332. *The Kinetics and Mechanism of the Decomposition of Michael Adducts: An Example of the* E1cB *Elimination.*

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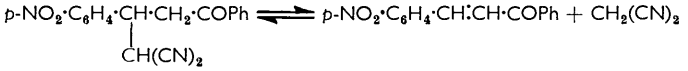
The kinetics of the decomposition, in methanol, of the Michael adduct of 4-nitrochalcone and malononitrile has been studied. It is concluded that the reaction belongs to the *E*1*cB* mechanistic class, the rate-determining step involving unimolecular decomposition of the conjugate base of the substrate, after ionisation of a proton from the α-carbon atom. Ionisation of the γ-hydrogen atom inhibits the reaction, as also does addition of strong or weak acids. The reaction sequence of the decomposition is, in accordance with the principle of microscopic reversibility, the exact reversal of the accepted mechanism for the Michael condensation.

In spite of its wide scope, the Michael reaction [1] and its reversal have been the subject of only a few kinetic studies. Ingold [2a] suggested that the reverse reaction may be of the *E*1*cB* mechanistic type, and this was suggested also by Hine and Kaplan [3] for the decomposition of 1,1,1,3-tetranitro-2-phenylpropane to nitroform and β-nitrostyrene. In general, *E*1*cB* eliminations from a saturated compound have been studied kinetically only in a small number of cases.[4] These investigations were conducted in basic or acid solutions, and no work was reported for neutral media. We have studied the elimination of malononitrile from 4,4-dicyano-3-*p*-nitrophenyl-1-phenylbutan-1-one (*i.e.*, the Michael adduct formed from 4-nitrochalcone and malononitrile) in methanol:



$$p\text{-}NO_2\cdot C_6H_4\cdot \underset{\substack{|\\ CH(CN)_2}}{CH}\cdot CH_2\cdot COPh \rightleftharpoons p\text{-}NO_2\cdot C_6H_4\cdot CH{:}CH\cdot COPh + CH_2(CN)_2$$

Results

4,4-Dicyano-3-*p*-nitrophenyl-1-phenylbutan-1-one, obtained by Michael condensation of 4-nitrochalcone and malononitrile, was decomposed at 40° in absolute methanol. Even though great care was taken to repeat exactly the purification procedure for the solvent, up to ±25%

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[1] Bergmann, Ginsburg, and Papo, *Org. Reactions*, 1959, **10**, 179.

[2] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, 1953, (*a*) p. 695, (*b*) p. 423, (*c*) p. 462.

[3] Hine and Kaplan, *J. Amer. Chem. Soc.*, 1960, **82**, 2915.

[4] Cristol, Hause, and Meek, *J. Amer. Chem. Soc.*, 1951, **73**, 674; Hine, Wiesboeck, and Ramsay, *ibid.*, 1961, **83**, 1222; Kemp, *Diss. Abs.*, 1961, 2894.

difference in rate coefficients was observed with different batches. Accordingly, the same batch of methanol was used in all experiments, apart from those summarised in Table 5. The kinetics of the reaction were followed spectrophotometrically, the wavelength at which the 4-nitrochalcone absorbs most strongly being used for the measurements. The initial first-order rate coefficient for the decomposition decreased slowly, but constantly, with the increase in the substrate concentration (Table 1). Increasing the substrate concentration 120-fold (from $0{\cdot}75$ to 92×10^{-4} mole l.$^{-1}$) causes a nine-fold decrease of the first-order rate coefficient (from $2{\cdot}52$ to $0{\cdot}29 \times 10^{-5}$ sec.$^{-1}$). Higher concentrations of substrate could not be investigated owing to the limited solubility of the compound in methanol. The optical density–time plots were linear at least up to 3% reaction with the highest substrate concentrations used, and to considerably larger reaction percentages with lower concentrations, and the reproducibility of the experiments was good.

TABLE 1.

Effect of substrate concentration on the initial rate coefficients for the decomposition of 4,4-dicyano-3-*p*-nitrophenyl-1-phenylbutan-1-one (DPB) in methanol.

DPB (10^{-4} mole l.$^{-1}$) ...	0·75	1·32	1·88	3·96	4·73	6·60	9·46	11·9	47·6	92
10^5k_{obs} (sec.$^{-1}$) at 40° ...	2·52	2·36	2·25	2·08	2·02	1·84	1·56	1·43	0·54	0·29
at 30°	0·44			0·43						
at 50°		10·4		8·05						
$10^7k_{\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ l.$^{-\frac{1}{2}}$ sec.$^{-1}$) * at 40°	2·2	2·7	3·1	4·2	4·4	4·7	4·8	4·9	3·8	2·8

* Calc. by assuming that the reaction is of one-half order in the substrate (see Discussion).

The Effect of Malononitrile on the Rates.—Table 2 shows that addition of malononitrile to the reaction mixture causes a decrease in the rate coefficients. This was not due to a reversal of the reaction: in mixtures containing 10^{-3}—10^{-4} mole l.$^{-1}$ of 4-nitrochalcone and up to 10^{-2} mole l.$^{-1}$ of malononitrile, no change in the absorption could be detected during periods of up to 3 days, *i.e.*, under these conditions no measurable Michael condensation takes place.

TABLE 2.

Initial rate coefficients for the decomposition of $3{\cdot}1 \times 10^{-4}$ mole l.$^{-1}$ of 4,4-dicyano-3-*p*-nitrophenyl-1-phenylbutan-1-one in the presence of malononitrile (MN) in methanol at 40°.

MN (10^{-4} mole l.$^{-1}$)..................	0	0·11	5·08	10·9	20·4	50·0
10^5k_1 (sec.$^{-1}$)	2·15 *	2·15	1·66	1·27	1·08	0·80

* Interpolated from Table 1.

The Effect of Added Perchloric Acid on the Rates.—Very low concentrations of perchloric acid inhibit the reaction, and higher concentrations stop it completely (Table 3). Similarly, in a pyridine–pyridine hydrochloride buffer (apparent pH measured with a glass electrode in methanol ~2·5) the reaction was too slow to follow.

TABLE 3.

Initial rate coefficients for the decomposition of $2{\cdot}56 \times 10^{-4}$ mole l.$^{-1}$ of 4,4-dicyano-3-*p*-nitrophenyl-1-phenylbutan-1-one in the presence of perchloric acid in methanol at 40°.

$HClO_4$ (10^{-6} mole l.$^{-1}$)	0	0·64	1·6	6·4	16	48	5000
10^5k_1 (sec.$^{-1}$)	2·15	1·84	1·47	1·37	0·89	0·32	0

The Effect of Added Base or Buffer on the Reaction Rates.—Addition of sodium hydroxide in very low concentrations enhanced the reaction rate. However, owing to the high experimental error accompanying the use of very low base concentrations, these results were inconclusive as regards the order of the reaction in base. The first four values in Table 4 show that the reaction is accelerated in a linear manner by using a constant triethylamine hydrochloride concentration while increasing that of triethylamine. At a constant triethylamine : triethylamine hydrochloride ratio the rate increases linearly with the buffer concentration, pointing to general base-catalysis. When the initial concentration of the substrate was increased, with constant buffer concentration, the rate coefficients remained practically constant; a very slight decrease was observed only when the substrate concentration was of the same order of magnitude as the buffer concentration. For different buffer mixtures, the rate coefficients fell with the acidity of the medium.

TABLE 4.

Initial rate coefficients for the decomposition of 4,4-dicyano-3-*p*-nitrophenyl-1-phenylbutan-1-one (DPB), in the presence of various concentrations of triethylamine (TEA) and triethylamine hydrochloride (TEA,HCl) in absolute methanol at 40°.

DPB (10^{-4} mole l.$^{-1}$)	2·87	2·74	2·74	2·42	1·15	2·87	1·28	2·56	2·42
TEA (10^{-3} mole l.$^{-1}$)	13·9	26·7	41·5	55·5	13·9	13·9	27·8	27·8	41·3
TEA,HCl (10^{-3} mole l.$^{-1}$)	6·95	6·95	6·95	6·95	6·95	6·95	13·9	13·9	20·8
10^5k_1 (sec.$^{-1}$)	3·18	5·14	7·13	8·95	3·20	3·18	3·58	3·70	4·05
DPB (10^{-4} mole l.$^{-1}$)	0·98	2·46	4·92	27·5	50·8	1·0	5·0	10·0	
TEA (10^{-3} mole l.$^{-1}$)	10	10	10	10	10	5·1	5·1	5·1	
TEA,HCl (10^{-3} mole l.$^{-1}$)	5·1	5·1	5·1	5·1	5·1	5·1	5·1	5·1	
10^5k_1 (sec.$^{-1}$)	2·49	2·40	2·35	2·46	2·03	1·49	1·38	1·25	

The Effect of the Solvent Composition on the Reaction Rates.—Increasing the water content of methanol–water mixtures gave slower rates. The decrease is nearly linear in media containing up to 40% of water and is less pronounced in more aqueous mixtures (see Table 5). The total decrease is relatively small. The rate in pure methanol is about three times higher than in 2 : 3 v/v methanol–water.

Reaction rates for the decomposition were measured also in dimethylformamide at 40°, and again the rate coefficients decreased with increasing substrate concentration. The values were slightly lower than in methanol, 10^5k_1 being 2·06, 1·01, and 0·77 sec.$^{-1}$ at substrate concentrations of 1·01, 2·51, and 5·02 × 10^{-4} mole l.$^{-1}$, respectively.

TABLE 5.

Effect of added water on the initial first order rate coefficients for the decomposition of 2·6 × 10^{-4} mole l.$^{-1}$ of 4,4-dicyano-3-*p*-nitrophenyl-1-phenylbutan-1-one in methanol at 40°.

Water (% v/v)	1	2	6	10	14	20	26	30	36	40	46	50	56	60
10^5k_1 (sec.$^{-1}$) ...	2·52	2·42	2·32	2·28	2·02	1·78	1·59	1·43	1·03	0·98	0·95	0·84	0·85	0·70

Activation Energies.—The activation energies were calculated from the results given in Table 1 and were found to be 32·4, 29·6, and 29·8 kcal. mole^{-1} for the concentrations 0·75, 1·36, and 3·96 × 10^{-4} mole l.$^{-1}$, respectively.

The kinetic results for the decomposition of 4,4-dicyano-3-*p*-nitrophenyl-1-phenylpentan-1-one to 4-nitrochalcone and methylmalononitrile are given in Table 6. Although the reproducibility was poor (±25%) it is clear that the decomposition rates are higher than those of 4,4-dicyano-3-*p*-nitrophenyl-1-phenylbutan-1-one in similar concentrations and that the concentration of the compound has only a small effect on the measured rate coefficients.

TABLE 6.

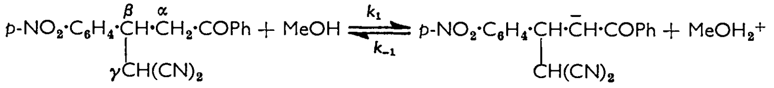
Initial rate coefficients for the decomposition of 4,4-dicyano-3-*p*-nitrophenyl-1-phenylpentan-1-one (DPP) in absolute methanol at 40°.

DPP (10^{-4} mole l.$^{-1}$)	1·74	2·03	3·48	7·76	12·2	28·4	30·6	41·8
10^5k_1 (sec.$^{-1}$)	5·5	4·8	5·4	4·6	5·7	4·5	4·4	4·0

Three runs on the decomposition of ethyl α-cyano-β-*p*-nitrophenyl-δ-oxo-δ-phenylvalerate were conducted in methanol at 40°. The rate coefficients were much smaller than in the case of the analogous compound with a second cyano- instead of an ethoxycarbonyl group, the values being 7·6, 6·2, and 6·3 × 10^{-7} sec.$^{-1}$ for the decomposition of 0·97, 2·42, and 4·78 × 10^{-4} mole l.$^{-1}$ of the substrate.

DISCUSSION

The reversal of the reaction sequence generally accepted for the Michael condensation fits the results presented in the previous section:



$$\underset{\gamma\mathrm{CH(CN)_2}}{p\text{-}NO_2{\cdot}C_6H_4{\cdot}\overset{\beta}{C}H{\cdot}\overset{\alpha}{C}H_2{\cdot}COPh} + MeOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathrm{CH(CN)_2}}{p\text{-}NO_2{\cdot}C_6H_4{\cdot}CH{\cdot}\bar{C}H{\cdot}COPh} + MeOH_2^+ \qquad (1)$$

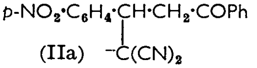
(I) (II)

$$\text{(II)} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} p\text{-}NO_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COPh + {}^-CH(CN)_2 \qquad (2)$$

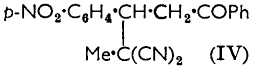
(III)

$$^-CH(CN)_2 + MeOH_2^+ \text{ (or MeOH)} \rightleftharpoons CH_2(CN)_2 + MeOH \text{ (or } MeO^-) \qquad (3)$$

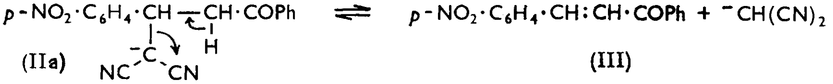
Step (1) is the formation of a carbanion by loss of a proton from the α-carbon atom. Although, as judged by the acidity of malononitrile [5] (p$K \sim 11$) as compared to that of acetophenone [6] (p$K \sim 19$), the formation of the isomeric carbanion (IIa) with loss of a proton from the γ-position must be much faster and thermodynamically more favoured,



(IIa)



(IV)



(IIa) (III) (4)

we believe that there is no reasonable route through which (IIa) is able to react to give the chalcone (III). A proton transfer from (IIa) to give (II) is kinetically (and mechanistically) indistinguishable from the steps proposed above, while a direct four-centre reaction of (IIa) to give (III) (equation 4) cannot be excluded *a priori* but is probably unimportant as a four-centre reaction of this type cannot occur with compound (IV) which nevertheless gives the same reaction somewhat faster than (I), showing that obstruction of the pathway (IIa $\rightleftharpoons$ III) does not influence the feasibility of the reaction. We believe therefore that the reaction of both compounds (I) and (IV) takes place through a similar mechanism, *i.e.*, by steps 1—3.

Obviously in step (1) the abstraction of the proton may occur both by methanol molecules and methoxide ions. However, the effect of added acids on the rate (Table 3) shows that methoxide ions are relatively unimportant. The rate coefficients in $1{\cdot}6 \times 10^{-6}$M- and $1{\cdot}6 \times 10^{-5}$M-acid are about 70% and 40% of that in pure methanol, showing that the original methoxide-ion concentration (about 10^{-8} mole l.$^{-1}$ in neutral solution) cannot be a major factor in the proton abstraction. The same conclusion was reached by Hine and Kaplan [3] for a similar system.

Addition of malononitrile to compound (I) lowered the reaction rates when constant substrate concentrations (Table 2) were used. As it was shown that no measurable reaction takes place between malononitrile and compound (I) this cannot be due to a reversal of step (2). We attribute the effect again to the acidity of malononitrile, *i.e.*, to inhibition by common (hydrogen) ions, similarly to that by perchloric acid and by the γ-hydrogen atom of the substrate itself. The inhibition (in similar concentrations) by malononitrile is somewhat smaller than that by the substrate itself. This may be due to the difference in the acidity of the γ-hydrogen atom of compound (I) on the one hand and of malononitrile on the other. It is also possible that the effect of the γ-hydrogen atoms is the larger, as they are in a favoured position and may exert their influence by intramolecular proton transfer leading to the unreactive ion (IIa).

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

[6] Conant and Wheland, *J. Amer. Chem. Soc.*, 1932, **54**, 1212.

The lowering of the first-order rate coefficients by increased substrate concentrations can be explained, therefore, as auto-inhibition caused by the common-ion effect of the equilibrium ($I \rightleftharpoons IIa$) on the equilibrium ($I \rightleftharpoons II$), *i.e.*, lowering the concentration of (II) in the solution and promoting the reverse reaction ($II \longrightarrow I$). This effect seems to be qualitatively independent of the nature of the solvent and appears also in the aprotic solvent dimethylformamide.

In a methanolic, neutral triethylamine–triethylamine hydrochloride buffer the first-order rate coefficients are practically independent of the substrate concentration and start to fall again only at substrate concentrations which are similar to that of the buffer, *i.e.*, when the buffer becomes relatively ineffective. In more acid buffered solutions, decrease in the coefficients is again observed but is less than in the unbuffered solution (Table 4, last three values).

The most conclusive evidence for the inhibiting effect of the γ-hydrogen on the rates is that replacing the latter by a methyl group gives a system in which the rate decrease with increasing concentration of the substrate is only very slight, somewhat irregular, and possibly within the experimental error for this compound (Table 6).

Steady-state treatment of equations (1) and (2) [we neglect the reverse of step (2), which was found to be immeasurably slow under the conditions employed] gave expression (5) for the reaction velocity:

$$v = k_1k_2[\mathrm{I}]/(k_2 + k_{-1}[\mathrm{MeOH_2^+}]). \tag{5}$$

As the substrate (I) is a weak acid in methanol, the concentration of protons or $MeOH_2^+$ ions in the medium is given by $[MeOH_2^+]^2 = K_A[I]$, where K_A is the acid dissociation constant of (I). Inserting this value into eqn. (5) gives:

$$v = k_1k_2[\mathrm{I}]/(k_2 + k_{-1}\sqrt{K_A}\sqrt{[\mathrm{I}]}). \tag{6}$$

An attempt was made to test equation (6) by correlating it with the observed values of the reaction velocity in Table 1, *i.e.*, $v = dx/dt = k_{obs}[I]$. Inserting this value into equation (6) and rearranging the terms gives:

$$1/k_{obs} = 1/k_1 + k_{-1}\sqrt{K_A}\sqrt{[\mathrm{I}]}/k_1k_2. \tag{7}$$

Plotting $1/k_{obs}$ against $\sqrt{[I]}$ gave a reasonably linear correlation for all points except the last two pertaining to the highest substrate concentrations.

The use of half-order rate coefficients (Table 1) can be justified as follows: The term k_2 in the denominator of equation (6) can be neglected as it is much smaller than the term $k_{-1}\sqrt{K_A}\sqrt{[I]}$. The order of magnitude of k_2 is, to a first approximation, equal to that of the observed overall rate, *i.e.*, $\sim 10^{-5}$; the protonation rate coefficient k_{-1} of similar pseudo-acids [7] is 10^8—10^9 l. mole^{-1} sec.$^{-1}$; K_A for malononitrile is $6{\cdot}5 \times 10^{-12}$ (*i.e.*, $\sqrt{K_A} \sim 2{\cdot}5 \times 10^{-6}$) and $\sqrt{[I]}$ is about 10^{-2} in our experiments. Hence the value of the term $k_{-1}\sqrt{K_A}\sqrt{[I]}$ is at least 10^4—10^5 times higher than that of k_2, so that the latter can certainly be neglected in comparison with it. Accordingly, equation (6) becomes, to a first approximation,

$$v = k_1k_2[\mathrm{I}]/k_1\sqrt{K_A}\sqrt{[\mathrm{I}]} = k'\sqrt{[\mathrm{I}]}. \tag{8}$$

The corresponding half-order rate coefficients are given in Table 1 (see row headed $k_{\frac{1}{2}}$). The correlation of $k_{\frac{1}{2}}$ is much better than that of k_{obs} at various substrate concentrations. Taking into consideration the simplifications used and the complexity of the system, it seems that the qualitative approximation $v = k'\sqrt{[I]}$ is valid.

The results in Table 4 show that with a constant triethylamine hydrochloride concentration the rates are enhanced by adding more of the basic component of the buffer, *i.e.*, of triethylamine. This is obviously due to the simultaneous increase in the concentration

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[7] Patai, Zabicky, and Israeli, *J.*, 1960, 2038.

of both triethylamine and methoxide ions. On the other hand, the rates are also higher, although less pronouncedly so, when the concentration of the buffer (with its components in the same proportions) is larger. This shows that the reaction is general base-catalysed, but the efficiency of triethylamine for proton abstraction is much less than that of methoxide ions.

Step (2) of the reaction is the cleavage of the $\beta\gamma$-carbon–carbon bond with the formation of 4-nitrochalcone (III) and the carbanion $^{-}CH(CN)_2$. Protonation of the latter in the medium must be very fast, so that step (3) does not influence the reaction sequence.

It can be concluded that the decomposition of (I) to (III) and to $CH_2(CN)_2$ is an example of the *E*1c*B* mechanism [2b] (*i.e.*, a unimolecular elimination from the conjugate base of the substrate).

For the generalised case, where several bases are present in the reaction mixture (*i.e.*, methanol, methoxide ions, and added base) equation (5) can be written in the form:

$$v = k_2[\mathrm{I}]\sum k_{\mathrm{B}}[\mathrm{B}]/(k_2 + \sum k_{-\mathrm{B}}[\mathrm{BH}^+]), \tag{9}$$

where B is any base present, BH$^+$ its conjugate acid, and k_{B} and $k_{-\mathrm{B}}$ are the rate coefficients of proton abstraction by B and protonation by BH$^+$, respectively. It can be deduced from equation (9) that two limiting cases will exist.[3] If $k_2 \gg \sum k_{-\mathrm{B}}[\mathrm{BH}^+]$ (*i.e.*, in strongly basic solution), equation (9) reduces to $v = [\mathrm{I}]\sum k_{\mathrm{B}}[\mathrm{B}]$ and proton abstraction (step 1) will be rate-controlling. If $k_2 \ll \sum k_{-\mathrm{B}}[\mathrm{BH}^+]$ (*i.e.*, in strongly acidic solution) most of the carbanions (II) will be returned to (I) and step (2) becomes rate-controlling. Both limiting cases will be subject to general base-catalysis.

In the derivation of equation (8) it has been shown that for neutral solution the arguments brought for an acid medium are still valid, and step (2) is rate-determining. The following additional arguments point in favour of this assumption. The overall decomposition rate coefficients of (I) are about thirty times faster than those of the compound $EtO_2C\cdot CH(CN)\cdot CH(C_6H_4\cdot NO_2\text{-}p)\cdot CH_2\cdot COPh$ to 4-nitrochalcone and ethyl cyanoacetate in similar conditions. As the effect of the γ-substitution (*i.e.*, replacement of one cyano-group by an ethoxycarbonyl group) can hardly affect considerably the ionisation of the α-hydrogen atom, it is probable that the difference in the rate coefficients is due to the greater stability of the $^{-}CH(CN)_2$ than of the $^{-}CH(CN)\cdot CO_2Et$ carbanion [7] influencing the rate of step 2, the second product (III) being the same in both cases.

The rather high activation energy of the reaction (about 30 kcal. mole^{-1}) also points to a rate-determining fission of a carbon–carbon bond, as much lower activation energies would be expected if the rate-determining step were the ionisation of a carbon acid (*e.g.*, 20 kcal. mole^{-1}).[5,8] The frequency factor of the reaction was calculated from the values in Table 1, and $\log_{10} A$ was found to be 16. This is similar to the values obtained for unimolecular eliminations from positively charged ions.[2c] As the sign of the charge (positive or negative) should not alter the type of the reaction, it could be predicted that an *E*1c*B* reaction should be affected by changes in the solvent in the same way as an *E*1 reaction of a cation, *i.e.*, more solvation should cause a small decrease in the rates. This was observed in our case (see Table 5). Part of this effect might be the result of the enhanced dissociation of the γ-hydrogen atom in more aqueous solvents. The same two effects probably also operate when the solvent is changed to dimethylformamide, in which the rates, with similar concentrations of substrate, are lower and the auto-inhibition is more pronounced.

The reverse of the mechanism proposed in steps (1)—(3) is in complete agreement with that generally accepted for the Michael condensation.

EXPERIMENTAL

Materials.—" AnalaR " methanol was refluxed with magnesium turnings and iodine, then distilled, and the fraction boiling at 64·5°/720 mm. was used. Dimethylformamide from British

[8] Hine, Wiesboeck, and Ghirardelli, *J. Amer. Chem. Soc.*, 1961, **83**, 1219.

Drug Houses Ltd. was distilled twice under reduced pressure and the fraction boiling at 45—46°/12 mm. was collected. 4-Nitrochalcone,[9] malononitrile,[10] and methylmalononitrile [11] were prepared according to the literature.

Condensation of 4-*Nitrochalcone with Malononitrile.*—4-Nitrochalcone (2·5 g., 0·01 mole) was dissolved in boiling methanol (50 ml.) to which 2 drops of N-methanolic sodium methoxide had been added. Malononitrile (2 g., 0·03 mole) was then added to the solution which became red immediately. After cooling, the yellow crystals (2·3 g.) were filtered off. Addition of water to the mother-liquor gave an additional crop (0·5 g.; total 88%). Crystallisation from methanol gave 4,4-*dicyano*-3-p-*nitrophenyl*-1-*phenylbutan*-1-*one* as white needles, m. p. 158° (Found: C, 67·7; H, 4·1; N, 12·8. $C_{18}H_{13}N_3O_3$ requires C, 67·7; H, 4·1; N, 13·15%), $\lambda_{max.}$ (in MeOH) 250 mμ (ε 18,800).

If the reaction mixture (together with the precipitate) was not worked up immediately after cooling, an unidentified by-product, m. p. 259°, was also obtained.

Condensation of 4-*Nitrochalcone and* 1,1-*Dicyanoethane* (*Methylmalononitrile*).—To 4-nitrochalcone (5 g., 0·02 mole) in methanol (150 ml.) there were added 1,1-dicyanoethane (1·5 g., 0·019 mole) and 2 drops of N-methanolic sodium methoxide. After one day at room temperature, water was added. Crystallisation of the yellow precipitate (2·2 g., 35%) from methanol gave 4,4-*dicyano*-3-p-*nitrophenyl*-1-*phenylpentan*-1-*one* (1·8 g.), m. p. 124° (Found: C, 68·6; H, 4·8; N, 12·0. $C_{19}H_{15}N_3O_3$ requires C, 68·5; H, 4·5; N, 12·6%), $\lambda_{max.}$ (in MeOH) 246 mμ (ε 15,200).

Condensation of 4-*Nitrochalcone with Ethyl Cyanoacetate.*—To a boiling solution of 4-nitrochalcone (2·5 g., 0·01 mole) and ethyl cyanoacetate (2 g., 0·017 mole) in methanol (20 ml.), enough methanolic sodium methoxide was added to make the solution slightly alkaline. The tar which separated from the cooled solution was dissolved in hot ethanol and left for 24 hr. Yellow crystals, m. p. 118°, were obtained. Crystallisation from ethanol gave *ethyl* α-*cyano*-β-p-*nitrophenyl*-δ-*oxo*-δ-*phenylvalerate* (2·5 g., 69%), m. p. 124° (Found: C, 65·7; H, 4·65; N, 7·7. $C_{20}H_{18}N_2O_5$ requires C, 65·6; H, 4·9; N, 7·65%), $\lambda_{max.}$ (in MeOH) 247 mμ (ε 28,100).

Kinetic Procedure.—As the compounds used dissolved in methanol only slowly, while their decomposition was rather fast, the following procedure was adopted: A weighed amount of the compound was dissolved in tetrahydrofuran (1—2 ml.), and methanol (boiled before use to expel dissolved carbon dioxide, and cooled to the reaction temperature) was added to give 50 ml. of solution. This was diluted immediately with more methanol, and/or the solutions of the other reagents, to the desired concentration. It was found that no decomposition occurred in tetrahydrofuran even after 24 hr. at 40°, and that the tetrahydrofuran (0·2% or less in the final mixture) had no effect on the rate. The reaction mixture was placed in a ground-glass, stoppered, silica absorption cell in a thermostat-controlled spectrophotometer chamber, and a Beckman DU spectrophotometer was used with a Beckman Dual Thermospacer. The absorbance at 314 mμ, the wavelength of the maximum absorption of 4-nitrochalcone [ε 29,600; lit.,[12] $\lambda_{max.}$ 315 mμ (ε 30,000)] was measured. The relevant data for the other compounds used, at 314 mμ, were ε 1100 for 4,4-dicyano-3-*p*-nitrophenyl-1-phenylbutan-1-one, ε 2400 for the pentanone, and ε 620 for the valerate.

Treatment of Data.—The optical-density (*D*) values were plotted against time, and first-order rate coefficients were calculated from the graphs, only the initial straight portion of the line up to 5% reaction being used.

A sample run for $6·6 \times 10^{-4}$ mole $l.^{-1}$ of 4,4-dicyano-3-*p*-nitrophenyl-1-phenylbutan-1-one in methanol at 40° was:

Time (min.)	4	10·5	16·5	20	24	27	30	35·5	41·5	48
D	0·568	0·660	0·770	0·840	0·915	0·985	1·045	1·153	1·292	1·430

$\Delta D/\Delta t$ (from graph) $= 3·6 \times 10^{-4}$ sec.$^{-1}$.

$k_1 = \Delta D/(\Delta t \times \varepsilon \times C_0) = (3·6 \times 10^{-4})/(29{,}600 \times 6·6 \times 10^{-4}) = 1·84 \times 10^{-5}$ sec.$^{-1}$.

Product Analysis.—(*a*) 4,4-Dicyano-3-*p*-nitrophenyl-1-phenylbutan-1-one (200 mg.) was dissolved in methanol (30 ml.), and *p*-anisaldehyde (1 g.) was added to trap the malononitrile produced, as this compound tends to give side reactions in methanol. 0·1N-Methanolic sodium

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[9] Davey and Gwilt, *J.*, 1957, 1008.

[10] Corson, Scott, and Vose, *Org. Synth.*, Coll. Vol. II, 1943, p. 379.

[11] Strack and Schwaneberg, *Ber.*, 1934, **67**, 42.

[12] Walker and Young, *J.*, 1957, 2041.

methoxide (1 ml.) was added and the mixture was left for 4 hr. at 40°. Water was added to the solution; the precipitated oil crystallised from methanol. Fractional crystallisation gave *p*-methoxybenzylidenemalononitrile [13] as well as 4-nitrochalcone and starting material.

(*b*) The spectrum of a methanolic solution ($5{\cdot}82 \times 10^{-4}$ mole $l.^{-1}$) of 4,4-dicyano-3-*p*-nitrophenyl-1-phenylbutan-1-one at 40° was measured after various periods up to 24 hr. By using the absorption at four wavelengths (characteristic for the starting material and 4-nitrochalcone), it was found that the percentage formation of the latter is identical with the percentage decomposition of the starting material. The incursion of side reactions become noticeable only after 2—4 days.

Attempts to Follow the Condensation.—Methanolic solutions of 4-nitrochalcone (10^{-4}—10^{-3} mole $l.^{-1}$) and malononitrile (10^{-4}—10^{-2} mole $l.^{-1}$) were kept at 40°. Samples were taken and diluted at various times and the optical densities were measured. No decrease in the absorption of the 4-nitrochalcone within 3 days was found in any of these experiments.

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[13] Zabicky, *J.*, 1961, 683.