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# Michael Addition of Acetonitrile to Chalcones under Ultrasound Irradiation

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When chalcones were treated with potassium superoxide ($KO_2$) in acetonitrile under ultrasound irradiation, chalcone-acetonitrile adducts were obtained in moderate yields.

Since nitriles are hydrolyzed to give carboxylic acids or reduced to give primary amines, synthesis of nitriles is one of the most important chemical reactions. The synthesis of nitriles involving carbon-carbon bond formation is then extensively studied.$^{1,2)}$ Kohler et al. have reported that chalcone (<u>1a</u>) reacts with cyanoacetic ester under basic conditions to give cyanoacetic ester adduct, whose alkaline hydrolysis product, cyano acid, is thermally decomposed to give 4-cyano-1,3-diphenyl-1-butanone (<u>2a</u>).$^{3)}$ Boyer et al. have reported that cinnamonitrile reacts with acetophenone under CsF-Si(OMe)$_4$ catalysis to give <u>2a</u>.$^{4)}$ Recently, we have reported the cyanomethylation reaction of Schiff bases in acetonitrile in the presence of $KO_2$ under mild conditions.$^{5)}$ We report here a new and convenient method for the synthesis of chalcone-acetonitrile adducts <u>2a-g</u>.

Chalcone (<u>1a</u>) (0.48 mmol) and powdered $KO_2$ (1.41 mmol) were suspended in dry acetonitrile (50 cm$^3$) in a test tube (80 cm$^3$). The solution was then irradiated for 15 minutes in the water bath of an ultrasonic laboratry cleaner (45 kHz, 100 W). After the reaction, NaCl and water were added and the reaction mixture was extracted with ether and dried over $Na_2SO_4$. After the evaporation of the organic layer, the residue was separated by thin-layer chromatography (<u>n</u>-$C_6H_{14}$:$CHCl_3$=1:3). The products were identified on the basis of $^1H$ and $^{13}C$ NMR, mass, and IR spectra. Product determination was made by gas chromatography.

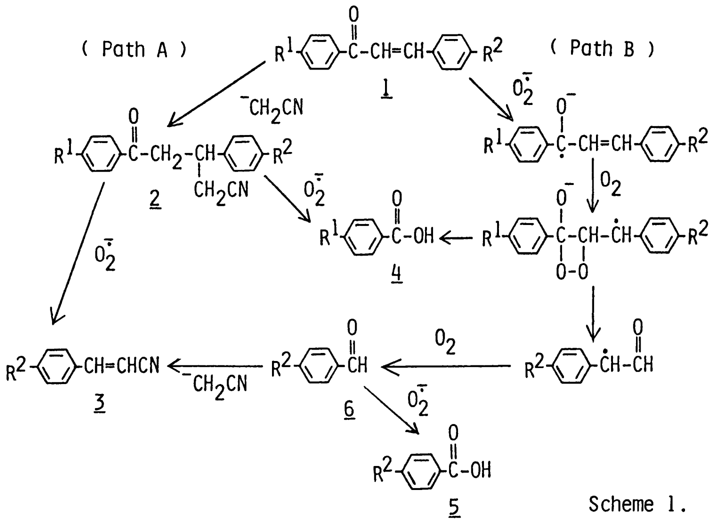
Table 1. Cyanomethylation of chalcones

| | Substituent | | Conversion | Yield / %$^{a)}$ | | | |
|---|---|---|---|---|---|---|---|
| Compound | $R^1$ | $R^2$ | % | <u>2</u> | <u>3</u> | <u>4</u> | <u>5</u> |
| <u>1a</u> | H | H | 53 | 64 | 5 | 18 | |
| <u>1b</u> | OMe | H | 82 | 47 | 8 | 7 | 4 |
| <u>1c</u> | Me | H | 68 | 40 | 8 | 14 | 5 |
| <u>1d</u> | Cl | H | 83 | 67 | 8 | 14 | 3 |
| <u>1e</u> | H | OMe | 82 | 33 | 5 | 3 | 3 |
| <u>1f</u> | H | Me | 100 | 54 | 4 | 19 | 10 |
| <u>1g</u> | H | Cl | 99 | 55 | 2 | 10 | 7 |

a) Yields were based on converted substrate.

The results of the reaction are summarized in Table 1. Chalcone-acetonitrile adduct 2a was obtained as the main product in 64% yield, accompanied by small amounts of cinnamonitrile (3a) and benzoic acid (4a). When MeO, Me, and Cl derivatives of chalcone 1b-g reacted under the same conditions, the corresponding acetonitrile adducts 2b-g were obtained in 33-67% yields.

A probable mechanism is shown in Scheme 1. Superoxide ion ($O_2^{\cdot-}$) acts as a Brønsted base and abstracts proton from acetonitrile to give cyanomethyl anion.6) The Michael addition of this anion to β-carbon atom of 1 gives 2 (path A). Since the active species produced in this system are cyanomethyl anion and $O_2^{\cdot-}$, there are two possibilities for the formation of 3, 4, and 5. One is the oxidative decomposition of 2 by $O_2^{\cdot-}$ followed by dehydration (path A). When adduct 2a was irradiated, 3a and 4a were produced in 3 and 21%, respectively. Another is the oxidation of 1 by $O_2^{\cdot-}$ to give 4 and 5 (path B).7, 8) Though aldehyde 6 is not isolated, it is easily converted into 3.9, 10)



Scheme 1.

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8) When 1a was stirred in acetonitrile at room temperature, 2a, 3a, and 4a were produced in 29, 14, and 22% yields, respectively (cf; Tab.1, run 1). This result suggests that ultrasound irradiation precedes path A.

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10) Ultrasound irradiation of 6a with acetonitrile in the presence of $KO_2$ gives 3a in 65% yeild.

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