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Ready Thermal DDQ Dehydrogenation of Some Methylcyclopropanes Activated by a Spiro-Fused Fluorene Group[†]

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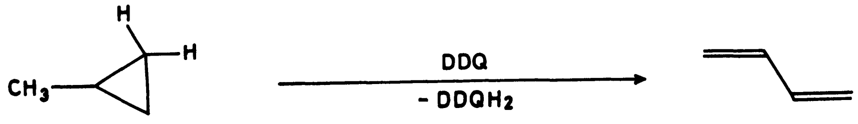
Some methylcyclopropanes activated by a spiro-fused fluorene group were readily dehydrogenated by DDQ, but not by chloranil, to give a butadiene derivative, which reacted further with DDQ to afford 7-(o,o'-biphenylene)-3,4-dichloro-1,6-dicyano-9-alkylbicyclo[4.4.0]deca-3,8-diene-2,4-dione. In contrast, methylcyclopropanes substituted merely by two phenyl groups were reluctant to undergo the dehydrogenation.

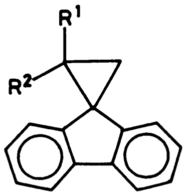
2,3-Dichloro-5,6-dicyano-p-benzoquinone (DDQ) and 2,3,5,6-tetrachloro-p-benzoquinone (chloranil) are well known dehydrogenating reagents and have been extensively used in the dehydrogenation of a wide variety of unsaturated compounds, such as steroidal ketones and hydroaromatic compounds.1) The reaction is usually carried out by refluxing a substrate with the quinone in benzene, dioxane or other appropriate solvents.

We recently found that DDQ very readily dehydrogenates certain methylcyclopropanes (**1**) substituted by a spiro-fused fluorene group (spiro-activated cyclopropanes)2) with a three-membered ring cleavage. The transformation can formally be described as shown below.



Thus, the reaction of 1-cyclopropyl-1-methyldibenzo[d,f]spiro[2.4]heptane (**1a**) with DDQ3) took place at room temperature in benzene. A product isolated in 56% yield was characterized as 7-(o,o'-biphenylene)-3,4-dichloro-1,6-dicyano-9-cyclopropylbicyclo[4.4.0]deca-3,8-diene-2,4-dione (**2a**),4) a Diels-Alder adduct of 9-(2-cyclopropyl-2-propenylidene)fluorene (**3a**) with DDQ. Besides **2a**, 9-methylenefluorene (**4**), 19%, and 2,3-dichloro-5,6-dicyano-p-hydroquinone (DDQH$_2$), 93%, were isolated and characterized. The same reaction proceeded more rapidly in acetonitrile, but the reaction was less clean and **2a** and **4** were isolated only in 20% and 7% yield, respectively.5)

[†] This paper is dedicated to late Professor Ryozo Goto, Kyoto University.



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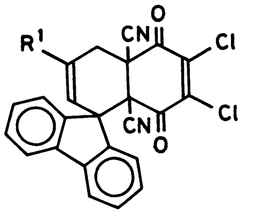

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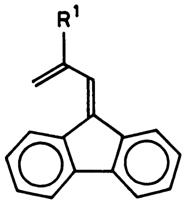

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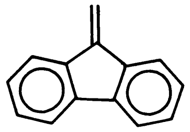

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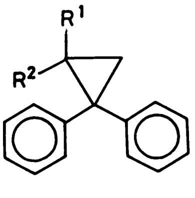


5

a : R^1 = cyclo-C_3H_5, R^2 = CH_3
b : R^1 = R^2 = CH_3
c : R^1 = R^2 = cyclo-C_3H_5

In marked contrast to high reactivity of **1a**, 1-cyclopropyl-1-methyl-2,2-diphenylcyclopropane (**5a**) did not react with DDQ under similar conditions. Furthermore, it was observed that chloranil failed to dehydrogenate otherwise highly reactive **1a** in the dark.

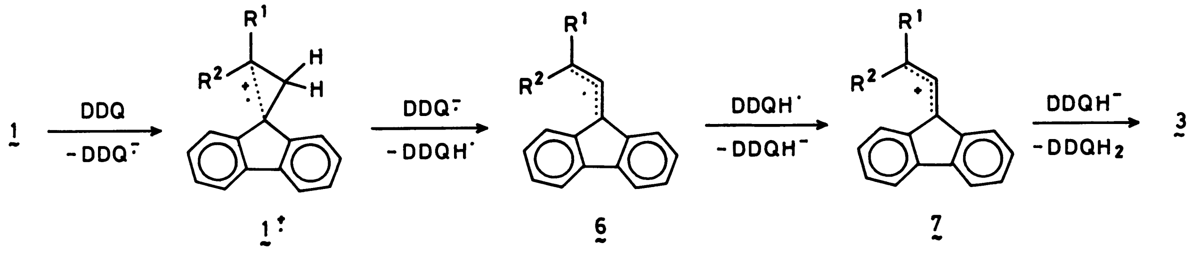
Thermal DDQ dehydrogenation of a spiro-activated 1,1-dimethyl derivative (**1b**) also proceeded smoothly in refluxing benzene, and **2b** was isolated in 78% yield. $DDQH_2$ was obtained quantitatively (96%), but **4** was not detected in the product mixture. The product **2b** was identical with an authentic specimen prepared from independently synthesized **3b** and DDQ. For the second time, chloranil was unable to dehydrogenate **1b** (5 d in refluxing benzene). The reaction of 1,1-dicyclopropyl derivative (**1c**) with DDQ was not clean, and a mixture composed of multicomponents was obtained.

On the contrary to the thermal reactions, both **1a** and **1b** were dehydrogenated by chloranil under illumination of visible light. Thus, the irradiation of a benzene solution of either **1a** or **1b** and chloranil$^{6)}$ with a halogen lamp resulted in the consumption of the starting material and **3** was produced. It is to be noted that chloranil does not have a high enough dienophilic reactivity to undergo the Diels-Alder reaction with **3**. Characterization of **3** was thus made by allowing it to react with DDQ, which was added to a crude hydrocarbon fraction of the product mixture. The yields of **2a** and **2b** in these photochemical reactions were, however, relatively low (20-27%).

The present thermal DDQ dehydrogenation is limited to the spiro-activated substrates. As mentioned above, **5a** failed to react with DDQ, although **5a** differs from **1a** only in that **5a** lacks a bond connecting the two phenyl groups. The inertness of gem-diphenyl derivatives was also noted in attempted reactions of 1,1-dimethyl-2,2-diphenylcyclopropane (**5b**) with DDQ. Thus, the presence of a planar biphenyl moiety in the substrate is essential for undergoing the dehydrogenation, and hence the present reaction is closely related to the reactions of these cyclopropanes with ethenetetracarbonitrile (TCNE).$^{2)}$ Accordingly, the reaction may involve a thermal single electron transfer (SET) at the very early stage of the transformation.$^{7)}$ Inability of chloranil to dehydrogenate the spiro-activated **1** is most probably due to its substantially low reduction potential (E_1 = +0.01 V vs. S.C.E.) relative to that of DDQ (E_1 = +0.51 V vs. S.C.E.).$^{8)}$ The facts that the photostimulation was effective in the reaction of **1** with chloranil are consistent with the SET initiated mechanism.$^{9)}$

Although it may be premature to consider the precise route for the overall transformation at this stage of investigations, the formation of **3** from $\mathbf{1}^{+\cdot}$ will most simply be depicted as shown in Scheme I, which is analogous to that suggested by Arnold$^{10)}$ for sensitized photochemical reaction of 1,1,2,2-tetraphenylcyclopropane. Namely, a proton abstraction from $\mathbf{1}^{+\cdot}$ by DDQ$^{\cdot-}$ will produce allylic radical **6**, which is oxidized by nearby DDQH$^{\cdot}$ to **7**, and **3** is ultimately formed from **7**. The fact that the reaction of **1c** gave the poor result may be associated with the formation of a strained methylenecyclopropane subunit at the diene-forming stage.

With regard to the pathway for **4**, it is hard to believe that **4** is produced after the proton abstraction, since there should be a partial double bond between C-1 and C-2 in the side chain of either **6** or **7**. A possible precursor for **4** may be $\mathbf{1}^{+\cdot}$, but further studies are undoubtedly neccessary to discuss the route for **4**.$^{11)}$



Scheme 1.

In conclusion, it was demonstrated that the spiro-activated methylcyclopropanes **1** were readily dehydrogenated thermally by DDQ, whereas **5** remained practically inert. It is proposed that the reaction will be initiated by SET, and a possible route for **3** is presented, although clarification of detailed pathways should be a subject of further investigations.

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References

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2) S. Nishida, M. Murakami, T. Mizuno, T. Tsuji, H. Oda, and N. Shimizu, J. Org. Chem., 49, 3428 (1984).
3) In a preliminary experiment, it was found that **1a** reacted with two moles of DDQ. Accordingly, the reactions described hereafter were carried out by using a twice

molar amount of DDQ relative to that of **1**.

4) All new compounds described hereafter gave satisfactory elemental analysis and spectroscopic data. Details will be reported in a full paper.

5) Since the reaction in benzene was cleanest, all other dehydrogenations were carried out in benzene.

6) On admixture of chloranil with **1a** or **1b** either in benzene or in dichloromethane, a new, relatively weak shoulder peak was observed in visible spectra at around 520 nm. This may be ascribable to the formation of a charge transfer complex between **1a** or **1b** and chloranil.

7) In benzene, radical ions may exist as a pair and the subsequent transformation will take place from it. It appears that the radical ions will more easily be apart in acetonitrile, and some side reactions may set in to make the yield of **2a** being relatively low.

With regard to the feasibility of thermal SET initiation of the reaction, it has been demonstrated that the isomerization of hexamethyl(Dewar benzene) to hexamethylbenzene catalyzed by electron acceptors can proceed with reasonable rates ($t_{1/2}$ = 2,300 s) at room temperature when ΔG_{ET} = 100 kJ (24 kcal/mol) (N. J. Peacock and G. B. Schuster, J. Am. Chem. Soc., 105, 3632 (1983)). In preliminary experiments, it was observed that the electrochemical oxidation of **1a** is irreversible and gave a wave with peak potential at about 1.0 V (vs. S.C.E.), which is significantly lower than that of **5a**, about 1.5 V. On the basis of these values, we can estimate approximate ΔG_{ET} for the pairs of reactants. The results are as follows: **1a**-DDQ = ca. 46 kJ (11 kcal/mol), **1a**-chloranil = ca. 96 kJ (23 kcal/mol), and **5a**-DDQ = ca. 96 kJ (23 kcal/mol). Accordingly, it may be reasonable to consider that the SET initiated reaction can easily take place between **1a** and DDQ, a matched pair of reactants, whereas there will be a significant energy barrier for the reactions of **1a** with chloranil and **5a** with DDQ.

8) M. E. Peover, J. Chem. Soc., 1962, 4540.

9) M. Julliard and M. Chanon, Chem. Rev., 83, 425 (1983).

10) D. D. M. Wayner and D. R. Arnold, Can. J. Chem., 63, 871 (1985). For the related photochemical reactions of phenylcyclopropane derivatives, see also: V. R. Rao and S. S. Hixson, J. Am. Chem. Soc., 101, 6458 (1979); K. Mizuno, J. Ogawa, and Y. Otsuji, Chem. Lett., 1981, 741; K. Mizuno, K. Yoshioka, and Y. Otsuji, ibid., 1983, 941.

11) In the mass spectra of **1a**, **1b**, **1c**, and their ring-dideuterio derivatives, a peak corresponding to 9-methylenefluorene (m/z = 178 or 180), or its alternative, was observed with relatively high intensity (30-60%). The results appear to support the assumption that $\mathbf{1}^{+\cdot}$ undergoes the fragmentation to give **4**.

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