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# Condensation of Ethyl Cinnamates with Benzyl Cyanides

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**Different substituted ethyl cinnamates reacted with substituted benzyl cyanides in the presence of sodium ethoxide at room temperature to give a single isomer of ethyl $\beta,\gamma$-diaryl-$\gamma$-cyanobutyrates. The reaction products were identified on the basis of their IR, NMR, MS, and elemental analysis data.**

## Introduction

In the course of our study on the reactivity of $\alpha,\beta$-unsaturated esters toward compounds having active methylene groups we reported the condensation of $\alpha$-phenyl-*p*-morpholinoacetophenone with ethyl arylpropiolates (*1*), as well as the condensation of ethyl arylpropiolates with cycloketones (*2*). The condensation of benzyl cyanides with ethyl phenylpropiolates (*3*) or ethyl arylpropiolates (*4*) has also been documented in the literature. Since the benzyl cyanides are good Michael donors and useful reagents for carbon–carbon bond formations the present work was intended to extend the study of the condensations of substituted ethyl cinnamates with benzyl cyanides.

## Experimental Section

Unless otherwise stated, IR spectra were measured with a Pye-Unicam SP 300 spectrophotometer for solutions in chloroform, ${}^1$H NMR spectra with a Brucker WP 80-SY spectrometer for solutions in deuterated chloroform containing tetramethylsilane as internal standard, and MS spectra with a 7070-E VG analytical organic mass spectrometer. Compounds were analyzed at the M-H-W-Laboratories, Phoenix, AZ. Melting points were determined with an electrothermal melting point apparatus and were uncorrected. Elemental analyses in agreement with theoretical values were obtained and submitted for review.

In each condensation, equimolar amounts of substituted benzyl cyanide and substituted ethyl cinnamates were added successively to a suspension of sodium ethoxide in dry ether (150 mL). The mixture was kept at room temperature for 3–7 days and then poured into water (250 mL) and extracted with ether. The ethereal extract yielded a crude solid which after recrystallization from the appropriate solvent afforded ethyl $\beta,\gamma$-diaryl-$\gamma$-cyanobutyrate. The alkaline aqueous layer was acidified with dilute sulfuric acid and extracted with ether and the ethereal solution was shaken with sodium hydrogen carbonate solution. Evaporation of the ether yielded a further amount of the desired product.

## Results and Discussion

Ethyl $\beta,\gamma$-diaryl-$\gamma$-cyanobutyrates (I) were obtained by the reaction of substituted ethyl cinnamates with substituted benzyl cyanides in the presence of sodium ethoxide at room temperature. Studies of the condensation products showed that the reaction proceeded through the Michael addition of the car-

Table I. Results for Ethyl $\beta,\gamma$-Diaryl-$\gamma$-cyanobutyrates (Ia–j)

| compd | reaction time, days | cryst solvent | mp, °C | yield, % | NMR ($CDCl_3$) $\delta$ (protons) |
|---|---|---|---|---|---|
| Ia | 3 | EtOH | 94–95 | 66 | 1.15 (3 H, t)<br>4.08 (2 H, q)<br>2.82 (2 H, d)<br>3.45 (1 H, m)<br>4.36 (1 H, d)<br>7.20 (9 H, m) |
| Ib | 4 | EtOH | 106–108 | 73 | 1.13 (3 H, t)<br>4.08 (2 H, q)<br>2.80 (2 H, d)<br>3.43 (1 H, m)<br>4.32 (1 H, d)<br>7.25 (9 H, m) |
| Ic | 6 | EtOH | 91 | 64 | 1.14 (3 H, t)<br>4.05 (2 H, q)<br>2.89 (2 H, d)<br>3.63 (1 H, m)<br>4.63 (1 H, d)<br>7.25 (9 H, m) |
| Id | 4 | EtOH | 113–115 | 83 | 1.25 (3 H, t)<br>4.15 (2 H, q)<br>3.00 (2 H, d)<br>3.83 (1 H, m)<br>4.33 (1 H, d)<br>7.55 (11 H, m) |
| Ie | 7 | MeOH | 207–208 | 53 | 0.76 (3 H, t)<br>3.97 (2 H, q)<br>2.98 (2 H, d)<br>3.48 (1 H, m)<br>4.82 (1 H, d)<br>7.25 (7 H, m) |
| If | 7 | aq EtOH | 148–149 | 80 | 1.23 (3 H, t)<br>4.19 (2 H, q)<br>2.94 (2 H, d)<br>3.49 (1 H, m)<br>4.34 (1 H, d)<br>7.48 (10 H, m) |
| Ig | 4 | MeOH | 118–120 | 58 | 1.26 (3 H, t)<br>4.20 (2 H, q)<br>3.09 (2 H, d)<br>3.75 (1 H, m)<br>4.28 (1 H, d)<br>7.30 (11 H, m) |
| Ih | 5 | aq MeOH | 128 | 58 | 1.08 (3 H, t)<br>4.08 (2 H, q)<br>2.82 (2 H, d)<br>2.24 (3 H, s)<br>3.34 (1 H, m)<br>4.32 (1 H, d)<br>7.50 (9 H, m) |
| Ii | 6 | MeOH | 74–75 | 59 | 1.05 (3 H, t)<br>3.94 (2 H, q)<br>2.64 (2 H, d)<br>2.24 (3 H, s)<br>3.43 (1 H, m)<br>4.45 (1 H, d)<br>7.37 (8 H, m) |
| Ij | 4 | MeOH | 118 | 71 | 1.12 (3 H, t)<br>4.08 (2 H, 6)<br>3.01 (2 H, 6)<br>2.25 (3 H, s)<br>3.81 (1 H, m)<br>4.35 (1 H, d)<br>7.70 (1 H, m) |

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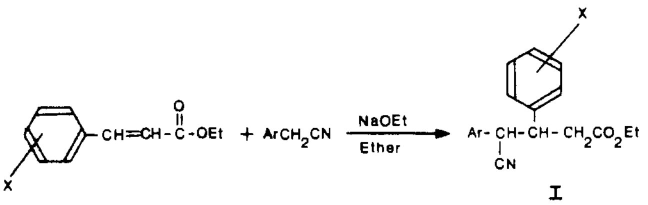
banion ArCHCN to the ethyl cinnamates as shown in the following scheme.



I

| | X | Ar |
|---|---|---|
| a. | H | $p$-Cl·$C_6H_4$– |
| b. | H | $p$-Br·$C_6H_4$– |
| c. | H | $o$-F·$C_6H_4$– |
| d. | H | α-naphthyl |
| e. | $o,p$-dichloro | $p$-Cl·$C_6H_4$– |
| f. | $o,p$-dichloro | α-naphthyl |
| g. | $p$-Br | α-naphthyl |
| h. | $p$-$CH_3$ | $p$-Br·$C_6H_4$– |
| i. | $p$-$CH_3$ | $o$-F·$C_6H_4$– |
| j. | $p$-$CH_3$ | α-naphthyl |

Although a priori two diastereomers are possible, the condensation under these conditions proceeded with the formation of only one single isomer. The structure of the reaction products was deduced from their spectral data as well as their elemental analysis. The infrared spectral data showed an absorption band at 2240 $cm^{-1}$ which corresponds to the cyano group, and the band at 1730 $cm^{-1}$ was characteristic of the ester carbonyl stretching frequency (*5*). The proton nuclear magnetic resonance spectral data (Table I) gave evidence for the structure of the ethyl β,γ-diaryl-γ-cyanobutyrates. The carbethoxy group appeared as triplet and quartet δ 1.15 and 4.08 integrating for three and two protons, respectively. A doublet at 4.36 integrating for one proton was attributed to the γ-methine proton. The β-methine proton appeared as multiplet at 3.45. This high degree of spin–spin splitting is expected due to the presence of the two diastereomeric protons at the α-carbon (*6*). Another doublet at 2.82 integrating for two protons corresponding to the α-methylene protons was observed. The aromatic protons appeared as multiplet at 7.20. The mass spectroscopy of these compounds showed exact molecular ion peaks $M^+$ and the elemental analysis of these compounds was in good agreement with the theoretical values.

**Registry No.** Ia, 100899-37-4; Ib, 100899-38-5; Ic, 100899-39-6; Id, 17532-78-4; Ie, 100899-40-9; If, 100909-01-1; Ig, 100899-41-0; Ih, 100899-42-1; Ii, 100899-43-2; Ij, 100899-44-3; $p$-$ClC_6H_4CH_2CN$, 623-03-0; $p$-$BrC_6H_4CH_2CN$, 623-00-7; $o$-$FC_6H_4CH_2CN$, 394-47-8; $PhCH{=}CHCOOEt$, 103-36-6; $p$-$BrC_6H_4CH{=}CHCOOEt$, 15795-20-7; $p$-$MeC_6H_4CH{=}CHCOOEt$, 20511-20-0; 2,4-$Cl_2C_6H_3CH{=}CHCOOEt$, 1504-68-3; α-naphthylacetonitrile, 132-75-2.

### Literature Cited

(1) Shandala, M. Y.; Al-Khashab, A.; Al-Arab, M. M. *J. Iraqi Chem. Soc.* **1977**, *2*, 53.
(2) Shandala, M. Y.; Al-Khashab, A.; Al-Jobour, N. H.; Al-Arab, M. M. *J. Prakt. Chem.* **1979**, *6*, 321.
(3) Al-Jallo, H. N.; El-Kholy, I.; Shandala, M. Y.; Al-Hajjar, F. *J. Chem. Soc., C* **1969**, 915.
(4) Shandala, M. Y.; Al-Jallo, H. N., Al-Jobour, N. H.; Al-Hajjar, F. H. *J. Chem. Eng. Data* **1979**, *21*, 115.
(5) Nakanishi, K.; Solomon, P. H. "Infrared Absorption Spectroscopy", 2nd ed.; Holden-Day: San Francisco, 1977; p 40.
(6) Pavia, D. L.; Lampman, G. M.; Kriz, G. S. "Introduction to Spectroscopy"; Saunders: Philadelphia, 1979; p 152.

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# Synthesis and Spectroscopic Data of 3,3′,5,5′-Tetrabromo-4,4′-diaminodiphenyldibromomethane

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**3,3′,5,5′-Tetrabromo-4,4′-diaminodiphenyldibromomethane has been synthesized and its spectral and thermal characteristics have been examined.**

Diaminodiphenylmethane (DADPM) is widely used in the synthesis of polyamides (*1*) and polyurethanes (*2*) and as a cross-linking agent for epoxy resins (*3*, *4*) and polyurethane elastomers (*5*, *6*). Since bromine compounds are used to promote flame retardancy in polymers (*7*, *8*), the bromo derivative of DADPM can act as a cross-linking agent-cum-fire retardant. Recently, tetrabromobisphenol-A has been used as such an additive in COCl-terminated polybutadiene (*9*).

Bromination of DADPM gives 3,3′-dibromo-4,4′-diaminodiphenylmethane (*10*, *11*) and 3,3′,5,5′-tetrabromo-4,4′-diaminodiphenylmethane (TB-DADPM) (*10*–*13*); the latter has been used as a flame retardant additive in polyamides (*14*) and polyurethanes (*12*). The synthesis of a hexabromo derivative of DADPM, which will be a more effective flame retardant because of its high bromine content, is not reported so far. In the present communication, the synthesis, characterization, and thermal stability of 3,3′,5,5′-tetrabromo-4,4-diminodiphenyldibromomethane (HB-DADPM) are discussed.

## Experimental Section

DADPM was synthesized according to the procedure of Scalan (*15*). HB-DADPM was prepared as follows. To a dilute HCl solution of DADPM (500 mg) bromine entrained in $N_2$ at room temperature was passed until the reaction mixture begins to show charring. The solid thus obtained was thoroughly washed with water and recrystallized from benzene (yield 800 mg).

IR spectra were recorded as Nujol mull on a Perkin-Elmer 597 spectrophotometer. $^1H$ NMR spectra were recorded on a 60-MHz Varian T-60 spectrometer at ambient temperature in $Me_2SO$-$d_6$ containing $Me_4Si$ as internal standard; $^{13}C$ NMR spectra were recorded on a Bruker WH-270 FT spectrometer at room temperature. The solvent $Me_2SO$-$d_6$ provided the required deuterium lock. The solutions (ca. 10% w/v) contained

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