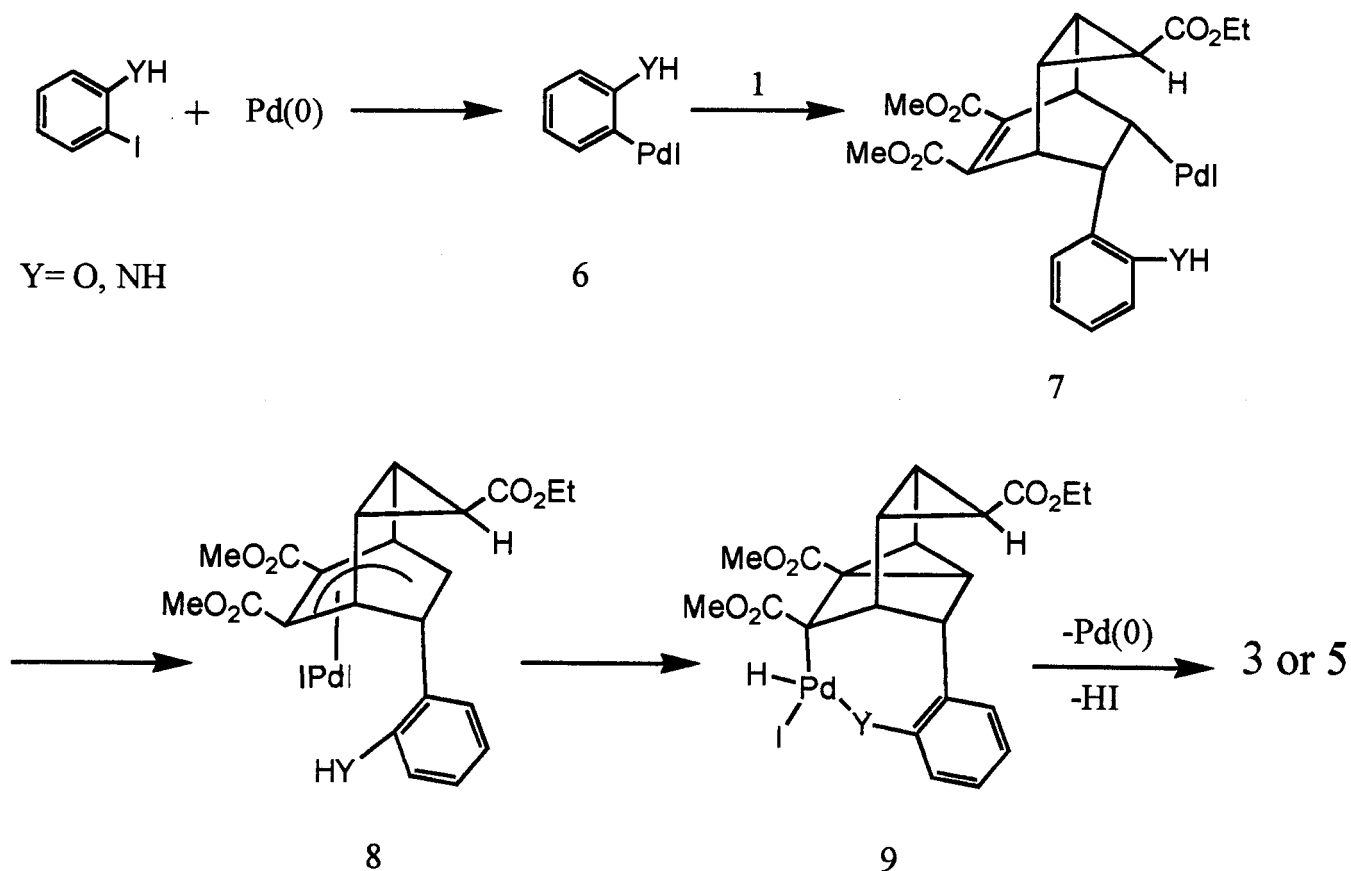
6,7-Dicarbomethoxytricyclo[3.2.2.0^{2,4}]nona-6,9-diene (1) reacted with three molar equivalents of phenol (2a) in ethyl acetate in the presence of an equimolar amount of palladium(II) acetate and five molar equivalents of sodium acetate under refluxing for 11 days. After a removal of palladium complexes, the reaction mixture was stripped on a rotary evaporator and the residue was isolated with column and thin layer chromatographed on silica gel to give a cyclic ether compound (3) in 11% yield. The analogous reaction but using 2-iodophenol (2b) instead of phenol (2a) in acetonitrile improved the yield of 3 to 49%.⁸



Though the yield was poor, the reaction with aniline derivatives gave almost the same result as the case of phenol. Thus, a reaction with aniline under the same reaction conditions as above resulted in a quantitative recovery of 1, but a reaction with 2-iodoaniline (4) afforded a cyclic amine compound (5) in 4% yield.⁹

Structures of the products (3), (5) were deduced on the basis of their spectral properties, especially NMR spectral properties and supported by the good resemblance of their spectral properties with those of the analogous compounds.¹⁰ The structure of the cyclic ether compound (3) was finally confirmed by single crystal X-Ray analysis.

The reaction mechanism is not clear now, but we tentatively propose the following mechanism. The reduction of palladium(II) acetate to Pd(0) is an established reaction. Oxidative addition of the aryl halide to Pd(0) formed an arylpalladium intermediate (6). The addition of 6 to the less substituted part of the homo-conjugated compounds (1) generated a palladium σ -complex (7),¹⁰ which was then transformed to a palladium π -complex (8).^{3,11} The subsequent insertion of the olefinic bond formed a palladium complex (9). Finally, the reductive elimination of Pd(0) from the complex (9) can generate the final products (3 and 5).



Further investigation on analogous reactions using a variety of homo-conjugated compounds and aryl iodides are now in progress. The detailed results of these researches will be reported in due course.

ACKNOWLEDGEMENT

The authors are indebted to Prof. Hideki Masuda of Nagoya Institute of Technology for his measurement of single crystal X-Ray analysis.

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8. 3: colorless crystal. mp 199.5–200.5 °C. HRMS m/z: 398.1337. Calcd for C₂₂H₂₂O₇ m/z: 398.1359. MS m/z (rel intensity): 398.4 (M⁺, 59), 334.2 (70), 309.1 (45), 260.1 (100). IR (KBr): 2955, 1725 cm⁻¹. ¹H NMR (CDCl₃) δ ppm: 1.29 (t, 3H, J= 7.2 Hz, Me), 1.68 (m, 1H), 2.00 (m, 2H), 2.28 (m, 2H), 2.75 (d, 1H, J= 4.6 Hz), 2.90 (s, 1H), 3.65 (s, 3H, Me), 3.97 (s, 3H, Me), 4.18 (q, 2H, J= 7.2 Hz, CH₂), 6.82 (dt, 1H, J= 1.5, 7.5 Hz), 6.94 (m, 2H), 7.14 (dt, 1H, J= 1.5, 7.5 Hz). ¹³C NMR (CDCl₃) δ ppm: 14.1, 18.5, 21.6, 23.1, 28.0, 35.0, 36.9, 37.0, 39.3, 52.1, 52.8, 60.8, 86.4, 116.5, 120.4, 126.4, 127.0, 128.8, 151.5, 168.8, 170.6, 171.6. Anal. Calcd for C₂₂H₂₂O₇: C, 66.32; H, 5.57. Found: C, 66.24; H, 5.71.
9. 5: brown viscous oil. MS m/z (rel intensity): 398.4 (M⁺, 59), 334.2 (70), 309.1 (45), 260.1 (100). IR (NaCl): 2961, 1722 cm⁻¹. ¹H NMR (CDCl₃) δ ppm: 1.28 (t, 3H, J= 7.2 Hz, Me), 1.62 (m, 1H, J= 4.6 Hz), 1.92 (m, 4H), 2.64 (d, 1H, J= 4.6 Hz), 2.82 (s, 1H), 3.62 (s, 3H, Me), 3.89 (s, 3H, Me), 4.18 (q, 2H, J= 7.2 Hz, CH₂), 5.02 (brs, 1H, NH), 6.62 (m, 2H), 6.85 (d, 1H, J= 7.5 Hz), 7.02 (t, 1H, J= 7.5 Hz). ¹³C NMR (CDCl₃) δ ppm: 14.1, 19.3, 21.7, 22.4, 24.2, 35.3, 36.9, 41.0, 41.0, 51.7, 52.7, 60.7, 66.9, 115.0, 117.6, 125.8, 126.4, 128.2, 141.3, 171.5, 171.8, 172.1.
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