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New Method for Oxidative Carbon-carbon Bond Formation by the Reaction of Allyl Ethers, 2,3-Dichloro-5,6-dicyano-p-benzoquinone(DDQ) and Silyl Carbon Nucleophiles

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Allyl ethers are oxidized by DDQ to generate the corresponding cationic species, which in turn react with silyl carbon nucleophiles in the presence of a catalytic amount of lithium perchlorate to afford the coupled products in a one-pot procedure in good yields.

Oxidation is one of the most fundamental reactions1) in organic synthesis, and recently various reagents have been developed for the selective oxidation of organic compounds. Among these, there are known a limited number of oxidants which can generate cationic species by hydride abstraction. There is a profound study about carbocations, however, these oxidatively generated cationic species have been rarely employed in further transformations. Therefore, the investigation of a novel oxidative carbon-carbon bond forming reactions by treating the above mentioned cationic species with carbon nucleophiles should lead to interesting new synthetic methods.

In this context we have already reported reactions2,3) of this type using trityl cation as an oxidant, in which isolable cationic species, generated by the hydride abstraction of ethylene acetals with trityl cation, are treated with lithium organo compounds,3) silyl carbon nucleophiles,4) and enamines4) to form the desired products with the formation of a new carbon-carbon bond.

In order to establish these reactions as a useful synthetic tool, the following points should be modified. Firstly, it is generally necessary either to isolate the cationic species in pure form, or to add the nucleophile after oxidation is completed because trityl cation is readily scavenged by the reaction with the nucleophile. Therefore, to simplify the reaction, it is desirable to carry out both oxidation and addition processes in a one-pot procedure. Another problem is the limitation in the structure of substrates smoothly oxidized by trityl cation.5) To overcome these problems, another hydride abstracting reagent, DDQ,6) was examined and in this communication, we wish to disclose a successful oxidative carbon-carbon bond forming reaction between allyl ether and silyl carbon nucleophiles in a one-pot procedure.

It is well known that DDQ is useful for the oxidation of allyl alcohols7) and benzyl alcohols.7) In order to acccomplish the desired carbon-carbon bond forming

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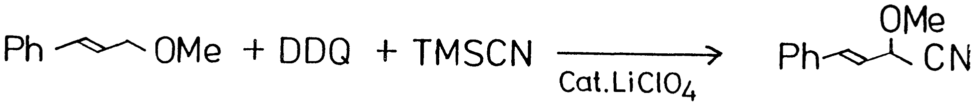
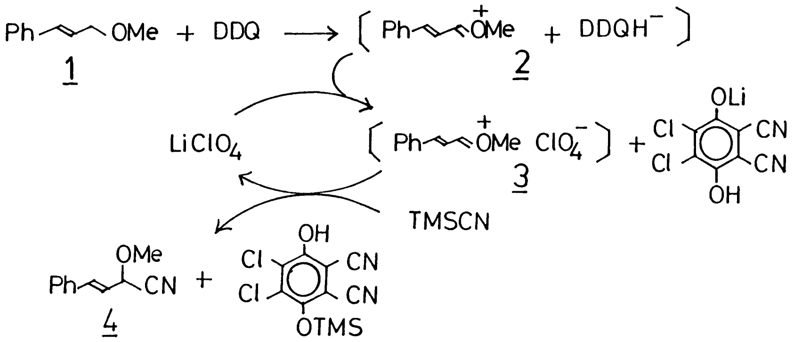
reaction, we have searched for suitable nucleophiles, which are able to react smoothly with the cationic species formed by hydride abstraction from allyl alcohols.

First, the reactions of cinnamyl alcohol and DDQ with various kinds of nucleophiles were examined but what was obtained was only cinnamaldehyde, probably because the cationic imtermediate is unstable and quickly transforms to aldehyde before reacting with a nucleophile. In order to stabilize the intermediate, allyl ether was used instead of allyl alcohol in the above reaction, and it was found that the desired product was obtained when trimethylsilyl cyanide was used as a nucleophile. That is, 1-cyano-1-methoxy-3-phenyl-2-propene was obtained in 60% yield along with cinnamaldehyde in 23% yield by the reaction of DDQ and cinnamyl methyl ether with trimethylsilyl cyanide. In the product only one isomer is detectable by ^{1}H -NMR, though there is a possibility of forming two regio isomers. In order to improve the yield the reaction conditions and additives were screened in detail, and $LiClO_4$ was found to be quite beneficial to the present reaction, the yield was increased to 82% in its presence. Moreover, a catalytic amount of $LiClO_4$ is enough to complete the reaction.



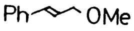
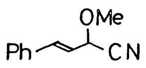
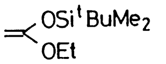
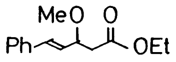
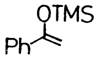
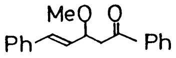
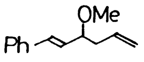
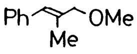
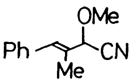
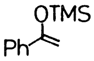
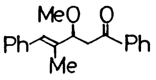
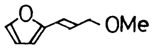
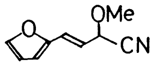
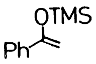
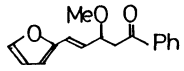
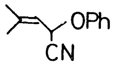
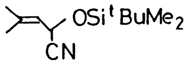
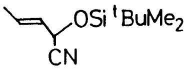
This substantial effect of $LiClO_4$ can be explained as follows: On adding cinnamyl methyl ether 1 to the solution of DDQ, ion pair 2 is formed and when $LiClO_4$ is present, the exchange of counter ions can take place to produce a new ion pair 3.[8] The ion pairs 2 and 3 might exist in the equilibrium and ion pair 3, a better electrophile, reacts with a nucleophile smoothly to afford the desired product 4 along with the regeneration of $LiClO_4$.



In this reaction, other silyl carbon nucleophiles such as silyl enol ether, ketene silyl acetal and allyl silane can also be employed and the results of the reactions between these nucleophiles and various allyl ethers are summarized in the Table. The following points deserve comments.

1) This oxidative carbon-carbon bond forming reaction is dependant on the characteristic ability of DDQ as an oxidant. When electron donating substituent such as phenyl or furyl group is attached to the allyl ethers, the reaction proceeds smoothly to afford the products in higher yields.

Table. Oxidative Coupling Reactions between Ally Ethers and Nucleophiles$^{a)}$

Entry	Allyl ether	Nucleophile	Product	Time/h	Yield/%	Method$^{b)}$
1		TMSCN		1	82	A
2	"	"	"	1	60	C
3	"			1	72	B
4	"			1	84	B
5	"	"	"	1	38	D
6	"	$Ph_3SnCH_2CH=CH_2$		1	79	B
7	"	$TMSCH_2CH=CH_2$	"	2	60	A
8	"	"	"	4	7	C
9		TMSCN		1	94	A
10	"			1	94	B
11		TMSCN		1	88	A
12	"			1	85	B
13		TMSCN		24	20	A
14		"		18	40	A
15		"		18	20	A

a) Molar ratio, DDQ : Allyl ether : Nucleophile : $LiClO_4$ = 1 : 0.9 : 2-3 : 0.1. Reaction is done at room temperature using CH_2Cl_2 as solvent.

b) A: To the solution of DDQ and $LiClO_4$, first the nucleophile, then the allyl ether are added.

B: To the solution of DDQ and $LiClO_4$, first the allyl ether, then after 5 min, the nucleophile are added.

C: The same reaction conditions as A without $LiClO_4$.

D: The same reaction conditions as B without $LiClO_4$.

2) The order of addition of reagents is crucial in this reaction: That is, trimethylsilyl cyanide and allyl trimethylsilane are inert to DDQ, so that it is possible to add these nucleophiles before adding an allyl ether (method A). In the cases of silyl enol ether, ketene silyl acetal and allyl stannane, which readily react with DDQ, it is necessary to add the nucleophile after the allyl ether is oxidized (method B).

3) In the allylation, allyl stannane gave a better result than allyl silane because of its stronger nucleophilicity.

4) In every case, $LiClO_4$ is essential for the effective promotion of this reaction and in the absence of $LiClO_4$, the yield decreased dramatically (Entries 1 and 2, 4 and 5, 7 and 8).

5) Both oxidation and addition processes are carried out in a one-pot procedure and it is not necessary to isolate and purify the intermediate cationic species, so that the experimental procedure becomes very simple.

Typical procedure of entry 1 of the table is as follows: To a dichloromethane solution (6 cm^3) of DDQ (0.45 mmol) and $LiClO_4$ (0.08 mmol) was added trimethylsilyl cyanide (1.2 mmol) and cinnamyl methyl ether (0.42 mmol) in dichloromethane (1.5 cm^3) successively at room temperature. After the reaction mixture was stirred at this temperature for an hour, the reaction was worked up by adding aqueous sodium hydrogencarbonate and the organic materials were extracted with dichloromethane. After the organic layer was dried and evaporated, the residue was purified by thin layer chromatography to give 1-cyano-1-methoxy-3-phenyl-2-propene (82%).

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