Vinyl Carbanions. Part I. Kinetics of Hydrogen–Deuterium Exchange in Fluoren-9-ylideneacetonitrile catalysed by Sodium Ethoxide

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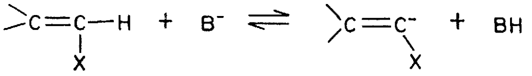
The kinetics of hydrogen–deuterium exchange in fluoren-9-ylideneacetonitrile in ethyl [^{2}H]alcohol, catalysed by sodium ethoxide, have been studied. The observed rate equation is (i) where k_{ex} = 1.15 ± 0.05 l mol^{-1} min^{-1} at

$$R = k_{ex}[\text{Olefin}][\text{EtO}^-\text{Na}^+] \qquad (i)$$

30°. N.m.r. did not show any formation of the addition product of ethyl alcohol to this olefin. Hydrogen–deuterium exchange of the *cis*- and *trans*-isomers of 3-(2-bromophenyl)-3-phenylacrylonitrile, under comparable conditions, occurs without any isomerization. It is suggested, therefore, that exchange takes place *via* the derived vinyl carbanion and not by an addition–elimination mechanism.

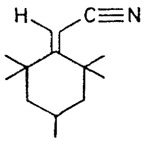
THE mechanism of nucleophilic additions to activated olefins has been extensively studied.[1,2] However, an acid–base equilibrium (1), which may exist in Michael addition reactions, was not taken into account in any of the kinetic studies of this reaction.



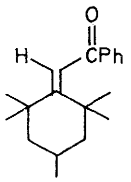
$$>C{=}\underset{X}{\underset{|}{C}}{-}H + B^- \rightleftharpoons >C{=}\underset{X}{\underset{\backslash}{C^-}} + BH \qquad (1)$$

X = electronegative group

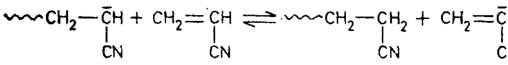
Some recent results indicate that vinyl carbanions may be formed from olefins in the presence of bases. It has been suggested that the derived vinyl carbanion is involved in the conversion of 2-nitro-1,1-diphenylethylene into 1,1,4,4-tetraphenylbutatriene, catalysed by potassium t-butoxide.[3] Vinyl carbanions are intermediates in the base-catalysed hydrogen–deuterium exchange of the vinyl hydrogens of 2,2,4,6,6-pentamethylcyclohexylideneacetonitrile (I)[4] and the corresponding acetophenone (II).[5] A chain transfer reaction to monomer took place during the anionic homogeneous polymerization of acrylonitrile leading to formation of a vinyl carbanion [reaction (2)].[6] Terminally unsaturated dimers of the type $CH_2{=}C(CO_2R)CH_2CO_2R$ are formed in good yield in ethyl alcohol by nucleophilic addition of the acrylic carbanion $CH_2{=}\bar{C}CO_2R$ to the double bond of an acrylic ester[7] in the presence of sodium ethoxide. An unsaturated dimer derived from ethyl crotonate, $CH_3CH{=}C(CO_2Et)CH(CH_3)CH_2CO_2Et$, was similarly formed in the presence of strong base.[8] Base-catalysed hydrogen–deuterium exchange reactions of the vinyl-α-hydrogen atom have been carried out with α,β-unsaturated esters[9] and nitriles,[9–11] which are also capable of undergoing a Michael addition reaction. The alternative addition–elimination mechanism (3) cannot be excluded in cases where the olefin is not sterically hindered at Cβ.



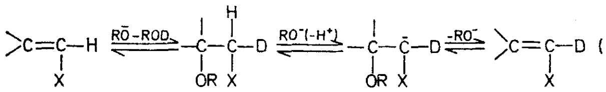
(I)



(II)



$$\sim\sim CH_2-\underset{CN}{\underset{|}{\bar{C}H}} + CH_2{=}\underset{CN}{\underset{|}{CH}} \rightleftharpoons \sim\sim CH_2-\underset{CN}{\underset{|}{CH_2}} + CH_2{=}\underset{CN}{\underset{|}{\bar{C}}} \qquad (2)$$

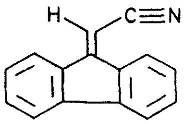


$$>C{=}\underset{X}{\underset{|}{C}}{-}H \underset{}{\overset{R\bar{O}-ROD}{\rightleftharpoons}} -\underset{OR}{\underset{|}{\overset{|}{C}}}-\underset{X}{\underset{|}{\overset{H}{\overset{|}{C}}}}-D \overset{RO^-(-H^+)}{\rightleftharpoons} -\underset{OR}{\underset{|}{\overset{|}{C}}}-\underset{X}{\underset{|}{\bar{C}}}-D \overset{-RO^-}{\rightleftharpoons} >C{=}\underset{X}{\underset{|}{C}}{-}D \qquad (3)$$

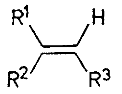
In view of the vast application of Michael additions in organic chemistry it is of importance to compare quantitatively and mechanistically simultaneous nucleophilic addition to the double bond and possible abstraction of the vinyl hydrogen at Cα in such reaction systems. The present work reports the kinetics and mechanism of the acid–base equilibrium (1) without involvement of the nucleophilic addition.

RESULTS AND DISCUSSION

Some preparative hydrogen–deuterium exchange experiments were carried out prior to the kinetic measurements involving the following β,β-disubstituted olefins:



(III)



(IV) $R^1 = R^2 = Ph$, $R^3 = CN$
(V) $R^1 = Ph$, $R^2 = 2\text{-}BrC_6H_4$, $R^3 = CN$
(VI) $R^1 = 2\text{-}BrC_6H_4$, $R^2 = Ph$, $R^3 = CN$
(VII) $R^1 = R^2 = Ph$, $R^3 = NO_2$

fluoren-9-ylidene-acetonitrile (III), 3,3-diphenylacrylonitrile (IV), *cis*- (V) and *trans*-3-(2-bromophenyl)-3-phenylacrylonitrile (VI), and 2-nitro-1,1-diphenylethylene (VII). The exchange reactions were carried out in

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[1] S. Patai and Z. Rappoport, ' The Chemistry of Alkenes,' ed. S. Patai, Interscience, New York, 1964, p. 469.

[2] C. Fyfe, ' The Chemistry of the Hydroxyl Group,' ed. S. Patai, Interscience, New York, 1971, p. 62.

[3] W. M. Jones and C. D. Broaddus, *J. Org. Chem.*, 1961, **26**, 2316.

[4] H. M. Walborsky and L. M. Turner, *J. Amer. Chem. Soc.*, 1972, **94**, 2273.

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[6] B. A. Feit and A. Zilkha, *J. Appl. Polymer Sci.*, 1963, **7**, 287.

[7] B. A. Feit, *Eur. Polymer J.*, 1967, **3**, 523.

[8] J. Shabtai and H. Pines, *J. Org. Chem.*, 1965, **30**, 3854.

[9] M. F. Zinn, T. M. Harris, D. G. Hill, and C. R. Hauser, *J. Amer. Chem. Soc.*, 1963, **85**, 71.

[10] L. C. Leitch, *Canad. J. Chem.*, 1957, **35**, 345.

[11] B. A. Feit and R. Paznichevsky, unpublished results.

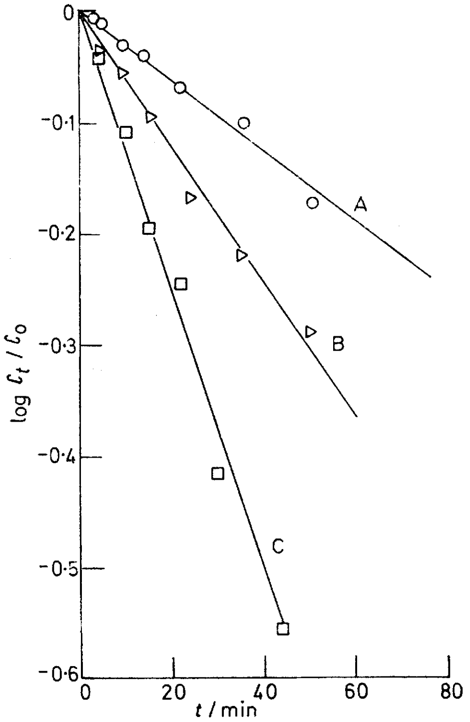
methyl or ethyl [^{2}H] alcohol and catalysed by the derived sodium alkoxide. The absorption bands of the α-vinyl hydrogens in the n.m.r. spectrum of olefins (III)—(VI) τ 4.1—4.3 (s), disappeared after exchange, and no new bands corresponding to addition products were formed. No isomerization occurred during exchange of the isomeric α,β-unsaturated nitriles (V) and (VI). This fact combined with the n.m.r data led us to the conclusion that base-catalysed hydrogen–deuterium exchange of the β,β-disubstituted acrylonitriles (III)—(VI), takes place *via* vinyl carbanion intermediates and not by the addition–elimination mechanism (3) which should lead to isomerization in the case of olefins (V) and (VI). It should be mentioned in this connection that hydrogen–deuterium exchange of the unsaturated nitrile (I) occurred with 99.3% retention of configuration.[4] This result and the lack of isomerization in the case of nitriles (V) and (VI), clearly indicate that vinyl carbanions derived from α,β-unsaturated nitriles have a high configurational stability. The reaction of the nitro-olefin (VII) with sodium methoxide in methyl [^{2}H]alcohol resulted in a mixture of the exchanged olefin and the exchanged addition product of methanol to this olefin $Ph_2C(OMe)$-CD_2NO_2. In spite of the steric hindrance at Cβ, nucleophilic addition of the alcohol takes place in the case of the nitro-olefin (VII) and not in the case of the β,β-disubstituted acrylonitriles. This may be due to the much higher activating affect of the nitro-group compared with the nitrile.*

The rates of the hydrogen-deuterium exchange were followed by measuring the i.r. absorption of the product at 815 and 678 cm^{-1}. These absorptions were due to $\rangle$C=C–H and $\rangle$C=C–D out-of-plane deformations, respectively.[12] The concentration of the unexchanged olefin at time t is given by $C_t = C_0(100 - \%D)/100$ where %D is the deuterium percentage obtained by using calibration plots based on mass spectral data. The rates of H–D exchange were measured at 30, 10, and —10 °C. Good first-order plots were obtained for each kinetic run on plotting logC_t/C_0 against time (Figure). Pseudo-first-order rate constants were derived from the slopes of these plots. Second-order rate constants were obtained by dividing the pseudo-first-order rate constants by the concentration of the catalyst. The results of the kinetic rate measurements are summarized in the Table.

The observed rate equation is (4). A similar second-order rate equation could be derived based on the Scheme

$$R = k_{ex}[\text{Olefin}][\text{EtO}^-\text{Na}^+] \qquad (4)$$

According to this Scheme the vinyl hydrogen of (C–H) is removed in the first step by a solvated ethoxide ion to yield the hydrogen-solvated vinyl carbanion ($C^- \cdots H$), Solvent reorganization then takes place to yield the deuterium-solvated vinyl carbanion ($C^- \cdots D$), which captures deuterium to give the exchanged olefin (C–D). This is essentially the mechanism proposed by Cram[13] and by Walborsky and Motes[14,15] for hydrogen–deuterium exchange of carbon acids.



First-order plots of log C_t/C_0 against time for H–D exchange in fluoren-9-ylideneacetonitrile at 30°. C_t and C_0 (3.44 × 10^{-2}M) are the concentrations of olefin at time t and 0, respectively: A, [EtO$^-$Na$^+$] 0.8 × 10^{-3}M; B, [EtO$^-$Na$^+$] 1.2 × 10^{-2}M; C, [EtO$^-$Na$^+$] 2.4 × 10^{-2}M

Rate constants for the H–D exchange of fluoren-9-ylideneacetonitrile in [^{2}H]alcohol catalysed by sodium ethoxide

T/°C	10^2[olefin]/M	10^2[EtO$^-$Na$^+$]/M	K_1/min^{-1}	K_2/l mol^{-1} min^{-1}
30	3.44	0.68	(7.2 ± 0.4) × 10^{-3}	1.06 ± 0.05 [a]
30	3.44	1.20	(1.4 ± 0.1) × 10^{-2}	1.17 ± 0.09
30	3.44	2.40	(2.9 ± 0.2) × 10^{-2}	1.20 ± 0.10
10	3.00	2.58	(4.3 ± 0.3) × 10^{-3}	(1.7 ± 0.1) × 10^{-1}
—10	2.50	2.40	(1.05 ± 0.08) × 10^{-4}	(4.4 ± 0.4) × 10^{-3}

[a] Average value at 30° of the observed second-order rate constant 1.15 ± 0.05 l mol^{-1} min^{-1}

Due to the extraordinarily fast back reaction of nitrile[16] and due to the high basicity of carbanion

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* Compare, for example the pK_a values of nitromethane (pK_a 10) and acetonitrile (pK_a 25).

[12] L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1960, pp. 51—52.

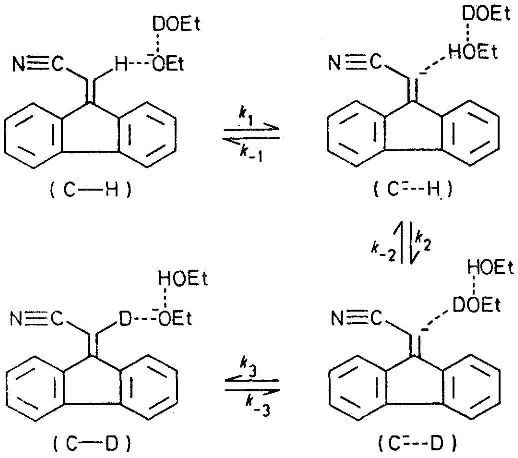
[13] D. J. Cram and L. Gosser, *J. Amer. Chem. Soc.*, 1964, **86**, 2950.

[14] H. M. Walborsky and J. M. Motes, *J. Amer. Chem. Soc.*, 1970, **92**, 2445.

[15] J. M. Motes and H. M. Walborsky, *J. Amer. Chem. Soc.*, 1970, **92**, 3697.

[16] R. G. Pearson and K. L. Dillon, *J. Amer. Chem. Soc.*, 1955, **75**, 2439.

($C^- \cdots D$) compared with that of the ethoxide ion, it can be assumed that $k_{-1} \gg k_1$ and $k_3 \gg k_{-3}$. It was also concluded from the observation of low or negative isotope effects in base-catalysed hydrogen-isotope exchange in carbon acids that $k_{-1} \gg k_2$.[17,18] This was the case, for example, in hydrogen–deuterium exchange of 2-methyl-3,3-diphenylpropiononitrile [14] (k_H/k_D 2.60), of 2,2-diphenylcyclopropanecarbonitrile [14] (k_H/k_D 1.50), and of the α,β-unsaturated nitrile (I)[4] (k_H/k_D 2.05). If the conclusion that $k_{-1} \gg k_2$ is accepted, it might be well assumed that $k_3 \gg k_{-2}$. The rate equation (5) was derived from the Scheme by applying the steady-state approximation and by assuming that $k_3 \gg k_{-3}$ and $k_3 \gg k_{-2}$. It follows from equations (4) and (5) that the



SCHEME

$$R = -\,\mathrm{d}[(\mathrm{C{-}H})]/\mathrm{d}t$$
$$= k_1k_2[(\mathrm{C{-}H})][\mathrm{EtO^-Na^+}]/(k_{-1} + k_2) \qquad (5)$$

rate constants for the exchange k_{ex} is given by $k_{ex} = k_1k_2/(k_1 + k_2)$. Three distinct conditions may be associated with the mechanism in the Scheme. (a) If $k_2 \gg k_{-1}$, $k_{ex} = k_1$. In this case proton abstraction (k_1) is the rate-determining step. (b) If $k_{-1} \gg k_2$, $k_{ex}\,k_1/k_{-1}k_2 = Kk_2$, where K is the equilibrium constant for the proton removal–recapture equilibrium. In this case, solvent reorganization is the rate-limiting step, while the rate of exchange is determined by the product Kk_2. (c) If k_2 and k_{-1} are of the same order of magnitude equation (5) cannot be simplified. No conclusion can be made, based on the kinetic data, on which of these three conditions applies to the reaction studied. This was due to the fact that the derived rate equation in each case is similar to the experimentally obtained equation (4). However, the activation parameters for the exchange clarify to some extent the problem of the mechanism. The value of the Arrhenius activation energy was derived from the slope of the straight line obtained on plotting k_{obs} against $1/T$. E_a 23 kcal mol^{-1} was obtained. The relatively high positive value of the activation entropy ($\Delta S^\ddagger$ 8 ± 1 cal mol^{-1} K^{-1}) indicates, although not conclusively, that solvent reorganization (k_2) is the rate-limiting step. This may be the case, since positive activation entropies are known to be associated with unimolecular transition states, or with the breaking of a solvent shell.[19] It should be mentioned in this connection that positive values of activation entropies were obtained for the methoxide-catalysed hydrogen–deuterium exchange of the olefinic nitrile (I)[4] ($\Delta S^\ddagger$ 9 ± 1 cal mol^{-1} K^{-1}) and for the methoxide-catalysed racemization of 2,2-diphenylcyclopropanecarbonitrile [14] ($\Delta S^\ddagger$ 7.2 cal mol^{-1} K^{-1}). It was of interest to compare the overall rate constants for the exchange of the two α,β-unsaturated nitriles (I) and (III). $k_{ex} = 6.18 \times 10^{-7}$ l mol^{-1} min^{-1} was obtained for olefin (1),[4] whereas the olefin (III) has $k_{ex} = 1.15$ l mol^{-1} min^{-1}.

The greater acidity of carbon acid (III) is due to the strong electron-withdrawing capacity of the fluorene system, compared with that of the cyclohexane system of (I).

EXPERIMENTAL

Materials.—Fluoren-9-ylideneacetonitrile was prepared [20] by condensation of fluorenone and acetonitrile in presence of butyl-lithium, followed by dehydration. β,β-Diphenylacrylonitrile was prepared by treating benzophenone with acetonitrile in the presence of sodium metal.[21] 2-Nitro-1,1-diphenylethylene was prepared by reacting diphenylmethyleneamine with nitromethane.[22] Methyl [^{2}H]alcohol was prepared from dimethyl carbonate and deuterium oxide in presence of dimethyl sulphate.[23] Absolute dry ethyl [^{2}H]alcohol (99.9% D j Miles-Yeda) was used. Alcoholic sodium alkoxide solutions were prepared by adding sodium metal to methyl or ethyl [^{2}H]alcohol under reflux. The base concentration was determined by titration with hydrochloric acid using phenolphthalein as indicator. Liquid materials and solutions were kept under pure nitrogen in flasks fitted with self-sealing rubber caps. Aliquot portions were removed from these flasks with syringes by applying a nitrogen pressure.

cis- *and* trans-3-(2-*Bromophenyl*)-3-*phenylacrylonitrile*.—These compounds were synthesized according to the method described for the preparation of 3-(4-bromophenyl)-3-phenylacrylonitrile.[24] An ethereal suspension of sodium amide was prepared by standard methods by reacting sodium metal (1.04 g, 0.044 mol) with liquid ammonia. A solution of acetonitrile (1.8 g, 0.043 mol) in ether (30 ml) was added dropwise into the stirred suspension of sodium amide in ether (100 ml). This was followed by a dropwise addition of a solution of 2-bromobenzophenone (10.5 g, 0.04 mol) in ether. The mixture was stirred and refluxed for 90 min and then poured into crushed ice. The organic layer was separated, and the aqueous layer was acidified with hydrochloric acid and extracted with ether. The combined ethereal

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[17] D. J. Cram and L. Gosser, *J. Amer. Chem. Soc.*, 1961, **85**, 3696.

[18] R. Stewart, J. P. O'Donell, D. J. Cram, and B. Rickborn, *Tetrahedron*, 1962, **18**, 917.

[19] L. L. Schaleger and F. A. Long, *Adv. Phys. Org. Chem.*, 1963, **1**, 23.

[20] E. H. Kaiser and R. Hauser, *J. Org. Chem.*, 1968, **33**, 3402.

[21] A. Uchida, S. Saito, and S. Matsuda, *J. Chem. Soc. Japan*, 1969, **42**, 2989.

[22] G. Charles, *Bull. Soc. chim. France*, 1963, 1573.

[23] A. Streitwieser, L. Verbit, and P. Stang, *J. Org. Chem.*, 1964, **29**, 3706.

[24] C. Runti and L. Sindellari, *Bull. Chim. Farm.*, 1960, **99**, 499.

solutions were dried and the ether evaporated off. The residue was crystallized from benzene to yield 3-(2-bromophenyl)-3-hydroxy-3-phenylpropiononitrile (8 g, 66%), m.p. 106—107°. The hydroxy-compound (8 g, 3.6×10^{-2} mol) was refluxed in 85% phosphoric acid (200 ml) for 90 min. The mixture was then poured into crushed ice and extracted with ether. The ethereal solution was washed with water, dried, and the ether evaporated. The residue was crystallized from ethyl alcohol to yield a mixture of two olefins (5.2 g, 73%) (t.l.c. and n.m.r.) (Found: C, 88.4; H, 4.8; N, 6.65. Calc. for $C_{15}H_{10}N$: C, 88.2; H, 4.95; N, 6.85%). This mixture was passed down an alumina column with benzene–light petroleum (40 : 60) as eluant. *cis*-3-(2-Bromophenyl)-3-phenylacrylonitrile (higher R_F) had m.p. 120–121°, τ ($CDCl_3$) 4.48 (1 H, s, C=CH) and 2.90–2.94 (9H, m, ArH). The *trans*-isomer had m.p. 101—102°, τ ($CDCl_3$) 4.02 (1 H, s, C=CH), 2.96—2.80 (8 H, m, ArH), and 2.55—2.25 (1 H, m, phenyl 2′-H).*

[α-^{2}H]*Fluoren-9-ylideneacetonitrile*.— Fluoren-9-ylideneacetonitrile (1.5 g, 7.4 mmol) was dissolved in sodium methoxide (1M) in methyl [^{2}H]alcohol (20 ml). This solution was heated for 12 h at 90° in a sealed stainless steel container. The alcohol was then evaporated and deuterium oxide and chloroform were added to the residue. The organic layer was separated, dried, and chloroform was evaporated. The residue was recrystallized from methanol to yield a product, (1.1 g, 74%), m.p. 111°. The deuterium content of this product was 0.83 D atom molecule^{-1}, as determined from its mass spectrum. The n.m.r. spectrum showed no absorption of the α-vinyl hydrogen at τ 4.1. The i.r. spectrum showed a very weak absorption at 815 cm^{-1} due to the $\mathrm{>C{=}C{-}H}$ group.

[α-^{2}H]$\beta\beta$-*Diphenylacrylonitrile*.— $\beta\beta$-Diphenylacrylonitrile (1.5 g, 7.3 mmol) was heated for 1 h under the conditions described above. The alcohol was then evaporated and deuterium oxide was added to the residue. The mixture was then extracted with dry ether. $\beta\beta$-Diphenylacrylonitrile recovered from the ethereal extracts (0.9 g, 60%) showed no absorption band in the i.r. spectrum at 830 cm^{-1}.

Kinetics.—The hydrogen–deuterium exchange reaction was carried out in a 150 ml flask connected to high vacuum and nitrogen lines. The flask was fitted with a self-sealing rubber cap through which liquids were introduced by syringes. The system was dried, evacuated, and flushed with dry nitrogen prior to the introduction of solvent and reactants. The required amount of fluoren-9-ylideneacetonitrile and ethyl [^{2}H]alcohol were introduced into the flask which was then immersed in a constant temperature bath. A solution of sodium ethoxide in ethyl [^{2}H]alcohol was added. Portions of the homogeneous mixture were withdrawn at measured intervals through a capillary stopcock, by applying a nitrogen pressure. The sample withdrawn was quenched immediately with D_2SO_4 in methyl [^{2}H]alcohol and the solvent was evaporated. The residue was extracted with chloroform and the solution was dried, filtered, and evaporated. This residue was subjected to quantitative i.r. measurements, to determine the extent of H–D exchange.

Attempted Isomerization of cis- *and* trans-3-(2-*Bromophenyl*)-3-*phenylacrylonitrile*.—Attempted isomerization of the *trans*-isomer was carried out in the same system used for rate measurements. Absolute ethyl alcohol, an ethanolic solution of sodium ethoxide (3.7×10^{-3}M), and olefin (3.52×10^{-2}M) were introduced into the reaction flask which was immersed in a constant temperature bath at 30 ± 0.1°. Samples withdrawn from the reaction flask were quenched with a dilute solution (5%) of hydrochloric acid in isopropyl alcohol and the olefin was recovered from this mixture. T.l.c. and n.m.r. indicated that no isomerization occurred within 3 h. Refluxing of the reaction mixture for an additional 3 h did not result in any isomerization. Attempted isomerization of the *cis*-isomer was carried out at reflux temperature under anhydrous conditions. A solution of the *cis*-olefin (2.5×10^{-2}M) and sodium ethoxide (5×10^{-3}M) in absolute ethyl alcohol was refluxed for 3 h and no isomerization was detected.

The attempted isomerizations were also carried out in ethyl [^{2}H]alcohol under the same conditions. α-Deuteriated non-isomerized olefins were recovered (t.l.c. and n.m.r.).

Quantitative I.r. Analysis.—The base-line density method [26] was used to determine the percentage deuterium (%D) in the samples withdrawn from the reaction mixture. Several samples composed of mixtures of weighted amounts of deuteriated and non-deuteriated nitrile (III) were each dissolved in CS_2, the i.r. spectrum of the solution recorded, and the transmittance at 678 cm^{-1} determined. This absorption band was due to the $\mathrm{>C{=}C{-}D}$ bond. The % D of the same samples was also determined from their mass spectra. A standard curve for quantitative i.r. analysis was then prepared by plotting $C_{CS_2}{}^{-1} \log T$ against % D for each sample, C_{CS_2} being the concentration of (III) in CS_2 and T the transmittance at 678 cm^{-1}. The i.r. spectra of olefin mixtures from the kinetic runs were similarly recorded and their % D was directly read from the standard curve.

N.m.r. spectra were recorded on a JEOL 60 MHz spectrometer. I.r. spectra were taken with a Perkin-Elmer 177 spectrometer.

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* The assignments of n.m.r. data to the *cis*- and *trans*-isomers were based on the n.m.r. spectra of fluoren-9-ylidene-malononitrile [25] and -acetonitrile, the latter giving τ ($CDCl_3$) 4.09 (1 H, s, C=CH), 2.10—2.90 (7 H, m, ArH), and 1.40—1.80 (1 H, m, fluorene 1-H).

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[26] C. N. R. Rao, 'Chemical Applications of Infrared Spectroscopy,' Academic Press, New York, 1963, p. 538.