Notes

Studies on Copper(II) Complexes of *ortho*-Quinone Mono-oximes: Reaction of Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) with Dimethyl Acetylenedicarboxylate under Various Experimental Conditions

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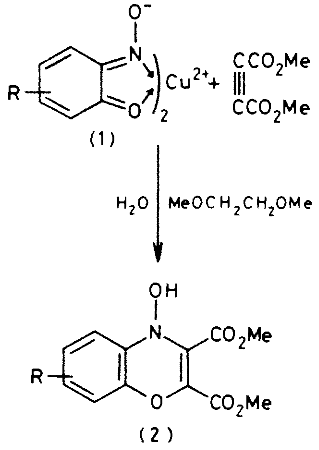
In anhydrous methanol the title complex reacts with dimethyl acetylenedicarboxylate to give methyl 5-chloro-1,3-benzoxazole-2-carboxylate instead of 6-chloro-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine as in aqueous solution. The role of water in such reactions is examined and discussed.

It is known that copper(II) complexes of *o*-quinone mono-oximes react with dimethyl acetylenedicarboxylate in hot aqueous 1,2-dimethoxyethane to give the corresponding benzoxazines (Scheme 1).[1] Here we describe the results obtained under different experimental conditions.

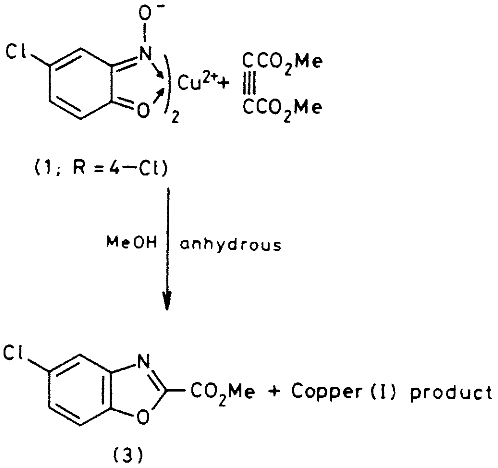


Scheme 1.

Results and Discussion

In anhydrous methanol the [4 + 2] cycloaddition does not occur and compound (1; R = 4-Cl) reacts with dimethyl acetylenedicarboxylate to give methyl 5-chloro-1,3-benzoxazole-2-carboxylate (3) (Scheme 2), instead of the benzoxazine (2; R = 6-Cl). In the course of the reaction a diamagnetic residue of Cu^I is formed and the NO oxime group undergoes deoxygenation. Analogous results have recently been reported for other reactions of compounds (1),[2] and a likely interpretation of the copper reduction has been proposed.[2a]

The dryness of the methanol used is critical: water, even in very small amounts, causes the cycloaddition which, in 99.5% methanol, occurs faster than in 1,2-dimethoxyethane. The role of water, following McKillop and Sayer,[1] could be related to the hydration energy of the copper ion, and/or to the formation of a square pyramidal adduct. In connection with our researches on the Lewis acidity of compound (1; R = 4-Cl),[3] we looked for a water adduct.



Scheme 2.

Addition of water to a previously boiled solution of compound (1; R = 4-Cl) in 1,2-dimethoxyethane, methanol, or other water-miscible solvents resulted in a colour change from dark purple to deep green. Spectrophotometric study of this equilibrium is not possible owing to the continuous slow separation of a green solid. Moreover, the characterization of the green precipitate is also not possible because of its extreme instability: when removed from the mother-liquor it reverts to the purple starting complex (confirmed by analysis and *X*-ray powder diffractogram). However, some deductions can be made from a comparison of the spectrum of the green aqueous solution with that of the compound (1; R = 4-Cl) and its adducts in the ligand-field region (Table).

The main visible envelope is slightly shifted toward lower wavelengths in going from chloroform to better donor solvents; a larger shift in the same direction is produced by chelating ligands. On the contrary, in an aqueous solution a very broad band appears at much higher wavelengths. In our opinion these features cannot be explained on the basis of the different basicities of the ligands or the different geometries of the adducts formed, but reflect a more significant alteration of the molecule (1; R = Cl) produced by water. The significance of the geometry of the reacting species was then examined by carrying out the cycloaddition in the presence of pyridine (py) or 2,2′-bipyridine (bipy) which form, with

Table. Solution spectra of (1; R = 4-Cl) and its chelated adducts in the region 400—700 nm

Compound	Medium	$\lambda_{max.}$/nm	
(1; R = 4-Cl)	$CHCl_3$	420	544
	MeCN	419	540
	Pr^iOH	420	541
	EtOH	413	538
	MeOH	413	536
1 : 1 bipy adduct [a]	MeCN	430(sh)	500
1 : 1 phen adduct [a,b]	MeCN	430(sh)	500
Green aqueous solution		424(sh)	635—674

[a] See ref. 3*c*. [b] phen = 1,10-Phenanthroline.

(1; R = 4-Cl), 1 : 1 adducts of different structure: square pyramidal with py [4] and *cis*-octahedral with bipy.[3b] In both cases the cycloaddition occurs readily (provided water is present), indicating that the geometry of the formed adduct is of no relevance. Therefore we believe that the role of water does not consist in the formation of a square-pyramidal adduct; a different interaction with the molecule (1; R = 4-Cl) and/or a thermodynamic effect due to hydration of Cu^{2+} seems to be more likely.

Furthermore, we examined the reactivity of dimethyl acetylenedicarboxylate toward the bis(4-chloro-1,2-benzoquinone 2-oximato)nickel(II): in the presence of water, cycloaddition occurs, although much more slowly than with (1; R = 4-Cl); in anhydrous methanol there is no reaction, in agreement with the reluctance of Ni^{II} to undergo reduction to Ni^{I}. Therefore it seems correct to assume that the first step in the synthesis of the benzoxazole (3) from (1) and dimethyl acetylenedicarboxylate in anhydrous methanol follows a pathway analogous to that suggested in ref. 2*a*.

Experimental

Preparation of Starting Materials.—Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II), bis(4-chloro-1,2-benzoquinone-2-oximato)(pyridine)copper(II), and bis(4-chloro-1,2-benzoquinone 2-oximato)nickel(II) were prepared as described previously.[5] (2,2′-Bipyridine)bis(4-chloro-1,2-benzoquinone 2-oximato) copper(II) was prepared by stirring stoicheiometric amounts of compound (1; R = 4-Cl) and bipy in MeCN and slowly evaporating the solution obtained.[3]

Reaction between Compound (1; R = 4-Cl) *and Dimethyl Acetylenedicarboxylate in Methanol.*—(*a*) The complex (0.65 g) and dimethyl acetylenedicarboxylate (1 cm^3) *in anhydrous methanol* (60 cm^3) were heated under reflux for about 1 h; the reaction mixture was filtered, treated with activated charcoal, and evaporated under vacuum to give a crude oil, from which pure *methyl* 5-*chloro*-1,3-*benzoxazole*-2-*carboxylate* was isolated by column chromatography [silica gel, carbon tetrachloride-ethyl acetate (19 : 1)] and repeated crystallizations from n-hexane, m.p. 120—121 °C (Found: C, 51.15; H, 2.85; N, 6.65. Calc. for $C_9H_6ClNO_3$: C, 51.1; H, 2.85; N, 6.60%); δ_H ([$^2H_6$]acetone) 4.06 (3 H, s), 7.67 (1 H, dd, *J* = 9.0 and 2.0 Hz), 7.87 (1 H, br), and 7.99 (1 H, br) (assignments confirmed by comparison with a sample of the compound prepared according to ref. 6). The solid residue was diamagnetic.

(*b*) In 99.5% methanol the 6-chloro-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine was formed in about 30 min; the reaction mixture was filtered and evaporated to dryness to give the crude product which was crystallized from ethyl acetate-n-hexane (identity confirmed by analysis, m.p., and i.r. spectroscopy). The solid residue was paramagnetic.

Physical Measurements.—Absorption spectra were recorded with a Carlo Erba 601 Spectracomb spectrophotometer, i.r. spectra of Nujol mulls with a Perkin-Elmer 1330 spectrophotometer, and ^1H n.m.r. spectra with a Bruker WP80SY spectrometer equipped with an Aspect 2000 computer.

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