A NOVEL CATALYST SYSTEM FOR THE ULLMANN CONDENSATION IN AQUEOUS SOLUTION.REACTION OF A HALOGENOANTHRAQUINONE WITH ANILINE

Tran Dinh TUONG

(Institute of Industrial Science,University of Tokyo,Roppongi,Minato-ku,Tokyo 106) and Mitsuhiko HIDA

(Faculty of Technology, Tokyo Metropolitan University, Fukusawa, Setagaya-ku, Tokyo 158)

The yield of the Ullmann condensation of sodium 1-amino-4-bromoanthraquinone-2-sulfonate with aniline in an alkaline aqueous solution was improved markedly by using the system $[Cu^{2+} + metal redu$ cing agent (such as Fe²⁺, Ti³⁺, Sn²⁺)] compared with the conventional procedures using only copper(Cu²⁺ or Cu⁺) salts.

Although the Ullmann condensation reaction has been used widely in the syntheses of diarylamines, diarylethers, etc. , the selection of the copper catalyst is still largely empirical due to the lack of knowledge of the true catalytic species. Thus, while suggestion has been made that cuprous copper is responsible for the catalytic effect ¹⁾ in some cases, cupric salts have also been pointed out to be more effective²⁾ in other instances. In this paper, we report that in the Ullmann condensation reaction of sodium 1-amino-4-bromoanthraquinone-2-sulfonate with aniline in an alkaline solution, the yield of the reaction was markedly improved by using the catalyst system [Cu²⁺ + metal reducing agent (such as Fe²⁺, Ti³⁺, Sn²⁺)].

The yields of the reaction promoted by various catalysts were summarized in Table 1 (following page).

It was also found that cupric sulfate and cuprous chloride gave almost the same yields when used $alone^{3}$ and that ferrous, titanous and stannous salts did not promote the reaction in the absence of a copper salt.

Kinetic studies revealed that the metal reducing agents accelerated the cupric catalyzed reaction during the earlier stage, and the rate decreased with time, and



(Major product)

(By-product)

TABLE 1 a,b)

Catalyst	Cu ²⁺	$Cu^{2+} + Fe^{2+}$	Cu ²⁺ + Ti ³⁺	$Cu^{2+} + Sn^{2+}$
Ym ^{c)}	21.50	70.02	86.95	95.28
Y _b d)	0.25	1.88	0.70	0.95

a) $[I]_{o}=1.25 \times 10^{-2} \text{ mol/l}, [PhNH_2]_{o} = 0.30 \text{ mol/l}, [Cu^{2+}] = [Fe^{2+}] = [Ti^{3+}] = [Sn^{2+}] = 2.50 \times 10^{-4} \text{ mol/l}$ (The metal ions were introduced in the reaction system in the form of an aquoeous solution of cupric sulfate, ferrous sulfate, titanous chloride and stannous chloride, respectively), pH = 9.94 (borax-sodium carbonate buffer), T = 46°C, reaction time: 30 min. Runs in a nitrogen atmosphere.

b) The reaction products were separated (paper) chromatographically and determined quantitatively by spectrometric measurements ($\lambda_{max}(I) = 484 \text{ nm}, \lambda_{max}(II) = 604 \text{ nm}, \lambda_{max}(III) = 540 \text{ nm}$) c) Yield of the major product (= 100 [II]/[I]₀)

d) Yield of the by-product (= 100 [III]/[I]₀)

finally, the reaction seemed to proceed at the same rate as in the system where only cupric (or cuprous) salt was used. The kinetic profile is shown in Figure 1 (following page) where the pseudo-first order plots for the two systems (one catalyzed by Cu^{2+} , the other by Cu^{2+} + Fe²⁺) are illustrated.

These observations suggest that an interaction between the cupric ion and the metal reducing agent occurred and yielded a highly catalytically reactive intermediate species, and that the latter was consumed in an irreversible process.



The interaction was in fact proved by electron spin resonance measurements. Thus, it was found that while the ESR absorption of Cu²⁺ species in the Cu^{2+} (only) catalyzed system remained unchanged during all the reaction time, 4) the addition of, for example, ferrous sulfate caused the intensity of the signal due to Cu²⁺ species to decrease monotonously, and finally, to disappear after ca. 5 minutes.

The ESR spectra recorded for the sys-

tem $[Cu^{2+} + Fe^{2+}]$ in pure water proved that the interaction between the metal ions did not occur in the low pH range.

The ESR and kinetic data could be understood by the assumption that in the alkaline aqueous solution, an electron transfer process took place via a briged intermediate [C] possessing high catalytic activity in the Ullmann condensation:

$$Cu^{2+} + Fe^{2+} \xrightarrow{OH} Cu^{-} Fe \longrightarrow Cu^{+} + Fe^{3+}$$
[C]

The postulated intermediate [C] is thought to collapse to cuprous species(the catalytic effect of which is comparable to the Cu^{2+} salt initially used³⁾) and ferric salts by an irreversible process. This latter assumption is justified by

the observation that while the cupric salt (only) catalyzed system was homogeneous, a precipitate was formed as the result of the introducing of ferrous sulfate. The precipitate was proved to contain ferric species by ESR measurements.

Further studies are being carried out to establish the synthetic utility of the findings reported in this paper and to contribute to the understanding of the mechanism of the Ullmann condensation which has not yet fully elucidated.

The authors thank Mr. T.Tabei of the Nihon Kayaku,Co.,Ltd., for his helps in some experiments.

REFERENCES

1)H. Weingarten, J. Org. Chem. 29, 978, 3624 (1964).

2)T. Tomita et al, Chem. Pharm. Bull. (Japan), <u>13</u>, 1341(1965).

3)T. D. Tuong and M. Hida, Bull. Chem. Soc. Japan, 44, 765(1971).

4)T. D. Tuong and M. Hida, ibid., <u>43</u>, 1763(1970).

(Received January 22, 1973)

366