Vinyl Anions. Part 9.† Vinyl Carbanions Derived from Acrylic Esters and their β-Phenyl Derivatives

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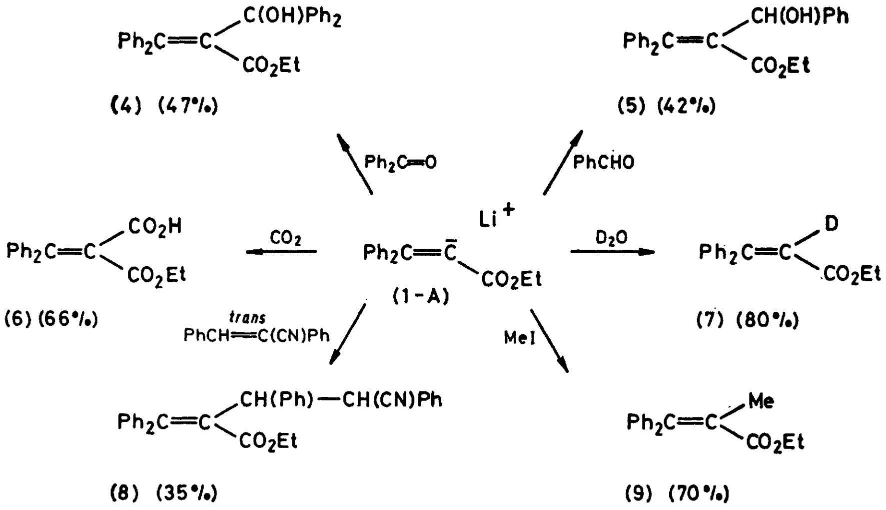
Ethyl ββ-diphenylacrylate, ethyl *cis*- and *trans*-cinnamate, methyl and ethyl maleate, ethyl fumarate, and methyl acrylate were treated with a strong base at low temperatures to yield the derived vinyl carbanions. The vinyl carbanions were treated with various electrophiles to give the corresponding α-substituted derivatives. Ethyl *cis*- and *trans*-cinnamate gave mostly β-substituted products having *trans*-geometry. The products obtained from the maleic esters were the corresponding fumarate derivatives. Deuteriation of ethyl *cis*-cinnamate gave the α-deuteriated ethyl *cis*-cinnamate. In the absence of an added electrophile dimers and trimers were isolated in the case of ethyl *cis*- and *trans*-cinnamate. Solvent, base, and temperature effects were also studied.

SOME aspects related to the formation of vinyl carbanions derived from activated olefins[1-6] and their synthetic applications as nucleophiles[7-14] have recently been studied. Theoretical calculations aimed at determining the site of deprotonation of several 1,2-substituted olefins were satisfactorily in accordance with experimental results.[6] Little is known regarding the effects of structure and medium on the configurational stability of vinyl carbanions, although the configurational stability of sp^3-type carbanions[15] and cyclopropyl[16] carbanions has been thoroughly studied.

It was the purpose of the present work to add some information on vinyl carbanions derived from αβ-unsaturated esters, with respect to their formation, site of deprotonation, reaction with electrophiles, and configurational stability. Methyl acrylate, ethyl *cis*- and *trans*-cinnamate, ethyl ββ-diphenylacrylate, and fumaric and maleic esters were deprotonated with bases in aprotic solvents at low temperature and the intermediates reacted with electrophiles.

RESULTS AND DISCUSSION

Ethyl ββ-Diphenylacrylate (1).—This was deprotonated by lithium di-isopropylamide (LDA) in THF at −78 °C to give the derived vinyl carbanion $Ph_2C{=}\bar{C}(CO_2Et)\ Li^+$ (1-A). Addition of a dilute DCl–D_2O solution to this reaction mixture resulted in a high yield (>80%) of the α-deuteriated olefin, indicating that the conversion of (1) into (1-A) was high. Some representative nucleophilic addition and substitution reactions were carried out by reacting (1-A) with carbonyl compounds, with an activated olefin, and with an alkyl iodide as the electrophiles. The expected α-substituted derivatives of (1) were obtained (Scheme 1).



SCHEME 1

Reaction products having a second electronegative substituent at C_α reacted further with the LDA present. A hydride transfer from LDA to the activated double bond of such products took place.[17] Thus the final reaction product of (1-A) with *e.g.* methyl benzoate was not the olefinic phenyl ketone (2) formed but rather the saturated derivative (3)[17] (Scheme 2). Reaction of

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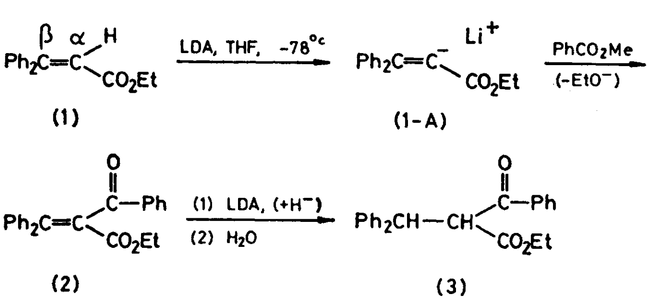
† For part 8 see ref. 13.

(1-A) with benzophenone and benzaldehyde gave benzhydryl alcohol and benzyl alcohol, respectively, as by-products. A hydride transfer from LDA was again responsible for the formation of these by-products.[18] It was possible to prepare the α-substituted olefin (2) by using an amide which had no hydrogen atoms at C_α. The lithium salt of 2,2,6,6-tetramethylpiperidine (LTMP) was used for this purpose.



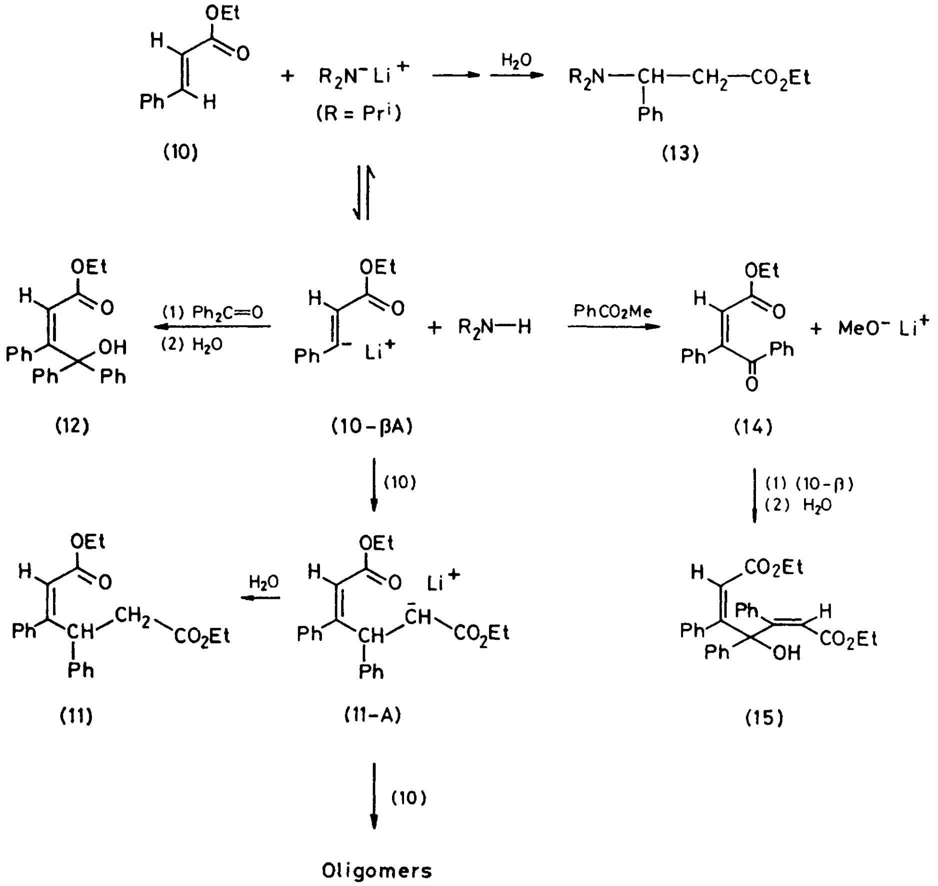
Scheme 2

Dimeric products resulting from a nucleophilic attack of (1-A) at C_α of (1) were not formed. This was in contrast to ββ-diphenylacrylonitrile, where products of such a reaction were formed.[5]

Ethyl trans-*Cinnamate* (10).—The (10)–base–THF reaction system differed from that of the corresponding ethyl ββ-diphenylacrylate reaction in three main features: (*a*) The equilibrium concentration of the derived vinyl carbanion was very low; (*b*) the thermodynamically controlled deprotonation of (10) took place at C_β and not at C_α; (*c*) Michael addition reactions of LDA and of the vinyl carbanion derived from (10) to the double bond of this olefin occurred.

Addition of D_2O or MeOD to the (10)–LDA–THF reaction mixture at —100 °C did not result in any deuteriation of the isolated olefin, indicating that the equilibrium concentration of the derived vinyl carbanion was very low. In accordance with this, none of the expected reaction products was formed when various electrophiles (MeI, cyclohexenone) were added to the (10)–LDA reaction mixture. However, on adding carbonyl compounds such as benzophenone and methyl benzoate, together with the olefin, into the LDA–THF solution, the diphenylmethanol derivative (12) and the phenyl ketone derivative (14) were the reaction products obtained. In the absence of any added electrophile, (10) was quantitatively converted into a complex mixture of a dimeric addition product (11), and unidentified oligomers (Scheme 3).

Formation of (11), (13), and (15) (Scheme 3) represent some of the competing side reactions which might occur in the (10)–base–electrophile reaction system, under the experimental conditions employed. It was obvious



Scheme 3

that a Michael addition–elimination mechanism could not be responsible for the formation of the β-substituted (10) derivatives (in which the *trans*-geometry is retained).

Compounds (11), (12), (14), and (15) were all formed *via* the C_β vinyl carbanion (10-βA), with retention of the *trans*-geometry of the double bond. This indicates that the C_β vinyl carbanion derived from (10) is configurationally stable under the conditions employed.

Compounds (11), (12), and (14) were formed in spite of the fact that the equilibrium concentration of (10-βA) was very low. This suggests that (10-βA) adds to the carbonyl group of benzophenone, methyl benzoate, and (10) itself, in a practically irreversible reaction, shifting the (10) $\rightleftharpoons$ (10-βA) equilibrium slowly in the direction of these products (Scheme 3). Various experimental conditions were applied for the (10)–LDA–Ph$_2$C=O system in order to increase the yield of (12) by increasing the equilibrium concentration and reactivity of the (10-βA) lithium salt (Table 1). Thus, the yield of (12) was higher in THF than in diethyl ether (DEE), since organolithium compounds in DEE exist mostly as contact ion-pairs, but as the much more reactive solvent-separated ion-pairs in THF.[19] Addition of a solvating agent (tetramethylenediamine) which increases ionization of the C—Li$^+$ ion-pair, the use of a stronger base (LTMP) instead of LDA, and longer reaction times all resulted in relatively higher yields of (12).

Ethyl cis-*Cinnamate* (16).—In contrast to the case of (10), where no deuteriation of the olefin took place, addition of MeOD to the (16)–base equilibrium mixture

TABLE 1

Reaction of αβ-unsaturated esters with electrophiles in the presence of base [a]

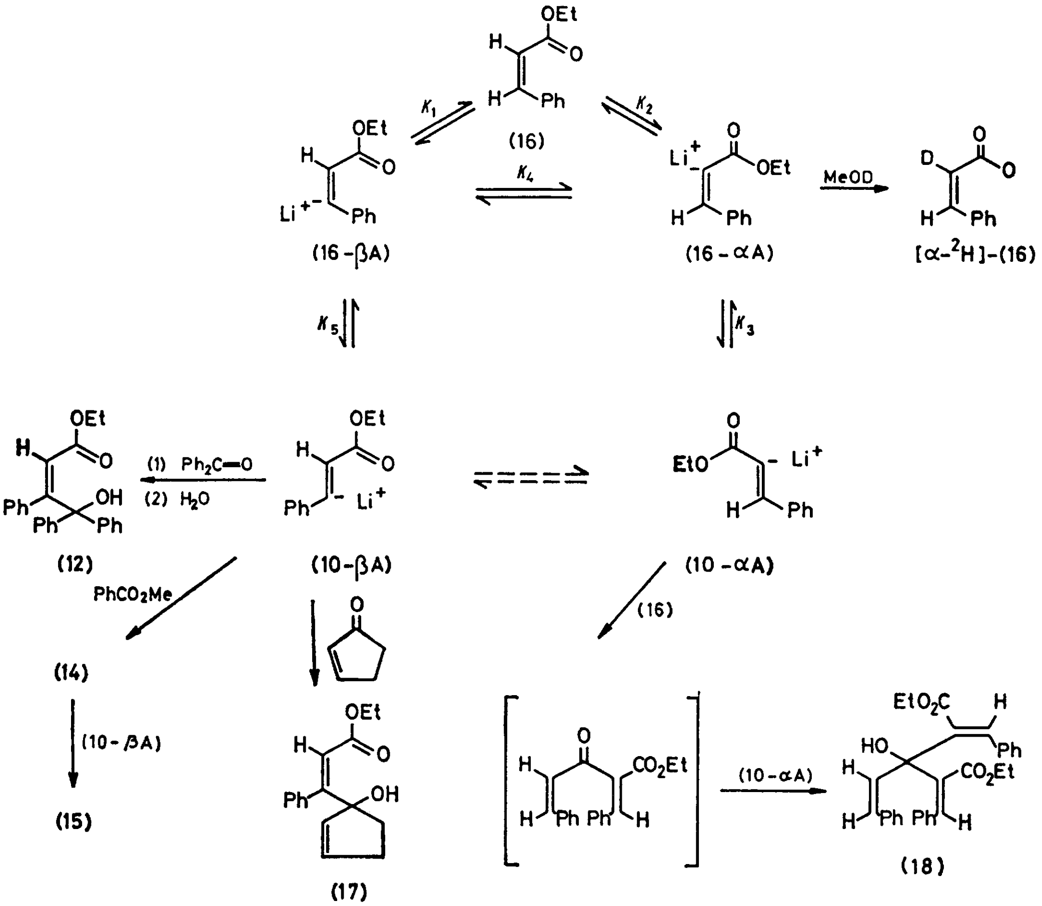
Olefin	Amount (mmol)	Base	Amount (mmol)	Electrophile	Amount (mmol)	Temperature (°C)	Solvent	time/min ($t_1 + t_2$)	Products (g; %)
(1)	2	LDA	6	Ph$_2$C=O	5	−78	THF	15	(4) (0.42; 47)
	2		6	PhCHO	5				(5) (0.30; 42)
	2		6	CO$_2$	excess				(6) (0.30; 66)
	2		6	D$_2$O–DCl	excess				(7) (0.40; 80)
	2		6	*trans*-PhCH=C(CN)Ph	4			30	(8) [b] (0.32; 34)
	2		6	MeI	5			15	(9) (0.38; 70)
(10)	10	LDA	30	Ph$_2$C=O	15	−100	DEE	20 + 60	(12) (0.27; 8)
	10		30		15		THF	20 + 60	(12) (0.70; 19)
	5		15 [c]		7.5			20 + 60	(12) (0.48; 27)
	5		15		7.5			15 + 960	(12) (0.85; 50)
	10		30		15			15 + 300	(12) (1.50; 43)
	10		15					0 [d] + 120	(11) (0.27; 15) [e,g]
	3.3	LTMP	10	Ph$_2$C=O	5			15 + 60	(11) (0.27; 50) [f]
	5	LDA	15	PhCO$_2$Me	10			15 + 60	(14) (0.18; 10) (13) (0.12; 9) (15) (0.11; 8) [g]
(16)	3.3	LTMP	10	Ph$_2$C=O	5			15 + 60	(12) (1.16; 90—100)
	3.3		10		5		DEE	15 + 60	(12) (0.73; 61)
	1.6		5	MeOD [j]	25		THF	0 [h] + 10	[α-^{2}H]-(16) (0.035; 12) [i]
	5	LDA	15	PhCO$_2$Me	10	−90		15 + 60	(14) [k] (0.52; 37) (15) (0.30; 26) [g]
	5		15	Cyclopent-2-enone	10			15 + 45	(17) (0.44; 50) [g]
	5		5			−100		0 [d] + 45	(18) [g] (1.40; 58) (16) (0.37; 42)
(19)	10		15		7.5	−80	THF	15 + 10	(20) [g] (0.20; 7.5) (21) (0.09; 3.6)
	5		15		10			15 + 10	(20) [g] (0.24; 17.6) (21) (0.25; 20)
	5	Bu^{t}Li	15		10	−100		15 + 10	(20) [g] (0.06; 4.8)
(23)	6.1	LTMP	5	Ph$_2$C=O	7.5		THF	20 + 30	(26) (0.47; 24)
	5		11		10			20 + 30	(26) (0.72; 44)
	12		11		15	−10		15 + 30	(26) (0.38; 20)
	5		5		7.5	−80	DME [m]	20 + 30	(26) (0.70; 40)
(24)	5		5		7.5	−100	THF	20 + 30	(27) (0.35; 20)
	10	LDA	40		20			20 + 30	(27) (1.23; 35)
(23) + (24)	2.5 + 2.5	LTMP	5		5	−90	DEE	0 [d] + 60	(23) : (24) = 1 : 9 [l]
(25)	10	LDA	15		10	−80	THF	15 + 20	(27) (1.47; 41)
(25)	2.5	LDA	7.5		2.75	−78	DEE–hexane (2 : 1)	15 + 20	(27) (0.30; 32)

[a] Two general procedures for these reactions are described in the Experimental section. [b] *trans*-1-Cyano-3-ethoxycarbonyl-1,2,4,4-tetraphenylbut-1-ene was a second product obtained with (8). Yield 0.31 g (34%); m.p. 145—147 °C (from CCl$_4$–PE); τ (CDCl$_3$) 9.25 (t, 3 H, *J* 6 Hz, CO$_2$CH$_2$*Me*), 6.25 (q, 2 H, *J* 6 Hz, CO$_2$C*H*$_2$Me), 5.95 (d, 1 H, *J* 10 Hz, C*H*CO$_2$Et), 5.10 (d, 1 H, *J* 10 Hz, C*H*Ph$_2$), and 3.50—2.50 (m, 20 H, 4 × Ph). [c] Tetramethylenediamine (22.5 × 10^{-3} mol) was first added to the LDA–THF solution. [d] The olefin was added to the base–THF solution in one portion. [e] Two fractions of mixtures of lower (0.60 g, 30%) and higher (1.05 g, 55%) oligomers were also obtained. [f] The yield of (12) in this experiment was determined from the ^{1}H n.m.r. spectrum of the crude mixture of the reaction products. [g] The pure products were isolated from the crude mixture of reaction products by column chromatography. [h] The electrophile was added in one portion. [i] Half of the (16) recovered (0.07 g, 25%) was the α-deuteriated derivative [α-^{2}H]-(16). [j] A detailed procedure is given in the Experimental section. [k] The actual yield of (12) was 63% because compound (15) was in fact formed from (14) (see Scheme 3). [l] This is the ratio of unreacted (23) and (24) as determined from the ^{1}H n.m.r. spectrum of the crude product mixture. [m] DME = dimethoxyethane.

in THF at −100 °C resulted in deuteriation of the olefin which was isolated from the mixture of products obtained. Deuteriation took place at the α-position and not at C_β. The ethyl cinnamate isolated (25%, including the fraction of the α-deuteriated derivative), was the *cis*-isomer only. Since no [α-^{2}H]-(10) was detected (t.l.c.) we suggest that [α-^{2}H]-(16) was formed *via* the vinyl carbanion (16-αA), and not by the alternative addition–elimination mechanism. The extent of deuteriation of the (16) isolated was *ca.* 50%, as was evident from its ^{1}H n.m.r. spectrum. It is, therefore, obvious that the equilibrium concentration of the *cis*-C_β-vinyl carbanion (16-αA) in the (16)–base mixture is quite high, and that the concentration of the *cis*- and *trans*-C_α-vinyl carbanions (if any), as well as that of the *trans*-C_α-vinyl carbanion, are very low. Another significant observation of this experiment was that of the high configurational stability of (16-αA) under the experimental conditions employed.

The reaction of (16) with several electrophiles (benzophenone, methyl benzoate, and cyclopentenone) in the presence of LDA (Scheme 4) resulted only in the corresponding β-substituted derivatives of (10) [(12), (14), and (17), respectively]. The phenyl ketone (14) further reacted *in situ* with (10-βA) to give the by-product (15) (Scheme 4). These observations might well be explained by interconnected equilibrium reactions (Scheme 4). The relationship between the equilibrium concentrations of the vinyl carbanions involved might be qualitatively summerized as follows: $K_2 \gg K_1$, K_3 and $K_4 \ll 1$, $1 \gg K_5 > K_4$.

Since (16-αA) was the vinyl carbanion initially formed before the addition of an electrophile (the deuteriation experiment), it must be assumed that in the presence of the electrophiles, (10-βA) was formed from (16-αA), and that the reaction of the electrophiles used with (10-βA) was practically irreversible (Scheme 4). (16-βA) is one possible intermediate for the conversion of (16-αA) into (10-βA).



SCHEME 4

The reaction of (16) with benzophenone in THF to give the product (12) was almost quantitative, while all attempts to get high yields in the case of (10) failed. Similarly, the yields of (16) and (15) were much higher on reacting methyl benzoate with the (16)–base system, as compared to the (10)–base system (Table 1). These higher yields, and formation of [α-^{2}H]-(16) and not of [α-^{2}H]-(10), suggest that (16) is more acidic than (10). Relief of steric interaction on deprotonation might contribute to the increased acidity of (16).

A trimeric product (18) having three double bonds was obtained at a relatively high yield (*ca.* 60%) in the absence of any added electrophile. The structure and stereochemistry of (18), based on ^1H n.m.r. data (Table 2), are discussed later. A possible mechanism for the formation of (18) is presented in Scheme 4. We suggest that a diolefinic ketone is first formed by a nucleophilic addition–elimination reaction of (10-αA) on an ester group of a molecule of (16). This is followed by a second addition of a (10-αA) carbanion to the relatively more reactive diolefinic ketone. A similar addition reaction was that of (10-βA) to the ketone (14) to give the allyl alcohol derivative (15).

It was surprising to find that the α-diphenyl alcohol derivative of (16) was not formed at all, in spite of the high equilibrium concentration of (16-αA). It is possible that the nucleophilic reactivity of (10-βA) towards certain electrophiles is much greater than than of (16-αA), or that the reaction of (16-αA) with benzophenone is slower than its isomerization to (10-βA). It has been shown for alkali salts of carbanions of the type $(R{-}CH_2{-}\bar{C}HX)M^+$ ($X = CN$, CO_2Me, 2-pyridyl, phenyl) that the 2-pyridyl, cyano, and methoxycarbonyl derivatives are much tighter contact ion-pairs and have substantially lower dissociation constants, as compared with the phenyl derivative. This was ascribed to an increased cation–anion coulombic attraction in the contact ion-pair due to delocalization of the negative charge onto the electronegative heteroatoms.[20–23] In view of this, it is reasonable to assume that (16-αA) is a much tighter ion-pair and (therefore) a less reactive carbanion salt than (10-βA). The co-ordination of the Li^+ of (10-βA) by the ester group [6] will further increase the ionic character and the reactivity of this salt. It seems that this co-ordination is also responsible for the formation and the observed configurational stability of (10-βA) as compared with that of (16-βA).

As mentioned above, the *cis*-geometry of (16) did not change on reacting its derived vinyl carbanion with MeOD. This suggests that vinyl carbanion lithium salts at C_α of αβ-unsaturated esters have a certain configurational stability in THF and in DEE at low temperatures, which might be due, at least to some extent, to co-ordination of the $C_\alpha{}^-Li^+$ bond by the $2p_z$ orbital of the carbonyl oxygen. The very low configurational stability of the C_α-vinyl carbanion derived from *cis*-cinnamonitrile, for which this type of co-ordination is impossible, is in accordance with this explanation. The reaction of this olefin in THF at −100 °C in the presence of LTMP with MeOD and benzophenone, gave *trans*-Ph–CH=CD–CN and the α-diphenylmethanol derivative of *trans*-cinnamonitrile, respectively.[24]

Methyl Acrylate (19).—The preparation of vinyl carbanions derived from acrylic esters and their reaction with electrophiles are expected to be complicated by the facile involvement of these olefins in Michael addition reactions and in anionic polymerization.

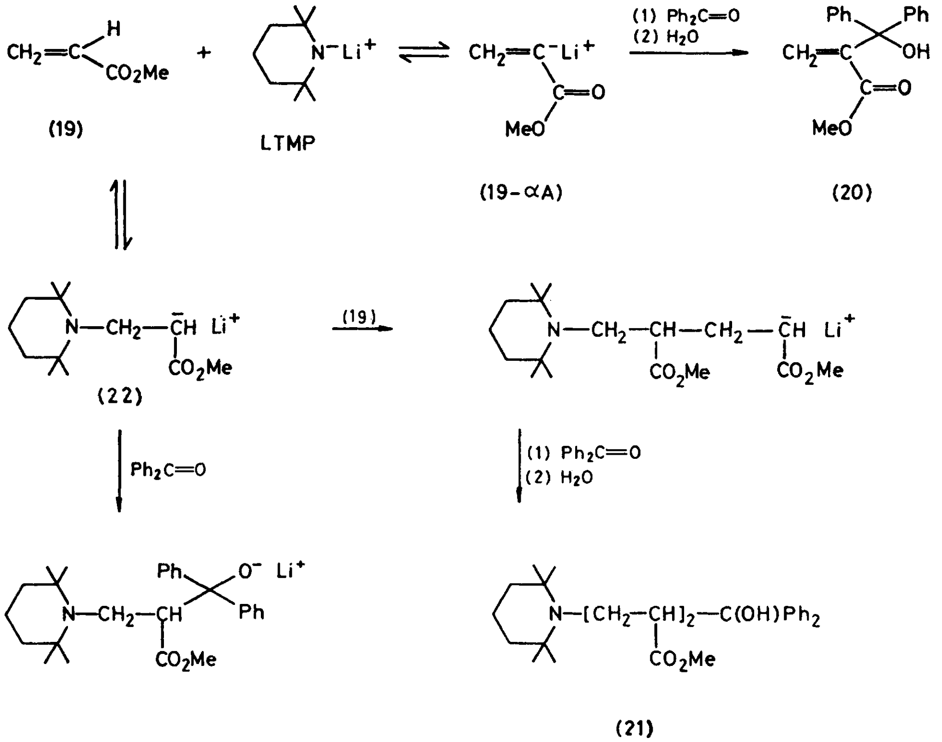
The derived vinyl carbanion formed might easily add to the neutral olefin. In fact, such a reaction has been reported for acrylic [25] and crotonic [26] esters. In order to depress such nucleophilic additions, an excess of LTMP was used. A solution of methyl acrylate and benzophenone was added dropwise into a cooled (−80 °C) LTMP–THF solution. All the olefin reacted yielding a mixture of several products, which was separated by chromatography. Two of the products identified were 1,1-diphenyl-2-methoxycarbonylprop-2-en-1-ol (20) and a dimer (21) formed by anionic oligomerization initiated by LTMP and terminated by benzophenone (Scheme 5).

Formation of these two compounds indicates that (19) is involved in both an acid-base type reaction to yield the vinyl carbanion (19-αA), and in nucleophilic addition reactions. Compound (19) is being deprotonated at C_α as is evident from the reaction products obtained, *i.e.* (20) and diethyl α-methyleneglutarate.[25] It could be argued that (20) could have been formed by reaction of the carbanionic intermediate (22) with benzophenone, followed by prototropy (or deprotonation) and elimination (Scheme 5). However, formation of (20) when Bu^tLi is used as a base (Table 1) is in favour of the vinyl carbanion (20-αA) reaction pathway, because elimination of a t-butyl carbanion is unexpected.

The possibility of co-ordination of the $C_\beta{}^-Li^+$ bond by the ester group is not sufficient to promote deprotonation of the C_β–H bond of methyl acrylate, unless its acidity is being increased by substituents at C_β. Indeed the *trans*-β-alkyl ether and the β-pyrrolidin-1-yl derivatives of ethyl acrylate and *NN*-diethylacrylamide, are preferentially deprotonated at C_β.[6–10,14] Such a combined effect of the phenyl group at C_β and the ester group at C_α, might be responsible for the favoured deprotonation of (10) at C_β, as compared to the C_α-H deprotonation in the case of (16) and (19).[6] However, with *trans*-cinnamonitrile, where such co-ordination of the C_β–Li bond is missing, deprotonation and reaction with various electrophiles takes place only at C_α in THF at −100 °C.[12]

Methyl Maleate (23), *Ethyl Fumarate* (24), *and Ethyl Maleate* (25).—These were reacted with benzophenone in the presence of LDA and LTMP at low temperature (Table 1). The same α-diphenyl alcohol derivative (27) was obtained from each of the two ethyl esters (24) and (25). *cis–trans* Isomerization of the vinyl carbanions derived from the maleic esters (23) and (25) took place, resulting in the products (26) and (27) having a *trans*-geometry. Increasing the reaction temperature to −10 °C, or carrying out the reaction in diethyl ether–hexane (2 : 1) or dimethoxyethane (which is a better solvating medium than THF) also resulted in the corresponding *trans*-products on starting from the maleic esters (Table 1). This preferred *cis–trans* isomerization of the vinyl carbanion lithium salts (23-A) and (25-A) into the corresponding fumaric ester salts might be due to the possibility of stabilization of (24-A) [but not of (25-A)] by the carbonyl group (Scheme 6), asoccurs in the case of (10-βA).

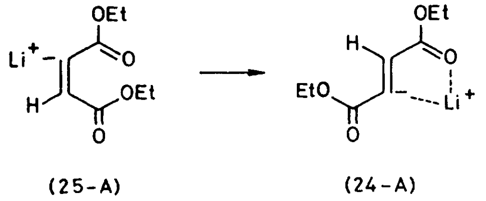
On reacting a mixture of equimolar quantities of methyl maleate and ethyl fumarate with benzophenone in DEE (at −90 °C) in the presence of LTMP (Table 1)



SCHEME 5

the ratio of the unreacted olefins isolated was (23) : (24) = 1 : 9. This might indicate that the *cis*-isomer is more acidic than the *trans*-isomer, as is the case with ethyl *cis*- and *trans*-cinnamates. A consecutive substitution of the two vinyl hydrogens could not be achieved by use of 1 or 2 equiv. of base per vinyl hydrogen. The only result was increased yield of (26) and (27).

The stereochemistry and structure of the olefinic products were not rigorously established, but could be tentatively assigned on the basis of their ^{1}H n.m.r. spectra. The data available in the literature [27-29] (Table 2, footnote *d*) indicate that the chemical shifts of the vinyl hydrogens of alkyl *cis*- and *trans*-cinnamates, $Ph{-}CH_\beta{=}CH_\alpha{-}CO_2R$, are very little affected by substituting either one of the vinyl hydrogens by an alkyl or phenyl group. We have also assumed that a vinyl carbanion derived from ethyl *trans*-cinnamate does not isomerize to the corresponding *cis*-anion, whereas the opposite isomerization takes place readily. This assumption is quite reasonable because identical products [(11), (12), (14), (15), (17)] were obtained on reacting either (10) or (16) with the same electrophiles in the presence of a base, (Table 1). We therefore suggest that these monosubstituted ethyl cinnamates have a *trans*-geometry. The chemical shifts of the vinyl hydrogen of these products [τ(CDCl$_3$): (11), 3.30 (s, 1 H); (12), 3.55 (s, 1 H); (15), 3.10 (s, 2 H); (17), 3.25 (s, 1 H): no absorption bands at τ 2.4—2.6 typical of H_β of alkyl *trans*-cinnamates] suggest that all of them are β-substituted derivatives of ethyl *trans*-cinnamate. The chemical shift of the vinyl hydrogen of (14) was at a very low field (τ 2.15—1.85) due to the deshielding effect of the carbonyl group. By analogy to the other compounds derived from (10), we suggest that it is a β-phenyl ketone derivative of (10).



SCHEME 6

The n.m.r. spectrum of the trimeric product (18) shows the presence of two CO_2Et groups, two vicinal vinyl hydrogens [τ 3.70(d, *J* 13 Hz) and 3.17 (1 H, d, *J* = 13 Hz)], a multiplet at 2.75—2.30 (17 H) which might be due to three phenyl groups and two vinyl hydrogens, and an OH group (τ 5.60, s, 1 H). A possible mechanism for the formation of (18), based on its ^{1}H n.m.r. spectrum, is presented in Scheme 4. Comparison with the chemical shifts of monosubstituted ethyl *cis*- and *trans*-cinnamates (Table 2, footnote) indicates that the COH group is attached to two ethyl *trans*-cinnamate moieties at C_α.

The same product (27) was obtained on reacting either ethyl fumarate (24) or ethyl maleate (25) with benzophenone in the presence of LDA. Assuming again that the *trans*-vinyl carbanion lithium salt is much more stable than the *cis*-lithium salt (25-A), we suggest that both (26) and (27) have a *trans*-geometry.

TABLE 2

^{1}H N.m.r. data of reaction products from αβ-unsaturated esters and electrophiles in the presence of base

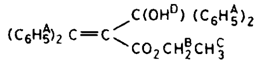
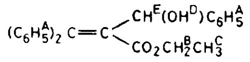
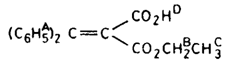
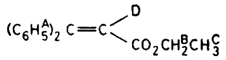
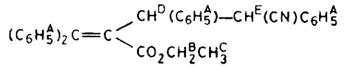
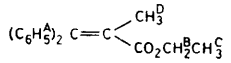
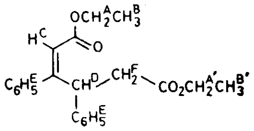
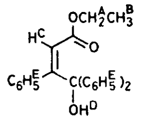
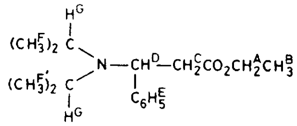
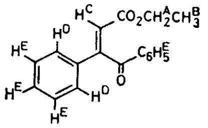
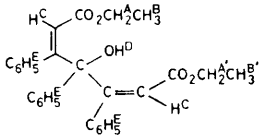
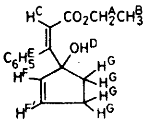
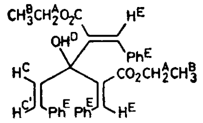
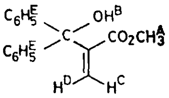
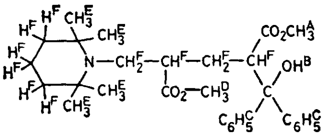
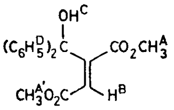
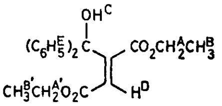
		H^{A} $H^{A'}$	H^{B} $H^{B'}$	H^{C} $H^{C'}$	H^{D}	H^{E}	H^{F} $H^{F'}$	H^{G}
(4)		3.00—2.10 (m, 20 H)	6.45 (q, 2 H)	9.35 (t, 3 H)	6.30 (s, 1 H)			
(5)		2.60—2.10 (m, 15 H)	6.15 (q, 2 H)	9.30 (t, 3 H)	5.65 (d, 1 H)	5.35 (d, 1 H) [a]		
(6)		2.80—2.20 (m, 10 H)	5.85 (q, 2 H)	9.00 (t, 3 H)	1.00 (brs, 1 H)			
(7)		3.00—2.20 (m, 10 H)	5.90 (q, 2 H)	8.90 (t, 3 H)				
(8)		3.70—2.20 (m, 20 H)	6.50 (q, 2 H)	9.40 (t, 3 H)	5.80 (d, 1 H)	4.85 (d, 1 H)		
(9)		3.20—2.60 (m, 10 H)	6.35 (q, 2 H)	9.20 (t, 3 H)	8.10 (s, 3 H)			
(11)		6.15 (q, 2 H) 5.95 (q, 2 H)	9.10 (t, 3 H) 8.90 (t, 3 H)	3.30 (s, 1 H)	5.65 (t, 1 H)	2.90—2.10 (m, 10 H)	7.10 (d, 2 H)	
(12)		6.07 (q, 2 H)	9.15 (t, 3 H)	3.55 (s, 1 H)	4.97 (s, 1 H)	2.70—2.20 (m, 15 H)		
(13)		5.95 (q, 2 H)	8.82 (t, 3 H)	7.40 (d, 2 H)	5.45 (t, 1 H)	2.87—2.37 (m, 5 H)	9.00 (d, 6 H) 9.08 (d, 6 H)	6.82 (heptet, 2 H)
(14)		5.78 (q, 2 H)	8.85 (t, 3 H)	2.15—7.15 [b]	2.15—1.82 (m, 3 H) [b]	2.88—2.22 (m, 8 H)		
(15)		5.98 (q, 4 H)	9.05 (t, 6 H)	3.10 (s, 2 H)	4.67 (s, 1 H) [c]	2.85—2.42 (m, 15 H)		
(17)		5.85 (q, 2 H)	8.91 (t, 3 H)	3.25 (s, 1 H)	7.15 (s, 1 H) [c]	2.75—2.50 (m, 5 H)	4.00—3.75 (m, 1 H) 4.25—4.00 (m, 1 H)	8.20—7.25 (m, 4 H)
(18)[d]		5.92 (q, 4 H)	8.98 (t, 6 H)	3.80 (d, *J* 13 Hz, 1 H) 3.17 (d, *J* 13 Hz, 1 H)	5.65 (s, 1 H) [c]	2.75—2.30 (m, 17 H)		

TABLE 2 (*continued*)

		H^A $H^{A'}$	H^B $H^{B'}$	H^C $H^{C'}$	H^D	H^E	H^F $H^{F'}$	H^G
(20)		6.27 (s, 3 H)	4.85 (s, 1 H) [c]	4.80 (s, 1 H)	3.56 (s, 1 H)	2.85—2.20 (m, 10 H)		
(21)		6.35 (s, 3 H)	5.32 (s, 1 H) [c]	2.90—2.25 (m, 10 H)	6.50 (s, 3 H)	9.20; 9.15 (2 s, 12 H)	9.00—7.25 (m, 12 H)	
(26)		6.33 (s, 3 H) 6.28 (s, 3 H)	4.27 (s, 1 H)	5.75 (s, 1 H) [c]	2.82—2.37 (m, 10 H)			
(27)		5.80 (q, 2 H) 5.87 (q, 2 H)	8.92 (t, 3 H) 8.75 (t, 3 H)	5.55 (s, 1 H) [c]	4.30 (s, 1 H)	3.00—2.35 (m, 10 H)		

[a] The doublet changed to a singlet on addition of D_2O. [b] H^C may be present in the τ 2.15—1.85 multiplet which is due to the two H^D and the one H^C atoms. [c] Disappears on addition of D_2O or MeOD. [d] The following are n.m.r. data (*cf.* refs. 27—29) of mono-substituted alkyl *cis*- and *trans*-cinnamates: *trans*-Ph–CH_β=CH_α–CO_2R, τ ($CDCl_3$) H_α 3.68, H_β 2.44; τ (CCl_4) H_α 3.87, H_β 2.63: *trans*-Ph–CH=C(Ph)–CO_2R, τ (CCl_4) H_β 2.51; *trans*-Ph–CH=C(Me)–CO_2R, τ (CCl_4) H_β 2.65: *trans*-Ph–C(Me)=CH–CO_2R, τ (CCl_4) 3.88; Ph_2C=CH–CO_2R, τ ($CDCl_3$) H_α 3.55; *cis*-Ph–CH=CH–CO_2R: τ ($CDCl_3$) H_α 4.17; H_β 3.20; Ph-C(Me)=CH–CO_2R, τ (CCl_4) H_α 4.20; Ph–CH=C(Ph)–CO_2R, τ ($CDCl_3$) H_β 3.80.

TABLE 3

Analytical and spectroscopic data of the products

Compound	M.p.[a] (°C)	Formula	Anaysis (%) Found (Required)			$\nu_{max.}$/cm^{-1}	$\lambda_{max.}$/nm (ε)	*m/e*
			C	H	N			
(4)	149 (CCl_4)	$C_{30}H_{26}O_3$	82.85 (82.96)	6.0 (5.99)		3 530, 3 010, 1 710, 1 600, 1 210		343
(5)	95 (PE)	$C_{24}H_{22}O_3$	80.3 (80.46)	6.1 (6.14)		3 450, 3 010, 1 710, 1 600, 1 210		358
(6)	142 (CCl_4)	$C_{18}H_{16}O_4$				3 010, 1 720, 1 610, 1 210		296
(7)		$C_{17}H_{15}DO_2$						252, 253
(8)	180 (CCl_4–PE)	$C_{32}H_{27}NO_2$	83.9 (84.04)	5.9 (5.90)	3.05 (3.06)	3 000, 2 200, 1 700, 1 610, 1 200		457
(9)	87 (CCl_4) [b]					3 000, 2 200, 1 700, 1 600		266
(11)		$C_{22}H_{24}O_4$	74.75 (74.98)	7.0 (6.86)		3 000, 1 730	263 (1.77 × 10^4), 258 (1.77 × 10^4)	352
(12)	99	$C_{24}H_{22}O_3$	80.25 (80.42)	6.1 (6.19)		3 480, 3 100, 1 690, 1 630, 1 600, 1 220		358
(13)			73.3 (73.66)	9.7 (9.74)	4.75 (5.05)	2 980, 1 680, 1 640, 1 200		277
(14)	91	$C_{18}H_{16}O_3$	77.45 (77.16)	5.8 (5.71)		3 010, 1 700, 1 670	280 (1.67 × 10^4), 254 (1.77 × 10^4)	280
(15)		$C_{29}H_{28}O_5$	76.4 (76.33)	6.25 (6.14)		3 620, 3 010, 1 710, 1 630, 1 600, 1 220		456
(17)		$C_{16}H_{18}O_3$	74.1 (74.15)	7.35 (7.33)				259
(18)		$C_{31}H_{30}O_5$	77.25 (77.19)	6.25 (6.22)				482
(20)		$C_{17}H_{16}O_3$	76.05 (76.10)	6.0 (6.01)		3 490, 3 010, 1 690, 1 200		268
(21)	126—127 (PE–EA)	$C_{30}H_{41}O_5N$	72.6 (72.70)	8.4 (8.34)	2.75 (2.82)	3 620, 2 940, 2 760, 1 710, 1 620, 1 600		495
(26)	139 (PE–EA)	$C_{19}H_{18}O_5$	69.8 (69.93)	5.6 (5.56)		3 490, 3 010, 1 720, 1 640, 1 210		321
(27)	87 (PE)	$C_{21}H_{22}O_5$	71.25 (71.17)	6.3 (6.26)		3 600, 3 010, 1 720, 1 220		354

[a] Solvent of crystallization also given (PE = light petroleum; EA = ethyl acetate). [b] W. H. Johnson and A. Goldman, *J. Am. Chem. Soc.*, 1945, **67**, 430.

EXPERIMENTAL

Materials.—Ethyl ββ-diphenylacrylate (1) [30,31] and ethyl *cis*-cinnamate (26) [32] were prepared according to known methods. Ethyl *trans*-cinnamate, methyl maleate, ethyl fumarate, and methyl acrylate were dried and fractionally distilled before use. THF was first refluxed over sodium and then distilled. A solution of sodium naphthalene or sodium benzophenone ketyl in the distilled THF was then prepared. The required amount of THF was distilled directly from these coloured solutions into the reaction flask. Diethyl ether (DEE) and dimethoxyethane (DME) were kept over sodium and directly distilled into the reaction flask.

The Reaction of αβ-*Unsaturated Esters with Electrophiles in the Presence of Base.—General Procedures*. The following data are given in Table 1 for each experiment: solvent, reaction temperature, and reaction time; olefin, base, and electrophile used, and their concentrations; the reaction products and their yields. The structure of the products obtained, their melting points and solvent used for crystallization, ^{1}H n.m.r. data, and results of elementary analysis are given in Tables 2 and 3. The bases used were either LDA or LTMP, and were prepared by adding an equimolar amount of Bu^{t}Li (dissolved in hexane) to the derived amine–THF solution. All manipulations and the reaction itself were carried out under nitrogen and anhydrous conditions. Method A was applied to ethyl ββ-diphenylacrylate, and Method B to the rest of the olefins studied.

Method A. Ethyl ββ-diphenylacrylate, (1) dissolved in THF (10 ml) was added dropwise during 5 min to LDA–THF (25 ml) at −78 °C. The solution, which became dark brown-red, was further stirred for 10 min. The electrophile (E) dissolved in THF (3—5 ml) was introduced in one portion, and the mixture was then stirred for 15—20 min at −78 °C. Dilute hydrochloric acid was then added, the mixture extracted with ether or chloroform, the organic layer dried, and the solvent evaporated. The residue was recrystallized from the appropriate solvent.

Method B. A solution of the olefin and the electrophile in the required solvent (10 ml) was added dropwise during t_1 min (see Table 1) to the cooled base–solvent (30 ml) solution. The coloured reaction mixture was further stirred for t_2 min (see Table 1) at the reaction temperature, and then extracted with water–chloroform. The organic layer was washed with water, dried, and the solvent evaporated. The crude residue was subjected to either crystallization or column chromatography to give the pure products.

Reaction of Ethyl cis-*Cinnamate* (16) *with Methan*[^{2}H]*ol in the Presence of LTMP*.—A solution of (16) (0.28 g, 1.6 mmol) in THF (10 ml) was added in one portion to a solution of LTMP (5.0 mmol) in THF (30 ml) at −100 °C. The reaction mixture which immediately darkened was stirred for 1 min and absolute methan[^{2}H]ol (1 ml, 25 mmol) was then added in one portion. The reaction mixture was stirred for another 10 min and the solvent evaporated. The crude product mixture (which consisted of six compounds according to t.l.c.) was separated by column chromatography. The ^{1}H n.m.r. of the fraction corresponding to (16) (0.07 g, 25%) indicated that *ca.* 50% of the isolated (16) was [α-^{2}H]-(16); τ($CDCl_3$) of the (16)–[α-^{2}H]-(16) mixture: 5.85 (q, 2 H), 9.98 (t, 3 H), 4.07 (d, 0.5 H), 3.08 (d, 0.5 H), 3.05 (br s, 0.5 H), and 2.85—2.30 (m, 5 H).

The Reaction of Methyl Acrylate with Benzophenone in the Presence of LTMP.—A solution of methyl acrylate (0.42 g, 5.0 mmol) and benzophenone (1.36 g, 7.5 mmol) in THF (10 ml) was added dropwise during 15 min to a cooled (−80 °C) solution of LTMP (15 mmol) in THF (30 ml). The dark mixture formed was further stirred for 10 min at −80 °C. Water–chloroform was then added, and the organic layer was dried and evaporated. The viscous residue solidified after treatment with light petroleum. The precipitate (0.05 g) was filtered off, and the filtrate evaporated. The residue left behind was separated by column chromatography to give (20) as a colourless viscous liquid (0.24 g, 17.6%), and (21) (0.25 g, 20%) as colourless crystals, m.p. 126—127 °C (from ethyl acetate–light petroleum).

The Reaction of (12) *with LDA*.—A solution of (12) (0.72 g, 2.0 mmol) in THF (10 ml) was added dropwise during 5 min to a cooled (−78 °C) solution of LDA (8.0 mmol) in THF (40 ml). The mixture was stirred for 40 min at −78 °C, then dilute hydrochloric acid was added, followed by extraction with chloroform. The solid residue obtained from the chloroform solution was chromatographed on silica gel. Elution with light petroleum–chloroform (3 : 1) gave (12) (0.65 g, 90%), benzophenone (0.025 g, 6.9%), and unidentified products (0.08 g). No ethyl cinnamate was detected.

We thank Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for financial support.

[0/099 *Received*, 18*th January*, 1980]

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