73. *Nucleophilic Attacks on Carbon–Carbon Double Bonds. Part IV.*[1] cis–trans-*Isomerisation of Ethyl α-Cyano-β-*o-*methoxyphenylacrylate by Various Nucleophiles.*

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The isomerisation of ethyl *cis*-α-cyano-β-*o*-methoxyphenylacrylate to the corresponding *trans*-compound in ethanol has been found to be strongly catalysed by various nucleophiles. Hydroxyl ions and the carbanions formed from active methylene compounds are very strong catalysts and even the cyanoform anion is quite effective. Sodium perchlorate, perchloric acid, and the amount of water in the medium have practically no effect on the isomerisation rates. The mechanism of the reaction is discussed.

AMONG the reaction paths given in the generalised scheme in Part I [2] of this series, the isomerisation reaction (path e) is the simplest, involving only the addition of the nucleophile to the double bond, and its subsequent elimination, permitting the isomerisation of the compound. *cis*–*trans*-Isomerisations in the presence of cationic reagents or radicals, as well as photochemical isomerisations, have been thoroughly investigated [3] but only a

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[1] Part III, preceding paper.

[2] Part I, *J.*, 196, 377.

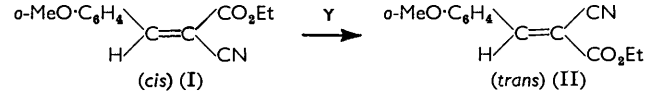
[3] Crombie, *Quart. Rev.*, 1952, **6**, 108; Nozaki and Ogg, *J. Amer. Chem. Soc.*, 1941, **63**, 2583; Davies and Evans, *Trans. Faraday Soc.*, 1956, **52**, 74.

few cases of nucleophilic isomerisations are mentioned in the literature.[4,5] We did not find any systematic kinetic work on an isolated nucleophilic isomerisation alone.

The present paper deals with the nucleophilic isomerisation of ethyl *cis*-α-cyano-β-*o*-methoxyphenylacrylate (I) to the *trans*-isomer (II).

In Parts II and III of this series we showed that in the presence of hydroxyl ions, compound (II) is hydrolysed to *o*-methoxybenzaldehyde and ethyl cyanoacetate.[1] The present paper gives results on the isomerisation (I) ⟶ (II) concurrent with hydrolysis, as well as on the isomerisation alone in conditions in which practically no hydrolysis took place. Compound (I) was the only substance studied in these series where a *cis*-isomer could be prepared.

The overall reaction where Y is the nucleophilic reagent is:



(*cis*) (I) (*trans*) (II)

RESULTS

The rate of the isomerisation of the *cis*-ester (I) at 40° in 95% ethanol was found spectrophotometrically to be of the first order in the concentration range studied (see Table 1).

TABLE 1.

First-order initial rate coefficients (k_1 in sec.$^{-1}$) for the isomerisation of ester (I) in 95% ethanol at 40°.

Concn. (10^{-4} mole l.$^{-1}$)	0·5	1	2
10^5k_1 (sec.$^{-1}$)	1·79	1·88	1·94

Effect of Added Triethylamine(TEA)—*Triethylamine Hydrochloride* (TEA,HCl) *Buffer on the Isomerisation Rate.*—Good linear correlation was found to exist between the buffer concentration and the overall rate constants (k'). Extrapolation to zero buffer concentration from the straight-line plot of k' against buffer concentration gave the value of 0·64 × 10^{-4} sec.$^{-1}$ for the rate coefficient due to ethanol, water, and the corresponding anions in the medium. Subtraction of this value from the k' values gave the coefficients k for the part of the reaction due to the buffer, which was found to be proportional to the concentration of the latter (Table 2).

TABLE 2.

Overall (k') and buffer-dependent (k) first-order initial rate coefficients of the isomerisation of ester (I) (10^{-4} mole l.$^{-1}$) at various concentrations of TEA–TEA,HCl buffer * in 95% ethanol at 40°.

TEA–TEA,HCl (10^{-3} mole l.$^{-1}$)	1	2	4	7	10
$10^4k'$ (sec.$^{-1}$)	1·16	2·09	2·88	4·72	6·15
10^4k (sec.$^{-1}$)	0·52	1·45	2·24	4·08	5·51

* Each component at the concentration stated.

Effect of Nucleophiles on the Isomerisation Rate.—Table 3 shows that the rate of the reaction is enhanced by the presence of various types of nucleophilic reagent. A nearly linear rate–concentration relation is obtained by using either triethylamine or malononitrile (up to 3·6 × 10^{-3} mole l.$^{-1}$) as the nucleophile. Added ethyl cyanoacetate or potassiotricyanomethane, $KC(CN)_3$, also enhanced the isomerisation rate. In the presence of both the amine buffer (TEA–TEA,HCl) and an active methylene compound the rate coefficients were higher than the sum of the coefficients corresponding to each alone. In buffered solutions, with identical concentration of buffer and active methylene compound, malononitrile enhanced the isomerisation rates about 35 times more than ethyl cyanoacetate. No Michael-type adducts were found as a result of these reactions.

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[4] Jones, Morris, Vernon, and White, *J.*, 1960, 2349.
[5] Miller and Yonan, *J. Amer. Chem. Soc.*, 1957, **79**, 5931.

TABLE 3.

Initial first-order rate coefficients (k_1, in sec.$^{-1}$) for the isomerisation of ester (I) (10^{-4} mole l.$^{-1}$) in the presence of triethylamine (TEA), malononitrile (MN), ethyl cyanoacetate (ECA), $KC(CN)_3$, and buffer (TEA–TEA,HCl) at 40° in 95% ethanol.

Nucleophile (10^{-3} mole l.$^{-1}$)	10^4k_1	Nucleophile (10^{-3} mole l.$^{-1}$)	10^4k_1	Nucleophile (10^{-3} mole l.$^{-1}$)	TEA–TEA,HCl (10^{-3} mole l.$^{-1}$)	10^4k_1	$10^4k_1'$
None	0·19	0·8 MN	1·15	None	4	2·82	0
1 TEA	3·51	1·2 MN	1·44	2 ECA	4	3·62	0·80
2 TEA	6·20	1·6 MN	1·92	10 ECA	4	11·2	8·4
5 TEA	13·7	2·0 MN	2·16	20 ECA	4	18·6	15·8
10 TEA	25·2	3·6 MN	3·78	100 ECA	4	35·1	32·3
100 ECA	15·9	8·0 MN	4·79	2 MN	4	30·6	27·8
4 $KC(CN)_3$	1·21						

k_1' = Coefficient due to active methylene compound alone.

Effect of Added Salt on the Reaction Rate.—Low concentrations of sodium perchlorate had no effect on the rate either in ethanol alone or in the presence of the buffer TEA–TEA,HCl. Higher salt concentrations had a very slight accelerating effect (Table 4).

TABLE 4.

The effect of sodium perchlorate on the isomerisation rates (k_1, in sec.$^{-1}$) of ester (I) (10^{-4} mole l.$^{-1}$) in the presence of buffer (2×10^{-3} mole l.$^{-1}$) at 40° in 95% ethanol.

$NaClO_4$ (mole l.$^{-1}$)	0	0·001	0·005	0·012	0·06	0·12
10^4k_1	2·09	2·07	2·13	2·40	2·20	2·38

Effect of Added Acid on the Isomerisation Rate.—The effect of added perchloric acid up to 0·2 mole l.$^{-1}$ on the isomerisation rates was within the experimental error. In 2M-acid the rates were decreased by about 25% (Table 5).

TABLE 5.

Relative rates for the isomerisation of ester (I) (10^{-4} mole l.$^{-1}$) in presence of perchloric acid at 40° in 95% ethanol.

$HClO_4$ (mole l.$^{-1}$)	0	0·000032	0·0016	0·004	0·04	0·2	2
Relative rate	1	1·03	1·08	1·08	0·96	0·92	0·77

Effect of Changing the Water Content of the Medium on the Reaction Rates.—This was studied at 48° and was found to be rather small (Table 6). The effects of 0·02 mole l.$^{-1}$ of perchloric acid in 20%, 30%, and 40% water–ethanol mixtures were negligible.

TABLE 6.

Initial first-order rate coefficients for the isomerisation of ester (I) (10^{-4} mole l.$^{-1}$) in ethanol–water mixtures at 48°.

Water (% v/v)	1	10	20	30	40	50
10^4k_1 (sec.$^{-1}$)	0·303	0·365	0·360	0·373	0·356	0·395

Effect of Added Base on the Reaction Rates.—Addition of low concentrations (up to 8×10^{-5} mole l.$^{-1}$) of sodium hydroxide enhanced the reaction rate. The error was rather high (±25%) although carbon dioxide was removed from the ethanol used. The rate coefficients were approximately proportional to the (low) base concentration, and no simultaneous hydrolysis was observed. At higher base concentrations, concurrent hydrolysis of the double bond was also observed and was measured spectrophotometrically. The rate coefficients for the hydrolysis of the system undergoing simultaneous isomerisation (k_2 = 2·7—3·0 $\times 10^{-4}$ mole l. sec.$^{-1}$) were somewhat higher than those obtained in the hydrolysis of the pure *trans*-compound [1] (k_2 = 1·98 $\times 10^{-4}$ mole l. sec.$^{-1}$). At base concentrations higher than 10^{-4} mole l.$^{-1}$ the hydrolysis became very rapid and only approximate values could be calculated for the isomerisation. In all cases the rate coefficients for the isomerisation were higher than those for the concurrent hydrolysis (Table 7).

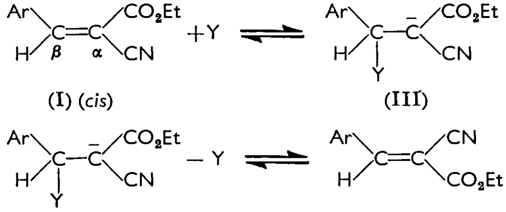
TABLE 7.

Initial first-order rate coefficients for the isomerisation (k_{isom}) and the hydrolysis (k_{hydr}) of ester (I) (10^{-4} mole l.$^{-1}$) in the presence of sodium hydroxide at 40° in 95% ethanol.

[NaOH] (10^{-5} mole l.$^{-1}$)	2	4	6	8	10	20
10^4k_{isom} (sec.$^{-1}$) (±25%)	0·57	1·4	2·10	3·20	7·1	20·8
10^4k_{hydr} (sec.$^{-1}$)	very slow	very slow	very slow	0·107	2·7	5·95

DISCUSSION

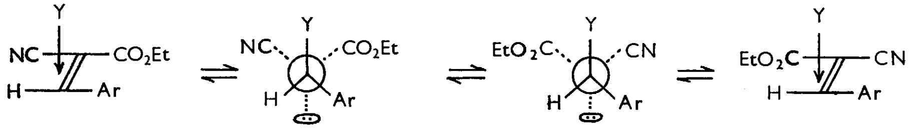
We propose the following mechanism for the isomerisation reaction under the influence of various nucleophilic reagents (Y):



(I) (*cis*) (III)

(II) (*trans*)

In the first and rate-determining step, the positively polarized β-carbon atom of the double bond is attacked by the nucleophilic reagent. The resulting carbanion has the conformation (IIIa) which is the diastereoisomer of the carbanion (IIIb). The transformation (IIIa) $\rightleftharpoons$ (IIIb) occurs readily because it involves only an inversion of configuration in a carbanion, a process which is assumed to be easy.[6] Elimination of Y *trans* to the electron pair from (IIIb) results in formation of the *trans*-isomer (II).



(I) (IIIa) (IIIb) (II)

The results of Miller and Yonan,[5] namely, that a nucleophilic replacement going through a carbanion intermediate may take place on a carbon–carbon double bond with almost complete retention of configuration, isomerisation being a much slower process, cannot be relevant to our case. The following argument shows that in the present case the inversion of configuration of the carbanion must be very fast: The rate of isomerisation is almost unaffected by acid concentrations up to 2 mole l.$^{-1}$. As the protonation of a free carbanion of this type is known to be extremely fast and protonation of the carbanion must inhibit its inversion, we conclude that the rate of inversion is considerably higher than that of the protonation, *i.e.*, very high indeed. The fact that the final products of the condensations of ethyl cyanoacetate with aromatic aldehydes are always the *trans*-isomers [although both (IIIa) and (IIIb) are formed as intermediates] also supports the view that the transformation (a $\rightleftharpoons$ b) is fast with the equilibrium overwhelmingly on the side of (b), the thermodynamically more stable and sterically less hindered carbanion which on *trans*-elimination of Y gives the *trans*-isomer (II). Thus, the stereochemistry of the product in the condensation or in the isomerisation is probably controlled by the conformation in the elimination stage, as proposed by Zimmerman and Ahramjian for related types of reaction.[7]

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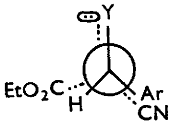
[6] Leffler, " The Reactive Intermediates of Organic Chemistry," Interscience, New York, 1956, p. 196; Wittig, *Experientia*, 1958, **14**, 389; Ziegler and Wentz, *Chem. Ber.*, 1950, **83**, 354; Letsinger, *Angew. Chem.*, 1958, **70**, 151.

[7] Zimmerman and Ahramjian, *J. Amer. Chem. Soc.*, 1959, **81**, 2086.

Identical results would be obtained also by assuming that in our case a *cis*-elimination takes place from the primarily formed carbanion (IIIa), in its eclipsed conformation (IIIc). Although this is a relatively high-energy conformation, the energy needed for its formation from (IIIa) is probably of the same order of magnitude as that needed for the inversion of (IIIa) to (IIIb). Moreover, when Y is a neutral molecule (*e.g.*, H_2O), after the attack it gains a positive charge, and the electrostatic attraction between the two opposed charges in (IIIa) will favour formation of the rotational isomer (IIIc). Overlapping of orbitals in (IIIc) may be the main factor in the *cis*-elimination, as shown by Zimmerman *et al.* for the Perkin reaction.[7] On the basis of our experimental results there seems to be no possibility of deciding which of the two mechanisms is operative.



(IIIc)

Five nucleophilic reagents which can attack the double bond were shown to increase the rate of the isomerisation in ethanol. These range from the very strong nucleophile OH^- to the very weak cyanoform anion, which still enhanced the rate of isomerisation by a factor of 6. We believe, therefore, that the reaction is catalysed by practically all types of nucleophilic reagents.

The reaction in aqueous ethanol proceeds by nucleophilic attack by water (and possibly ethanol) molecules, and not by the small concentrations of hydroxide (or ethoxide) ions, which exist in such solutions. This can be seen from the effect of added acid on the reaction rates (Table 4). In 95% ethanol–water the inhibition even by large concentrations of acid is very small (and may be within experimental error), and therefore it is clear that neutral molecules and not the corresponding anions are involved in the initial attack. If we assume a common initial step in both reactions, this gives further support for the conclusion in Part II of this series that the hydrolysis in ethanol–water mixtures also involves undissociated solvent molecules and not their anions. The small decrease in the isomerisation rate at high acid concentrations may be due to incursion of a different and possibly slower mechanism (analogous to that studied by Noyce *et al.*[8]). Alternatively, at high concentrations protonation of the intermediate carbanion may compete effectively with the isomerisation.

Effect of Various Nucleophiles.—Tables 2 and 3 show that addition of various nucleophiles enhanced the rate of isomerisation in all the cases studied. On the other hand, with relatively high concentrations (0·01—0·1 mole l.$^{-1}$) of perchlorate, which is known to be an extremely weak nucleophile (Table 4), the small difference in the rates is probably due to a rather weak salt effect.

From the good linearity of the rate with the TEA–TEA,HCl buffer concentration (cf. values of *k* in Table 2) it is concluded that the reaction is general base-catalysed. The rate in the presence of triethylamine alone is also an approximate linear function of the base concentration, but increases much more steeply than with the buffer concentration, owing to the simultaneous increase in the concentration of hydroxyl ions caused by addition of triethylamine. Ethyl cyanoacetate at low concentrations gave a relatively small rate enhancement, but at higher concentration (0·1 mole l.$^{-1}$) the catalysed rate was almost a hundred-fold that in ethanol alone. Malononitrile was a more active catalyst than ethyl cyanoacetate and gave an approximately linear dependence in the low concentration range. In order to ascertain whether the undissociated active methylene compounds or their carbanions are involved in the isomerisation, the reaction was studied with these in the presence of TEA–TEA,HCl buffer. It can be seen (Table 3) that the rate increase is much larger than the sum of the effects of the two nucleophiles (buffer and active methylene compound) separately. In our opinion this is clear evidence that the carbanions are involved as nucleophiles in the attack by the active methylene compound and, further, that these are much more effective nucleophiles than triethylamine, as the sum of the carbanions and the free base is constant $(Et_3N + CH_2XY \rightleftharpoons Et_3NH^+ + {}^-CHXY)$.

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[8] Noyce, Pryor, and King, *J. Amer. Chem. Soc.*, 1959, **81**, 5423.

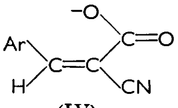
We believe, therefore, that the attack in the unbuffered solutions is also due to the anions produced by the dissociation of the active methylene compound. At constant concentrations of buffer and active methylene compound the rate enhancement by malononitrile is by about one power of ten greater than that by ethyl cyanoacetate, in good agreement with the dissociation constants for the two active methylene compounds given by Pearson and Dillon.[9] With malononitrile, the spectrophotometric measurements gave some indication that concurrently with the isomerisation, some "arylmethylene transfer" (see Part I) also occurs: $\mathrm{Ar{\cdot}CH{=}C(CN){\cdot}CO_2Et + CH_2(CN)_2 \rightleftharpoons Ar{\cdot}CH{=}C(CN)_2 + NC{\cdot}CH_2{\cdot}CO_2Et}$.

The enhancement of the isomerisation rate by ethyl cyanoacetate, alone or in the presence of base, may give an alternative explanation for the fact that in carbonyl–methylene condensations only the *trans*-isomer of the product is isolated, which was taken as evidence for the specificity of the elimination step.[10,11] Our present results point to a further possibility, namely, that even if the *cis*-compound is formed in part, this may be isomerised rapidly by unchanged methylene compound (or by any base, if present, and even by the solvent itself) to the thermodynamically more stable *trans*-isomer.

As in the hydrolysis of carbon–carbon double bonds by nucleophilic attack (see Part II) no considerable salt effect was observed. This is taken as an indication that no great difference exists in the charge separation between the initial and the transition state.

Changing the water content of the medium has practically no effect on the rate. Possibly this is caused by the similar nucleophilic activity of water and ethanol in the present case, and also by the absence of medium effects as discussed above in the case of added salt.

It is interesting that Baker and Howes [11] obtained *cis*-α-cyano-β-*o*-methoxyphenylacrylic acid from 3-cyanocoumarin in the presence of 1 mole l.$^{-1}$ of sodium hydroxide. Although we found that higher yields could be obtained by shortening the reaction time and lowering the temperature, it is still surprising that no complete isomerisation takes place. It is possible that the electrostatic repulsion by the charge on the carboxylate anion (IV) largely inhibits the attack by the hydroxyl ions. Moreover, the presence of a negative charge in the molecule must lower considerably the electrophilic character of the β-carbon atom.



(IV)

Isomerisation and Hydrolysis.—Incursion of concurrent hydrolysis of the double bond becomes appreciable only at relatively high base concentrations (*i.e.*, $>8 \times 10^{-5}$ mole l.$^{-1}$), the isomerisation rates being then already very fast. No attempt was made to correlate the two rates in view of the large experimental errors under these conditions. That isomerisation is always much faster than hydrolysis shows that only a very small fraction of the intermediate (III) enters the reaction sequence resulting in hydrolysis, while most of it either reverts to compound (I) or gives compound (II). Moreover, the hydrolysis is specific hydroxyl-ion-catalysed and does not take place in the presence of buffer, active methylene compounds, or $\mathrm{KC(CN)_3}$, while these (*i.e.*, bases in general) catalyse the isomerisation. Hydrolysis of the *cis*-compound is probably somewhat faster than that of the *trans*-compound, as shown by the slightly higher hydrolysis rates observed in the mixture containing both isomers (*i.e.*, concurrently with the isomerisation) than with the hydrolysis rate of the pure *trans*-isomer.[1] Owing to experimental difficulties arising from the fast isomerisation, we could not determine the hydrolysis rate of the pure *cis*-isomer.

EXPERIMENTAL

Materials.—Ethanol was purified as described in Part II of this series. Triethylamine was dried over potassium hydroxide and distilled twice. Triethylamine hydrochloride was

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[9] Pearson and Dillon, *J. Amer. Chem. Soc.*, **1953**, **75**, 2439.

[10] Zabicky, *J.*, **1961**, 683, 687.

[11] Baker and Howes, *J.*, **1953**, 119.

prepared by saturating a benzene solution of triethylamine with hydrogen chloride; the precipitate was filtered and crystallised from ethanol; it melted (with preliminary sublimation) at 253°. Sodium perchlorate (B.D.H.) was dried for 24 hr. at 120° before use. Perchloric acid solutions were prepared from 70% acid (Baker's analysed). Potassium cyanoform was prepared according to Cox and Fontain.[12]

Ethyl trans-*α-Cyano-β-*o*-methoxyphenylacrylate* (II).—This was prepared by condensing 0·1M-ethanolic *o*-methoxybenzaldehyde with an equimolar amount of ethyl cyanoacetate and one drop of 0·1M-sodium hydroxide. It was crystallised from ethanol to constant m. p.[11] (77°) and constant spectrum.

Ethyl cis-*α-cyano-β-*o*-methoxyphenylacrylate* (I).—α-Cyano-β-*o*-methoxyphenylacrylic acid was prepared as described by Baker and Howes.[11] Higher yields (65%) were obtained by limiting the time of treatment by base to 15 min. at 15° instead of 1 hr. at 25—30°. The acid (4 g.) was dissolved in 5% aqueous sodium hydrogen carbonate (20 ml.) and treated with aqueous silver nitrate until no more precipitate was formed. The yellow silver salt was washed with water and ether, dried *in vacuo*, and then added to ethyl iodide (6 g.) in ether (50 ml.). The mixture was stirred for 6 hr. in the dark, then filtered and evaporated under reduced pressure. The crude yellow residue (m. p. 50°) was dissolved in tetrahydrofuran (20 ml.), filtered, concentrated to 5 ml., and kept at 0° for 24 hr. Pale yellow crystals of the *ethyl ester* separated (1·5 g., 33%), having m. p. 74·5—75° (mixed m. p. with the *trans*-isomer, 55°) (Found: C, 67·6; H, 5·95; N, 5·6. $C_{13}H_{13}NO_3$ requires C, 67·5; H, 5·7; N, 6·05%).

Spectra.—Infrared spectra were measured by using a Baird spectrophotometer with a potassium bromide prism. The following characteristic peaks were found for the *cis*- and *trans*-esters (I) 5·88, 8·90, 9·20, 10·73, 12·70, 12·92, 14·95 μ; (II) 5·83, 8·90, 12·25, 13·13 μ.

Ultraviolet data were determined in a Beckman DU spectrophotometer. Data for the *cis*- and the *trans*-ester are: (I) λ 215 (max.) (ε 4000), 256 (min.) (ε2500), 295 (max.) (ε 9700), 326 (min.), 7100 (ε 339·5) (isosbestic point with II, ε 7900), 370 (ε 5300), 380 mμ (ε 3500); (II) λ 255 (min.) (ε 1300), 300 (max.) (ε 12,600), 330 (min.) (ε 5600), 339·5 (ε 7900), 360 (max.) (ε 11,800), 370 (ε 9300), 380 mμ (ε 6700).

Stability of Stock Solutions.—A solution of *cis*-ester (5×10^{-3} mole $l.^{-1}$) was prepared in dried benzene, in a brown flask. At 40°, the absorption of these stock solutions, after dilution by ethanol, was found to increase slightly, but constantly, with time. Therefore, the stock solutions were kept frozen at 0° and brought to 40° immediately before use, and frozen again as soon as the sample was taken. Even so, during one week the absorption increased by 4—6%, and new stock solutions were prepared each third day.

Product Analysis.—(*a*) In the relatively fast runs, solutions (10^{-4} mole $l.^{-1}$) of *cis*-ester were kept overnight at the reaction temperature and the final spectra were measured; they were identical with that of the *trans*-compound with 95—100% conversion. (*b*) The *cis*-compound (0·01 mole $l.^{-1}$) in ethanol was kept for 48 hr. at 40°. Most of the alcohol was removed under reduced pressure. The crystals which separated were identified as *trans*-ester by m. p. and mixed m. p.

Kinetic Procedure.—Solutions were made up from the stock solution of the *cis*-compound and other reagents in ethanol. The mixture was placed in a ground-glass-stoppered silica absorption cell in a spectrophotometric chamber (thermostat) (Beckman Dual Thermospacer). Absorptions were usually measured for at least three wavelengths concurrently: at 370 and 380 mμ for the actual rate measurements and at 339·5 mμ which is the isosbestic point of the *cis*- the *trans*-compound. In some runs measurements were made also at 360 mμ, the wavelength of maximum absorption of the *trans*-compound.

Treatment of Results.—Initial rate coefficients were calculated as follows: At a certain wavelength, C_0 denotes the initial concentration and C the concentration at the time t of the *cis*-compound. D_0 and D are the optical densities of the solution in the beginning of the reaction and at the time t, ε_{cis} and $\varepsilon_{\text{trans}}$ are the molar extinction coefficients of the *cis*- and the *trans*-compound, respectively. The following relations hold, k being the initial rate coefficient:

$$k = (C - C_0)/C_0t; \qquad D_0 = C_0\varepsilon_{\text{cis}};$$

$$D = C\varepsilon_{\text{cis}} + (C_0 - C)\varepsilon_{\text{trans}};$$

hence

$$C - C_0 = (D - D_0)/(\varepsilon_{\text{cis}} - \varepsilon_{\text{trans}}).$$

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[12] Cox and Fontain, *Bull. Soc. chim. France*, 1954, 948.

Inserting the last into the first equation gives

$$k = (D - D_0)/(\varepsilon_{\text{cis}} - \varepsilon_{\text{trans}})tC_0.$$

Values of ($\varepsilon_{\text{cis}} - \varepsilon_{\text{trans}}$) are 3960 and 3230 at 370 and 380 mμ, respectively, as determined from the absorption spectra of the two pure isomers. By using the values of $(D-D_0)/t$ from the optical density–time graphs, initial rate coefficients were calculated for each run separately from the values obtained at 370 and 380 mμ. The mean value of the two coefficients (which were as a rule identical within 5—8%) so obtained is given in the Tables. This procedure was used in order to obtain more reliable results in view of the close spectral values of the two components, which increases the experimental error, and also to detect the occurrence of side reactions such as " arylmethylene transfer " in the isomerisation catalysed by malononitrile. No hold-up of any intermediate was detected by this procedure.

From the decrease in the optical density at the isosbestic point of the *cis*- and the *trans*-compound (339·5 mμ) the rate of concurrent hydrolysis was calculated. At this wavelength any decrease in absorption is due to the disappearance of the double bond by hydrolysis alone.

A sample run is recorded in the annexed Table.

Isomerisation of *cis*-ester (I) (10^{-4} mole l.$^{-1}$) in presence of $KC(CN)_3$ (4×10^{-3} mole l.$^{-1}$).

Time (min.)	1	12	18·5	24	30	36	42·5	48	54	60
log (I_0/I) at 370 mμ...	0·508	0·535	0·550	0·569	0·588	0·604	0·620	0·636	0·655	0·670
Time (min.)	1·5	12·5	18	24·5	30·5	36·5	42	48·5	54·5	60·5
log (I_0/I) at 380 mμ...	0·320	0·345	0·359	0·372	0·389	0·401	0·415	0·431	0·447	0·460

Initial rate (slope/C_0 . $\Delta\varepsilon$):

at λ = 370 mμ, $k_1 = 1{\cdot}18 \times 10^{-4}$ sec.$^{-1}$;
at λ = 380 mμ, $k_1 = 1{\cdot}24 \times 10^{-4}$ sec.$^{-1}$;
mean $k_1 = 1{\cdot}21 \times 10^{-4}$ sec.$^{-1}$.

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[*Received, July 24th*, 1961.]