SECTION B

Physical Organic Chemistry

Nucleophilic Attacks on Carbon–Carbon Double Bonds. Part X.[1] Nucleophile-catalysed *cis–trans* Isomerisation of *cis*-4-Nitrochalcone and of Diethyl Maleate in 95% Ethanol

By Zdenka Grünbaum, Saul Patai, and Zvi Rappoport

The catalytic *cis–trans* isomerisation of 4-nitrochalcone and of diethyl maleate in the presence of various nucleophiles has been studied spectrophotometrically in 95% ethanol. The reactivity order was: OH^- > piperidine > N_3^- > Bu^nNH_2 > $C_6H_{11}\cdot NH_2$, benzylamine > Pr^n_2NH > Pr^i_2NH $\ggg$ Bu^n_3N, C_5H_5N, Br^-. The isomerisation is of overall second order (first order in each the substrate and the nucleophil) at low nucleophil concentrations, but the second-order rate coefficients fall with increase in the catalyst concentration. The kinetic behaviour, mechanism and factors influencing the reaction are discussed.

THE study of nucleophilic *cis–trans* isomerisation of compounds containing activated carbon–carbon double bonds is important to the understanding of other nucleophilic vinylic reactions, *e.g.*, substitutions and their stereochemistry.[2] With a highly reactive system such as ethyl α-cyano-β-*o*-methoxyphenylacrylate[3,4] the reaction is of the first order in the nucleophilic catalyst, both in 95% ethanol[3] and in benzene,[4] and secondary as well as tertiary amines are effective catalysts. On the other hand, in the isomerisation of the less reactive diethyl[5,6] or dimethyl[7] maleates (I) to the fumarates
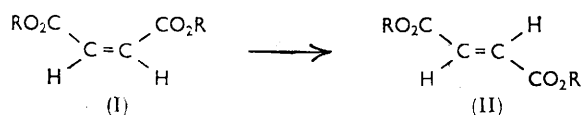
(II) in diethyl ether, tertiary amines were ineffective. The reaction is of second order in the catalytic amines,[6,7] and different mechanisms[4,6–9] were suggested to account for the role of the second amine molecule. The question arises whether in the isomerisation of systems intermediate in reactivity, a transition from first to second order in catalyst might be observed and whether a hydroxylic solvent might replace one of the amine
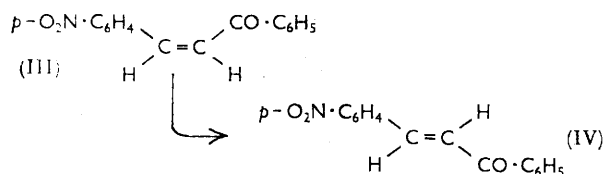
molecules required in the isomerisation. Hence the isomerisations of *cis*-4-nitrochalcone (III)[10] and of diethyl maleate were investigated in 95% ethanol.

RESULTS

The catalysed *cis–trans* isomerisation of *cis*-4-nitrochalcone (III) to the *trans* isomer (IV) in 95% ethanol at 33·8° was studied spectrophotometrically, in the presence of ten different nucleophiles. With 2×10^{-5}M-chalcone no isomerisation was detected after 2·5 hr. in the presence of 0·25—0·0025M-tri-n-butylamine. Under the same conditions, no isomerisation was observed with 0·02M-sodium bromide, or with 0·124—0·248M-pyridine, although isomerisation in pyridine was reported.[10]

Table 1 shows the first-order (k_1) and the second-order rate coefficients (k_{exp}, defined as k_1 divided by the stoicheiometric concentration of the catalyst) found with seven effective nucleophiles. The reaction is of first order each in the substrate and in the nucleophile. With 2×10^{-5}M-substrate and nucleophil concentrations *ca.* 0·001—0·2M the second-order k_{exp} values decreased on increasing the catalyst concentrations, but the decrease was not more than 30—50% on increasing the nucleophile concentration 20—30-fold. A plot of log k against log [nucleophile] was not straight, so comparisons of reactivity should be made only at similar nucleophile concentrations. The differences between the most reactive nucleophile, sodium hydroxide, and the least, di-isopropylamine, were three orders of magnitude.

To ascertain whether the decrease of the second-order rate coefficients in the presence of considerable concentrations of nucleophiles is due to the medium, an experiment was conducted with 0·02M-sodium azide and 4% cyclohexanone. The change was within the experimental error.

Sodium hydroxide, piperidine, or n-butylamine had no effect on *cis*-4-nitrostilbene under similar conditions.

The experiments with diethyl maleate (I) in 95% ethanol (Table 2) required a higher substrate concentration (0·01M) owing to the relatively small absorption of the two isomers, and have a higher experimental error. Nevertheless, the

[1] Part IX, Z. Rappoport and S. Gertler, *J. Chem. Soc.*, 1964, 1360.

[2] S. Patai and Z. Rappoport in S. Patai "The Chemistry of Alkenes," Interscience, New York, 1964, (*a*) p. 525, (*b*) p. 555.

[3] S. Patai and Z. Rappoport, *J. Chem. Soc.*, 1962, 396.

[4] Z. Rappoport, C. Degani, and S. Patai, *J. Chem. Soc.*, 1963, 4513.

[5] G. R. Clemo and S. B. Graham, *J. Chem. Soc.*, 1930, 213.

[6] K. Nozaki, *J. Amer. Chem. Soc.*, 1941, **63**, 2681.

[7] M. Davies and F. P. Evans, *Trans. Faraday Soc.*, 1955, **51**, 1506.

[8] E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., New York, 1962, p. 344.

[9] Ref. 2, p. 568.

[10] P. L. Southwick and R. J. Shozda, *J. Amer. Chem. Soc.*, 1959, **81**, 3298.

TABLE 1

First-order (k_1) and second-order $(k_{exp} = k_1/[\text{nucleophile}])$ rate coefficients for the nucleophile-catalysed isomerisation of 1.9—$2.1 \times 10^{-5}\text{M}$-*cis*-4-nitrochalcone to the *trans* isomer in 95% ethanol at 33·8° [a]

$10^2[\text{Nucleophile}]$ (M)	$10^5 k_1$ (sec.$^{-1}$)	$10^2 k_{exp}$ (l. mole^{-1} sec.$^{-1}$)
Sodium hydroxide		
0·009	4·42	49·2
0·02	11·0	55·0
0·05	23·5	47·0
0·1	43·2	43·2
0·2	70·5	35·3
Piperidine		
0·109	9·6	8·70
0·327	24·5	7·50
0·545	44·0	8·08
1·09	79·8	7·33
3·27	164·0	5·03
Sodium azide		
0·10	2·06	2·06
0·20	4·25	2·13
0·20	4·00 [b]	2·00
0·50	9·77	1·95
1·00	17·5	1·75
1·81	32·3	1·78
1·91	32·4	1·70
n-Butylamine		
0·202	2·00	0·99
0·606	5·75	0·95
1·01	9·45	0·93
2·02	16·05	0·79
5·05	26·0	0·52
Di-n-propylamine		
0·73	2·25	0·31
2·19	7·70	0·35
7·30	21·5	0·30
21·9	79·5	0·36
Cyclohexylamine		
0·826	2·61	0·32
2·47	6·8	0·28
4·13	10·1	0·25
8·26	16·9	0·20
16·5	27·9	0·17
Di-isopropylamine		
3·56	1·43	0·040
14·2	3·73	0·026
21·4	6·65	0·031

[a] Estimated experimental error for each run $\pm 3\%$; reproducibility $\pm 5\%$. [b] In this run the ethanol contains 4% (v/v) of cyclohexanone.

of the nucleophile on the double bond; (b) reactions of the intermediate thus formed (e.g., protonation, inversion, internal rotation); and (c) elimination of the nucleophile to form the more stable geometrical isomer. Most of the mechanistic problems arise in step (b). The relative importance and rates of the three steps determine the precise mechanism of the reaction. We have shown

TABLE 2

First-order (k_1) and second-order $(k_{exp} = k_1/[\text{amine}])$ rate coefficients for the amine-catalysed isomerisation of diethyl maleate to diethyl fumarate in 95% ethanol at 33·8° [a]

$10^2[\text{Amine}]$ (M)	$10^5 k_1$ (sec.$^{-1}$)	$10^2 k_{exp}$ (l. mole^{-1} sec.$^{-1}$)
Piperidine		
0·4	8·33	2·08
1·0	16·4	1·64
2·0	36·3	1·83
4·0	71·8	1·80
8·0	105·0	1·31
10·0	111·0	1·11
n-Butylamine		
1·01	3·48	0·345
2·02	6·25	0·310
10·1	18·9	0·187
20·2	33·4	0·165
40·4	31·2	0·077
Benzylamine		
9·17	11·7	0·128
14·6	21·8	0·149
18·4	21·5	0·117
36·7	28·5	0·078
Cyclohexylamine		
1·65	1·43	0·087
8·25	6·00	0·073
16·0	9·60	0·060
33·0	16·60	0·050
48·0	15·90	0·033
Di-n-propylamine		
2·19	1·19	0·054
3·65	1·80	0·049
5·84	2·87	0·049
7·30	3·39	0·046
10·95	6·38	0·058
14·60	6·90	0·047

[a] The estimated experimental error in the rate coefficients is $\pm 6\%$.

overall picture seems very much the same as with 4-nitrochalcone. The kinetics are of first order in the ester and of nearly first order in the amines, with k_{exp} (defined similarly to those of Table 1) generally falling at high catalyst concentrations. Decomposition of 4-nitrochalcone at high amine concentrations interfered with the measurements, but amine concentrations of up to 0·5M (5% v/v) could be employed with the maleate.

Diethyl maleate isomerises more slowly than 4-nitrochalcone. The value of the ratio $k_{exp}^{\text{chalcone}}/k_{exp}^{\text{maleate}}$ at comparable catalyst concentrations is between 2 and 5.

DISCUSSION

The mechanism of the nucleophilic isomerisation of carbon–carbon double bonds can usually be discussed in terms of three separate steps: [3,4] (a) reversible attack

that with strongly activated systems, such as ethyl α-cyano-β-o-methoxyphenylacrylate, among the processes occurring in step (b), protonation of the intermediate is mechanistically unimportant and only inversions and rotations have kinetic significance. However, when attack on the double bond is less favoured, the ratio of the rate of protonation of the unstable carbanion compared with its inversion and rotation may increase with the reactivity of the carbanion. The formation of a protonated intermediate followed by proton removal by a second nucleophile molecule was used to explain the overall third-order kinetics of the amine-catalysed maleate–fumarate isomerisation in ether.[4]

In the nucleophilic cleavage of the double bond by hydroxide ion, 4-nitrochalcone is 2000 times less reactive

than ethyl α-cyano-β-*o*-methoxyphenylacrylate and thus the former seems to be a suitable compound for study of the effect of the structure on the kinetics of isomerisation. This system also allows comparison of the isomerisation rates (k_{isom}) with the previously determined cleavage rates (k_{cleav}) and of this ratio with the one found for ethyl α-cyano-β-*o*-methoxyphenylacrylate.[3] Table 1 shows that although 4-nitrochalcone is less reactive, its kinetic behaviour is similar to that of ethyl α-cyano-β-*o*-methoxyphenylacrylate. We believe that the Scheme represents the main steps of the process (with *e.g.*, RR'NH as the nucleophile). The

Scheme

(I)—(II) $R^1 = R^2 = CO_2Et$; (III)—(IV) $R^1 = p\text{-}O_2N\cdot C_6H_4$, $R^2 = COPh$

order of the reaction in nucleophil [which in some cases may reflect its actual participation in the formation of the carbanion (V) or the corresponding intermediate addition compound, *e.g.*, $p\text{-}O_2N\cdot C_6H_4\cdot CH(NRR')\cdot CH_2\cdot CO\cdot C_6H_5$] remains unity, although some decrease is observed in the second-order rate coefficients with increased catalyst concentrations. When 4% of cyclohexanone were added to a mixture containing 4-nitrochalcone and sodium azide, the medium could be assumed to be similar to that with the highest amine concentration employed. Since only a very small change was observed in k_{exp} the absence of any considerable effect due to the medium can be assumed.

The rate decrease with the increase in the amine concentration could result from the lowering of the effectivity of the nucleophile with the increase in its stoicheiometric concentration. Thus, for instance, if k_{exp} reflects two concurrent reactions, one with the free amine molecules and the other with the strongly nucleophilic hydr-

oxide or ethoxide ion obtained from the equilibrium reaction of the nucleophile with the solvent (eqn. 4):

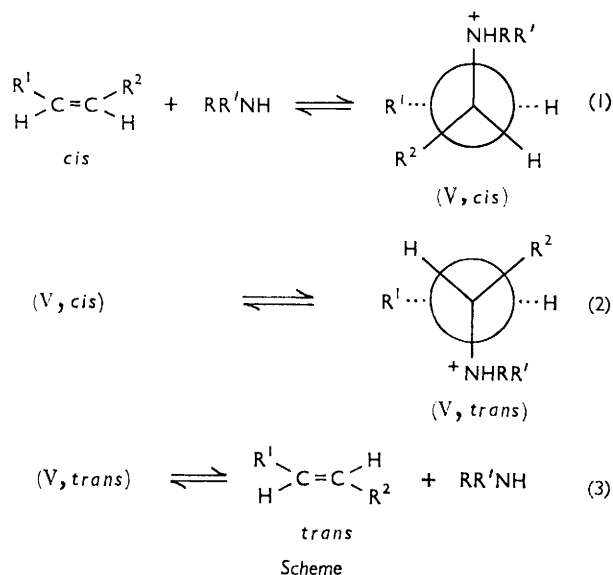$$EtOH + R'NH_2 \underset{}{\overset{K_b}{\rightleftharpoons}} EtO^- + R'NH_3^+ \qquad (4)$$

the rate equation would be:

$$(dx/dt) = (k_{R'NH_2}\, [R'NH_2] + k_{EtO^-}\, [EtO^-])[Substrate]$$

and the decrease in k_{exp} should reflect the diminishing contribution of the ethoxide-catalysed reaction to the total. This contribution can be evaluated, to a first approximation, as follows: pK_a for n-butylamine in ethanol [11] is 12·1 and pK of ethanol autoprotolysis [12] is 18 (or less [13]). Hence $pK_b = ca.$ 6, *i.e.*, $K_b = [EtO^-][BuNH_3^+]/[BuNH_2] = 10^{-6}$ in ethanol and $[EtO^-] = 10^{-3}\sqrt{[BuNH_2]}$. For 0·002 and 0·05M-BuNH$_2$ the calculated $[OEt^-]$ concentrations are 2·25 and 0·5% of that of the n-butylamine, respectively. The main anionic species in ethanolic sodium hydroxide is EtO^-,[13] and considering the values of Table 1 we used $k_{EtO^-}/k_{BuNH_2} = ca.$ 50. On this basis, with 0·002M-n-butylamine, half of the reaction is amine-catalysed and half is ethoxide-catalysed. With 0·05M-n-butylamine, the ethoxide-catalysed term contributes only one-fifth to the total, so k_{exp} should fall 40% between 0·002 and 0·05M-amine. The actual decrease is 50%. This treatment, with use of only approximate numbers and neglect of the presence of the second anionic nucleophil, the hydroxide ion, and other factors, is meant only as a qualitative demonstration for the importance and consequences of the amine–alcohol equilibrium.

In addition, the nucleophilicity of the amines could be slightly reduced at the higher concentration by hydrogen-bond formation between amine molecules. This explanation is not valid for the hydroxide and azide ions. In these two cases, incomplete dissociation at the higher concentrations of the salts in ethanol may be responsible for the lower rate coefficients, as found also for the reaction of azide ion with 1-chloro-2,4-dinitrobenzene in 95% ethanol.[14]

It was concluded [4] that the measured rate coefficient for the isomerisation is given by Kk_{rot}, where K is the equilibrium constant for the reversible attack of the nucleophile on the double bond (eqn. 1), and k_{rot} is the rate coefficient for the internal rotation in the intermediate carbanion (eqn. 2). It is worthwhile to compare the reactivity order obtained in our system with the results obtained in other nucleophilic vinylic reactions (relative reactivities given in parentheses): (*a*) Substitution of the halogen in *trans*-p-Me·C$_6$H$_4$·SO$_2$CH=CHCl in methanol [15] at 0°: Piperidine (300) > MeO$^-$(30) > Bu$^n_2$NH (15) > N$_3^-$, C$_6$H$_{11}$·NH$_2$ (1); (*b*) Isomerisation of ethyl maleate to ethyl fumarate in ether [6] at 25°: Piperidine (155) > Me$_2$NH (130) > MeNH$_2$ (75) > EtNH$_2$ (6) > Et$_2$NH (1) > Et$_3$N (0); (*c*) Isomerisation

[11] R. P. Bell, "The Proton in Chemistry," Cornell Univ. Press, Ithaca, New York, 1959, p. 44.
[12] W. K. McEwen, *J. Amer. Chem. Soc.*, 1936, **58**, 1124.
[13] E. F. Caldin and G. Long, *J. Chem. Soc.*, 1954, 3737.
[14] S. Patai and Y. Gotshal, *Israel J. Chem.*, 1965, **3**, 223.

[15] (*a*) L. Maioli and G. Modena, *Gazzetta*, 1959, **89**, 854; (*b*) G. Modena and P. E. Todesco, *ibid.*, 1959, **89**, 866; (*c*) G. Modena, P. E. Todesco, and S. Tonti, *ibid.*, 1959, **89**, 878; (*d*) Ref. 2, p. 544.

of ethyl *cis*-α-cyano-β-*o*-methoxyphenylacrylate in benzene [4] at 40°: Bu^n_2NH, Pr^n_2NH (70) > Pr^i_2NH (55) > Bu_3N (10) > Pyridine (1); (*d*) Isomerisation of *cis*-4-nitrochalcone in 95% ethanol at 33·8°: OH^- (700) > piperidine (160) > N_3^- (40) > Bu^nNH_2 (20) > $C_6H_{11}NH_2$, Pr^n_2NH (7) > Pr^i_2NH (1) >>> Et_3N, Pyridine, Bu_3N, Br^-, (0); (*e*) Isomerisation of diethyl maleate to diethyl fumarate in 95% ethanol at 33·8°: Piperidine (20) > n-$BuNH_2$ (3) > Benzylamine (2) > $C_6H_{11}·NH_2$ (1·5) > Pr^n_2NH (1). The relative reactivity order of most nucleophils studied in different reaction series is roughly the same.

It is expected that within a series of amines, both carbon basicity and hydrogen basicity should show the same order of relative reactivity. Therefore, the relative reactivities should be related to both the basic strength and the steric effects of the amines.

The strongly basic secondary amines show different degrees of reactivity, probably owing to variations in steric effects. Relatively small steric effects in conjunction with high inherent basicity explain the appearance of piperidine (when studied) at the beginning of each series. Secondary amines of low steric requirements should be more reactive than primary, but in some cases the weaker primary amines may be more reactive owing to their lower steric requirements. Branching of the amine decreases more the reactivity and di-iso-propylamine is the least reactive amine studied. Rates with tertiary amines, which are both weaker and more crowded than secondary, can be measured with the more reactive ethyl α-cyano-β-*o*-methoxyphenylacrylate.[4] They are effective with 4-nitrochalcone only when used as the reaction medium for the isomerisation for extended reaction times.[10] When the measured rate coefficient does not include the rotation step (as in vinylic substitution) a secondary amine is much more reactive than a primary.

It is not surprising that the small and highly basic hydroxide ion is the most reactive of the nucleophiles studied. The relatively high reactivity of the azide ion (which is more reactive than all the amines except piperidine) compared with the unreactivity of the bromide ion is in contrast to their similar reactivity in S_N2 reactions,[16–18] but it is in line with its high nucleophilicity relative to bromide in nucleophilic aromatic substitution.[17] The similarity between the aromatic and vinylic nucleophilic substitutions has been emphasised.[19] The differences in non-bonding interactions between the entering and the leaving groups are assumed to be among the main factors for the high N_3^-/Br^- reactivity ratio in S_NAr reactions.[17] The present case is one in which there is no leaving group, but the azide ion still shows high relative nucleophilicity. However, that the existence of a leaving group is important also in nucleophilic vinylic substitution is evident from the higher reactivity of azide ion than of di-n-propylamine

in the isomerisation, while in the substitution [15] di-n-butylamine (which is similar in reactivity to di-n-propylamine) [4] is more reactive than azide ion.

The formation of the carbanion (VI) is the first step both in the isomerisation of *cis*-4-nitrochalcone and in its cleavage to 4-nitrobenzaldehyde and acetophenone (eqn. 5). The ratio of the isomerisation (k_{isom}) to the cleavage (k_{cleav}) rate coefficients is governed by processes

$$p\text{-}O_2N·C_6H_4·CH(OH)·\bar{C}H·CO·C_6H_5 \longrightarrow$$
$$p\text{-}O_2N·C_6H_4·CHO + \bar{C}H_2·CO·C_6H_5 \quad (5)$$
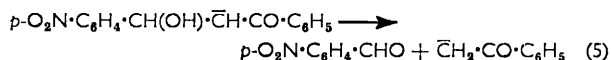
occurring during the life of the carbanion. Although the simultaneous cleavage of the *cis* isomer concurrent with its isomerisation was not studied, the rate coefficient for the cleavage of the *trans* isomer is known [20] to be $5·83 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$ in 95% ethanol at 35° in the presence of 0·05—0·2M-sodium hydroxide. This can be compared with k_{isom} of 35×10^{-2} l. mole^{-1} sec.$^{-1}$ for the isomerisation of the *cis* isomer in the presence of 0·002M-sodium hydroxide. Assuming that the rates of cleavage of the *cis* and the *trans* isomers are approximately the same (as is true with ethyl α-cyano-β-*o*-methoxyphenylacrylate [3]), we find $k_{isom}/k_{cleav} = 600$. Calculation of the corresponding ratio for the ethyl α-cyano-β-*o*-methoxyphenylacrylate is complicated by the occurrence of solvent-catalysed isomerisation and at the higher base concentrations this ratio is only about 3·5. The large difference in k_{isom}/k_{cleav} for the two systems indicates that the structure of the carbanion strongly influences the rate of carbon–carbon bond cleavage in which two carbanions of widely differing stabilities are formed, in a process of high energy requirements, and affects only slightly the rates of the free rotation or inversion, which have relatively low energy requirements unless the substituents are very bulky. A general conclusion, namely, that the lower the reactivity of an electrophilic double bond, the higher k_{isom}/k_{cleav}, seems to be indicated.

In the ethyl maleate–ethyl fumarate isomerisation the reaction in ether was of second order in the amine.[6,7] Explanations were given, *e.g.*, that one amine molecule gives the addition compound, $EtO_2C·CH(NRR')·CH_2·CO_2Et$, while the second removes the proton.[4] We hoped that the use of ethanol would simplify the reaction by decreasing association of the amine, by lengthening the life of the carbanion, and by assisting the deprotonation. Indeed, the order in the amine in ethanol solvent was somewhat less than unity, with k_{exp} falling with increasing amine concentrations. We believe that this drift is similar to the one suggested in the 4-nitrochalcone isomerisation, *i.e.*, a decrease in the relative concentration of ethoxide and hydroxide ions which contribute to the reaction rate. The effect in most cases is more pronounced here, owing to the use of higher concentrations of the amines. Moreover, the relative reactivity of ethoxide and hydr-

[16] A. J. Parker, *J. Chem. Soc.* (*A*), 1966, 220.
[17] B. O. Coniglio, D. E. Giles, W. R. McDonald, and A. J. Parker, *J. Chem. Soc.* (*B*), 1966, 152.

[18] C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, 1953, **75**, 141.
[19] J. F. Bunnett, in "Theoretical Organic Chemistry," Butterworths, London, 1959, p. 144.
[20] E. L. Walker and J. R. Young, *J. Chem. Soc.*, 1957, 2045.

oxide ions compared with the amines should be larger for the less reactive diethyl maleate than for the reactive 4-nitrochalcone system: a reactive substrate should discriminate less between a stronger and weaker nucleophil, while reaction of a non-reactive substrate should be strongly influenced by the nature and strength of the attacking agent. Hence, the relative importance of the ethoxide- and hydroxide-catalysed reaction should be larger with the maleate. At high amine concentrations, the decrease in the degree of dissociation would be manifest in the lower k_{exp} values, and enhance amine–amine hydrogen bonding should also be considered.

The identical order of reactivity of the various nucleophils with the two substrates makes it probable that a similar mechanism operates in both cases. The higher reactivity of the chalcone is expected both from the electron-attracting character of the groups flanking the double bond and from results for other nucleophilic vinylic reactions.[21]

The change of the order of the reaction in the amine from second with ether as solvent, to nearly first in nucleophil in ethanol is probably due to the solvating power of the alcohol which may make the presence of a second molecule of the amine superfluous in the transition state, either in the nucleophilic attack or during deprotonation. Actually, stabilisation of the intermediate carbanion by the hydroxylic solvent might give it a long enough life to complete the rotation and elimination steps without the appearance of a kinetically important protonated neutral intermediate.

EXPERIMENTAL

Materials.—95% Ethanol was purified as previously.[22] The amines were pure commercial grades, distilled, dried (KOH), and redistilled immediately before use. *cis*-4-

Nitrochalcone was prepared by the irradiation of a 2,3,3-trimethylpentane solution of the *trans* isomer.[23] Diethyl maleate (B.D.H.) was distilled before use.

Kinetics.—Spectrophotometry was in a Beckman DU spectrophotometer with a thermostated cell chamber. With 4-nitrochalcone, rate coefficients were calculated from measurements at 300 and 315 mμ, where the differences between the absorptions of the *cis* and the *trans* form were largest. In addition, the absorption was checked several times during each run at the isosbestic point ($\lambda = 281$ mμ) in order to ascertain the absence of side reactions which would change the optical densities. With 4-nitrochalcone and 0·11M-piperidine, fast decomposition of the chalcone was evident from the sharp changes in the absorption values at the isosbestic point.

Absorption values in runs with diethyl maleate were measured at 280 and 290 mμ. The rate coefficients were calculated from measurements at each wavelength separately, and the average of the two values was taken. Owing to the small differences between the absorption of the two isomers, the accuracy of k is about $\pm 3\%$ with 4-nitrochalcone and $\pm 6\%$ with diethyl maleate. The reproducibility of the individual runs was similar and several results in Tables 1 and 2 are averages of 2—3 runs. The rate coefficients were calculated as described previously.[4] In the 4-nitrochalcone–pyridine system no change was observed in the absorption, but the high absolute values at the isosbestic wavelength pointed to strong complex formation.

Some experiments were conducted with 2.75×10^{-5}M of *cis*-4-nitrostilbene in 95% ethanol at 33·8°. Measurements at 350 and 335 mμ and at the isosbestic point at 300 mμ showed no isomerisation after 24 hr. in the presence of 0·1M-*n*-butylamine, 0·01M-sodium hydroxide, or 0·044M-piperidine.

DEPARTMENT OF ORGANIC CHEMISTRY,
  THE HEBREW UNIVERSITY,
    JERUSALEM, ISRAEL. [6/824   *Received, June 29th*, 1966]

[21] N. H. Cromwell, P. L. Creger, and K. E. Cook, *J. Amer. Chem. Soc.*, 1956, **78**, 4412.

[22] S. Patai and Z. Rappoport, *J. Chem. Soc.*, 1962, 383.
[23] W. B. Black and R. E. Lutz, *J. Amer. Chem. Soc.*, 1953, **75**, 5990.