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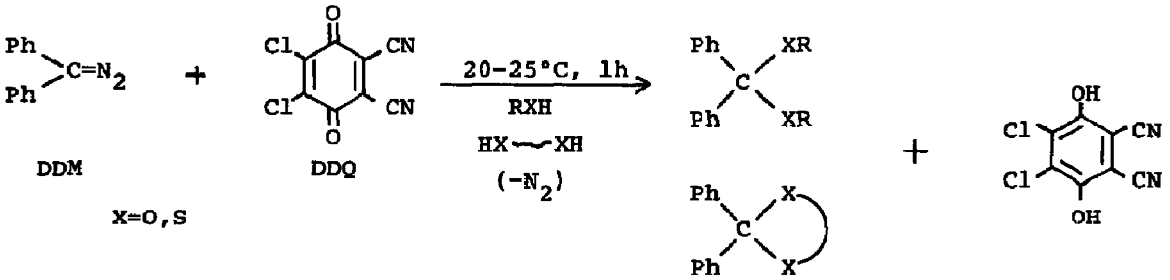
FACILE SYNTHETIC METHODS OF ACETALS AND CROWN ETHERS FROM THE REACTION OF DIPHENYLDIAZOMETHANE WITH 2,3-DICHLORO-5,6-DICYANOBENZOQUINONE IN THE PRESENCE OF ALCOHOLS

Takumi Oshima, Ryoji Nishioka, Toshikazu Nagai*
Institute of Chemistry, College of General Education,
Osaka University, Toyonaka, Osaka 560, Japan

Summary: The reaction of diphenyldiazomethane with 2,3-dichloro-5,6-dicyanobenzoquinone in the presence of alcohols and thiols gave the corresponding benzophenone acetals and thioacetals at 20-25°C in 1,2-dichloroethane. The mechanism of the reaction will be discussed.

Acetals are generally produced from the reactions between the alcohols and the carbonyl compounds with a Brønsted catalyst.[1]

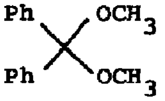
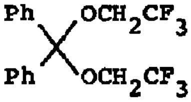
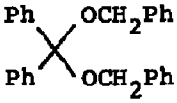
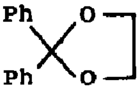
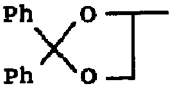
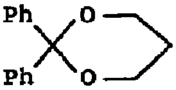
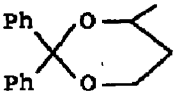
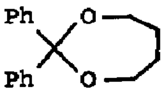
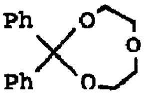
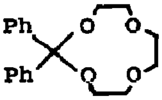
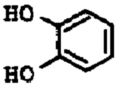
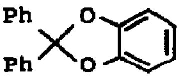
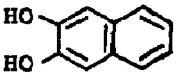
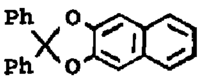
We now wish to report facile synthetic methods of acyclic or cyclic acetals including crown ethers under the mild conditions not requiring such a protic acid. The present methods utilize the decomposition of diphenyldiazomethane(DDM) by 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ) and the strong dehydrogenating ability of this quinone.[2] The reaction of DDM and a stoichiometric amount of DDQ in the presence of 3 to 5 fold molar excess of alcohols proceeds with a vigorous evolution of N_2 to give benzophenone acetals in good yields together with 2,3-dichloro-5,6-dicyanohydroquinone as seen in Scheme 1(Method A).

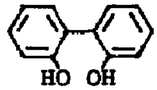
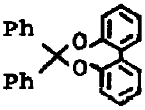
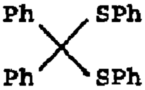
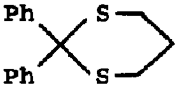


Scheme 1

This system was found to be efficient even if the alcohols were separately added after the complete reaction(Method B). Some examples are listed in Table 1.

Table 1. Formation of Acetals in the DDM–DDQ–Alcohols Systems.

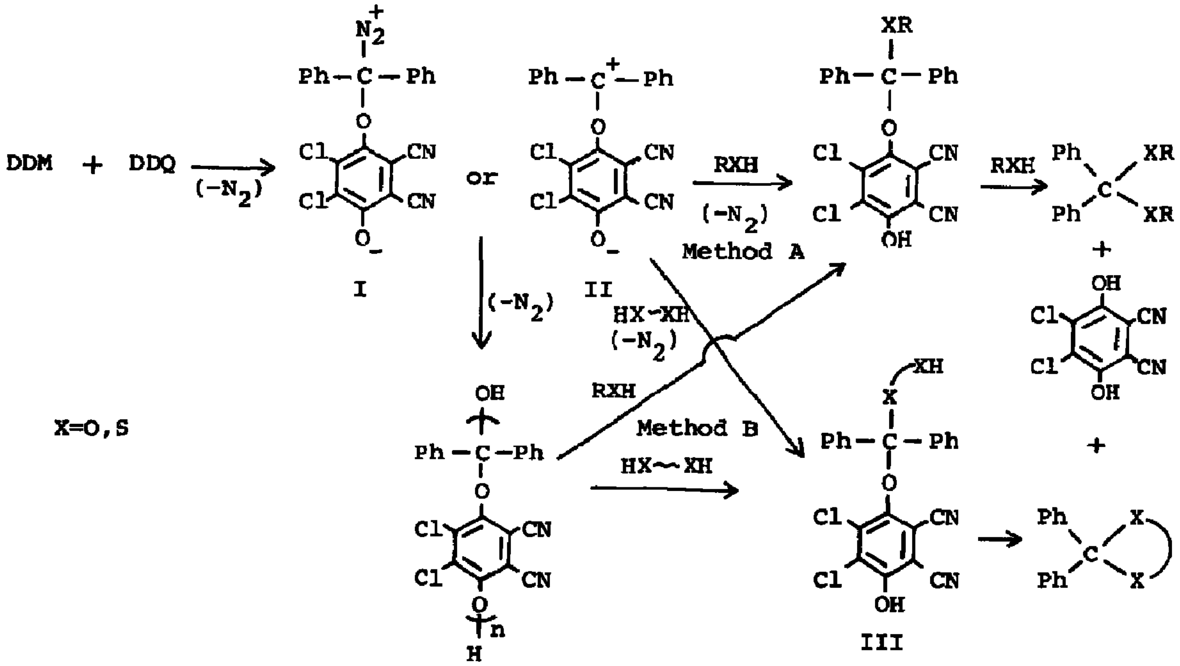
No.	Alcohols and Thiols	Methods	Products	Yield(%)[a]	Mp(°C)	Found(%)[b]	
						C	H
1	CH_3OH	A		87 85[c]	106–107	78.98 (78.92)	7.01 (7.06)
		B		78			
2	CF_3CH_2OH	B		54	95–96	56.26 (56.04)	4.08 (3.87)
3	$PhCH_2OH$	A		73	107–109	85.37 (85.22)	6.30 (6.37)
4	$HO(CH_2)_2OH$	A		81	54–55	79.66 (79.61)	6.22 (6.25)
5	$HOCH_2CH(OH)CH_3$	A		74	68–69	80.08 (79.96)	6.70 (6.72)
6	$HO(CH_2)_3OH$	A		84	113–115	79.88 (79.96)	6.65 (6.72)
7	$HOCH_2CH_2CH(OH)CH_3$	A		78	89–91	80.18 (80.27)	7.11 (7.15)
8	$HO(CH_2)_4OH$	A		75	124–126	80.19 (80.27)	7.03 (7.15)
9	$HO(CH_2CH_2O)_2H$	B		83	———	75.52 (75.52)	6.71 (6.72)
10	$HO(CH_2CH_2O)_3H$	B		76	———	72.58 (72.58)	7.06 (7.07)
11		B		65	93.5 –94.5	83.27 (83.18)	5.15 (5.15)
12		B		54	158 –159.5	85.15 (85.15)	4.95 (4.98)

13		B		50	166-167	85.68 (85.68)	5.13 (5.19)
14	PhSH	B		79	138-139	77.88 (78.07)	5.19 (5.25)
15	$HS(CH_2)_3SH$	A		53	111 -112.5	70.55 (70.53)	5.97 (5.93)
16	H_2O	B	$Ph_2C{=}O$	95	48-50		

a) Isolated yield based on DDM. b) Required values in the parenthesis.

c) Obtained from DDM-chloranil-CH_3OH system, ref.3.

Mechanistically, formations of acetals are well interpreted in terms of the occurrence of diazonium(I) or carbonium betaine(II) intermediate and the following nucleophilic attack of alcohols as well as the DDM-chloranil system[3] (Scheme 2). The resulting hydroquinone ethers(III) lead to the acetals by way of the external or the internal nucleophilic attack by the hydroxy and the mercapt groups. As was expected, presence of water(R=H, X=O) resulted in the formation of benzophenone given by the loss of water from the initial product,



Scheme 2

α,α-dihydroxydiphenylmethane(Table 1.No.16). In method B, it seems that I or II temporarily polymerizes and then the addition of alcohols and thiols causes the nucleophilic cleavage of the ether linkage to afford III.

The representative procedure is as follows. To a stirred suspension of DDQ(0.59g,2.60 mmol) in 1,2-dichloroethane(20 ml) was added 10 ml of 1,2-dichloroethane solution containing DDM(0.50g,2.60 mmol) and methanol(0.40g, 12.5 mmol) in one portion at 20°C. The characteristic purple color of DDM suddenly faded with the vigorous evolution of N_2. After stirring for 1h, the solvent was evaporated in vacuo and the pasty reaction mixture was triturated with 3×20 ml benzene. The combined benzene solution was washed several times with aqueous sodium carbonate(5%), dried over anhydrous sodium sulfate, and evaporated to give α,α-dimethoxydiphenylmethane(0.51g,87%) together with a small amount of benzophenone(0.04g,8.5%). The solidy residue was chromatographed (on silica gel) to afford 2,3-dichloro-5,6-dicyanohydroquinone(0.55g,92%) with benzene-ether mixture(4:1) as an eluent. In other cases, no effort to isolated the hydroquinone was made, namely, benzene(60 ml) was poured into the pasty or solidy reaction mixtures to extract the acetals. The benzene extract was washed with aqueous sodium carbonate(5%), dried over anhydrous sodium sulfate, and evaporated in vacuo. The fractional crystallization of the residue in ether or column chromatographic treatment on aluminium oxide using petroleum ether-benzene(4:1) as an eluent gave the analytically pure samples. The hygroscopic crown ethers were eluted with benzene-methanol(5:1) and dried in vacuo over 200°C(No.9 and 10).

REFERENCES

1. a) E. J. Witzemann, W. L. Evans, E. F. Schroeder, Org. Synth., II, 137 (1943)
   b) M. Renoll, M. S. Newman, Org. Synth., III, 502 (1955).
2. A. Schönberg et al. have obtained some benzophenone acetals in the long time reaction of diphenyldiazomethane(DDM) with alcohols under the influence of ninhydrin,where the formation mechanism has been obscure, Liebigs Ann., Chem., 711, 98 (1968).
3. T. Oshima and T. Nagai, Bull. Chem. Soc. Jpn., 53(1980), in press.

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