CHEMISTRY LETTERS, pp. 1977-1980, 1993.

Hydrogenolysis of *gem*-Diphenylcyclopropanes Fused with Trihalogenated Quinones

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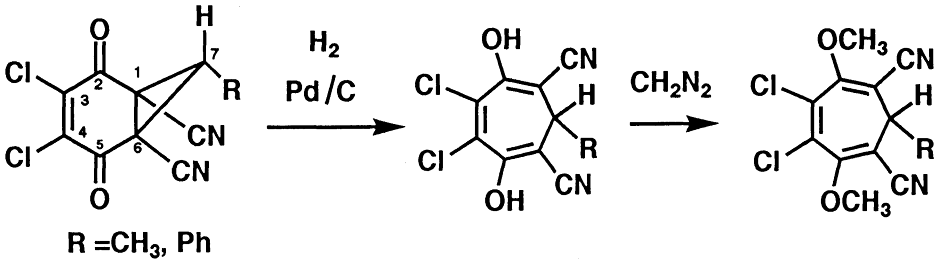
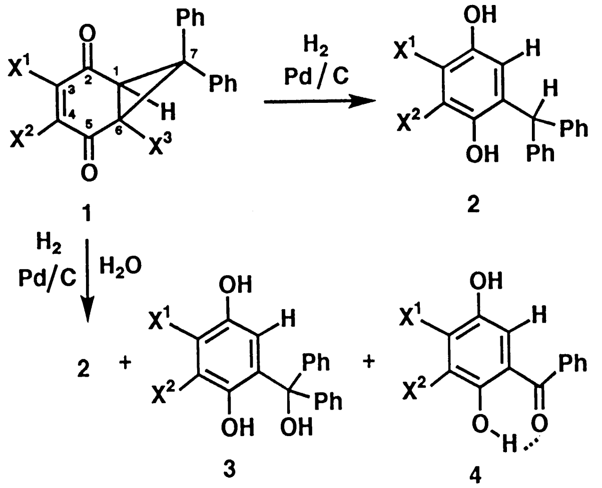
Palladium-catalyzed hydrogenolysis of *gem*-diphenylcyclopropanes fused with trihalogenobenzoquinones gave diphenylmethylhydroquinones. Water took part in the reaction to yield α-hydroxydiphenylmethyl- and benzoylhydroquinones. The selective ring-cleavage was interpreted in terms of the π-conjugative interaction of cyclopropane.

The hydrogenolysis of cyclopropanes is an important, well-established reaction which is frequently used in organic synthesis.[1)] A vast study has been made of the hydrogenolysis of variously substituted[2)] and ring condensed cyclopropanes,[3)] and the steric and electronic preferences in the reductive ring opening of cyclopropanes has been well documented. The simple generalization is that a cyclopropane ring can be cleaved at the least substituted and the weakest bond by catalytic hydrogenation. In addition, conjugative properties of the cyclopropane ring with an adjacent unsaturated bond must be taken into account, since the molecular orbitals of cyclopropane can overlap with such a π-system.[4)] In a previous paper,[5)] it was noted that 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ) fused cyclopropanes undergo the reductive ring cleavage at the C_1-C_6 bond to form the dienolized cycloheptatrienes on palladium catalyzed hydrogenolysis (Scheme 1).



Scheme 1.

We report here that the reactions of title cyclopropanes, **1**, proceeded entirely differently through a C_1-C_7 bond fission to give diphenylmethyl-substituted hydroquinones, **2**. It was also found that these reactions suffer a participation of additive water and yield α-hydroxydiphenylmethyl- and benzoyl-substituted hydroquinones, **3** and **4**[6)](Scheme 2 and Table).



Scheme 2.

a; $X^1=X^2=X^3=Cl$
b; $X^1=Br$, $X^2=X^3=Cl$
c; $X^1=X^3=Cl$, $X^2=Br$
d; $X^1=X^2=Cl$, $X^3=Br$
e; $X^1=X^2=X^3=Br$

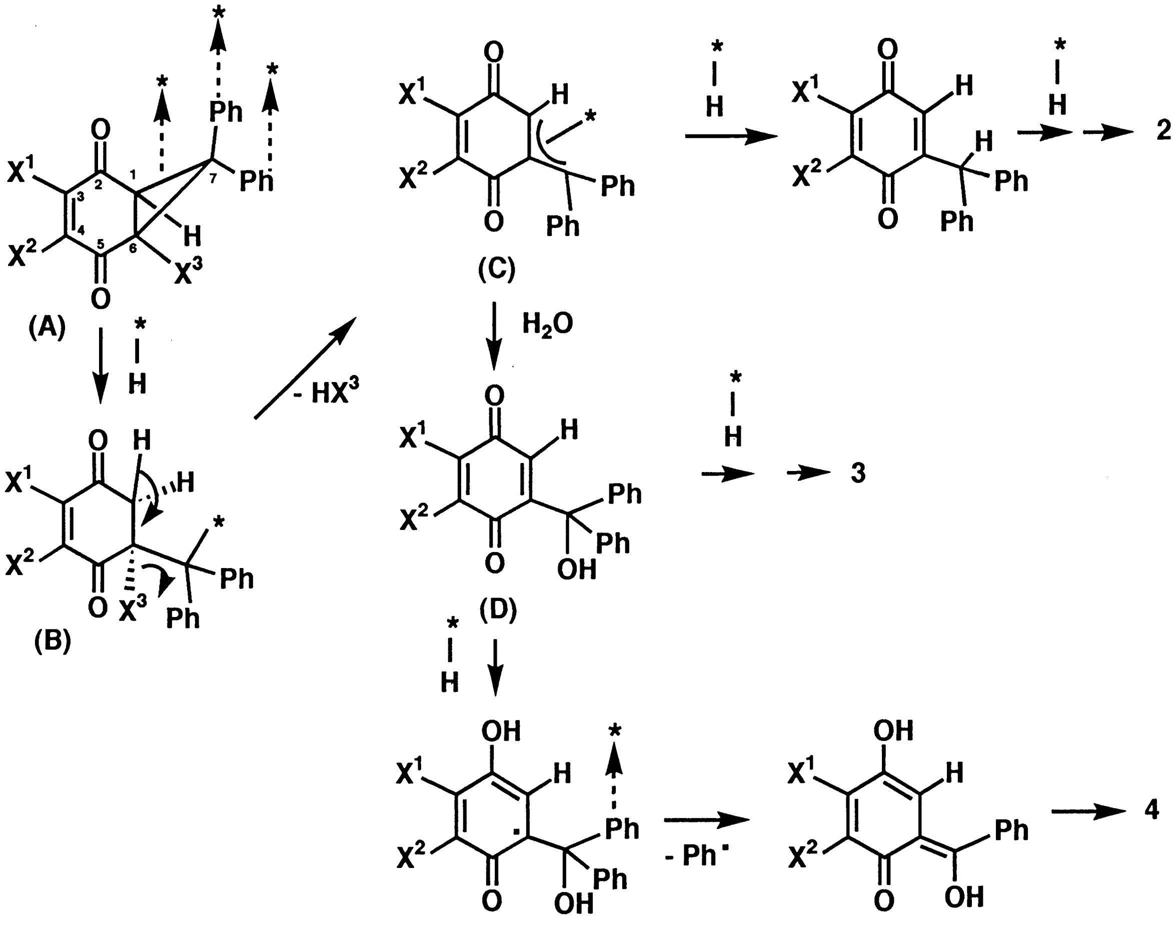
Table 1. Hydrogenolysis of Quinone-fused *gem*-Diphenylcyclopropanes (**1a-e**)[a]

Cyclopropane	Solvent	Additive (v/v)	Time h	Yield/ %[b] **2**	**3**	**4**
1a	1,4-Dioxane	-	6	100 [c]	-	-
1a	"	H_2O (1%)	2	35	12	42
1a	"	H_2O (2%)	2	13	11	59
1b	Benzene	-	6	100 [c]	-	-
1c	1,4-Dioxane	H_2O (1%)	6	56	9	27
1d	Benzene	-	6	100 [c]	-	-
1d	1,4-Dioxane	H_2O (2%)	2	6	15	75
1e	1,4-Dioxane	-	6	100 [c]	-	-
1e	"	H_2O (1%)	6	31	15	33

a) Under atmospheric pressure at room temperature. Substrate: 100 mg; Pd/C(10%): 30 mg; Solvent: 5 ml.
b) Unless otherwise noted, isolated yield. c) Based on ^{1}H NMR.

All the compounds, **2-4**, were found to lose a halogen X^3, and thus **1d**($X^{1,2}$=Cl, X^3=Br) gave the bromine-free products identical to those from **1a**($X^{1,2,3}$=Cl), but **1b**(X^1=Br, $X^{2,3}$=Cl) and **1c**($X^{1,3}$=Cl, X^2=Br) produced bromine-retained products. Of interest is that the compounds **4** are further devoid of one phenyl group. The lost aromatic ring was confirmed to be liberated as benzene by the GC-Mass analysis of the distillate of the reacting solution.[7] The structure of **4** is suited for an internal hydrogen bonding due to a favorable quasi six-membered ring as depicted in Scheme 2. In fact, ^{1}H NMR spectra of **4** showed two phenolic signals near at δ 5.3 and 12.2 ppm in $CDCl_3$, with the downfield signals apparently demonstrating such an interaction. Incidentally, no interconversion could be observed in these products, **2-4**, on extended standing of the mixture under hydrogenolytic conditions.

A probable pathway of hydrogenolysis of **1** is suggested in Scheme 3. The substrate is adsorbed on the catalyst by the unhalogenated C_1-C_7 bond. Such interaction is presumably favored owing to the formation of an aromatic donor-metal complex[8] as well as the environmental requirement avoiding a significant steric repulsion by halogen X^3. The adsorbate(A) will undergo the hydrogenolytic ring-opening by consecutive insertion of a Pd(0) species and hydrogen addition to the C_1 carbon atom, giving rise to an alkylpalladium hydride(B) which immediately leads to **2** by successive dehydrohalogenation, reductive elimination of zero-valent palladium from the possible π-allyl complex C, and hydrogenation and dienolization. In a competitive process, however, additive water may attack C to provide D which turns out to **3** in a similar manner as above. As to **4**, hydrogenation of D and the adsorption on the catalyst seem to be crucial for the extrusion of phenyl radical from the β-carbon atom.



Scheme 3.

We attribute the differences in the hydrogenolytic behavior of DDQ-fused cyclopropanes and the present substrates to the well-established ability of cyclopropane to enter into π-type conjugation with neighboring π-electron systems.[9] The substituents under consideration are the CO, CN and Ph groups and are all good π-electron acceptors with low-lying LUMOs. The important stabilizing interaction is the mixing of the acceptor

LUMO orbital into the antisymmetric HOMO Walsh orbital[10)] of cyclopropane as shown below. Thus, there is net electron transfer from cyclopropane to π-system. Of the above substituents, carbonyl group is expected to exert the conjugative effects less satisfactrily because of the conformational restriction. Consequently the antibonding interaction in the opposite bond **b** is weakened, i.e., this bond should become stronger, while the vicinal bonds **a** and **c** should be weakened due to the diminished bonding interaction. These electronic considerations well predict the preferential scission of the C_1-C_6 bond for the DDQ-fused dicyanocyclopropanes and of the C_1-C_7 or C_6-C_7 for the present diphenyl substituted cyclopropanes; here the C_1-C_7 prevails due to the reason mentioned above. Although other factors, e.g., the inductive and the steric effects as well as the chemisorption of the substituents also contribute to the hydrogenolysis of quinone-fused cyclopropanes, the dominant factor seems to us the conjugation with the adjacent π-electron system.

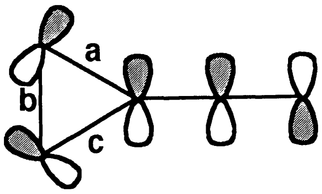


Fig. 1. Interaction of HOMO of cyclopropane with LUMO of π-acceptor substituent

We thank Professor H. Kurosawa of Osaka University for useful discussions.

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6) Satisfactory analytical and spectroscopic data were obtained for all new compounds described here.
7) For the sake of convenience, reduction of **1a** was carried out in volatile ether containing 2% volume of water.
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(Received August 19, 1993)