Nucleophilic Attacks on Carbon–Carbon Double Bonds. Part XVIII.[1,2] Reaction of 2-Dicyanomethyleneindane-1,3-dione with Anilines in Acetonitrile

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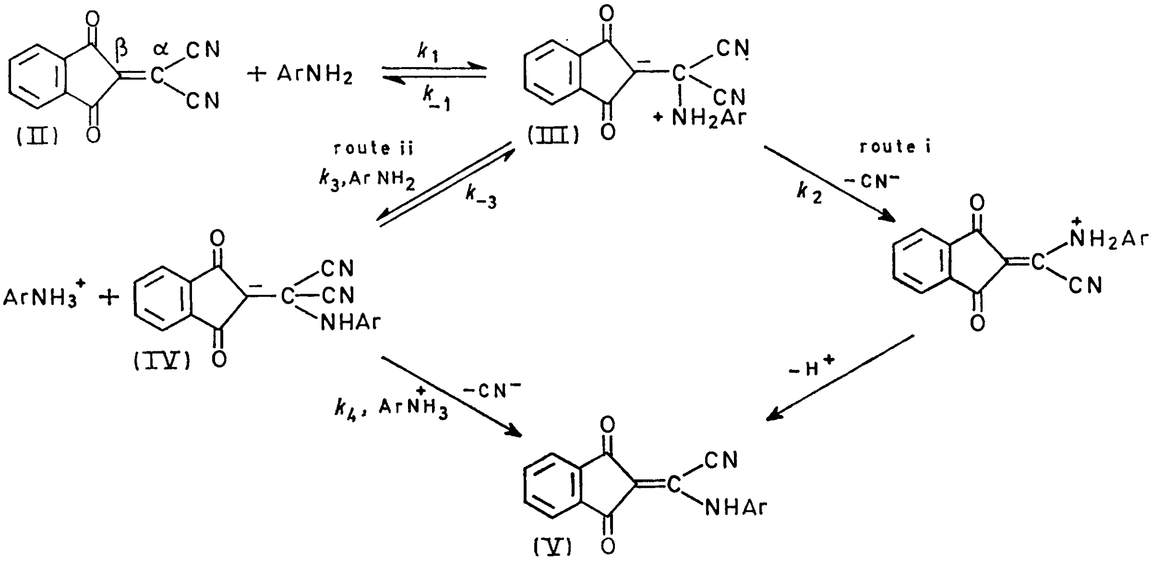
The replacement of one of the cyano-groups of 2-dicyanomethyleneindane-1,3-dione (II) by ring-substituted anilines in acetonitrile is of nearly second order in the amine, is catalysed by pyridines, and shows a Hammett ρ value of $-6{\cdot}9$ at 30°. A mechanism is suggested in which the zwitterion (III), formed initially by a reversible nucleophilic attack of the amine on (II), is reversibly deprotonated by a second amine molecule, followed by an anilinium ion-assisted expulsion of the cyanide ion. *NN*-Dimethyl-, *N*-methyl-, 2,5-dimethoxy-, and 2,6-dimethyl-anilines give *para*-addition products with (II).

THE reactions of amines with electrophilic olefins carrying a leaving group X, *e.g.* (I), are of kinetic order of one,[3] two,[1,4] or between one and two [1,3g,4a] in the amine. The kinetics are accommodated by Scheme 1, where the

$$p\text{-Me}_2\text{NC}_6\text{H}_4\text{C(X)}\colon\text{C(CN)}_2 \qquad \text{(I)}$$

initial bimolecular nucleophilic attack of the amine on the olefin [which is exemplified by 2-dicyanomethyleneindane-1,3-dione (II) [5]] forms the zwitterion (III). The C–X bond cleavage in (III) (where X = CN, and the negative charge is also delocalised on the oxygen atoms) is retarded by the electron-withdrawing α-ammonium residue. With good leaving groups C–X bond cleavage is faster than any other reaction of (III), nucleophilic attack becomes rate determining (route i) [6] and the reaction is first order in the amine.[3] When X is a sluggish leaving group (*e.g.*, CN, OEt, or F),[1,4] reversible deprotonation of the ammonium ion of (III) by another amine molecule may precede C–X bond cleavage (route ii). The further cleavage of the C–X bond in the carbanion (IV) is then much easier than that in the zwitterion (III).



SCHEME 1

A steady-state treatment of Scheme 1 gives equation (1), where $k_{\text{obs}}{}^2$ is the observed second-order rate coefficient. When $k_2 + k_3k_4[\text{Amine}]/(k_{-3} + k_4) > k_{-1}$ route i predominates [equation (2)] as found when X = Cl, Br,

$$k_{\text{obs}}{}^2 = k_1\,[k_2 + k_3k_4[\text{Amine}]/(k_{-3} + k_4)]/[k_{-1} + k_2 + k_3k_4[\text{Amine}]/(k_{-3} + k_4)] \qquad (1)$$

$$k_{\text{obs}}{}^2 = k_1 \qquad (2)$$

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[1] Part XVII, Z. Rappoport and P. Peled, *J.C.S. Perkin II*, 1973, 616.

[2] Presented in part at the 42nd Meeting of the Israel Chemical Society, Rehovoth, 1972; see Z. Rappoport and D. Ladkani, Abstracts of the 42nd Meeting of the Israel Chemical Society, 1972, p. 6.

[3] (*a*) G. Modena, P. E. Todesco, and S. Tonti, *Gazzetta*, 1959, **89**, 878; (*b*) G. Modena, F. Taddei, and P. E. Todesco, *Ricerca sci.*, 1960, **30**, 894; (*c*) L. Maioli, G. Modena, and P. E. Todesco, *Boll. sci. Fac. Chim. ind. Bologna*, 1960, **18**, 66; (*d*) A. Campagni, G. Modena, and P. E. Todesco, *Gazzetta*, 1960, **90**, 694; (*e*) F. Scotti and E. J. Frazza, *J. Org. Chem.*, 1964, **29**, 1800; (*f*) P. Beltrame, G. Favini, M. G. Cattania, and F. Guella, *Gazzetta*, 1968, **98**, 380; (*g*) Z. Rappoport and R. Ta-Shma, *J. Chem. Soc.* (*B*), 1971, 1461; (*h*) Z. Rappoport and A. Topol, *J.C.S. Perkin II*, 1972, 955.

[4] (*a*) Z. Rappoport and R. Ta-Shma, *J. Chem. Soc.* (*B*), 1971, 871; (*b*) Z. Rappoport and N. Ronen, *J.C.S. Perkin II*, 1972, 955.

[5] (*a*) S. Chatterjee, *Science*, 1967, **157**, 314; (*b*) *J. Chem. Soc.* (*B*), 1969, 725; (*c*) H. Junek and H. Sterk, *Tetrahedron Letters*, 1968, 4309.

[6] Z. Rappoport, *Adv. Phys. Org. Chem.*, 1969, **7**, 1.

$OSO_2C_6H_4Me$-*p*, $OSO_2C_6H_4Br$-*p*, OSO_2Me.[3,6] When $k_{-1} > k_2 + k_3k_4[\text{Amine}]/(k_{-3} + k_4)$ a linear $k_{obs}{}^2$–[Amine] relationship is expected. If we introduce a further simplification, *i.e.* $k_{-3} \gg k_4$, since proton transfer between an amine and an ammonium ion is very fast, equation (3) is obtained. The first term of the equation may predominate as observed with anilines and (I; X = Cl)[4] in acetonitrile, or the second term can predominate, giving overall third-order kinetics, as found with (I; X = F).[4] Equation (1) itself applies, giving a

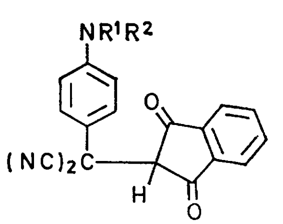
$$k_{obs}{}^2 = k_1k_2/k_{-1} + (k_1k_3k_4/k_{-1}k_{-3})[\text{Amine}] \qquad (3)$$

curved $k_{obs}{}^2$–[Amine] plot for (I; X = OEt) with morpholine.[1] It was of interest to study in detail a system where X = CN since the acidity of the conjugate acid of CN^- is intermediate between those of the conjugate acids of OEt^- and F^-. A previous study showed that in the reaction of piperidine and morpholine with (I; X = CN) in acetonitrile, route ii predominates.[1]

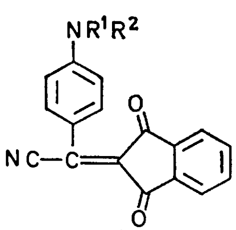
We have studied the reaction of anilines with 2-dicyanomethyleneindane-1,3-dione (II) which resembles (as an electrophilic olefin or as a π-acid)[5b] tetracyanoethylene (TCNE) which was studied earlier.[7] While this work was in progress Junek *et al.*[8] observed the same reaction and suggested a mechanism for it.

RESULTS

2-Dicyanomethyleneindane-1,3-dione reacted in acetonitrile with nine ring-substituted anilines and with *N*-methyl- and *NN*-dimethyl-aniline. In the preparative runs with excess of amine, the reaction mixtures turned blue immediately on mixing the reactants and then changed to yellow or red with the formation and precipitation of the final product. The disappearance of the blue colour was faster with the more basic anilines. Two types of products were formed. With the ring-monosubstituted anilines and with 2,4-dimethoxyaniline only the *N*-monosubstitution products (V) were obtained. With 2,5-dimethoxy-, 2,6-dimethyl-, *N*-methyl-, and *NN*-dimethylaniline the 1 : 1 adducts (VI) of (II) and the amine [*e.g.* (VIa)] were isolated and n.m.r. spectra showed that the addition took place exclusively *para* to the nitrogen atom. Attempts to obtain and isolate the *C*-substitution products (VIIa,b), either by reacting (II) and the anilines under more drastic conditions than required for *N*-substitution, or by reacting the adducts with excess of a strong amine for a long time failed. In both cases the isolated products were highly coloured [as expected for (VII)] but from their apparent ε values only a partial (VI) ⟶ (VII) transformation occurred, and separation of (VI) and (VII) was unsuccessful. For example, (II) (1 mmol) and *NN*-dimethylaniline (2·5 mmol) when refluxed in chloroform for 24 h gave a mixture of (VIa) and (VIIa) with $\lambda_{max.}$ (MeCN) 566 nm (ε 1760). By analogy with the ε value at the high wavelength absorption of (I; X = CN)[7a] or with the maximum ε value obtained for (VIIb), the percentage of (VIIa) in the product is 5—10%. When this reaction mixture was left for several days in acetonitrile, the absorption at 566 nm increased slightly but it was accompanied by new maxima of medium intensity at 390 and 712 nm. However, samples obtained under synthetic conditions, using higher concentrations, showed only minor absorptions at these wavelengths and these changes were not investigated further.



(VI) a; $R^1 = R^2 = Me$
b; $R^1 = Me, R^2 = H$



(VII) a; $R^1 = R^2 = Me$
b; $R^1 = Me, R^2 = H$

When (II) (1 mmol) and *N*-methylaniline (2·4 mmol) were refluxed in chloroform for 24 h, a mixture of (VIb) and (VIIb) was formed. From the apparent ε value of the mixture (18,500 at 536 nm in MeCN) the percentage of (VIIb) in the product is between 30 and 50%.

Kinetics.—The kinetics of the *N*-substitution of six of the ring-substituted anilines was followed spectrophotometrically in acetonitrile by measuring the increase in the absorption of the products (V) at their $\lambda_{max.}$ (380—390 nm) where (II) and the anilines have no absorption. The [Amine] : [II] ratios used were 10—400 and the reactions were followed to two or more half-lives. The pseudo-first-order rate coefficients (k_1') were calculated by the KINDAT programme,[9] which uses D_t (the optical density at the time *t*) and searches for the best D_∞. The correlation coefficients *r* were >0·999. The observed second-order coefficients $k_{obs}{}^2$ (= k_1'/[Amine]) increased linearly with the amine concentration [equation (4), Table 1] for all the amines.

$$k_{obs}{}^2 = k_2' + k_3'[\text{Amine}] \qquad (4)$$

The least squares intercepts and slopes at the two temperatures, their standard deviations, and the *r* values of the linear plots are in Table 2. The $k_3' : k_2'$ ratios are very high (*e.g.*, 180—7400 at 30°) and hence the error in the intercepts is very high. However, at 30° (but not at 45°) the k_2' values change systematically with the Hammett σ values[10] of the ring substituent, although a log k_2'–σ plot is not linear. The third-order coefficients $k_{obs}{}^3$ (= $k_{obs}{}^2$/[Amine]) are accordingly nearly constant (Table 1). Hammett log k_3'–σ plots for the anilines were linear with ρ −6·9 (*r* 0·980) at 30 and −6·7 (*r* 0·996) at 45°.

The reaction of (II) with *p*-toluidine was also studied in the presence of added pyridine or 3-methylpyridine. At constant *p*-toluidine concentration $k_{obs}{}^3$ increases linearly with the increase in the pyridine concentration (Table 3) as demonstrated in the Figure. The intercepts of these plots correspond (within the high experimental error) to the k_3' values for *p*-toluidine in the absence of added base. We found that all our reactions are highly sensitive to the batch of the acetonitrile used. For example, while linear log k_3'–[Pyridine] or log k_3'–σ (with the same ρ) plots were observed when using different batches of the solvent, the actual k_3' or k_2' values differed in the extreme cases by as much as 100%. Consequently, we do not present the activation parameters, since their significance seems to us questionable.

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[7] (*a*) Z. Rappoport, *J. Chem. Soc.*, 1963, 4498; (*b*) Z. Rappoport and A. Horowitz, *ibid.*, 1964, 1348; (*c*) Z. Rappoport and E. Shohamy, *Israel J. Chem.*, 1968, **6**, 865; (*d*) N. Ronen, M.Sc. Thesis, The Hebrew University, Jerusalem, 1971.

[8] H. Junek, H. Aigner, and H. Fischer-Colbrie, *Monatsh.*, 1972, **103**, 639.

[9] R. C. Williams and J. M. Taylor, *J. Chem. Educ.*, 1970, **47**, 129.

[10] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

TABLE 1

Second-order (k_{obs}^2) and third-order (k_{obs}^3) rate coefficients for the reactions of 6·6 × 10^{-5}M-(II) with anilines in acetonitrile

	At 30°					At 45°			
p-Anisidine									
10^4[Amine]/M	6·66	13·3	20·0			4·1	5·8	7·2	8·7
$10k_{obs}^2$/l mol^{-1} s^{-1}	3·6	6·9	9·7			4·2	5·0	5·6	8·3
k_{obs}^3/l^2 mol^{-2} s^{-1}	540	520	490			940	870	780	960
p-Toluidine									
10^4[Amine]/M	13·3	26·6	53·2 [a]	53·2	79·9	10·4	15·7	20·9	26·1
$10k_{obs}^2$/l mol^{-1} s^{-1}	0·87	1·49	2·95	2·75	3·90	1·17	1·94	2·34	3·09
k_{obs}^3/l^2 mol^{-2} s^{-1}	65	56	55	51	49	112	124	112	119
m-Toluidine									
10^4[Amine]/M	27·7	55·3	83·0	110·6		16·2	21·5	26·9	53·8
$10^2k_{obs}^2$/l mol^{-1} s^{-1}	1·29	2·63	3·89	5·57		5·2	5·4	7·6	15·0
k_{obs}^3/l^2 mol^{-2} s^{-1}	4·66	4·76	4·69	5·05		32·3	24·9	28·2	27·9
o-Toluidine									
10^4[Amine]/M	5·50	11·0	16·5	27·5					
$10^2k_{obs}^2$/l mol^{-1} s^{-1}	2·09	3·39	4·20	6·42					
k_{obs}^3/l^2 mol^{-2} s^{-1}	3·79	3·08	2·55	2·33					
Aniline									
10^4[Amine]/M	26·6	53·2	79·7	106·3		30·1	60·1	120·2	150·3
$10^2k_{obs}^2$/l mol^{-1} s^{-1}	0·51	1·00	1·56	2·11		6·6	11·1	19·4	26·2
k_{obs}^3/l^2 mol^{-2} s^{-1}	1·91	1·88	1·95	1·99		22·0	18·5	16·1	17·4
p-Chloroaniline									
10^4[Amine]/M	33·3	166·5	269·7			68·8	103·0	137·5	172·0
$10^2k_{obs}^2$/l mol^{-1} s^{-1}	0·07	0·29	0·43			0·56	0·58	0·79	0·92
k_{obs}^3/l^2 mol^{-2} s^{-1}	0·21	0·17	0·16			0·82	0·57	0·57	0·53

[a] [II] = 3·3 × 10^{-5}M.

We note in this connection that we were unable to get high reproducibility in the rate coefficients for the reaction of primary aromatic amines with TCNE,[7d] and from the data in the literature on the reaction of tricyanovinylbenzene with cyclopentadienylidenetriphenylphosphorane this also shows low reproducibility.[11]

TABLE 2

Kinetic data for the reaction of (II) with anilines $XC_6H_4NH_2$ [a]

	At 30°		At 45°	
X	$10^4k_2'$/ l mol^{-1} s^{-1}	k_3'/ l^2 mol^{-2} s^{-1}	$10^4k_2'$/ l mol^{-1} s^{-1}	k_3'/ l^2 mol^{-2} s^{-1}
p-MeO	626 ± 252	459 ± 18	258 ± 15 [b]	926 ± 222 [b]
p-Me	267 ± 19	45·8 ± 0·4	31·8 ± 180 [c]	118·6 ± 9·8 [c]
o-Me	110 ± 15	1·93 ± 0·09		
m-Me	18 ± 18	5·1 ± 0·2	19 ± 77 [c]	27·4 ± 2·3 [c]
H	5·1 ± 2·5	2·0 ± 0·03	161 ± 111 [c]	15·8 ± 1·1 [c]
p-Cl	2·35 ± 1·0	0·15 ± 0·01	27 ± 9	0·37 ± 0·07 [d]

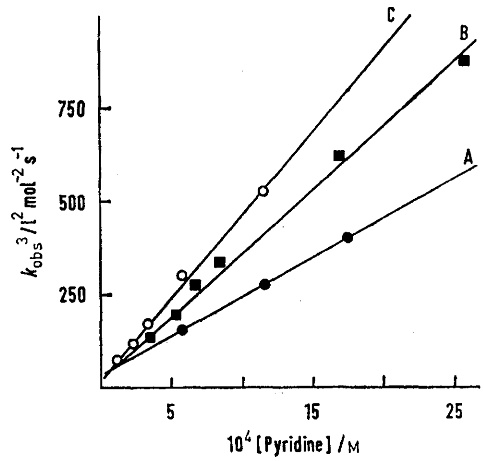
[a] Correlation coefficients of the linear plots $r > 0·999$ unless otherwise stated. A different batch of solvent was used at each temperature. [b] r 0·944. [c] r 0·994. [d] r 0·964.

TABLE 3

Third-order coefficients (k_{obs}^3) for the reaction of *p*-toluidine with (II) in the presence of pyridines in acetonitrile at 30°

10^4[*p*-Toluidine]/M	7·24	7·24	7·24	7·24	7·24	9·89	9·89
10^4[Pyridine]/M	1·15	2·31	3·46	5·77	11·53	3·42	5·13
k_{obs}^3/l^2 mol^{-2} s^{-1}	66	120	170	294	526	134	197
10^4[*p*-Toluidine]/M	9·89	9·89	9·89	9·89	14·48	14·48	14·48
10^4[Pyridine]/M	6·84	8·55	17·1	25·6	5·77	11·53	17·30
k_{obs}^3/l^2 mol^{-2} s^{-1}	271	328	612	880	156	275	398
10^4[*p*-Toluidine]/M	8·89	8·89	8·89	17·77	17·77	17·77	
10^4[3-Methylpyridine]/M	1·07	2·15	3·22	1·07	2·15	3·22	
k_{obs}^3/l^2 mol^{-2} s^{-1}	115	216	361	71	128	188	

Relative Reactivities of (II) *and TCNE*.—In a competition experiment 0·0015M-TCNE and -(II) reacted with 0·0012M-*p*-toluidine in acetonitrile. The only product isolated was *N*-tricyanovinyl-4-methylaniline,[12] while (II) was recovered unchanged.



A plot of k_{obs}^3 for the reaction of (II) with *p*-toluidine in the presence of different concentrations of added pyridine. A, [*p*-Toluidine] = 14·5 × 10^{-4}M; B, [*p*-Toluidine] = 9·9 × 10^{-4}M; and C, [*p*-Toluidine] = 7·2 × 10^{-4}M

When 4mM-(VIa) reacted with 0·1M-Et_3N in acetonitrile at 30°, the optical density at 398, 566, and 600 nm increased slowly. Assuming $\lambda_{max.}$ 566 nm (ε *ca.* 30,000) for (VIIa), the reaction progressed to the extent of 0·1% in 2 h. The half-life of *p*-$Me_2NC_6H_4C(CN)_2CH(CN)_2$ with 0·1M-pyridine at 24° in chloroform is 9 h.[13]

Reaction of (II) *with Diethylamine*.—Solutions of (II) and

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[11] E. Lord, M. P. Naan, and C. D. Hall, *J. Chem. Soc.* (*B*), 1970, 1401.

[12] B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Amer. Chem. Soc.*, 1958, **80**, 2806.

[13] F. G. Farrell and J. Newton, *J. Chem. Soc.* (*B*), 1970, 1630.

of diethylamine in acetonitrile were mixed in a u.v. absorption cell so that the final concentrations were 0·5mM-(II) and 3·8mM-Et_2NH. The spectrum which was recorded after 20—25 s showed the absence of the characteristic maxima of (II) at 271, 281, and 347 nm, and new maxima at 237 (ε 22,600), 260sh (8800), and 379 nm (19,000). This spectrum remained stable for a few hours. The new spectrum is identical with that of authentic 2-[cyano-(diethylamino)methylene]indane-1,3-dione (VIII).[14] The reaction was also conducted at higher concentrations in [$^2H_6$]acetone in an n.m.r. tube and followed by means of a 100 MHz instrument. At 31° (II) showed a narrow multiplet at δ 8·14—8·16. When 0·5M-Et_2NH were added to this solution at −33°, a narrow multiplet at δ 7·77—7·78, a quartet centred at 4·04 (*J* 7·5 Hz), and a triplet centred at 1·40 (*J* 7·5 Hz) in the ratio 2 : 2 : 3, respectively, were observed immediately, and no further change was observed on warming the mixture to +10°. This spectrum is identical with that of (VIII), showing that it is already completely formed at our first experimental point. At 30° additional signals at δ 7·63 (s) and 3·80 (q) are developed slowly, at the expense of those of (VIII). They are the main signals observed after 24 h, when the ratio of the total aromatic to the total methylene signals is still 1 : 1. These signals are ascribed to a further reaction product of (VIII) which was not investigated.

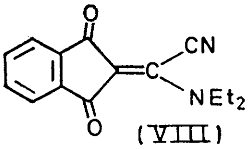
TABLE 4

Physical properties of compounds (V) and (VI)

		N.m.r.[a]				*m/e* (Relative abundance %)[b]				
Compound	$\lambda_{max.}$(MeCN)/nm (log ε)	Ar[c]		Me	CH,NH[d]	*M*	*M* − HCN	*M* − CO	*M* − 2CO	Other
Ar	*N*-Substituted products $C_6H_4(CO)_2C{=}C(CN)NHAr$ (V)[e]									
Ph	233 (4·30), 260 (4·13), 379·5 (4·35)	7·88	7·50			274 (100)	247 (52)	246 (40)	218 (18)	*f*
2-MeC_6H_4	237 (4·27), 264 (4·13), 375 (4·32)	7·88	7·41	2·44		288 (60)	261 (8)	260 (17)	232 (20)	*g*
3-MeC_6H_4	233 (4·33), 260 (4·16), 382 (4·38)	7·88	7·35	2·46		288 (100)	261 (38)	260 (45)	232 (35)	*h*
4-MeC_6H_4	235 (4·38), 264 (4·18), 390 (4·38)	7·86	7·37	2·43		288 (100)	261 (81)	260 (33)	232 (48)	*i*
4-$MeOC_6H_4$	236 (4·36), 262 (4·11), 391 (4·28)	7·86	7·31[j]	3·98		304 (100)	277 (86)	276 (8)		*k*
4-ClC_6H_4	236 (4·30), 264 (4·12), 385 (4·38)	7·88	7·46			308 (100)[l]	281 (63)[l]	280 (21)[l]		*m*
2,4-$(MeO)_2C_6H_3$	245 (4·26), 265 (4·06), 305sh (3·82), 426 (4·20)	7·88	7·71[n] 6·47[p]	3·99 4·02		334 (100)	307 (34)		278 (12)	*o*
$ArNR^1R^2$	*C*-*para*-Addition products $C_6H_4(CO)_2CHC(CN)_2ArNR^1R^2$-*p* (VI)[q]									
2,5-$(MeO)_2C_6H_2NH_2$	227 (4·73), 252 (4·28), 302 (3·86)	7·98	6·47[n] 6·93[n]	3·67 3·80	4·65,[n] 4·33[p]	361 (4)	334 (100)			*r*
2,6-$Me_2C_6H_2NH_2$	231 (4·63), 252 (4·34), 293 (3·50)	7·92	7·00—7·12	1·89	4·48, 4·15	329 (37)	302 (47)	301 (37)		*s*
C_6H_4NHMe	228 (4·63), 258 (4·33)	7·98	6·90[j]	2·68	4·50, 4·16	315 (41)	288 (87)	287 (78)	259 (32)	*t*
$C_6H_4NMe_2$	229 (4·58), 267 (4·27)	7·93	6·88[j]	2·87	4·54	329 (3)	302 (100)	301 (96)		*u*

[a] Data in δ (p.p.m.) downfield from tetramethylsilane. Data for compounds (V) in CF_3CO_2H and for compounds (VI) in [$^2H_6$]-acetone. The integration fits the assignments. [b] Only peaks with relative abundance of 20% or more at *m/e* values >120 are given, except for those specially assigned. [c] The first number refers to the C_6H_4 group and is usually a narrow multiplet or a singlet. The second number refers to the ArNH group and is usually a multiplet. [d] The first number refers to the CH signal and the second one to the NH or the NH_2 signal. The signals are broad and have approximately the correct integration. [e] For all compounds $\nu_{max.}$(Nujol) 2220—2230vw (C≡N), 1695—1700 and 1645—1650 (C=O), and 1600 cm^{-1} (C=C). [f] *m/e* 245 (54%, *M* − HCO), 229 (30), 219 (50, *M* − HCN − CO), and 190 (34). [g] *m/e* 259 (16%, *M* − HCO), 245 (12, *M* − CO − Me), 204 (23), 135 (100), 127 (60, cyanobenzocyclobutene$^+$), and 120 (60%). [h] *m/e* 273 (17%, *M* − Me), 245 (25, *M* − CO − Me), 243 (42), and 126 (21). [i] *m/e* 273 (17%, *M* − Me) and 245 (27, *M* − CO − Me). [j] AA′BB′ Quartet. [k] *m/e* 289 (6%, *M* − Me), 278 (16, *M* − CN), 262 (52, *M* − HCN − Me), and 233 (11, *M* − Me − 2CO). [l] Relative abundance of the peaks with ^{35}Cl. [m] *m/e* 273 (16%, *M* − Cl), 253 (30, *M* − HCN − CO), and 245 (27, *M* − CO − Cl). [n] A singlet for 1H. [o] *m/e* 319 (10%, *M* − Me) and 264 (16, *M* − HCN − CO − Me). [p] A signal for 2H. [q] For all compounds $\nu_{max.}$(Nujol) 2240—2250vw (C≡N) and 1745—1750 and 1705—1715 (C=O), and 3510 and 3410 cm^{-1} (NH) for the compounds with free NH_2 groups. [r] *m/e* 319 (70%, *M* − HCN − Me), 304 (97, *M* − HCN − 2Me), 288 (26, *M* − HCN − Me − OMe), 260 (13, *M* − HCN − Me − OMe − CO), 216 (18, *M* + 1 − indane-1,3-dione), 208 [21, (II)$^+$], 153 (51, 2,5-dimethoxyaniline$^+$), and 138 (94, 2,5-dimethoxyaniline − Me). [s] *m/e* 303 (34%, *M* − CN), 288 (37, *M* − Me − CN), 287 (51, *M* − Me − HCN), 185 [44, $H_2NC_6H_2Me_2CH(CN)_2{}^+$], 184 [100, $H_2NC_6H_2Me_2{=}C(CN)_2{}^+$], 170 [39, $H_2NC_6H_2MeCH(CN)_2$], 159 (31, $H_2NC_6H_2Me_2CHCN$), and 146 (32, indane-1,3-dione$^+$). [t] *m/e* 289 (63%, *M* − CN), 260 (28, *M* − HCN − CO), 261 (28, *M* − 2HCN), 258 (63, *M* − HCO − CO), 232 (33, *M* − HCN − 2CO), 171 [66, $MeNHC_6H_4CH(CN)_2{}^+$], and 170 [100, $MeNHC_6H_4{=}C(CN)_2{}^+$]. [u] *m/e* 330 (28%, *M* + 1), 315 (78, *M* + 1 − Me), 303 (31, *M* − CN), 288 (41, *M* − CN − Me), 287 (54, *M* − HCN − Me), 260 (24, *M* − 2HCN − Me), 258 (63, *M* − 2CO − Me), and 146 (30, indane-1,3-dione$^+$).

Spectral Properties of the Products.—The spectral properties of compounds (V) and (VI) are in Table 4. The highly conjugated enamines (V) show a bathochromic and hyperchromic change compared with (II), as also observed previously.[8] This is in contrast with the hypsochromic change observed with the transformation (I; X = Cl, F, or CN) ⟶ (I; X = ArNH).[1,4a] The lower $\lambda_{max.}$ of the *o*-



(VIII)

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[14] H. Ainger, H. Junek, and H. Sterk, *Monatsh.*, 1970, **101**, 1145.

toluidino-enamine compared with the *p*-toluidino-enamine is probably due to steric hindrance to planarity in the former. The long wavelength maxima are absent in the spectra of the adducts (VI).

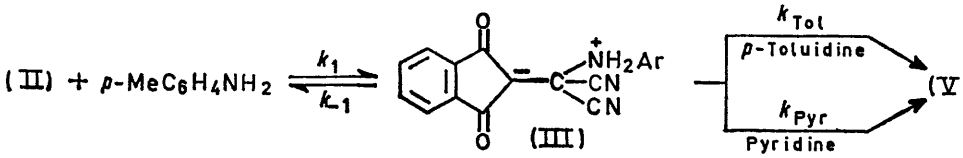
The i.r. spectra are characterised by the very low intensity (or the complete absence) of the cyano-absorption at 2220—2230 cm^{-1} for the conjugated compounds (V), and at 2240—2250 cm^{-1} for the unconjugated compounds (VI). This is characteristic of cyano-groups in systems which are heavily substituted by electron-attracting substituents.[15] The carbonyl absorption appears as a doublet, as also observed for 2-arylmethyleneindane-1,3-dione.[16] The appearance of the band at 1645—1650 cm^{-1} for the highly polar (V) is reminiscent of the low wavenumbers for the cyano-absorption in β-cyano-enamines.[4a]

Due to the low solubility of compounds (V) in the usual n.m.r. solvents the spectra were measured in CF_3CO_2H, where the absorption of the aryl group of the indane-1,3-dione is nearly constant, and the amino-proton is not observed. The n.m.r. of compounds (VI) in [$^2H_6$]acetone is consistent with attachment of (II) *para* to the amino-group. The CH and the NH signals appear as broad singlets.

In the mass spectra of compounds (V) the molecular peak is the base peak (except for the *o*-toluidine derivative), and loss of HCN, CO, and sometimes two CO molecules is of importance. The molecular peaks for the adducts (VI) are of relatively low intensity, and for (VIa) a peak with $M + 1$, which may be due to an ion–molecule reaction, was observed.

DISCUSSION

The linearity of the k_{obs}^2–[Amine] plots confirms our prediction that the cyano-function is a sluggish leaving group and that deprotonation of the zwitterion (III) precedes the C–CN bond cleavage. The very high $k_3' : k_2'$ ratios (Table 2) show that the substitution of 2-dicyanomethyleneindane-1,3-dione by amines follows route ii of Scheme 1 nearly exclusively, with a possible small contribution from the non-catalysed route i. The possibility of additional intermediates along the reaction co-ordinate is discussed below.

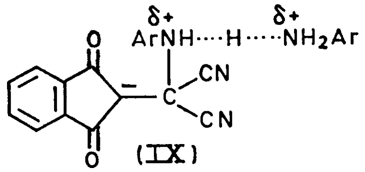


Scheme 2

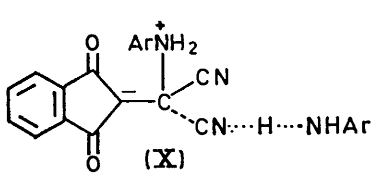
Two possible, if unlikely, transition states for the rate-determining step which are consistent with the kinetics are (IX) and (X). In (X), the NH proton of a second amine molecule electrophilically assists in the expulsion of the leaving group from (III), but this route is excluded by conducting the reaction in the presence of tertiary amines which are capable only of base catalysis.[4] As shown previously,[4] equation (5) applies for Scheme 2, where *p*-toluidine and an added pyridine compete in the transformation of (III) to (V) (by proton abstraction) and when the decomposition of the intermediate is rate determining, *i.e.* when $k_{-1} \gg k_{Tol}[Tol] + k_{Pyr}[Pyr]$. Consequently, a linear dependence of k_{obs}^3 on the added

$$k_{obs}^3 = k_1k_{Tol}/k_{-1} + k_1k_{Pyr}[Pyr]/k_{-1}[Tol] \qquad (5)$$

pyridine concentration at constant *p*-toluidine concentration, with a slope of $k_1k_{Pyr}/k_{-1}[Tol]$, an intercept of k_1k_{Tol}/k_{-1}, and a slope : intercept ratio of $k_{Pyr}/k_{Tol}[Tol]$ are predicted. This linear dependence has been indeed observed. From the plots at two different β-picoline and three different pyridine concentrations, the $k_{\beta\text{-picoline}} : k_{p\text{-toluidine}}$ ratio is 76 ± 10 and the $k_{pyridine} : k_{p\text{-toluidine}}$ ratio is 12 ± 3. Both the linear dependence and the higher catalytic efficiency of the stronger base establish the process as base catalysis, as also observed for the reactions of (I; X = F) with amines.[4b]



(IX)



(X)

Earlier we had suggested and brought evidence and analogies that the proton transfer step for (I; X = OEt or F) is not the single step k_3 but a fast pre-equilibrium followed by a slow detachment of the leaving group by the conjugate base of the amine.[1,4b] We suggest a similar scheme (Scheme 3) for our system, since the proton transfer between the amine and the substituted ammonium ion (III) is probably fast.[17] Electrophilic assistance for the detachment of the leaving cyano-group by substituted ammonium ions was recently suggested for the expulsion of the β-cyano-group from the carbanions $\mathrm{Ar}\underset{\beta}{\mathrm{C}}\mathrm{R(CN)}-\underset{\alpha}{\bar{\mathrm{C}}}\mathrm{(CN)_2}$ (R = CN or Me).[18]

Hammett Relationships.—The high negative Hammett

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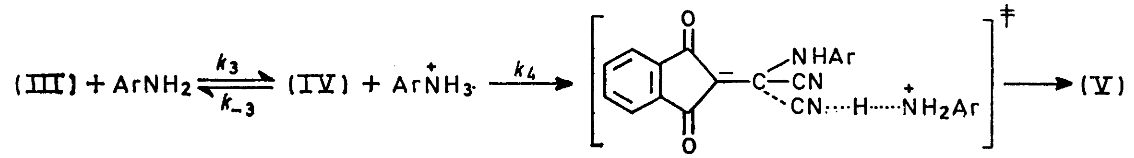
[15] (*a*) L. J. Bellamy, ' The Infrared Spectra of Complex Molecules,' Methuen, London, 1958, 2nd edn., p. 365; (*b*) R. M. Silverstein and G. C. Bassler, ' Spectrophotometric Identification of Organic Compounds,' Wiley, New York, 1963, 1st edn., p. 68; (*c*) Z. Rappoport and E. Shohamy, *J. Chem. Soc.* (*B*), 1969, 77.

[16] (*a*) I. Agranat, R. M. J. Loewenstein, and E. D. Bergmann, *Israel J. Chem.*, 1969, **7**, 89; (*b*) J. Kaneti and I. Yuchnovski, *Tetrahedron*, 1970, **26**, 4397.

[17] J. J. Delpeuch, B. Bianchin, and C. Beguin, *Chem. Comm.*, 1970, 1186; J. J. Delpeuch, G. Serratrice, A. Strich, and A. Veillard, *ibid.*, 1972, 817.

[18] (*a*) Z. Rappoport and E. Shohamy, *J. Chem. Soc.* (*B*), 1971, 2060; (*b*) M. Albeck, S. Hoz, and Z. Rappoport, *J.C.S. Perkin II*, 1972, 1248.

ρ values, which are based on k_3', are among the highest known to us. In terms of Scheme 1 these values are composite ($\rho = \rho_1 - \rho_{-1} + \rho_3 - \rho_{-3} + \rho_4$) since $k_3' = k_1k_3k_4/k_{-1}k_{-3}$. Moreover, even if the ρ values for all the pre-equilibrium steps are grouped together as ρ_{eq} for the reaction $2ArNH_2 + (II) \rightleftharpoons ArNH_3^+ + (IV)$ it is not obvious that a plot of k_3' against σ should be linear since k_4 itself involves a multiple variation within the reaction series; both the proton donor ($ArNH_3^+$) and the acceptor (IV) are simultaneously changed with the variation in the substituent.[4b] A linear Hammett plot is therefore expected only when log k_4 is linear in σ. The condition for this is that the two reaction series (a) various anilinium ions (superscript X) with the aniline substituted carbanion (subscript H) [equation (6)] and (b) anilinium ion (superscript H) with several carbanions (IV) (subscript X) [equation (7)] would both give linear Hammett plots with slopes ρ_a and ρ_b, respectively. The log k_X^X values for the reaction of an aniline with an anilinium ion carrying the same substituent would be then given



SCHEME 3

$$\log k_H^X = \log k_H^H + \sigma\rho_a \quad (6)$$

$$\log k_X^H = \log k_H^H + \sigma\rho_b \quad (7)$$

$$\log k_X^X = \log k_X^H + \sigma\rho_a = \log k_H^H + \sigma(\rho_a + \rho_b) \quad (8)$$

by equation (8) and it would be linear in σ with a slope $\rho_a + \rho_b$.* Hence, $\rho = \rho_{eq} + \rho_a + \rho_b$.

We have found no ρ value for an equilibrium addition of anilines to a double bond, while the ρ values for nucleophilic additions or substitutions [3h,4,19] are usually lower than our values of −6·7 to −6·9. It is difficult to find an appropriate model for evaluating ρ_{eq}. If $\rho = -3{\cdot}4$ for the equilibrium protonation of anilines in 82% dioxan [20] is taken as an approximation for our ρ_{eq}, k_4 can be rate determining only when the C–CN bond cleavage in the transition state progresses much further than the N–H bond cleavage. This is a corollary of the fact that in reaction series (a), where ρ_a is positive, the hydrogen at the reaction centre is directly attached to the aryl group, while in reaction series (b), where ρ_b is negative, the CN at the reaction centre is separated from the aryl group by an additional carbon atom.

The lower reactivity of *o*-toluidine as compared with *p*-toluidine is due to the combination of steric effects in the nucleophilic attack step k_1, in the deprotonation step k_3, and in the assisted C–CN bond cleavage step k_4 which are slower for the more hindered *o*-substituted aniline. The behaviour is reminiscent of that observed in the analogous reaction of (I; X = F).[4a] The importance of the steric factor is emphasised by the formation of the carbon addition products (VI) when the amino-nitrogen atom is completely or partially hindered by *N*-substitution or by *o,o'*-disubstitution. However, even with a less hindered amino-group the reaction can be directed into the *para*-position, provided that this position is highly activated. This is the case with 2,5-dimethoxyaniline, where the *para*-position is activated by both the *p*-amino- and the *o*-methoxy-substituents. This *N*- *vs.* *C*-selectivity in the reaction of anilines with (II) is exactly analogous to that found for the reaction of anilines with TCNE.[7c]

Other Possible Intermediates.—We attribute the blue colours which were observed at the beginning of the reaction either in the preparative runs or when the mixture of the e.s.r. experiment was cooled, to the formation of π-complexes of the anilines with 2-dicyanomethyleneindane-1,3-dione. This is in analogy with the formation of the blue π-complexes in the reactions of tetracyanoethylene and tricyanovinyl chloride with anilines,[7a–c,21] and with the formation of π-complexes of (II) with aromatic donors.[5b] These complexes were not observed at our kinetic concentrations, and at present we have no evidence that they appear along the reaction co-ordinate.

The dependency of k_{obs}^2 on the batch of solvent and the detection of the tetracyanoethylene anion radical in the reaction of anilines with TCNE [21b] suggested the possibility that the radical anion of (II) is formed in the reaction course by electron transfer from the aniline to (II). However, we did not observe the signals of the known 2-dicyanomethyleneindane-1,3-dione anion radical [5a,b] when the reaction with *p*-toluidine was conducted in an e.s.r. tube either at room temperature or in a degassed acetonitrile matrix at low temperature.

Junek *et al.*[8] suggested Scheme 4 as the mechanism for the reaction of anilines with (II). The kinetics exclude this Scheme which calls for a first-order dependency on the amine, although it is possible that hydrogen bonding between the negatively charged oxygen and the ammonium ion of (III), *i.e.* (XIa), contributes to its relative stability. Nevertheless, (XIb) should be considered since Aigner *et al.*[14] claimed that they observed both (XIIa) and (XIIb) in the reaction of (II) with Et_2NH. They ascribed the following changes in the

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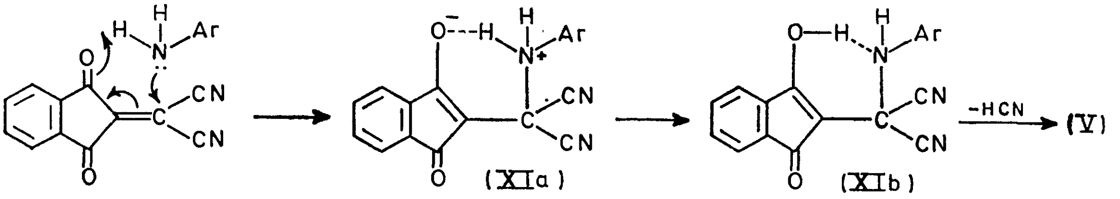
* We correct the misprint $\rho = \rho_a - \rho_b$ which appeared in ref. 4*b*.

[19] S. Hoz, M.Sc. Thesis, The Hebrew University, Jerusalem, 1969.

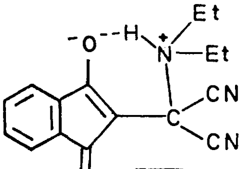
[20] J. C. James and J. G. Knox, *Trans. Faraday Soc.*, 1950, **46**, 254.

[21] (*a*) Z. Rappoport, P. Greenziad, and A. Horowitz, *J. Chem. Soc.*, 1964, 1334; (*b*) N. S. Issacs, *J. Chem. Soc.* (*B*), 1966, 1053; (*c*) S. Garbutt and D. L. Gerrard, *J.C.S. Perkin II*, 1972, 782.

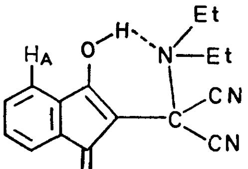
n.m.r. spectrum to the (II) → (XIIa) → (XIIb) → (VIII) reaction: (a) Et_2NH and (II) [δ 8·14 (s,Ar)] show at −30° in [$^2H_6$]acetone only a singlet at δ 7·62; (b) a new signal at 6 Hz higher field is formed at −20°; (c) at +10° H_A shows coupling with the other ring protons; (d) at 30° the two signals are at a ratio of 1 : 3; and (e) at 38° only the δ 7·62 signal reappears. This seemed to us improbable since the half-life of (II) in the presence of *p*-anisidine concentrations 500 times *lower* than those of the Et_2NH used by Aigner *et al.*[14] is only 6 min, while Et_2NH is a *stronger* base by 5·7 pK_a units. A rough estimate based on the k_3' values for the reactions of (I; X = F or OEt) with *p*-anisidine, piperidine, and diisopropylamine[1,4] suggested that the reaction of (II) with Et_2NH under the conditions of Aigner *et al.* would be complete in less than 10^{-3} s. We verified our conclusion by showing (both by u.v. and by n.m.r. methods, see Results section) that the formation of (VIII) is already complete before the first measurement. The spectral changes observed by Aigner *et al.* as well as by us, are due to further reactions of (VIII). Consequently, there is no evidence for the intermediacy of (XIb) or (XIIb) in the course of the substitution.



SCHEME 4



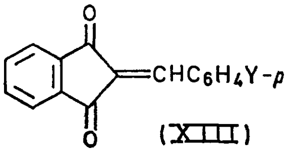
(XIIa)



(XIIb)

Reactivity Comparisons.—Comparing our k_3' value for *p*-anisidine with that for (I; X = CN) with piperidine and morpholine[1] and assuming that the same Brønsted relationship holds for the three amines, shows that the reaction of (II) is at least four orders of magnitude faster than that of (I; X = CN). This is due to the higher electrophilicity of (II) compared with that of (I; X = CN).

gem-Dicarbonyl groups spread a negative charge better than *gem*-dicyano-groups, as judged by the pK_a values of 2-phenylindane-1,3-dione (4·13)[22a] and phenylmalononitrile (5·80).[22b] Consequently, in vinylic systems (XIII; Y = H) is 4·4 times more reactive than (XIV; Y = H) on treatment with OH^-,[23] the equilibrium constant for the addition of n-butanethiol to (XIII; Y = H) is 460 times higher than addition to (XIV; Y = H),[23] and the equilibrium constant for the addition of MeO^- to (XIII; Y = NO_2) is 100 times higher than addition to (XIV; Y = NO_2).[24] Moreover, MO calculations[25] show that the α-carbon of (II) is more electrophilic than the β-carbon, and this is verified by the structure of our adducts (VI). We therefore expected tetracyanoethylene to be less reactive than (II) in nucleophilic reactions, in line with the bond order of the C_α–C_β bond which is 0·3900 for TCNE and 0·312 for (II).[25]



(XIII)

$p\text{-}YC_6H_4CH{=}C(CN)_2$

(XIV)

However, the reactions of anilines with TCNE are all faster than those with (II).[7d] For example, while the reaction of *p*-anisidine with TCNE is too fast to measure conventionally in acetonitrile, it is still slightly faster even in 1 : 9 acetonitrile–carbon tetrachloride than the reaction of *p*-anisidine with (II) in pure acetonitrile. This is emphasised by our result that only the *N*-tricyanovinyl product is formed when TCNE and (II) compete for a limited amount of *p*-toluidine. Since the discussion above suggests that k_1 or k_1/k_{-1} are higher in the reactions of (II), the (III) → (IV) step should be much slower for (II) than the analogous step for TCNE, so as to more than compensate the reactivity difference in the first step. This is consistent with the isolation of the adducts (VIa) and (VIb) and their very slow conversion to (VIIa) and (VIIb), while the elimination of HCN from the corresponding adducts (or σ-complexes) of *N*-methyl- and *NN*-dimethyl-aniline with TCNE is relatively fast.[7a,b,26] For example, our preliminary experiment shows that the Et_3N-catalysed elimination of HCN from (VIa) in acetonitrile is much slower than the pyridine-catalysed elimination of HCN from *p*-$Me_2NC_6H_4C(CN)_2CH(CN)_2$ in chloroform.[13] Finally, this reactivity difference fits Scheme 3 since the C–CN bond cleavage in (IV) would be much slower than that in $(NC)_2\bar{C}$–$C(CN)_2NHAr$, due to the reduced internal nucleophilicity in (IV), as observed in related systems.[27]

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[22] (*a*) H. F. Ebel, ' Die Aciditat der CH-Sauren,' Thieme Verlag, Stuttgart, 1969, p. 38; (*b*) H. D. Hartzler, *J. Amer. Chem. Soc.*, 1964, **86**, 2174.

[23] R. B. Pritchard, C. E. Lough, D. J. Currie, and H. L. Holmes, *Canad. J. Chem.*, 1968, **46**, 775.

[24] P. Schuster, O. P. Polansky, and F. Wessley, *Tetrahedron*, 1966, Supp. 8, Part II, 463.

[25] H. Sterk and H. Junek, *Tetrahedron*, 1970, **26**, 5361.

[26] F. G. Farrell and J. Newton, *Tetrahedron Letters*, 1964, 189.

[27] S. Hoz, M. Albeck, and Z. Rappoport, *Tetrahedron Letters*, 1972, 3511.

Comparison of the equilibrium constant ratio for the reaction of OH^- with (XIII; and XIV; $Y = NO_2$)[23] with the rate ratio for the reaction of MeO^- with (XIII; and XIV; Y = H)[24] also suggests a slower expulsion of a leaving group from a diketo-carbanion than from the analogous dicyano-carbanion.

EXPERIMENTAL

M.p.s were taken with a Fischer–Johns apparatus and are uncorrected. N.m.r. spectra were taken with a Varian T-60 or H/100 instrument, i.r. spectra with a Perkin-Elmer 337 instrument, and u.v. spectra with a Perkin-Elmer 450 instrument.

Materials.—2-Dicyanomethyleneindane-1,3-dione, $\lambda_{max.}$ (MeCN) 271 (ε 32,000), 281 (36,000), and 347 nm (ε 6600), m.p. 280—285°, was prepared according to Junek and Sterk[5c] and was crystallised from acetonitrile. The amines were commercial products. The liquid amines were kept overnight over KOH, then distilled twice, and the middle fraction was used. The solid amines were crystallised. The physical properties agree with the literature values.

TABLE 5

Analytical data for compounds (V) and (VI)

	M.p.(°C)[a]	Yield	Found(%) C	Found(%) H	Found(%) N	Formula	Required(%) C	Required(%) H	Required(%) N
Ar		*N*-Substituted products $C_6H_4(CO)_2C{=}C(CN)NHAr$ (V)							
Ph	218—220[b]	90	74·48	3·43	10·30	$C_{17}H_{10}N_2O_2$	74·45	3·67	10·21
$2\text{-}MeC_6H_4$	182	95	75·04	4·00	9·80	$C_{18}H_{12}N_2O_2$	74·99	4·20	9·72
$3\text{-}MeC_6H_4$	164—165	90	75·09	4·06	9·58	$C_{18}H_{12}N_2O_2$	74·99	4·20	9·72
$4\text{-}MeC_6H_4$	205—207	80	74·75	4·21	9·77	$C_{18}H_{12}N_2O_2$	74·99	4·20	9·72
$4\text{-}MeOC_6H_4$	203—204[c]	95	71·24	3·80	8·98	$C_{18}H_{12}N_2O_3$	71·05	3·97	9·21
$4\text{-}ClC_6H_4$	211—213[d]	70	66·29	2·67	8·80	$C_{17}H_9ClN_2O_2$	66·14	2·92	9·05
$2,4\text{-}(MeO)_2C_6H_3$	270	100	68·26	4·19	8·53	$C_{19}H_{14}N_2O_4$	68·26	4·22	8·38
$ArNR^1R^2$		*C-para*-Addition products $C_6H_4(CO)_2CHC(CN)_2ArNR^1R^2\text{-}p$ (VI)							
$2,5\text{-}(MeO)_2C_6H_2NH_2$	170	95	66·74	4·23	11·49	$C_{20}H_{15}N_3O_4$	66·48	4·18	11·63
$2,6\text{-}Me_2C_6H_2NH_2$	215	90	72·90	4·58	12·51	$C_{20}H_{15}N_3O_2$	72·94	4·59	12·76
C_6H_4NHMe	170	70	72·08	3·92	13·42	$C_{19}H_{13}N_3O_2$	72·37	4·16	13·33
$C_6H_4NMe_2$	172	80	72·87	4·64	12·46	$C_{20}H_{15}N_3O_2$	72·94	4·59	12·76

Compounds (V) were crystallised from MeCN. Compounds (VI) were crystallised from $MeCN\text{–}CCl_4$. Lit.,[8] m.p. 214—215°. [c] Lit.,[8] m.p. 202°. [d] Lit.,[8] m.p. 214°.

Solvent.—Acetonitrile (Baker Analysed) was dried overnight over an excess of P_2O_5, further refluxed for 1 h, and distilled using a fractionating column. The fraction boiling at 78—78·5° was used.

Reaction of (II) *with Anilines*.—Two molar equivalents of the aniline were added to one equivalent of (II) in the minimum quantity of acetonitrile required for the dissolution of (II). The mixtures turned blue immediately, then green, and after 5—20 min they were brown, yellow, or red. The substitution products (V) usually precipitated directly from the mixture, while carbon tetrachloride had to be added in order to precipitate the adducts (VI). The analyses of the cyano-enamines are in Table 5. 2-[Cyano(diethylamino)methylene]indane-1,3-dione, m.p. 104° (lit.,[14] 104°), $\lambda_{max.}$ (MeCN) 273 (ε 22,500), 260sh (8200), and 379 nm (21,000), δ ([$^2H_6$]acetone) 1·40 (6H, t, *J* 7·5 Hz, 2 × Me), 4·04 (4H, q, *J* 7·5 Hz, 2 × CH_2), and 7·7 (4H, s, ArH), was prepared by addition of diethylamine (220 mg, 3 mmol) to (II) (630 mg, 3 mmol) in acetonitrile (15 ml) at 5°. After 20 min the solvent was distilled *in vacuo*, the oil obtained crystallised on keeping overnight at room temperature, and was recrystallised from aqueous ethanol.

Kinetic Procedure and Product Analysis.—Stock solutions of (II) in acetonitrile were prepared daily. Their stability was dependent on the batch of solvent used. In commercial acetonitrile (Baker Analysed) the absorbance at all the wavelength maxima decreased by 19% after 2 h, while only 4% loss in the optical density was observed after 2 h in our 'dry' (by P_2O_5) solvent. However, (II) was usually stable during the time required for the completion of our reactions. In the presence of 3×10^{-4}M-3-methylpyridine the absorption of (II) at 347 nm in the dry solvent decreased by *ca*. 14% during one day, and some additional spectral changes were observed, but this did not interfere with the kinetic measurement of the much faster substitutions. Stock solutions of the amines were prepared daily and the reactants were kept and mixed at the reaction temperature. The reaction was followed spectrophotometrically in 1 cm cells at the $\lambda_{max.}$ of the products in a thermostat-controlled chamber of a Beckman DU spectrophotometer.

The u.v. spectra of the final mixtures corresponded to those of the enamines. In the reaction of *p*-toluidine with (II) the *p*-toluidino-enamine (1 mg) was isolated under the kinetic conditions and identified by m.p.

E.s.r. Experiment.—A mixture of 2×10^{-3}M-(II) and 2×10^{-2}M-*p*-toluidine in dry degassed acetonitrile was introduced immediately after mixing at liquid nitrogen temperature into an e.s.r. tube. The e.s.r. spectrum of the blue-green solution was taken at liquid nitrogen temperature with a Varian 4595 instrument in modulations between 100—1000 kHz at 3200 G. No e.s.r. signal was observed at the expected field for the radical-anions of (II). A similar negative result was obtained also when the experiment was conducted at room temperature.

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