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## Reaction of Cinnamoyl Chloride with a Dialkylcadmium Reagent

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and the aqueous layer made alkaline with aqueous sodium hydroxide. The amine was separated by ether extraction and the combined ether extracts were dried and stored over barium oxide. Derivatives prepared included the picrate (m.p. 215-225°) and the diacetyl derivative XVIIa (m.p. 301-305°).

*Anal.* Calcd. for  $C_{20}H_{22}N_2O_2$ : C, 74.5; H, 6.87; N, 8.69.  
Found: C, 74.3; H, 6.99; N, 8.6.

The pure amine was isolated by the same technique employed for isolation of the diphenyldiaminocyclobutane VIIIa.

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## Reaction of Cinnamoyl Chloride with a Dialkylcadmium Reagent<sup>1</sup>

KENNETH W. KRAUS<sup>2</sup>, RICHARD T. BOGAN AND RICHARD M. WEIER

*Abstract.* It was demonstrated that a dialkylcadmium reagent would successfully react with the unsaturated acid chloride, cinnamoyl chloride, under both ordinary conditions and at 0° in the presence of ferric chloride to give the alkyl styryl ketone in yields of 54% and 46% respectively. The *n*-butyl styryl ketone obtained in the reaction displayed infrared absorption at 5.92  $\mu$  (C=O) and at 6.04  $\mu$  (C=C). The dipole moment was found to be 3.16 D in benzene solution at 25°.

It has been reported (1) that alkyl styryl ketones were not isolated from the reaction of cinnamoyl chloride with dialkylcadmium reagents, although benzalacetophenone was obtained when the same acid chloride was treated with diphenylcadmium. It is significant however, that these attempts were made prior to important modifications in the reaction of organocadmium

<sup>1</sup> (a) Richard T. Bogan was an N.S.F. Undergraduate Research Participant during the summer of 1962 and the 1962-63 academic year; (b) Richard M. Weier was an N.S.F. Undergraduate Research Participant during the 1961-62 academic year.

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reagents with acid chlorides which were introduced by Cason (2).

Recently a quantity of *n*-butyl styryl ketone was desired and it was decided to reinvestigate this reaction. The attempt with di-*n*-butylcadmium under the ordinary conditions (3) was successful in producing a 54% yield of *n*-butyl styryl ketone.

It may also be pointed out that a 46% yield of the same product was obtained when the reaction was run at 0° in the presence of ferric chloride catalyst. The low temperature reaction of an organocadmium reagent in the presence of ferric chloride has been described (4) as useful in giving unrearranged product in an instance where the rearrangement of the intermediate acylium ion interfered with the normal organocadmium reaction. More recently the successful application of these conditions was reported for aliphatic and aromatic cadmium reagents with saturated aliphatic and aromatic acid chlorides (5).

The current success of an unsaturated acid chloride in the ordinary reaction with an organocadmium reagent and in the low temperature reaction in the presence of ferric chloride extends the potential synthetic utility of the organocadmium reaction.

It is interesting that several trials with cinnamoyl chloride at a reaction temperature of -10° in the presence of ferric chloride gave no ketone product, although this temperature was successful for saturated acid chlorides (4). Studies to determine just how critical the temperature is for various acid chlorides are currently in progress.

#### EXPERIMENTAL

*Cinnamoyl chloride* was prepared by refluxing 119 g. (0.8 mole) of cinnamic acid and 172 g. (1.45 moles) of thionyl chloride for three hours. Excess thionyl chloride was removed under reduced pressure and the residue was vacuum distilled. A total of 122 g. (90%) of white crystalline cinnamoyl chloride was obtained with a melting point of 34-35°; literature m.p. 35-36° (6).

*n*-Butyl styryl ketone (*Benzylidenemethyl n*-butyl ketone). (A) *Ordinary cadmium reaction.* The cadmium reagent was prepared in the usual way (3) from *n*-butylmagnesium bromide made from 63.8 g. (0.46 mole) of *n*-butyl bromide and 11.2 g. (0.46 mole) of magnesium turnings. After the ether was removed and replaced with benzene, 25 g. (0.15 mole) of cinnamoyl chloride in benzene solution was added over a 15 minute period. Finally the reaction was refluxed for one hour and it was stopped by the addition of ice and dilute sulfuric acid.

After a typical workup (3), the product was vacuum distilled to give 15.2 g. (54%) of n-butyl styryl ketone, b.p. 147.5–148.5° (8 mm.). After distillation the yellow product solidified and re-crystallization from ligroin with a Dry Ice-acetone bath gave white crystals, m.p. 37–38°, 2,4-dinitrophenylhydrazone m.p. 196–197° and phenylhydrazone m.p. 97–98°; literature m.p. 38–39° and literature phenylhydrazone m.p. 97.5–98.5° (7). The product displayed infrared absorption at  $5.92\mu$  ( $C=O$ ) and at  $6.04\mu$  ( $C=C$ ). The dipole moment was found to be 3.16 D.

(B) *Low temperature, ferric chloride catalyzed reaction.* The cadmium reagent was prepared from the same amounts of starting materials as in (A). Instead of removing the ether however, the cadmium reagent was cooled to  $-5^\circ$  and 3.6 g. (0.023 mole; 15 mole % based on acid chloride) of anhydrous ferric chloride dissolved in ether was added. Next 25 g. (0.15 mole) of cinnamoyl chloride dissolved in ether was added at a rate suitable to maintain a temperature of  $0^\circ$ . The reaction mixture was then stirred at  $0^\circ$  for 30 minutes and stopped by the addition of ice and dilute sulfuric acid. After the workup, the product was vacuum distilled to give a yield of 13 g. (46%) of n-butyl styryl ketone with the same physical properties as in (A).

*The dipole moment measurement and calculation.* The dipole moment was measured and calculated according to the method previously described by Rev. R. J. Dolter, et. al. (8).

The slope-intercept data for the dilute solutions of n-butyl styryl ketone in benzene at  $25^\circ$ ;  $\epsilon_1 = 2.2722$ ,  $\alpha = 6.0012$ ,  $d_1 = 0.8715$ ,  $\beta = 0.1673$ ,  $n_1 = 1.4979$ ,  $\gamma = 0.05718$ . The molar polarization was determined to be 265.1 and the molar refraction 57.3 ml.

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