VINYL CARBANIONS DERIVED FROM CIS-CINNAMONITRILE-REACTIONS WITH ELECTROPHILES AND CONFIGURATIONAL STABILITY

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(Received in U.K. 25 September 1980)

Abstract—Vinyl carbanions derived from *cis*-cinnamonitrile 1 were formed by reacting it with lithiur n-copropylamide (LDA) as a base in aprotic solvents at low temperatures; reaction with various electrophiles ($_,F$) sulted in the corresponding derivatives PhCH=C(E)CN. The configurational stability of the vinyl carbanions derived from 1 and the geometry of the reaction products was affected by the solvating properties of the medium. Retention of configuration was achieved in a poor solvating medium-diethyl ether-hexane (4:1). Addition of a crown ether or using THF as solvent resulted in products having trans geometry. The site of deprotonation of cinnamonitrile (*cis* and *trans*) was compared to that of cinnamic esters and discussed. Determination of the geometry of the products was based on their ¹H NMR spectra.

The use of vinyl carbanions derived from activated olefins as nucleophiles in organic synthesis, has been recently studied.¹⁻⁹ Vinyl carbanionic intermediates of

the type $\sum C = C \xrightarrow{L_{1}^{+}} C = C \xrightarrow{L_{1}^{+}}$

H-D exchange reactions in 2, 2, 4, 6, 6-pentamethylclohexylideneacetonitrile,¹⁰ in fluorene-9-ylideneacetonitrile,¹¹ and trans-cinnamonitrile,¹² which were kinetically studied. Vinyl carbanions (at C_{α}) derived from trans-B-(1-pyrrolidinyl)acrylonitrile,¹⁶ B, β -diphenylacrylonitrile⁵ and trans-cinnamonitrile⁶ were reacted with various electrophiles to yield the corresponding reaction products. The use of vinyl carbanions as nucleophiles is not a straightforward one because of certain complications and competing reactions, some of which are: (a) Nucleophilic addition of the base at C_{μ} of the olefin (Michael addition). (b) Nucleophilic addition at C_{α} when C_{β} is sterically hindered, followed by elimination of either an electronegative substitutent^{13,14} or H⁻¹⁴ from the intermediate carbanion. (c) Depending on the experimental conditions (e.g. reaction temp) deprotonation of each of the two vinyl hydrogens of a 1, 2-disubstituted ethylene (such as β substituted acrylic acid derivatives) is either kinetically or thermodynamically controlled resulting in different vinyl carbanions in each case.^{1b.15} (d) When an amide having an H atom at C_{α} is used in an olefin-baseelectrophile reaction system, a hydride transfer from the amide to certain reaction products may take place.¹⁶ (e) Vinyl carbanions like the isoelectronic ketimines,¹⁷ are capable of undergoing cis-trans isomerization.

This isomerization is obviously important for the application of vinyl carbanions in organic synthesis, because of its effect on the geometry of the expected products. The information on the configurational stability and stereochemistry of vinyl carbanions is limited and is mostly related to that of alkenyl and stilbenyl carbanions.¹⁸ Very little has been reported in this regard on vinyl carbanions having electronegative substituents at $C_{\alpha}^{7,9,10,19,20,21}$ Reactions of *cis*-cinnamonitrile 1 with various electrophiles (in presence of a base) were studied in the present work. The comparison of the stereochemistry of these reactions to that of *trans*-cinnamonitrile 2⁶ and to that of *cis*- and *trans*-ethylcinnamate,⁹ offers a good possibility to study some effects of solvent and of the nature of the electronegative substituent at C_{α} , on the configurational stability of the derived vinyl carbanions.

RESULTS AND DISCUSSION

Vinyl carbanions formed by reaction of *cis*-cinnamonitrile 1 with lithiumdiisopropylamide (LDA) at low temperatures (-80 to -100°), were applied as nucleophiles in some substitution and addition reactions. Methyl iodide, methanol-0-d, and ethanol-0-d, benzophenone, cyclopentenone and α -cyano- β , β -diphenylacrylonitrile were used as electrophiles. The reactions were carried out in most cases by adding a mixture of 1 and the electrophile into a cooled LDA solution. The experimental conditions applied and the results obtained are presented in Table 1. All the reaction products obtained were the C_{α} derivatives of cinnamonitrile. ¹H NMR data and elementary analysis of the reaction products are given in Table 2.

A profound solvent effect on the configurational stability of the derived vinyl carbanions was observed. All the reaction products formed in THF and benzene had a *trans* geometry, whereas a mixture of the corresponding *trans* (3, 13%) and *cis*(4, 23%) derivatives was obtained in DEE, using benzophenone as an electrophile (Exp. 3). A complete retention of configuration was observed on carrying out the reaction in a mixed solvent composed of DEE-hexane (4:1) (Exp. 4, 5). However, in the presence of a crown ether, a product having a *trans* geometry was obtained in this medium (Exp. 6).

In all the reactions carried out, Michael addition products of LDA to 1 were not detected at all. This fact combined with the retention of the *cis* geometry of the

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Table 1. Reaction of cis-cinnamonitrile with electrophiles in presence of LDA

| Exp. | Method | [<u>]]</u> mmole | LDA mmole | E | [E] mmole | Solvent | °C | t (min) (t ₁ +t ₂) ^a | Product | gr | (%) |
|-----------------|--------|----------------------|------------------|--------------------------------------|--------------|---------------------|------------------|---|--|------|------|
| 1 | A | 5 | 15 | Ph2C=0 | 7.5 | THF | -100 | 20+30 | A-C(OH)Ph2 ^b 3 | 1.40 | (92) |
| 2 | A | 5 ^C | 15 | Ph2C=0 | 7.5 | THF | -100 | 20+30 | A-C(OH)Ph ₂ | 0.83 | (54) |
| 3 ⁿ | | 5 | 15 | Ph ₂ C=0 | 7.5 | DEE | -80 | 20+30 | A-C(OH)Ph2 | 0.20 | (13) |
| | | | | | | | | | A'-C(OH)Ph ₂ <u>4</u> | 0.37 | (23) |
| 4 | A | 5 | 7.5 ^e | Ph ₂ C=0 | 5.5 | DEE-hexane (4:1) | -75 | 5+30 | A'-C(OH)Ph ₂ | 0.95 | (61) |
| 5 | A | 5 | 10 | Ph2C=0 | 7.5 | | -115 | 20+60 | A'-C(OH)Ph2 | 1.50 | (95) |
| б ^f | A | 5 | 7.5 | Ph ₂ C=0 | 7.5 | DEE-hexane (4:1) | -75 | 5+30 | A-C(OH)Ph ₂ | 0.70 | (45) |
| 7 | В | 5 | 7.5 | Ph ₂ C=0 | 7.5 | | -75 | 0 ¹ +60 | A-C(OH)Ph ₂ | 0.58 | (37) |
| 8 | A | 5 | 7.5 | Ph ₂ C=0 | 7.5 | Benzene | 0 | 5+30 | A-C(OH)Ph ₂ | 0.45 | (31) |
| 9 | A | 5+5 ⁹ | 5 | Ph ₂ C=0 | 10 | THF | -90 | 20+45 | A'-H : A-H =0.61 | | |
| 10 | A | 5+5 ⁹ | 5 | Ph ₂ C=0 | 10 | THF | -90 | 0+60 | A'-H : A-H =0.61 | | |
| 11 | В | 5 | 15 | $\square = 0$ | 7.5 | THF | -100 | 0+60 | A-(| 0.70 | (56) |
| 12 | В | 5 | 7.5 ^e | Ph ₂ C=C(CN) ₂ | 5 | THF | -100 | 0+15 | A-C(CN)2CHPh2 6 | 1.12 | (62) |
| 13 | 8 | 2.5 | 5 | снзі | 7.5 | THF | -100 | 0 ¹ +30 | A-CH ₃ <u>7</u> | | (72) |
| 14 ⁿ | ß | 5 | 15 | CH3I | 25 | THF | -100 | 0 ¹ +15 | A-CH3 | 0.08 | (10) |
| | | | | | | | | | A''-CH ₃ j <u>B</u> | 0.14 | (19) |
| 15 | B | 5 | 7.5 | сн ₃ т | 15 | THF | -100 | 20 ^K +30 | A-CH3 | | (35) |
| | | | | | | | | | A''-CH ₃ | | (7) |
| 16 | В | 5 | 7.5 | сн _з ор | | THF | -100 | 0 ¹ +10 | A-H+A-D | 0.28 | (43) |
| | | | | | | | | | A-H : A-D =35:65 | £. | |
| 17" | В | 5 | 7.5 | EtOD | | DEE-hexane | -75 ^C | 0 ¹ +5 ^m | A'-H+A'-D+A-H+A-D | 0.28 | (43) |
| | | | | | | (4:1) | | | A'-H:A'-D:A-H:A-D 4:17:26:53 ^t | = | |
| 18 | В | 5 | 7.5 | EtOD | | DEE-hexane | -75 | 0 ¹ +5 ^m | A'-H+A'-D+A-H+A-D | 0.30 | (46) |
| | | | | | | (4:1) | | | A'-H:A'-D:A-H:A-D 3:12:33:53 [£] | = | |

a. t_1 - the time of addition of a mixture of <u>1</u> and the electro- g. A mixture of <u>1</u> (S mumole) and <u>2</u> (S mumole) was used. h. When 2 was used the yield was 38%. phile into the LDA solution: t_2 - reaction time after

> i. The electrophile was added in one portion into the 1-LDA solution.

$$J \cdot A^{1/2} = \frac{Ph}{CH_3}C = C CN$$

- k. The electrophile was added dropwise during 20 min into the 1-LDA solution.
- 1. The ratio was determined by H-nmr.
- m. The solution of 1 was added dropwise during 20 min into the 1-LDA solution. The mixture was further stirred for 5 min and ethanol-0-d was then added in one portion.
- n. See experimental.

- addition of the 1-electrophile.
- $\frac{Ph}{H} > C = C < CN$ Ъ. А =
- c. Trans-cinnamonitrile (2) was used in this experiment.
- d. A' = $\frac{Ph}{H} c = c < CN$
- e. The base used was LTMP
- f. The reaction was carried out in the presence of dibenzo [12]-crown-4.

Table 2. Reaction products of cis-cinnamonitrile with electrophiles in presence of LDA

| | | Se la | | H-NMR da | ta ^a | | Analysis | ave |
|--------------|--|--------------------------------|--------------------------------------|------------------------|------------------------------------|--------------|---------------------------------|------------|
| | | , ()° | ۲Ħ | в ^н | ᄓᆂ | °± | (Found, Required) | (_ |
| | ₆ H ₅ ^{C(0H^B)(ε₆H₅) ₂} | 185-7 | 7.58 | 2.78 | 6.88-7.52 | | C, 85.09; H, 5.50; N, 4.51 | 311 |
| 0 1 | A C | (EA-PE) | (N1, 2) | (Hl, 2) | (m,15H) | _ | C, 84.86; H, 5.50; N, 4.50 | |
| | 0, HA , , c(0H ^B) (c ₆ H ₅) 2 | 155-7 | 7.13 | 2.88 | 7.25-7.60 | 7.65-7.85 | C, 84.34; H, 5.57; N, 4.56 | 311 |
| 41 | 5 " " " " " " " " | (EA-PE) | (H,s) | (Hl,s) | (m,13H) | (m,2H) | C, 84.86; H, 5.50; N, 4.50 | 1 |
| | ₹ Ωr. αr. | | 2.00-2.60 | 3.25-3.75 | 7.10-7.50 | | C. 79.60; H, 6.20; N, 6.63 | 211 |
| امر | | | (m,5H) | (m,2H) | (m,6H) | | C. 79.58; H. 6.28; N. 6.60 | |
| 9 | | 175-82(d) | 7.30 | 4.63 | 6.80-7.10 | 7.20-7.60 | C, 83.24; H, 4.78; N, 11.50 | 359 |
| 1 | $\frac{1}{4}$ $\frac{1}{6}$ $c = c - c + c + 2 - c + $ | | (Hl*s) | (Hl, s) | (m,2H) | (H()(m) | C, 83.58; H, 4.73; N, 11.69 | |
| P | C ₆ H ₅ CH ₃ b | | 2.10 | 7.13 | 7.34 | | | 143 |
| ~1 | BH ^C ⁻ CN | | (HE ' s) | (Hl,m) | (m,5H) | | | |
| 0 | c ₆ H5 CH ^A | | 1.87 | 2.35 | 7.00-7.30 ^c | | | 157 |
| 01 | | | (H£*s) | (HE, 2) | (m, 5H) | | | |
| - 21 Dilla - | z spectrum in CDC1 ₃ , TMS used as an isomers (2.04, 2.14 ppm) are given ir | internal star n the literat | ldard, § units ure. ²⁴ | . ^b Ref. 27 | . ^c The CH ₃ | absorption 1 | bands for the E(1.83, 2.36 ppm) |] |

products, under certain experimental conditions, suggest that a $cis-C_{\alpha}$ vinyl carbanion $1-\alpha A$ is the intermediate initially formed. This carbanion could then either react with an electrophile, or isomerize to the *trans-C_{\alpha}* vinyl carbanion $2-\alpha A$ prior to its reaction with the electrophile (Scheme).

The deuteration of 1 by methanol-0-d or ethanol-0-d was carried out by (Exp. 16-18) introducing the alcohol in one portion into the cooled LDA-olefin solution. The crude product consisted of deuterated and non-deuterated cinnamonitriles ($\sim 40\%$) and of a mixture of oligomeric products which was not identified. A mixture of trans-cinnamonitriles-2(35%) and $2-\alpha d(65\%)$, was recovered from the deuteration reaction in THF. The olefinic mixture recovered from the reaction in DEE: hexane (4:1) contained $1(\sim 4\%)$, $1-\alpha d(\sim 15\%)$, $2(\sim 30\%)$ and $2-\alpha d(\sim 50\%)$. The deuteration results again indicate that although the isomerization of $1-\alpha A$ to 2- αA is fast even in aprotic solvents of low dielectric constant, $1-\alpha A$ has a higher configurational stability in DEE-hexane mixed solvent as compared to THF. It is therefore obvious that a practical way to obtain the α -derivatives of 1, is to add the electrophile togetter with 1 (when this is possible) into the base-DEE: hexane solution. When done so, using benzophenone as an electrophile, the cis product 4, was obtained (Exp. 4, 5), whereas the trans product 3 was obtained on adding the ketone into the LDA-1 solution (Exp. 7).

The presence of non-deuterated 2 in the olefin mixture recovered from the deuteration mixtures, might be due to a partial protonation of $2-\alpha A$ by the diisopropyl amine present, or to the following proton transfer:

$$cis$$
-PhCH==CH-CN + $trans$ -PhCH== \overline{C} -CN
 $\Rightarrow cis$ -Ph-CH== \overline{C} -CN + $trans$ -PhCH==CH-CN.

There are indeed some indirect indications that 1 is more acidic than 2. The yield of 3 obtained in the 2-benzophenone-LDA-THF system was significantly lower (Exp. 2) than that obtained in the corresponding 1 system (Exp. 1). In addition to it, on reacting an equimolar mixture of 1 and 2 with benzophenone in the presence of LDA (Exp. 9), the consumption of 1 was much faster than that of 2. These observations might indicate that the acidity of the C_{α} -H bond of 1 is larger than that of 2. This phenomena could be attributed to the higher ground state energy of 1 as compared to that of 2.

The base-catalyzed deuteration of 1 in THF resulted in a product having a *trans* geometry-2- α d (Exp. 16), while the deuteration of *cis*-ethylcinnamate (CEC) under comparable conditions gave CEC- α d⁹. It turns out that besides the solvating properties of the medium, the functional group at C_{α} , is a significant factor which affects the configurational stability of a vinyl carbanion. It has been suggested that the stabilizing effect of the ester group on the configuration of the Li salt of CEC- αA , might be due to a coordination of the Li⁺ ion by the non-bonded 2Pz electrons of the CO group.⁹ The



configurational instability of $1-\alpha A$ in THF is thus interpreted as due to both the decreased coordination of the Li⁺ by the linear C = N group, and to the solvating properties of this medium.

The reaction products of 1 and 2⁶ in THF with electrophiles, in the presence of bases, were the C_{α} derivatives, PhCH = C(E)CN.

The corresponding products in the case of the CEC and *trans*-ethyl-cinnamate (TEC) under comparable conditions were always (except for the CEC-LDA-MeOD system) the C_{β} derivatives of TEC. *trans*-PhCE=CH-COOEt.⁹ This difference between cinnamonitrile and the cinnamic ester with regard to the site of the deprotonation may be again caused by the possible stabilization of the *trans* configuration of the C_{β} vinyl carbanion TEC- βA by the ester group, which is less pronounced with the nitrile group.^{1,15}



The reaction of 1 with MeI in THF in presence of LDA afforded the *trans* - α - methyl - cin namonitrile 7. In some cases the *trans*- α , β -dimethylcinnamonitrile 8 was formed as a by-product (Exp. 13-15). It was obviously formed by a further deprotonation (at C_{β}) of the already formed momethylation product, followed by methylation of the derived vinyl



carbanion. The dimethylation seems to depend on both the ratio and the concentrations of reactants (1, LDA, MeI) and the mode of addition (in one portion or dropwise) of the methyl iodide to the 1-LDA solution. A detailed study on how to direct the reaction towards dimethylation was not carried out. The *trans* geometry ascribed to the dimethyl derivative, was based on the ¹H NMR data previously described for the *cis* and *trans* isomers of 2-cyano-3-phenyl-but-2-ene.²⁴

¹H NMR spectra was used to determine the geometry of products 3-8 (Table 2). A deshielding effect of the -CN group was observed in the case of *cis*-1-cyano-2phenyl olefins (and not with *trans* isomers), causing a clear downfield shift of the absorption band of two out of the five H atoms of the phenyl group. Examples of this effect are shown in the NMR spectra of some unsaturated nitriles (δ , CDCl₃):

cis-Cinnamonitrile (5.40, d, 1H; 7.13, d, 1H; 7.10–7.55, m, 3H; 7.53–8.00, m, 2H), *trans*-cinnamonitrile (5.85, d, 1H; 7.35, d, 1H; 7.05–7.73, m, 5H), fluorene-9-yilideneacetonitrile (5.91, s, 1H; 7.10–7.90, m, 7H; 8.20–8.60, m, 1H),²⁵ fluorene-9-yilidenemalononitrile (7.18–7.43, m, 6H; 8.31, m, 2H),²⁶ α -methyl-*cis*-cinnamonitrile (2.06, s, 3H; 6.80, bs, 1H; 7.30, m, 3H; 7.60, m, 2H).²⁷

Based on this type of characterization of the geometry of cinnamonitrile derivatives, it is obvious that compound 4 is a derivative of *cis*-cinnamonitrile, while all other compounds (Table 2) are derived from the *trans* isomer.

EXPERIMENTAL

Materials. cis-Cinnamonitrile was prepared by isomerization of trans-cinnamonitrile.²⁸ THF was kept as a soln with sodium naphthalene or sodium benzophenone ketyl. Absolute hexane, diethyl ether (DEE) and benzene were kept over Na. The required amount of solvent was directly distilled from these stock solns into the reaction flask.

The reaction of cis-cinnamonitrile with electrophiles in presence of LDA

General procedures. The experimental conditions, the experimental methods and the results are given for each experiment in Table 1. Structures of the products obtained, their m.p., ¹H NMR data and elementary analysis are given in Table 2. The lithium amide used as base (LDA) was prepared by adding an equimolar amount of BuLi or t-BuLi (dissolved in hexane) into the diisopropylamine-solvent soln. All the manipulations and the reaction itself were carried out under N₂ and anhydrous conditions. Two types of procedures were used for the reaction of 1 with electrophiles in the presence of a base.

Method A. A soln of both 1 and the electrophile in the required solvent (10 ml) was added dropwise during t_1 min into the cooled LDA-solvent (40 ml) soln. The mixture which became colored, was stirred for another t_2 min at the reaction temp, and then extracted with a water-chloroform mixture. The organic layer was washed with water, dried and the solvent evaporated. The residue left behind was subjected to either crystallization or column chromatography to yield the pure products.

Method B. 1 dissolved in the required solvent (10 ml) was added dropwise during 5-10 min into the LDA-solvent soln (30 ml) at the reaction temp. A soln of the electrophile in the same solvent (10 ml) was then added in one portion ($t_1 = 0$) into the LDA-1 soln, and the whole mixture was then stirred for t_2 min at the reaction temp.

Further workup of the mixture was done as described for method A.

Deuteration of cis-cinnamonitrile (Exp. 17)

A solution of 1 (0.65 g, 5 mmole) in DEE-hexane (4:1) (10 ml) was added dropwise during 1 min into a cooled (-78°) solution of

LDA (7.5 mmole) in DEE-hexane (4:1) (40 ml). The mixture was stirred for 5 min and ethanol-0-d (3 ml) was added. Stirring was continued for 10 min, water-chloroform added, and the organic layer was separated, dried and evaporated. The residue was separated by column chromatography. A mixture of cinnamonitriles was obtained (0.28 g, 43%), its composition determined by its ¹H NMR spectrum (see Table 1).

The reaction of cis-cinnamonitrile (1) with benzophenone in DEE in presence of LDA (Exp. 3)

A soln of 1 (0.65 g, 5 mmole) and benzophenone (1.37 g, 7.5 mmole) in DEE (15 ml) was added dropwise during 20 min into a cooled (-80°) soln of LDA (10 mmole) in DEE (35 ml). The colored soln was further stirred for 30 min. A water-chloroform mixture was then added and the organic layer was dried and evaporated. The viscose residue was treated with a 1:1 mixture of EtOAc and petroleum ether. The ppt formed was filtered off and crystallized to give 3 (0.20 g, 13%) m.p. 185-7° (from 1:1 EA-PE). The combined filtrates were evaporated and the residue was crystallized to give 4 (0.37 g, 23%) m.p. 155-7° (from 1:1 EA-PE).

The reaction of cis-cinnamonitrile with methyliodide in THF in presence of LDA (Exp. 14)

1 (0.65 g, 5 mmole) dissolved in THF (10 ml) was added dropwise during 10 min into a cooled (-100°) soln of LDA (15 mmole) in THF (40 ml). The mixture was stirred for 5 min and MeI (0.61 g, 25 mmole) was then added in one portion. Stirring was continued for 15 min (at -100°) and a water-chloroform mixture was then added. The residue solidified after treatment with an EA-PE mixture. The yellow ppt formed was a quaternary ammonium salt. The residue recovered from the filtrate (0.74 g) was separated by column chromatography to give the monomethyl derivative 7 (0.08 g, 10%) and the dimethyl derivative **8** (0.14 g, 19%).

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