The Configurational Stability of Vinyl Carbanions Derived from Monosubstituted Activated Ethylenes

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The configurational stability of vinyl carbanions derived from the 1-substituted activated ethylenes, acrylonitrile and methyl acrylate, was investigated. The pure *cis*-isomers of the corresponding β-deuterio-olefins were treated with benzophenone in the presence of a base in several solvents (diethyl ether, tetrahydrofuran, and diethyl ether–hexane). *cis–trans* Mixtures of the corresponding α-[hydroxy-[(diphenyl)methyl] derivatives formed were isolated and their composition determined. The mechanism of the formation of the two isomeric products is discussed. The vinyl carbanion derived from the β-deuterioacrylonitrile was configurationally stable, while that derived from the corresponding acrylic ester was configurationally unstable.

Vinyl carbanions derived from 1,2-disubstituted activated ethylenes by an acid–base type reaction [equation (1)] have been recently used as nucleophiles in organic synthesis.[1a—l]


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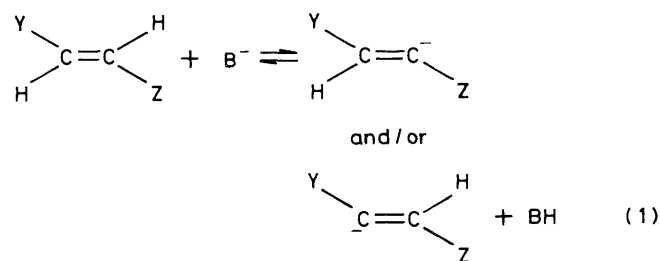
Z and Y = electronegative substituents

One problem with this is the need to prevent the isomerization of the vinyl carbanion formed, prior to its reaction with an electrophile, so that the original geometry of the olefin is preserved in the reaction product. This, of course, will depend on the configurational stability of the vinyl carbanions, which in turn should be affected by the structure of the carbanion, the ion-pairing characteristics of the carbanion metal salt, the solvating properties of the reaction medium, and the electronegative substituents. The effects of these factors on the configurational stability of sp³-type carbanion salts have been widely studied,[2] but very little work has been reported for vinyl carbanions.[1h,3a—c]

Recent results indicate that one of the substituents of 1,2-disubstituted ethylenes of the type YC(2)H=C(1)HZ (Z,Y=CN, Ph;[1h] CN, OEt;[4a] CN, NR₂;[4b] CO₂R,NR₂;[1a] CO₂R, SR;[4c] CO₂R, Ph;[1l] or CO₂R, OR[4d]) affects the configurational stability of the vinyl carbanion salt on the neighbouring carbon atom by a preferential stabilization of one configuration (mostly the *trans*). This was explained by the crowding effect in the ground state of the *cis*-isomer, and a relatively efficient internal co-ordination of the carbanion metal salt by this substituent. We have investigated the effect of an electronegative substituent Z, in the absence of any influence from the β-substituent, on the configurational stability of a vinyl carbanion derived from an activated olefin >C(β)=C(α)HZ.

Results and Discussion

Monosubstituted ethylenes such as CH₂=CHZ were used in order to avoid any influence from a β-substituent. The *cis*- or

(1b)
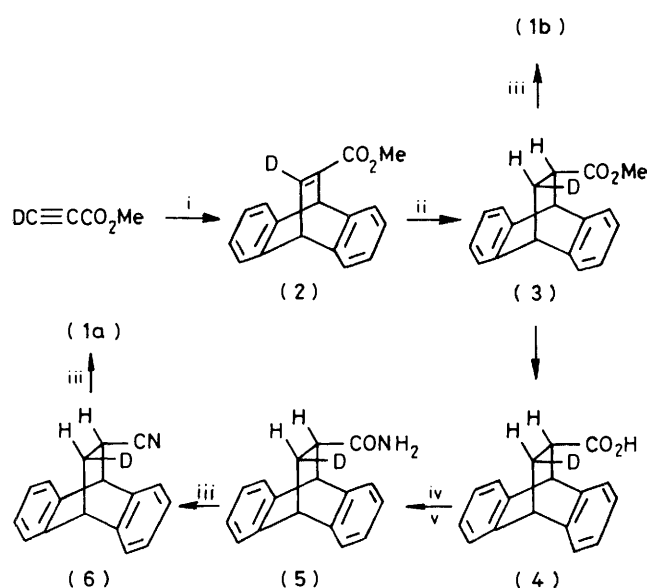
Scheme 1. *Reagents:* i, C₁₄H₁₀; ii, H₂, Pd–C; iii, 300 °C; iv, SOCl₂; v, NH₃

trans-isomer of the β-deuterio derivative, CHD=CHZ, were suitable for the present work. *cis*-β-Deuterioacrylonitrile (1a) and methyl *cis*-β-deuterioacrylate (1b) were used.

Synthesis of the cis-*Isomers of* β-*Deuterioacrylonitrile* (1a) *and Methyl* β-*Deuterioacrylate* (1b).—The synthetic sequence used to prepare (1a) and (1b) is summarized in Scheme 1. The synthesis of the nitrile (1a) was based on the work of Hill and Newkome;[5] methyl acrylate stereospecifically deuteriated at the β-position was prepared by the catalytic hydrogenation of the Diels–Alder adduct of methyl 3-deuteriopropiolate and anthracene (2), and the reduced adduct (3) pyrolysed at 300 °C to yield pure methyl *cis*-β-deuterioacrylate (1b). Improved procedures described by Cristol and Noreen[6] for the deuteriation of methyl propiolate and for the preparation of the adduct (2) were used in the present work.

Pure isomers of β-deuterioacrylonitrile have not been obtained by any of the available methods. These include deuteriation of cyanoacetylene over a Lindlar catalyst[7] and reduction of propiolamide or deuteriated propiolamide using chromous chloride–D₂O or LiAlD₄ as reducing agents.[8a,b]
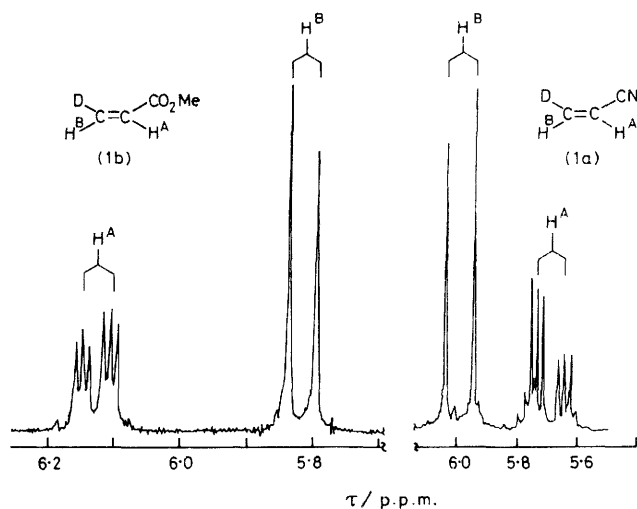
Figure. ¹H N.m.r. spectra of cis-β-deuterioacrylonitrile (1a) and methyl cis-β-deuterioacrylate (1b)

a; Z = CN
b; Z = CO₂Me

Reagents: i, Base; ii, CHCl₃–H₂O

The pure isomer (1a) was prepared in the present work by an extension of the method of Hill and Newkome. The hydrogenated adduct (3) was hydrolysed to the corresponding acid (4); this was converted into the amide (5) which was dehydrated to the nitrile (6). This nitrile was pyrolysed to yield pure cis-β-deuterioacrylonitrile (1a). The ¹H n.m.r. spectra of (1a) and (1b) are given in the Figure.

A severe practical difficulty associated with the formation of vinyl carbanions by treating monosubstituted activated ethylenes with bases is the very facile anionic polymerization of such olefins for which the base and/or the derived vinyl carbanions [9] might act as initiators. Because of this very effectively competing anionic polymerization reaction, all studies on the formation, chemistry, and stereochemistry of vinyl carbanions derived from activated olefins have been carried out with 1,2-disubstituted and 1,2,2-trisubstituted activated ethylenes, which undergo anionic polymerization much less readily if at all. However, this difficulty was satisfactorily circumvented in a recent study, in which optimal experimental conditions were established for the reaction of a vinyl carbanion derived from acrylonitrile with benzophenone.[10]

The Reaction of cis-β-Deuterioacrylonitrile (1a) and cis-β-Deuterioacrylate (1b) with Benzophenone in the Presence of Base.—A solution of each of the deuteriated olefins (1a) and (1b) together with an electrophile (benzophenone) was added dropwise to a solution of lithium di-isopropylamide (LDA) [for (1a)] or lithium tetramethylpiperidide (LTMP) [for (1b)] at low temperatures [(equation (2)].

The crude mixture of the reaction products was separated into its constituents by column chromatography. The proportions of the cis- and trans-isomers in the fraction containing the product was quantitatively determined from its ¹H n.m.r. spectra. This was done by comparing the relative intensities of the absorption bands of the trans C(β)-H (τ 4.15) of (7a) and the cis C(β)-H (τ 3.83) of (8a), and those of the trans C(β)-H (τ 4.81) of (7b) and the cis C(β)-H (τ 3.60) of (8b) (Table 1).

A study on the configurational stability of a vinyl carbanion derived from an acrylonitrile derivative was recently carried out, using the cis-cinnamonitrile–LDA–benzophenone–solvent system.[1h] It was confirmed that a relatively good solvating
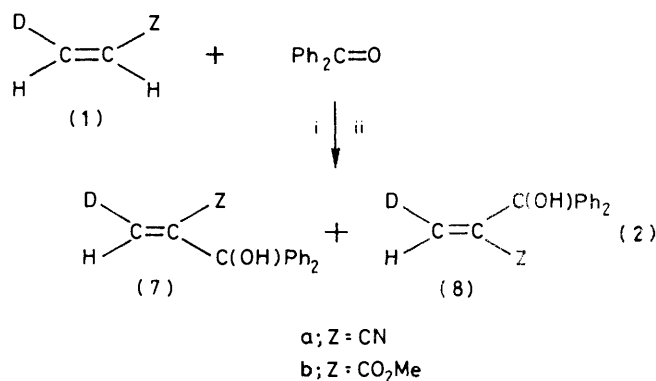
medium [tetrahydrofuran (THF) [11]] led to complete isomerization of the derived vinyl carbanion, while the cis geometry of the double bond was unchanged in the reaction product [PhCH=C(CN)C(OH)Ph₂] in a poorly solvating medium (diethyl ether–hexane, 4 : 1 [11]). In view of this, (1a) was treated under comparable conditions with benzophenone in diethyl ether (DEE), THF, DEE–hexane (4 : 1), and DEE containing an effective solvating agent hexamethylphosphoric triamide (HMPT). The results are summarized in Table 2. The ratio of (7a) : (8a) for each run was practically constant (ca. 7 : 3) irrespective of the reaction medium used.

A reasonable conclusion from the partial retention of configuration was that the vinyl carbanion (1a)′ derived from (1a) was involved in the formation of at least part of the product (7a) obtained. It was the mechanism by which the trans-product (8a) was formed that required an explanation. The fact that the (7a) : (8a) ratio was independent of the solvating properties of the reaction medium presented another problem, because the configurational stability of carbanion salts would be expected to be dependent on their ion-pairing characteristics.[2]

Three possible reaction pathways for the formation of the mixture of (7a) and (8a) are outlined in Scheme 2. (a) An addition–elimination reaction pathway [(1a) —→ (10a)′ —→ (11a)′ —→ (12a)′ —→ (7a) + (8a)].
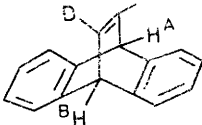
(b) A vinyl carbanion reaction pathway [(1a) —→ (1a)′ —→ (9a)′ —→ (7a) + (8a)].

(c) A combined addition–elimination/vinyl carbanion pathway [(1a) —→ (10a)′ —→ (1a) + (9a) —→ (1a)′ ⊢ (9a)′ —→ (7a) + (8a)].
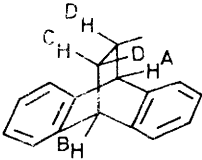
In spite of the fact that the addition products (10a) and (11a) were not detected at all in the crude mixture of the reaction products, either one of the two addition–elimination reaction pathways (a) or (c) could still be considered to be responsible for the formation of (8a) assuming that either $k_4 \gg k_{-3}$ and k_5 or $k_{-3} \gg k_3$ and k_5, respectively. The non-deuteriated compound (11) was synthesized [10] and subjected to the typical experimental conditions under which (1a) was treated with benzophenone (THF, excess of LDA, −78 °C) to yield the mixture of (7a) and (8a). No reaction took place and practically all the starting material was recovered,[10] indicating that neither (8a) nor (7a) was formed by the reaction pathway (a). On treating a mixture of (7a) and (8a) (3 : 2) with an excess of LDA in THF at −78 °C for 1 h, no other products were obtained and the starting mixture with the same composition was recovered. This might indicate that no interconversion of (7a) and (8a) takes place in the (1)–LDA–benzophenone reaction system.

The formation of a mixture of (7a) and (8a), with (7a) in excess, could have resulted from pathway (b) if isomerization of (1a)′ to (9a)′ took place to some extent, followed by con-
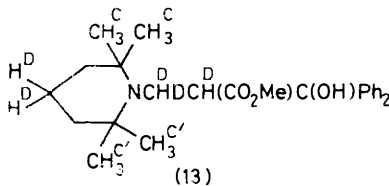
Table 1. ^{1}H N.m.r.,^{a} i.r., and mass spectral data ^{b} for compounds (1)—(8) and (13)


(2)　　　　　　(3)—(6)　　　　　　(13)

Compd.	H^A	H^B	H^C	H^D	CO$_2$CH$_3$	Benzene H	CO$_2$H or OH	M/z	V$_{max.}$ (cm^{-1})
(2)	4.25 (s, 1 H)	4.71 (s, 1 H)			6.30 (s, 1 H)	3.05—2.40 (m, 8 H)			
(3)	5.27 (s, 1 H)	5.65 (d, 1 H)	8.00 (bdd, 1 H)	7.13 (dd, 1 H)	6.40 (s, 1 H)	3.00—2.45 (m, 8 H)		265 (C$_{18}$H$_{15}$DO$_2$)	1 735
(4)	5.29 (d, 1 H)	5.63 (d, 1 H)	8.00 (bdd, 1 H)	7.10 (dd, 1 H)		3.00—2.40 (m, 8 H)	1.00 (bs, 1 H)	251 (C$_{17}$H$_5$DO$_2$)	
(5)	5.25 (d, 1 H)	5.60 (d, 1 H)	8.20 (dd, 1 H)	7.25 (dd, 1 H)		2.90—2.20 (m, 8 H)			
(6)	5.40 (d, 1 H)	5.59 (d, 1 H)				3.00—2.30 (m, 8 H)		232 (C$_{17}$H$_{12}$DN)	2 240
(1b)^e	3.877 (dt, 1 H, J 11.70, J 2.69)	4.185 (d, 1 H, J 1.47)			6.250 (s, 3 H)				
(7b)^d and (8b)	3.60^f (s, 0.5 H)	4.81^g (s, 0.5 H)			6.27 (s, 3 H)	2.66—2.60 (m, 10 H)	4.80^j (s, 1 H)	269 (C$_{17}$H$_{15}$DNO$_3$)	
(1a)^e	4.317 (dt, 1 H, J 11.72, J 2.68)	3.340 (d, 1 H, J 11.47)							
(7a)^d and (8a)	3.83^h (s, 0.28 H)	4.15^i (s, 0.72 H)				2.62—2.60 (m, 10 H)	6.88^j (s, 1 H)	236 (C$_{16}$H$_{12}$DND)	3 460 2 240 2 280w
(13)			9.05, 9.12 (2 s, 12 H)	8.60 (m, 8 H)	6.40 (s, 3 H)	2.75—2.25 (m, 10 H)	4.92 (bs, 1 H)	4.10 (C$_{26}$H$_{34}$DNO$_3$)	3 500 1 710

^{a} τ Values (CDCl$_3$) using a 60 MHz spectrophotometer; the spectrum of (5) was measured in (CD$_3$)$_2$SO; the spectra of (1a) and (1b) were measured on a 250 MHz spectrophotometer. J Values are in Hz. ^{b} Elemental analyses were all in accord with the formulae given for the compounds. ^{c} Labelling for the assignments of compounds (1a) and (1b) is given in the Figure. ^{d} ^{1}H N.m.r. data of a mixture of the cis- and trans-isomers. ^{e} The structures assigned to the cis-β-deuteriated olefins (1a) and (1b) are based on the stereochemistry of the retro Diels–Alder reactions of (3) and (6), respectively (Scheme 1), and on the ^{1}H n.m.r. data for the vinylic hydrogen atoms of the α,β-dideuterio olefins (A)—(C) (see below): (A), τ (neat) 3.7;^{5} (B), τ (CCl$_4$) 4.20;^{5} τ (CDCl$_3$) 3.81;^{8b} (C), τ (CDCl$_3$) 3.96.^{8b} ^{f} Absorption band of the cis-C(β)-H (cf. ref. 5 and footnote e). ^{g} Absorption band of the trans-C(β)-H (cf ref. 5 and footnote e). ^{h} Absorption band of the cis-C(β)-H (cf. ref. 8b and footnote e). ^{i} Absorption band of the trans-C(β)-H (cf. ref. 8b and footnote e).

(A)　　　　　　(B)　　　　　　(C)
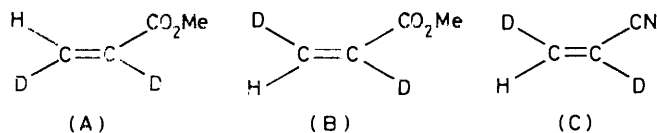
version of (1a)′ into (7a) and (9a)′ into (8a) at equal rates (k_s). It might, however, be reasonably assumed that the vinyl-carbanion (1a)′ cannot have a partial configurational stability under the same conditions (DEE–hexane, 4 : 1, –80 °C, LDA) as those in which the vinyl carbanion derived from cis-cinnamonitrile showed a 100% retention of configuration.^{1h} In fact, the configurational stability of (1a)′ would be expected to be larger than that of the β-phenyl derivative. The formation of (8a) by pathway (b) to more than a minor extent can therefore be ruled out.

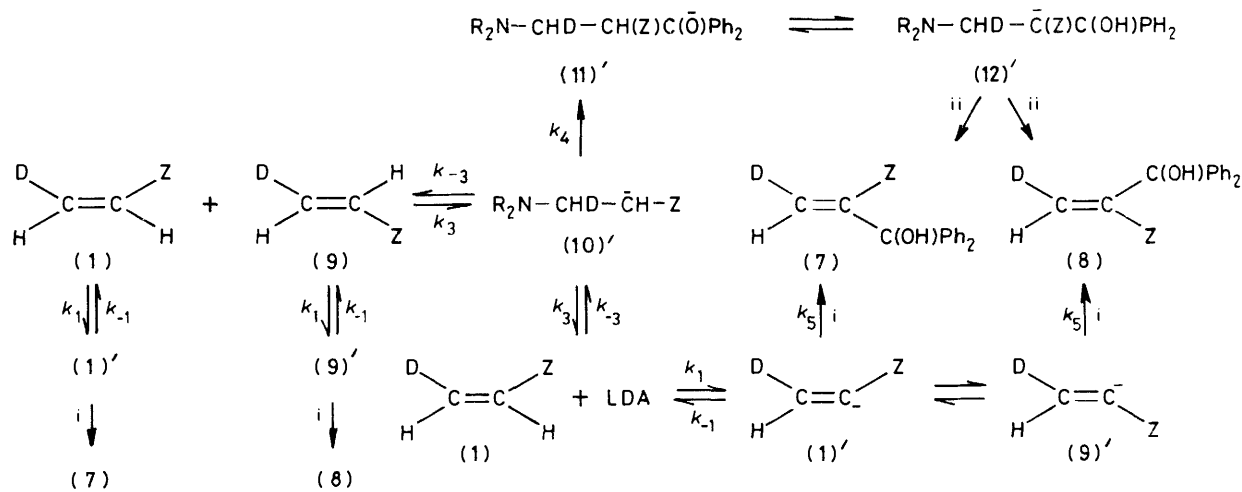The configurational stability of a carbanion salt should decrease in relation to the type of ion-pairing in the order :

contact ion-pair > solvent-separated ion-pair > free ion.$^{12a-e}$ This decreasing order parallels the increasing order of the solvating properties of the solvents used: DEE–hexane (4 : 1) < DEE < THF < DEE–HMPA.^{13} The constancy of the (7a) : (8a) ratio observed in all these solvents (Table 2) is not in accord with the expected effect of the reaction medium on the configurational stability of (1a)′, and hence on the (7a) : (8a) ratio.

The lithium salt of (10a)′ is involved in reaction pathway (c) which is the remaining alternative for the formation of (8a). Cram and his co-workers ^{14,12a} observed a high degree of retention of configuration of a carbanion derived from an

Table 2. Reaction of cis-β-deuterioacrylonitrile (1a) and methyl cis-β-deuterioacrylate (1b) with benzophenone in presence of a base [a]

Olefin	Amount (mmol)	Benzo-phenone (mmol)	Solvent	Temp. (°C)	Reaction products (g, %)		Ratio (7) : (8)
(1a)	4.12	6.0	DEE	−80	(7a) + (8a) (0.170, 17.5)		71 : 29
	4.12	6.0	THF	−80	(7a) + (8a) (0.300, 31)		68 : 32
	4.12	6.0	DEE–hexane (4 : 1)	−80	(7a) + (8a) (0.180, 18.5)		73 : 27
	3.09	4.0	DEE [b]	−80	(7a) + (8a) (0.120, 16.5)		74 : 26
	3.09	4.0	THF	−110	(7a) + (8a) (0.090, 12.3)		70 : 30
(1b)	2.50	3.75	DEE	−80	(7b) + (8b) (0.180, 27)	(13) (0.120, 13) (14) (0.210, 36.8)	1 : 1
	2.44	3.43	DEE	−115	(7b) + (8b) (0.160, 24.4)	(13) (0.160, 13.2) (14) (0.320, 57)	1 : 1
	4.00	6.00	DEE–hexane (4 : 1)	−80	(7b) + (8b) (0.040, 4)	(13) (0.180, 12) (14) (0.360, 39)	1 : 1
	2.40	3.43	THF	−80	(7b) + (8b) (0.160, 24.8)	(13) (0.150, 16.9) (14) (0.250, 45.6)	1 : 1

[a] The reactions of (1a) and (1b) were carried out in the presence of LDA and LTMP, respectively. [b] A solvating agent, HMPT (3.09, mmol), was used.

$$R_2N-CHD-CH(Z)C(\bar{O})Ph_2 \rightleftharpoons R_2N-CHD-\bar{C}(Z)C(OH)Ph_2$$

(11)′   (12)′

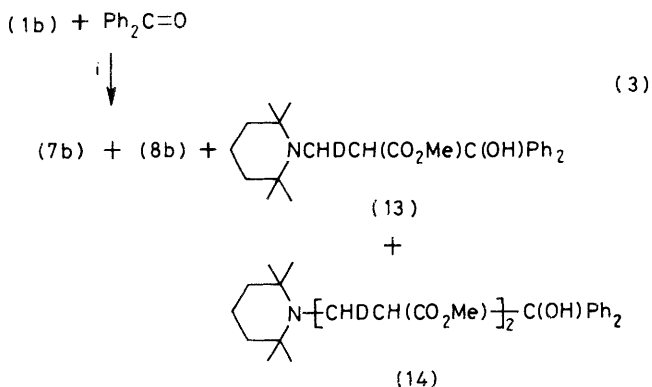**Scheme 2.** *Reagents:* i, $Ph_2C=O$; $^-NR_2{}^-$

optically active carbon acid in a nonpolar aprotic medium when an amine was used to deprotonate the acid. In such a case, the high rate of reprotonation of the asymmetric carbanion by the corresponding ammonium ion resulted in the retention of configuration. However, complete racemization was observed when the anion was used as base due to the relatively slow reprotonation of the carbanion by the neutral conjugate acid. It might therefore be assumed that complete isomerization of (10a)′ occurs prior to the elimination of LDA, leading to its conversion into a 1 : 1 mixture of cis- and trans-β-deuterioacrylonitrile (1a) and (9a); this mixture, after deprotonation to (1a)′ and (9a)′ by the LDA present, followed by reaction with the benzophenone present, might yield a 1 : 1 mixture of (7a) and (8a).

If this mechanism applies, increasing the extent of the addition of the amide ion to the cis-olefin on account of its deprotonation to the derived vinyl carbanion (by decreasing steric hindrance on either the nucleophile or on the β-carbon of the olefin), should increase the yield of the trans-isomer. Indeed, on treating the sterically less hindered lithium diethylamide with cis-cinnamonitrile (as a cis-olefin model) and benzophenone in DEE–hexane (4 : 1), a mixture of the cis- and trans-isomers of the product PhCH=C(CN)C(OH)Ph₂ was

obtained in the ratio 3 : 2; this contrasts with the previously reported complete retention of the cis-geometry when LDA was used as the base.[1h] Similarly, and in line with the above mechanistic conclusion, the reaction of the sterically unhindered [at C(β)] cis-β-deuterioacrylonitrile (1a) with benzophenone in the presence of LDA in DEE–hexane (4 : 1), resulted in a mixture of the cis- and trans-products (7a) and (8a) containing ca. 30% of the trans-isomer, while the cis-β-phenyl-substituted acrylonitrile yielded the corresponding cis-isomer only.[1h]

To summarize, on the basis of the above results and considerations, we suggest for the acrylonitrile–LDA–benzophenone reaction system that: (i) the cis-product (7a) was formed by both reaction pathways (b) and (c), while the trans-product (8a) was formed predominantly by pathway (c). Both (7a) and (8a) were formed via the corresponding vinyl carbanion intermediates, and not by an addition–elimination mechanism; and (ii) the vinyl carbanion (1a)′ derived from (1a) [as well as (9a)′] is configurationally very stable, which might be the reason for the observed independence of the (7a) : (8a) ratio of the solvating properties of the reaction medium.

The reaction of methyl cis-β-deuterioacrylate (1b) with

(1b) + $Ph_2C=O$

i |

(7b) + (8b) + [structure: $NCHDCH(CO_2Me)C(OH)Ph_2$] (13)

+

[structure: $N-[CHDCH(CO_2Me)]_2-C(OH)Ph_2$] (14)

(3)

Reagents: i, LTMP, solvent

benzophenone was carried out in THF, DEE, and DEE–hexane (4 : 1) using LTMP as base. The expected hydroxy-(diphenyl)methyl derivatives (7b) and (8b) were obtained, as well as two additional products (13) and (14) [equation (3)].

A 1 : 1 mixture of (7b) and (8b) was obtained in all the solvents used. The yields of this mixture were low compared with the yields of (13) and (14). The latter compounds were obviously formed by the addition of LTMP to the olefin (1b) followed by reaction of the intermediate carbanion with benzophenone to give (13), or, by its consecutive addition to (1b), to give the corresponding dimeric carbanionic intermediate; reaction of this with benzophenone would then give (14).

If all the 1 : 1 mixtures of (7b) and (8b) are formed by the vinyl carbanion reaction pathway (b) [(1b) —→ (1b)′ —→ (9b)′ —→ (7b) + (8b)] it should be concluded that the vinyl carbanion derived from methyl acrylate is not configurationally stable under the experimental conditions used. Neither of the reaction products (7b) and (8b) was formed on treating (13) with an excess of LDA in THF at −78 °C (see Experimental section). This indicated that the mixture of (7b) and (8b) could not be formed by the addition–elimination pathway (a) [(1b) —→ (10b)′ —→ (11b)′ —→ (12b)′ —→ (7b) + (8b)], in spite of the fact that the addition of LTMP to (1b) took place to a relatively high extent (Table 2). It might, therefore, be assumed that at least part of the mixture of (7b) and (8b) was formed *via* the reaction pathway (c) [(1b) —→ (10b)′ —→ (1b) + (9b) —→ (1b)′ + (9b)′ —→ (7b) + (8b)]. The sp³-type carbanionic intermediate (10b)′ is configurationally unstable under the experimental conditions used.[12a,14] It follows that the fraction of (1b) that reacts by pathway (c) is isomerized to a 1 : 1 mixture of (1b) and (9b), which further reacts *via* (1b)′ and (9b)′ to give a 1 : 1 mixture of (7b) and (8b). Since the deprotonation of (1b) and (9b) to give the corresponding vinyl carbanion is an essential part of pathway (c), the rest of the 1 : 1 mixture of (7b) and (8b) must be formed *via* the vinyl carbanion reaction pathway (b) which would also give a 1 : 1 equilibrium mixture of (1b)′ and (9b)′. This leads to the conclusion that the vinyl carbanion derived from an acrylic acid ester is configurationally unstable under the experimental conditions used. The results of previous studies support this conclusion. The H–D exchange reaction of 2,2,4,6,6-penta-methylcyclohexylidene–acetonitrile in $CH_3OD–MeO^-Na^+$ solution took place with complete retention of configuration of the derived vinyl carbanion;[3a] the vinyl carbanion derived from the corresponding acetophenone derivative was only partially stable under the same conditions.[3b] A recent relevant theoretical study claims that the $CH_2=\overset{-}{C}-CN$ carbanion is configurationally much more stable than that derived from an acrylic ester.[15]

Experimental

Materials.—THF was refluxed over sodium and then distilled. A solution of sodium diphenylketyl in the distilled THF was prepared and the required amount of THF was distilled directly from this solution into the reaction flask. DEE and hexane were kept over sodium and directly distilled into the reaction flask. LDA and LTMP were prepared in the reaction flask by adding an equimolar amount of BuLi or Bu^{t}Li (dissolved hexane) into the corresponding amine–solvent solution. All manipulations, and the reactions of the olefins with benzophenone in the presence of a base, were carried out under nitrogen and anhydrous conditions. Ether refers to diethyl ether. Light petroleum refers to the fraction with b.p. 40—60 °C.

Synthesis of Methyl cis-β-Deuterioacrylate (1b) and cis-β-Deuterioacrylonitrile (1a).—Methyl 3-deuteriopropiolate. This was prepared by a procedure previously described for the preparation of the corresponding ethyl ester.[6] No signal for a proton at C-3 appeared in the ^{1}H n.m.r. spectrum of the product obtained.

Methyl 11,12-cis-12-deuterio-9,10-etheno-9,10-dihydroanthracene-11-carboxylate (2). This was prepared by a procedure previously used for the preparation of the corresponding ethyl ester.[6] Methyl 3-deuteriopropiolate (12.75 g, 0.15 mol), anthracene (11.10 g, 0.062 mol), hydroquinone (0.10 g), and dry benzene (200 ml) were placed in a sealed steel bomb heated at 210 °C for 5 h. The steel bomb was then cooled to room temperature, opened, and the reaction mixture filtered to separate precipitated anthracene. The solvent was evaporated from the filtrate, and the residue was chromatographed on a silica gel column to give the product (2) (11.75 g, 72%), m.p. 174—175 °C (lit.,[16] m.p. 174—175 °C) (from ethanol).

Methyl 11,12-cis-12-deuterio-9,10-ethano-9,10-dihydro-anthracene-11-carboxylate (3). A solution of (2) (10 g, 0.038 mol) in ethyl acetate (300 ml) was hydrogenated for 16 h in the presence of Pd–C (5%) catalyst at a pressure of 35—40 lb in^{-2} to give (3) (8.8 g, 87%), m.p. 117—118 °C (lit.,[6,17] 117—118 °C) (from methanol).

11,12-cis-12-*Deuterio-9,10-ethano-9,10-dihydroanthracene-11-carboxylic acid (4).* A mixture of the ester (3) (16.70 g, 0.066 mol), ethanol (120 ml), potassium hydroxide (3.90 g, 0.069 mol), and water (240 ml) was refluxed for 1 h. Water (1.2 l) was then added and the mixture filtered. The filtrate was acidified with concentrated hydrochloric acid and the precipitate collected, washed with water, dried, and crystallized from ethanol to give (4) (12.10 g, 73%), m.p. 181—182 °C (lit.,[18] m.p. 183—185 °C).

11,12-cis-12-*Deuterio-9,10-ethano-9,10-dihydroanthracene-11-carboxamide (5).* A solution of (4) (12.10 g, 0.048 mol), freshly distilled thionyl chloride (4.37 ml), and pyridine (0.06 ml) in dry benzene (55 ml) was refluxed under nitrogen for 2 h. More thionyl chloride (1 ml) was added and heating continued for 20 min. The hot reaction mixture was filtered under nitrogen, the filtrate was cooled in an ice-bath, and gaseous ammonia was bubbled into it. The precipitate, which was immediately formed, was filtered off, washed with water, dried, and dissolved in chloroform. The solution was evaporated to give (5) (8.7 g, 72%), m.p. 234—237 °C (lit.,[19] m.p. 238—239 °C).

11,12-cis-12-*Deuterio-9,10-ethano-9,10-dihydroanthracene-11-carbonitrile (6).* A mixture of (5) (8.7 g, 0.035 mol) and thionyl chloride (40 ml) was refluxed for 6 h. The reaction mixture was evaporated to dryness and water–chloroform added to the residue. The organic layer was dried, and the solvent evaporated. The residue left behind was pure (6) (6.0 g, 79%), m.p. 147—149 °C.

Methyl cis-β-deuterioacrylate (1b). This was prepared as

previously described [5] by heating (3) (8 g, 3 mmol) under nitrogen at 290—300 °C at atmospheric pressure. The volatile ester (1b) was slowly released and was collected in a cooled receiver. The distillate was redistilled affording pure (v.p.c.) (1b) (2.5 g, 98%). An ethereal solution (15 ml) of (1b) was used in further experiments.

cis-β-*Deuterioacrylonitrile* (1a). This was prepared from (6) (6 g, 0.026 mol) using the same experimental conditions as those used for decomposing (3). The pure product (1a) obtained (1 g, 73%) was dissolved in ether (10 ml) and this solution was used in all experiments involving (1a).

Reaction of cis-β-*Deuterioacrylonitrile* (1a) *with Benzophenone in the Presence of LDA.*—A solution of (1a) (0.22 g, 4.12 mmol) and benzophenone (1.0 g, 6 mmol) in THF (10 ml) was added dropwise during 20 min to a cooled solution (−80 °C) of LDA (7.5 mmol) in THF (40 ml). The colourless solution became dark. The reaction mixture was stirred at −80 °C for another 20 min, during which time the colour changed to green and then to yellow. Chloroform–water was then added and the precipitated polyacrylonitrile was separated by filtration. The oily residue recovered from the organic layer of the filtrate was subjected to column chromatography to give a mixture of cis- and trans-β-deuterio-α-hydroxy(diphenyl)-methylacrylonitrile (7a) and (8a) (0.30 g, 31%) in the ratio of 68 : 32 and benzhydrol (0.21 g, 19%).

Reaction of Methyl cis-β-*Deuterioacrylate* (1b) *with Benzophenone in the Presence of LTMP.*—A solution of (1b) (0.22 g, 2.5 mmol) and benzophenone (0.68 g, 3.76 mmol) in DEE (10 ml) was added dropwise during 15 min to a cooled solution (−80 °C) of LTMP (7.5 mmol) in DEE (40 ml). The reaction mixture was further stirred at −80 °C for 15 min and chloroform–water added. The residue recovered from the organic layer was separated by column chromatography to give a 1 : 1 mixture of (7b) and (8b) (0.18 g, 27%), an addition product (13) (0.12 g, 13%), m.p. 137 °C (from light petroleum–ethyl acetate), and a dimeric addition product (14) (0.21 g, 37%), m.p. 126—127 °C (from light petroleum–ethyl acetate) (lit.,[1i] m.p. of the non-deuteriated derivative 126—127 °C); m/z (for $C_{30}H_{39}D_2NO_5$) 497.

Reaction of the Ester (13) *with LDA.*—A solution of methyl [3-²H]-2-hydroxy(diphenyl)methyl-3-(2,2,6,6-tetramethyl-piperidyl)propanoate (13) (0.040 g, 0.1 mmol) in THF (10 ml) was added dropwise during 20 min to a solution of LDA (0.2 mmol) in THF (40 ml) at −78 °C. The reaction mixture was stirred for a further 1 h, and chloroform–water was then added. The residue recovered from the organic layer (0.035 g) was the starting material (13) (m.p., t.l.c., ¹H n.m.r., and mass spectra).

Reaction of cis-*Cinnamonitrile with Benzophenone in the Presence of* Et₂N⁻Li⁺.—A solution of cis-cinnamonitrile (0.325 g, 2.5 mmol) and benzophenone (0.546 g, 3.0 mmol) in DEE–hexane (4 : 1) was added dropwise during 10 min to a solution of lithium diethylamide (5.0 mmol) in the same solvent mixture (40 ml) at −80 °C. The reaction mixture was further stirred at −80 °C for 45 min and CHCl₃–H₂O was added. A crude oily residue (0.85 g) was obtained after several extractions with chloroform. Addition of light petroleum to this residue precipitated a cis–trans mixture of the reaction product (0.65 g, 83%). This mixture was crystallized to give trans-2-cyano-3-hydroxy-1,3,3-triphenylprop-1-ene (0.25 g, 41%), m.p. 184—186 °C (from 1 : 1 EA–PE). The filtrate left

behind was evaporated and the residue was crystallized to give cis-2-cyano-3-hydroxy-1,3,3-triphenylprop-1-ene (0.36 g, 59%), m.p. 154—156 °C [1h] (from 1 : 1 ethyl acetate–light petroleum).

Reaction of a Mixture of Isomers (7a) *and* (8a) *with LDA.*—A solution of a mixture of (7a) and (8a) (0.0479 g, 0.2 mmol) in THF (10 ml) was added dropwise during 20 min to a cooled solution (−78 °C) of LDA (1 mmol) in THF (40 ml). The cooled reaction mixture was further stirred for 1 h and water–chloroform was then added. The crude product (0.04 g) recovered from the organic layer consisted of a mixture of (7a) and (8a) only (t.l.c.), in the ratio 3 : 1 (¹H n.m.r. spectrum).

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