Heterodiene Syntheses.   Part 23.[1]   Zwitterions as Intermediates in the Formation of Michael Adducts or as Stable Products of the Reaction between 2-Oxoindolin-3-ylidene Derivatives with Enamines or Aminals

By **Gianfranco Tacconi,*** **Massimo Leoni, Pierpaolo Righetti,** and **Giovanni Desimoni,** Istituto di Chimica Organica dell'Università, 27100 Pavia, Italy
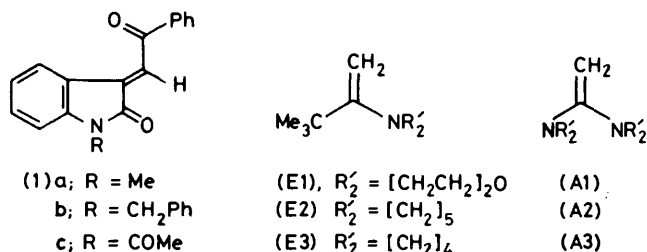**Roberta Oberti,** Centro di Studio per la Cristallografia Strutturale del CNR, 27100 Pavia, Italy
Fabio Comin, Istituto di Cristallografia dell'Università, 27100 Pavia, Italy

1-t-Butyl-1-aminoethylenes [(E1)—(E3)] react with *N*-substituted 2-oxoindolin-3-ylidene derivatives (1a—c) to give Michael-type adducts but the reactivity of diaminoethylenes [(A1)—(A3)] depends on the nature of substituents. 1,1-Dimorpholinoethylene (A1) undergoes Michael reaction with all the substrates tested but 1,1-dipiperidinoethylene (A2) only with the *N*-methyl- and *N*-benzyl-derivatives (1a and b). However, stable zwitterions are formed by (A2) with the *N*-acetyloxoindoline derivative (1c) and by 1,1-dipyrrolidinoethylene (A3) with all substrates. Their structure, determined by chemical and spectroscopic methods and by X-ray analysis, is the same as that of the intermediates proposed for the reaction between αβ-unsaturated carbonyl compounds and enamines. The reason for the alternative products, *i.e.* Michael adducts or stable zwitterions, is discussed in terms of the effect of substituents in stabilizing the charges of the zwitterion and also in terms of frontier-orbital interaction.

IN previous papers of this series [2,3] we discussed the reaction of 2-oxoindolin-3-ylidene derivatives which gave 1,2- or 1,4-cycloadducts with aldehyde-enamines and Michael-type adducts with cyclopentanone-enamines.

This behaviour was rationalized in terms of frontier orbitals interactions between the HOMO (highest-occupied molecular orbital) of the enamine and the LUMO (lowest unoccupied molecular orbital) of the oxindoline derivative. This involved the effect of the electron-attracting substituents in lowering the LUMO of the αβ-unsaturated carbonyl system and also the effect of the α-alkyl group in increasing the HOMO of the keto-enamine. The electron transfer favoured by the lower orbital-energy separation,[4] and the parallel asymmetry of the enamine coefficients, are both conducive to the zwitterionic pathway[5] required to give rise to a Michael adduct.

As a further development of this research we now discuss the reactivity of *N*-substituted 2-oxoindolin-3-ylideneacetophenones (1) with two classes of 'high HOMO' enamines, 1-t-butyl-1-aminoethylenes [(E1)—(E3)] and 1,1-diaminoethylenes [(A1)—(A3)] (better known as keten-aminals). Both enamines and aminals were tested carrying morpholine, piperidine, and pyrrolidine as amino-groups; these are known to increase the HOMO energy in this order.[6,7]

butyl-1-aminoethylenes (E1)—(E3)] and colourless adducts were obtained. These were sometimes isolated in the solid state, and sometimes handled in solution only.

The i.r. spectra (Table 1) show the presence of both lactam and ketonic carbonyl in addition to the enaminic double bond, a Michael-type reaction is therefore suggested.

TABLE 1

I.r. data (cm^{-1}) for the adducts (2)—(4)

Compound	ν(C=C) (enamine)	ν(C=O)		
		Lactam	Ketone	Acetyl
(2a) [a]	1 625m	1 715s	1 688m	
(3a) [a]	1 620m	1 721s	1 686m	
(4a) [a]	1 628w	1 718s	1 685m	
(2b) [a]	1 620m	1 711s	1 688m	
(3b) [a]	1 620m	1 720s	1 686s	
(4b) [a]	1 630w	1 709s	1 684s	
(2c) [b]	1 620m	1 758s	1 683s	1 700s
(3c) [b]	1 620w	1 767s	1 685s	1 708s
(4c) [b]	1 622w	1 756s	1 678s	1 700s

[a] In spectroscopic-grade benzene; NaCl cell, path length 0.10 mm, concentration 0.15M.   [b] Nujol mull.

The n.m.r. spectra of the adducts (2)—(4) show the H$_a$ proton as a broad doublet at *ca.* δ 4.0 and H$_b$ and H$_c$ as a multiplet at *ca.* δ 5.5. These spectra, which are consistent with the proposed structure, are poorly resolved particularly
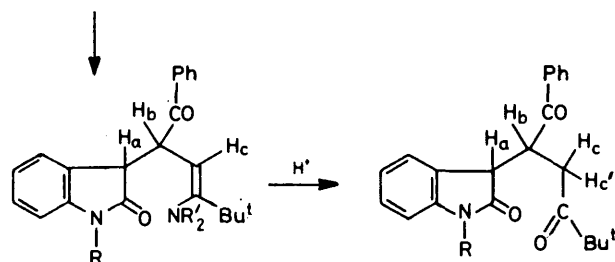
(1a-c) + (E1)-(E3)

RESULTS

Reaction with 1-t-Butyl-1-aminoethylenes.—All the oxo-indoline-acetophenones (1a—c) reacted with the 1-t-

(1)a; R = Me
b; R = CH$_2$Ph
c; R = COMe

(E1), R$_2'$ = [CH$_2$CH$_2$]$_2$O   (A1)
(E2) R$_2'$ = [CH$_2$]$_5$ (A2)
(E3) R$_2'$ = [CH$_2$]$_4$ (A3)

(2a–c); R$_2'$ = [CH$_2$CH$_2$]$_2$O
(3a–c); R$_2'$ = [CH$_2$]$_5$
(4a–c); R$_2'$ = [CH$_2$]$_4$

(5a); R = Me
(5b); R = CH$_2$Ph
(5c); R = COMe

TABLE 2

N.m.r. data for the enamine hydrolysis products (5)

| Compound | Chemical shifts (δ) | | | | | | | Coupling constants/Hz | | | |
	H_a	H_b	H_c	$H_{c'}$	Bu^t	R	Aromatic	J_{ab}	J_{bc}	$J_{bc'}$	$J_{cc'}$
(5a)	3.75(d)	4.85 [a]	2.85	3.32	1.02(s)	Me 3.26(s)	6.7—8.3(m)	2.5	5.0	8.2	−18.5
(5b)	3.74(d)	4.90 [b,c]	2.75 [c]	2.92 [c]	1.01(s)	CH$_2$Ph δ$_A$ 4.80, δ$_B$ 5.05, (J$_{AB}$ −15.3)	6.7—8.3(m)	2.6	d	d	−19.15
(5c)	3.63(d)	4.81 [e]	2.85 [f]		1.03(s)	COMe 3.23(s)	6.7—8.3(m)	2.8	13.4 [g]		d

[a] Seven lines. [b] Overlapped by NCH$_2$Ph signal. [c] Determined by decoupling. [d] Not determined. [e] Sextet. [f] Less sharp doublet. [g] $J_{bc} + J_{bc'}$.

those of the adducts which were not isolated in the solid state. The presence of two diastereoisomers (in a *ca.* 3 : 2 ratio) was shown in the spectra of the more stable solid adducts (4a—c) by the signals of the acetyl and t-butyl groups.

TABLE 3

I.r. spectra (cm⁻¹) for the adducts (6a—c) and (7a, b) [a]

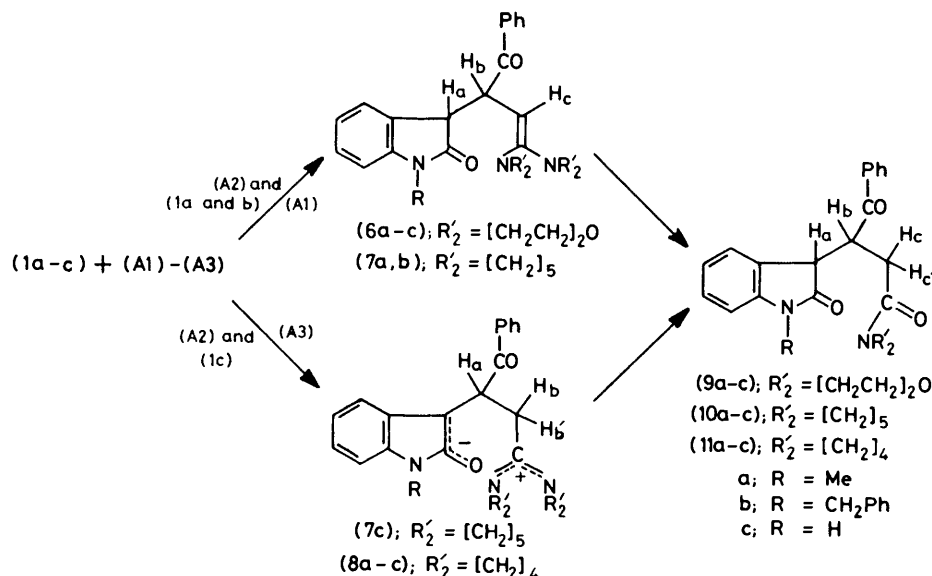| Compound | ν(C=C) (enamine) | ν(C=O) | | |
		Lactam	Ketone	Acetyl
(6a)	1 625m	1 711s	1 687s	
(6b)	1 620m	1 717s	1 682s	
(6c)	1 628m	1 761s	1 679s	1 699s
(7a)	1 622m	1 699s	1 680s	
(7b)	1 620m [b]	1 710s	1 671s	

[a] Nujol mulls. [b] Shoulder.

Hydrolytic cleavage of all the nine adducts (2)—(4), with loss of the base, gave only three t-butyl ketones (5a—c), whose structures were confirmed by n.m.r. spectroscopy (Table 2).

isolated in each case and five of them [all those from 1,1-dimorpholinoethylene (A1) and the adducts from 1,1-di-piperidinoethylene (A2) with (1a and b)] were the usual colourless Michael adducts (6a—c) and (7a and b) as shown by i.r. (Table 3) and n.m.r. spectra (Table 4).

The three adducts from 1,1-dipyrrolidinoethylene (A3) and that of 1,1-dipiperidinoethylene (A2) with the *N*-acetyloxoindoline derivative (1c), [(7c) and (8a—c)], were *orange-red* 1 : 1 *adducts* which sometimes retained water or ethanol of crystallization but, especially *N*-acetyl-substituted (7c) and (8c), could be isolated as pure crystalline compounds from acetonitrile.

The i.r. spectra were unusual; the ketonic carbonyl absorbed at about 1 670 cm⁻¹ but the acetyl group on (7c) and (8c) occurred at very low frequency (1 625 cm⁻¹) and a strong band in the range 1 585—1 605 cm⁻¹ could not be due to the benzene rings alone.

The n.m.r. spectra elucidated the structure. A proton at a chemical shift consistent with it being =C*H*−COPh occurred as a doublet of doublets, and is therefore coupled

(1a–c) + (A1)–(A3)

(A2) and (1a and b) / (A1)

(6a–c); R$_2'$ = [CH$_2$CH$_2$]$_2$O
(7a,b); R$_2'$ = [CH$_2$]$_5$

(A2) and (1c) (A3)

(7c); R$_2'$ = [CH$_2$]$_5$
(8a–c); R$_2'$ = [CH$_2$]$_4$

(9a–c); R$_2'$ = [CH$_2$CH$_2$]$_2$O
(10a–c); R$_2'$ = [CH$_2$]$_5$
(11a–c); R$_2'$ = [CH$_2$]$_4$
a; R = Me
b; R = CH$_2$Ph
c; R = H

In spite of the increased electron-donating effect of the α-t-butyl group, the behaviour of (E1)—(E3) is very similar to that of 1-pyrrolidinocyclopentene [3] and only Michael adducts were isolated. It seemed hard to imagine a more ' zwitterionic ' pathway than a Michael reaction.

Reaction with 1,1-Diaminoethylenes (A1)—(A3).—The reaction with the aminals (A1)—(A3) was performed under the same experimental conditions. Solid 1 : 1 adducts were

to two protons. These two protons were overlapped by N[CH$_2$]$_2$ signals, as shown by decoupling experiments, but the most significant point is that they are acidic, since simply by adding D$_2$O they exchanged and the doublet of doublets collapsed to a singlet. This would not be the case for a Michael adduct. The significant n.m.r. data are reported in Table 5.

The above data are consistent only if the acidic protons

are α to a $N\overset{+}{=}C=N$ group, the presence of which is further supported by the deshielding of the signal of the α-methylenes of the base.[8] Therefore the i.r. data can be interpreted in terms of a $C=C=O$ group which absorbs at very low frequency (about 1 600 cm⁻¹) and is also responsible for the dampening of the acetyl absorption.

Both Michael adducts and zwitterions (6)—(8) can be easily hydrolysed to the corresponding amides (9)—(11), and the spectroscopic data of these are reported in the Experimental section.

longer (1.24 vs. 1.20 Å), respectively, than the C–C=O system of oxoindoles.[11] Both (a) and (b) can both be interpreted as the result of a delocalized negative charge between $C=C=O$ which diminishes the π character of the carbonyl but increases the π character of the C–C bond. (c) Both C(14) and C(23) are sp^3 hybridized as shown by bond angles of 110, 114, and 107° for C(14) and 117° for C(23), even though some of them are distorted by steric hindrance. (d) C(23, C(24), N(25), and N(31) identify plane C, hence C(24) must be sp^2 hybridized, which is confirmed by its

TABLE 4

N.m.r. data for the adducts (6a—c) and (7a, b)

Compound	Chemical shifts (δ)							Coupling constants/Hz	
	H_a	H_b	H_c	R	CH_2–N–CH_2	CH_2–O–CH_2 or $[CH_2]_2$	Aromatic	J_{ab}	J_{bc}
(6a)	3.90(d)	5.04(dd)	3.74	Me 3.16(s)	2.45—3.1(m)	3.4—3.85(m)	6.65—8.35(m)	4.2	10.2
(6b)	4.04(d)	5.15(dd)	3.73 *	CH_2Ph $δ_A$ 4.76, $δ_B$ 5.03 (J_{AB} −15.9)	2.4—3.15(m)	3.35—3.8(m)	6.6—8.35(m)	4.1	10.1
(6c)	3.98(d)	5.10(dd)	3.75 *	COMe 2.67(s)	2.5—3.15(m)	3.45—3.8(m)	7.1—8.35(m)	4.1	10.2
(7a)	3.89(d)	4.94(dd)	3.71(d)	Me 3.18(s)	2.4—3.15(m)	1.25—1.8(m)	6.65—8.25(m)	4.0	10.5
(7b)	4.02(d)	5.06(dd)	3.82(d)	CH_2Ph $δ_A$ 4.88, $δ_B$ 4.99 (J_{AB} −14.7)	2.35—32.5(m)	1.25—1.85(m)	6.55—8.3(m)	4.2	10.6

* Partially overlapped by CH_2–O–CH_2 signal, but confirmed by decoupling.

TABLE 5

N.m.r. data for the zwitterions (7c) and (8a—c)

Compound	Chemical shift (δ)						Coupling constants/Hz	
	H_a	H_b and $H_{b'}$ [a]	R	N–CH_2	$[CH_2]_n$ [b]	Aromatic	J_{ab}	$J_{ab'}$
(7c)	5.15(dd) [c]	3.3	COMe 2.77(s)	3.1—3.55(m)	1.25—1.7(m)	6.45—8.3(m)	5.9	9.3
(8a)	5.28 [c,d]	3.3	Me 3.30(s)	3.1—3.85(m)	1.4—2.15(m)	6.5—8.3(m)	d	d
(8b)	4.98(dd) [c]	3.3	CH_2Ph 4.94(s)	2.6—3.75(m)	1.4—2.1(m)	6.5—8.3(m)	3.9	10.7
(8c)	5.22(dd) [c]	3.3	COMe 2.77(s)	3.1—3.8(m)	1.4—2.0(m)	6.4—8.3(m)	4.6	9.9

[a] Determined by decoupling since overlapped by the $N[CH_2]_2$ signal. [b] $n = 2$ or 3. [c] Collapsed to singlet either by irradiating $H_{b'}$ signal or by adding D_2O. [d] Not sufficiently well resolved to determine the coupling constants.

Because of the significance of isolating stable zwitterions, which in general are only suggested as intermediates and never isolated in similar reactions,[9] the structure suggested by the chemical and spectroscopic evidence was confirmed by an X-ray analysis of the dipiperidino-derivative (7c).

Crystal Structure.—The crystal-structure refinement yielded a final R of 6.4%. The results of the anisotropic refinement (see Experimental section) are shown in the Figure.[10] Bond lengths and angles not involving hydrogen atoms, together with the more relevant torsion angles, are listed in Tables 6 and 7. An analysis of the planarity of the conjugated systems and of the rings is provided in Table 8.

Some interesting points arise from the above data which clearly support the zwitterionic nature of (7c). (a) Torsion angles involving C(14) and C(3) with the oxoindole atoms are nearly 0° or 180° and this, added to the presence of plane (A) (average distance of atoms 0.02 Å) requires sp^2 hybridization of C(3). (b) The C(2)—C(3) and C(2)—O(13) bond lengths are considerably shorter (1.39 vs. 1.52 Å) and

bond angles of 121, 119, and 120°. (e) C(23)—C(24) is largely a single bond (1.51 Å) but C(24)—N(25) and C(24)—N(31) have an average bond length of 1.33 Å, considerably shorter than the average value (1.48 Å) found for N-substituted piperidines.[12-15] Both points (d) and (e) can be interpreted as the result of a localized positive charge between the nitrogens and C(24).

Therefore the proposed structure is supported by the X-ray data, and by the presence on the difference-Fourier map of the required hydrogen atoms only.

The piperidine α-carbons are not on plane C; plane D which includes them deviates considerably from planarity with an average distance of atoms from the plane of 0.31 Å. This is the result of largely sp^3 hybridization at the nitrogen atoms, as shown by the bond angles at nitrogen with the α-carbons (113°). This is not unusual in piperidine salts.[16]

Even through strong molecular interactions could be expected in zwitterions, no significantly short intermolecular distance was found in the cell.

TABLE 6

Bond lengths (Å; e.s.d. <0.005 Å) and bond angles (°; e.s.d. <0.4°)

(a) Bond lengths

N(1)–C(2)	1.485	C(17)–C(22)	1.368
N(1)–C(9)	1.419	C(18)–C(19)	1.387
N(1)–C(10)	1.395	C(19)–C(20)	1.372
C(2)–C(3)	1.387	C(20)–C(21)	1.350
C(2)–O(13)	1.246	C(21)–C(22)	1.388
C(3)–C(4)	1.427	C(23)–C(24)	1.508
C(3)–C(14)	1.504	C(24)–N(25)	1.324
C(4)–C(5)	1.398	C(24)–N(31)	1.333
C(4)–C(9)	1.414	N(25)–C(26)	1.481
C(5)–C(6)	1.383	N(25)–C(30)	1.489
C(6)–C(7)	1.384	C(26)–C(27)	1.508
C(7)–C(8)	1.381	C(27)–C(28)	1.515
C(8)–C(9)	1.384	C(28)–C(29)	1.514
C(10)–C(11)	1.520	C(29)–C(30)	1.517
C(10)–O(12)	1.217	N(31)–C(32)	1.493
C(14)–C(15)	1.532	N(31)–C(36)	1.481
C(14)–C(23)	1.542	C(32)–C(33)	1.523
C(15)–C(16)	1.215	C(33)–C(34)	1.502
C(15)–C(17)	1.501	C(34)–C(35)	1.551
C(17)–C(18)	1.399	C(35)–C(36)	1.479

(b) Angles

C(2)–N(1)–C(9)	108.3	C(15)–C(17)–C(18)	117.5
C(2)–N(1)–C(10)	127.3	C(15)–C(17)–C(22)	124.4
C(9)–N(1)–C(10)	124.3	C(18)–C(17)–C(22)	118.1
N(1)–C(2)–C(3)	105.7	C(17)–C(18)–C(19)	120.0
N(1)–C(2)–O(13)	122.3	C(18)–C(19)–C(20)	120.4
C(3)–C(2)–O(13)	131.9	C(19)–C(20)–C(21)	119.8
C(2)–C(3)–C(4)	110.0	C(20)–C(21)–C(22)	120.4
C(2)–C(3)–C(14)	121.6	C(17)–C(22)–C(21)	121.2
C(4)–C(3)–C(14)	128.4	C(14)–C(23)–C(24)	116.6
C(3)–C(4)–C(5)	133.2	C(23)–C(24)–N(25)	120.7
C(3)–C(4)–C(9)	107.8	C(23)–C(24)–N(31)	118.7
C(5)–C(4)–C(9)	118.1	N(25)–C(24)–N(31)	120.5
C(4)–C(5)–C(6)	119.9	C(24)–N(25)–C(26)	124.1
C(5)–C(6)–C(7)	120.8	C(24)–N(25)–C(30)	123.1
C(6)–C(7)–C(8)	121.0	C(26)–N(25)–C(30)	112.7
C(7)–C(8)–C(9)	118.4	N(25)–C(26)–C(27)	112.2
N(1)–C(9)–C(4)	107.2	C(26)–C(27)–C(28)	110.9
N(1)–C(9)–C(8)	131.0	C(27)–C(28)–C(29)	110.2
C(4)–C(9)–C(8)	121.8	C(28)–C(29)–C(30)	111.2
N(1)–C(10)–C(11)	118.9	N(25)–C(30)–C(29)	110.0
N(1)–C(10)–O(12)	120.2	C(24)–N(31)–C(32)	123.5
C(11)–C(10)–O(12)	120.8	C(24)–N(31)–C(36)	123.1
C(3)–C(14)–C(15)	110.1	C(32)–N(31)–C(36)	113.0
C(3)–C(14)–C(23)	113.7	N(31)–C(32)–C(33)	108.3
C(15)–C(14)–C(23)	107.3	C(32)–C(33)–C(34)	112.2
C(14)–C(15)–O(16)	120.8	C(33)–C(34)–C(35)	109.4
C(14)–C(15)–C(17)	119.2	C(34)–C(35)–C(36)	110.7
C(16)–C(15)–C(17)	119.9	N(31)–C(36)–C(35)	112.5

DISCUSSION

How can the different behaviour of 1-t-butylenamines and aminals, and the effect of substituents in producing stable and isolable zwitterions which are also the intermediates of the Michael reaction, be rationalized?

An explanation in terms of increased charge-transfer between the acceptor oxoindole and the donor aminoethylene can be given since the increased proximity of the energy levels of the frontier orbitals vary in the order: (E1)—(E3) < (A1)—(A3) (in general aminals have HOMO's higher than those of enamines),[17] (A1) < (A3) (pyrrolidine increases the i.p. more than piperidine and this more than morpholine) [6,7] and (1a) < (1c) (an electron-attracting group lowers the LUMO).

An alternative explanation can be given simply in terms of stabilization of the positive or negative end of the zwitterion.

An electron-attracting group stabilizes the negative end of the zwitterion (MeCO > CH_2Ph > Me) and a second amine residue (X = NR'_2) stabilizes the positive end of the zwitterion more than a t-butyl group. Considering the nature of NR'_2, since the basicity order morpholine < piperidine < pyrrolidine is well known,
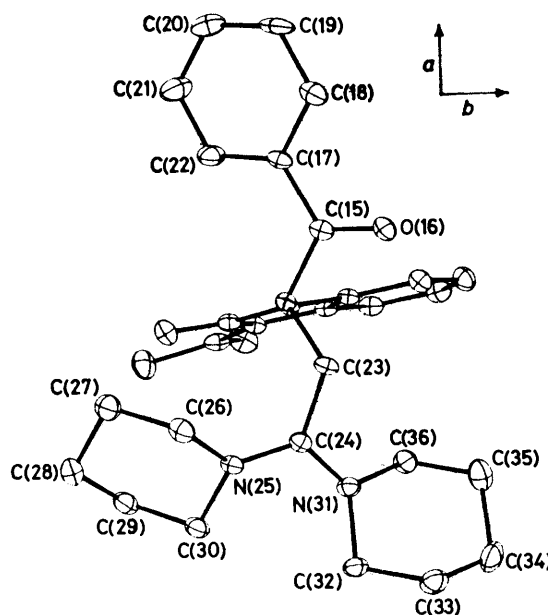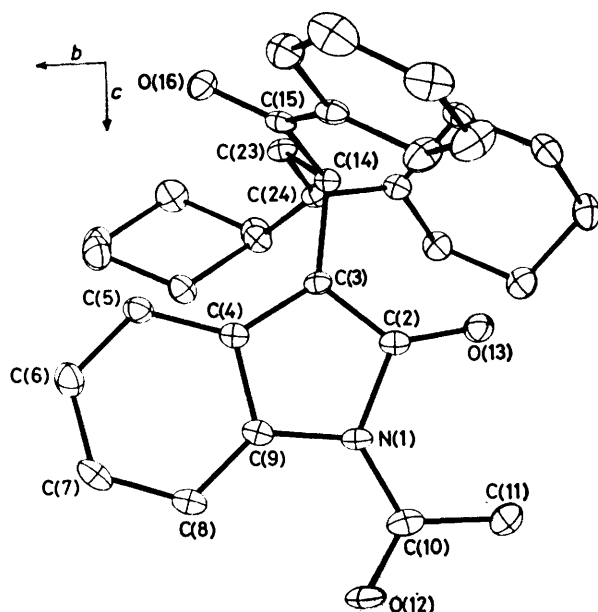
TABLE 7

Significant torsion angles (°) (e.s.d. 0.5°)

C(10)–N(1)–C(2)–O(13)	175.0
C(10)–N(1)–C(2)–C(3)	−3.8
N(1)–C(2)–C(3)–C(14)	2.7
O(13)–C(2)–C(3)–C(14)	−176.0
O(13)–C(2)–C(3)–C(4)	3.0
C(14)–C(3)–C(4)–C(5)	179.6
C(14)–C(3)–C(4)–C(9)	−2.6
C(9)–N(1)–C(10)–C(11)	−6.3
C(9)–N(1)–C(10)–O(12)	175.3
C(2)–N(1)–C(10)–O(12)	−1.8
C(2)–N(1)–C(10)–C(11)	176.6
C(2)–C(3)–C(14)–C(15)	49.8
C(2)–C(3)–C(14)–C(23)	−70.6
C(3)–C(14)–C(15)–C(17)	−105.2
C(23)–C(14)–C(15)–C(17)	19.0
C(3)–C(14)–C(15)–O(16)	77.2
C(23)–C(14)–C(15)–O(16)	−158.6
C(3)–C(14)–C(23)–C(24)	122.6
C(15)–C(14)–C(23)–C(24)	0.6
C(14)–C(15)–C(17)–C(22)	−179.7
C(14)–C(15)–C(17)–C(18)	−1.1
O(16)–C(15)–C(17)–C(18)	176.5
O(16)–C(15)–C(17)–C(22)	−2.1
C(14)–C(23)–C(24)–N(31)	−60.3
C(14)–C(23)–C(24)–N(25)	116.3
C(23)–C(24)–N(31)–C(32)	−42.9
C(23)–C(24)–N(31)–C(36)	145.4
N(25)–C(24)–N(31)–C(32)	140.4
N(25)–C(24)–N(31)–C(36)	−31.3
C(24)–N(31)–C(36)–C(35)	−64.1
N(31)–C(36)–C(35)–C(34)	−125.8
C(36)–C(35)–C(34)–C(33)	125.6
C(35)–C(34)–C(33)–C(32)	−122.9
C(34)–C(33)–C(32)–N(31)	122.4
C(33)–C(32)–N(31)–C(24)	63.7
C(33)–C(32)–N(31)–C(36)	−123.8
N(31)–C(24)–N(25)–C(26)	−22.6
N(31)–C(24)–N(25)–C(30)	157.9
C(23)–C(24)–N(25)–C(26)	160.8
C(23)–C(24)–N(25)–C(30)	−18.7
C(24)–N(25)–C(26)–C(27)	−54.3
C(30)–N(25)–C(26)–C(27)	125.2
N(25)–C(26)–C(27)–C(28)	−125.9
C(26)–C(27)–C(28)–C(29)	124.9
C(27)–C(28)–C(29)–C(30)	−123.0
C(28)–C(29)–C(30)–N(25)	123.4
C(29)–C(30)–N(25)–C(24)	54.9
C(29)–C(30)–N(25)–C(26)	−124.7

TABLE 8

Angles between planes (°)

Planes [defining atoms]	A (Oxoindole)	B (Benzoyl)	C (Positive part)
A [C(1)—C(14)]			
B [C(15), O(16), and C(17)—C(22)]	98.0		
C [C(23), C(24), N(25), N(31)]	64.4	137.6	
D [Plane C + C(26), C(30), C(32), C(36)]	63.7	133.6	4.1

ORTEP views of the molecular skeleton of the zwitterion (7c) (hydrogen atoms not included); the thermal ellipsoids (representing 25% probability) are depicted according to the output of the last least-squares cycle (see text)

zwitterions become stable enough to be isolated when X and NR′$_2$ are both pyrrolidine groups, independent of the nature of R, and when the former are piperidine only if the latter is an acyl group.
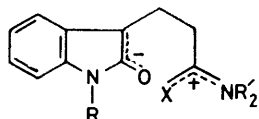
In order to distinguish between these two possibilities, we considered a reaction between two reagents which have different frontier-orbital separation, but are affected by a very similar stabilization to the ends of the zwitterion.

The reaction was performed between 1,1-dipiperidino-ethylene (A2) and 1-acetyl-3-benzylideneoxoindole (12) which react to give a zwitterion with the same charge stabilization as (7c). However the frontier-orbital separation is higher than that of (1c) and (A2) since the electron-attracting benzoyl group of (1c) gives a lower LUMO than that caused by the phenyl group of (12). This comparison was chosen since the reaction between (1c) and (A2) is the separation point between Michael reaction and formation of stable zwitterions.

The colourless adduct obtained (13) has the typical i.r. and n.m.r. spectra of a Michael adduct (see Experimental section for details).

Conclusion.—From these results it therefore seems more reasonable to rationalize the reactivity in terms of molecular orbitals of the reactants rather than stabilization of the intermediate by the substituents.

The reaction of 2-oxoindolin-3-ylidene derivatives with enamines and diaminoethylenes gives different heterodienic pathways: 1,4- and 1,2-cycloadditions, Michael reactions, and stable zwitterions can be obtained.

The variation in reaction pathway depends on the frontier-orbital interactions between the HOMO of the nucleophilic olefin and the LUMO of the oxoindoline derivative.[18] The lower the separation of the orbitals, the greater is the degree of electron transfer from the donor to the acceptor, and the stronger is the zwitterionic character of the reaction.

This is true if the amplitude of the coefficients at the reaction centres can be taken as constant.[19] If this is not the case, since they appear in the numerator of the general perturbation equation,[20] they must be taken into account. However, this will be the topic of a future paper in the field of heterodienic reactions.
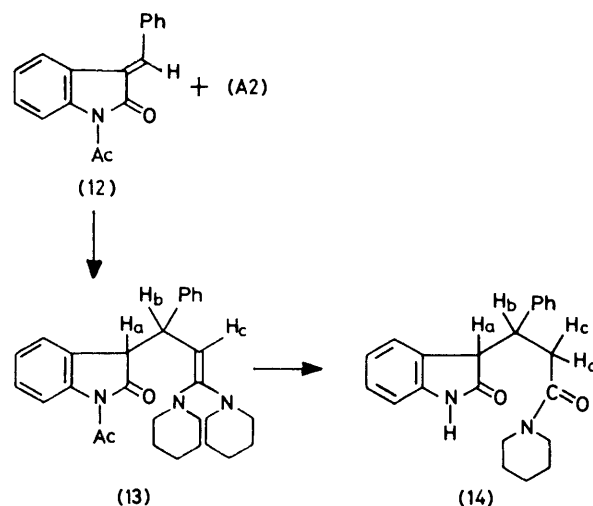
EXPERIMENTAL

I.r. spectra were determined for Nujol mulls, unless otherwise stated, with a Perkin-Elmer 257 spectrophotometer. N.m.r. spectra were obtained with a Perkin-Elmer

R 12A spectrometer (CDCl$_3$ as solvent) by Dr. A. Gamba Invernizzi.   Microanalyses were performed by Dr. L. Maggi Dacrema.

2-*Oxoindolin*-3-*ylideneacetophenones*   (1a—c).—1-Methyl-,[21] 1-benzyl-,[2] and 1-acetyl-2-oxoindolin-3-ylideneacetophenones (1a—c) [22] were prepared by reported methods.

Enamines (E1)—(E3).—3,3-Dimethyl-2-morpholinobut-1-ene (E1) was prepared by a reported method.[23]   The same

C, 78.6; H, 12.35; N, 9.3.   C$_{10}$H$_{19}$N requires C, 78.35; H, 12.5; N, 9.15%).

Diaminoethylenes (A1)—(A3).—1,1-Dimorpholinoethene (A1),[24] 1,1-dipiperidinoethane (A2),[24] and 1,1-bis-(1-pyrrolidinyl)ethene (A3) [25] were prepared by the reported methods.

Reaction of the Oxoindolinylidene Derivatives (1a—c) *with the Enamines* (E1)—(E3).—The reaction was performed as

TABLE 9

Reactions of the 2-oxoindolin-3-ylideneacetophenones (1a—c) with enamines (E1)—(E3)

Product	Enamine	Method (see text)	Reaction time [Ratio (mmol) of (1) to enamine]	Physical aspect [yield (%)]	M.p. (°C)	Formula	Elemental analysis (%) Found (required)
(2a)	(E1)	B	7 [d] (1 : 8)	a			
(2b)	(E1)	B	2 [d] (1 : 8)	a			
(2c)	(E1)	A	6 [d]	White crystals [70]	109—111 [b]	C$_{28}$H$_{32}$N$_2$O$_4$	C, 73.45; H, 7.1; N, 6.2 (C, 73.05; H, 7.0; N, 6.1)
(3a)	(E2)	B	3 [d] (1 : 4)	a			
(3b)	(E2)	B	2 [d] (1 : 4)	a			
(3c)	(E2)	A	1 [h] (1 : 2.5)	Pale pink crystals [81]	102—105 [b]	C$_{29}$H$_{34}$N$_2$O$_3$	C, 76.45; H, 7.65; N, 6.3 (C, 75.95; H, 7.45; N, 6.1)
(4a)	(E3)	C	6 [h] (1 : 2)	a			
(4b)	(E3)	C	4 [h] (1 : 2)	a			
(4c)	(E3)	A	20 min (1 : 1.5)	Pale pink crystals [90]	84—85 [b]	C$_{28}$H$_{32}$N$_2$O$_3$	C, 76.05; H, 7.35; N, 6.35 (C, 75.65; H, 7.25; N, 6.3)

[a] Not separated, the solution being directly hydrolysed.   [b] Crude sample dried for 6 h at room temperature and 0.1 mmHg.

TABLE 10

Hydrolytic cleavage of the adducts (2)—(4)

Product	Physical aspect [yield (%)] [a]	M.p. (°C)	Formula	Elemental analysis (%) Found (required)	I.r. ν(C=O) (lactam)	ν(CH$_2$C=O) (ketone)	ν(C=O) (acetyl)	ν(Ph—C=O) (ketone)
(5a)	White crystals [65, 65, 86] [d]	101—102 [b,c]	C$_{23}$H$_{25}$NO$_3$	C, 76.35; H, 7.25; N, 3.9 (C, 76.00; H, 6.95; N, 3.85)	1 715s			1 687s
(5b)	White crystals [62, 75, 95] [d]	163 [e]	C$_{29}$H$_{29}$NO$_3$	C, 79.25; H, 6.7; N, 3.1 (C, 79.25; H, 6.65; N, 3.2)	1 710s			1 681s
(5c)	White crystals [65, 80, 90] [d]	101—102 [e,f]	C$_{24}$H$_{25}$NO$_4$	C, 73.6; H, 6.7; N, 3.65 (C, 73.65; H, 6.45; N, 3.6)	1 758s	1 706s		1 677s

[a] The yields are given starting from (2), (3), and (4) respectively.   [b] From di-isopropyl ether.   [c] Dried for 3 h at 70 °C and 0.1 mmHg.   [d] The yield is determined from the starting 2-oxoindolin-3-ylideneacetophenone (1).   [e] From ethanol.   [f] From light petroleum–benzene (2 : 1).

method, but starting from 3,3-dimethylbutan-2-one and piperidine or pyrrolidine, was used to prepare the following enamines: 3,3-*dimethyl*-2-*piperidinobut*-1-*ene* (E2), colourless liquid, 70% yield, b.p. at 13 mmHg 79—80 °C; δ 1.08 (9 H, s, Bu^t), 1.4—1.75 (6 H, m, ring [CH$_2$]$_3$), 2.45—2.75 (4 H, m, ring CH$_2$–N–CH$_2$), and 4.54 and 4.74 (2 H, 2 s, =CH$_2$) (Found: C, 79.15; H, 12.9; N, 8.55. C$_{11}$H$_{21}$N requires C, 78.95; H, 12.65; N, 8.35%); and 3,3-*dimethyl*-2-(1-*pyrrolidinyl*)*but*-1-*ene* (E3), colourless liquid, 75% yield, b.p. at 12 mmHg 74—75 °C; δ 1.20 (9 H, s, Bu^t), 1.6—1.95 (4 H, m, ring [CH$_2$]$_2$), 2.8—3.2 (4 H, m, ring CH$_2$–N–CH$_2$), and 3.78 and 4.10 (2 H, 2 br s, =CH$_2$) (Found:

follows. (a) Freshly distilled enamine and powdered oxoindolinylidene derivative (1) (1 mmol) were mixed and stirred at room temperature until a cream coloured solid was formed, then set aside at low temperature for 12 h. The adduct was separated by grinding the resulting mass with cold light petroleum (b.p. 60—80 °C) and filtering off the crystalline solid.

(b) To a stirred solution of (1) (1 mmol) in anhydrous benzene (5.0 ml) was added freshly distilled enamine at room temperature. Stirring was continued for the required time and the solution was directly hydrolysed as described below.

TABLE 11

Reaction of the 2-Oxoindolin-3-ylideneacetophenones (1a—c) with (A1) and (1a and b) with (A2)

Product	Ratio (mmol) of (1) to (A1) or (A2)	Physical aspect [yield (%)]	M.p. (°C)	Formula	Elemental analysis (%) Found (required)
(6a)	1 : 1.05	Pale yellow crystals [70]	139—140 *	$C_{27}H_{31}N_3O_4$	C, 69.85; H, 6.75; N, 9.3 (C, 70.25; H, 6.75; N, 9.1)
(6b)	1 : 1.05	Pale yellow crystals [80]	158 *	$C_{33}H_{35}N_3O_4$	C, 73.45; H, 6.7; N, 7.95 (C, 73.7; H, 6.55; N, 7.8)
(6c)	1 : 1.5	Pale pink crystals [98]	96—97 *	$C_{28}H_{31}N_3O_5$	C, 68.35; H, 6.45; N, 8.8 (C, 68.7; H, 6.4; N, 8.6)
(7a)	1 : 2	Pale yellow crystals [77]	117 *	$C_{29}H_{35}N_3O_2$	C, 76.1; H, 7.9; N, 9.15 (C, 76.1; H, 7.7; N, 9.2)
(7b)	1 : 2	Pale yellow crystals [82]	123 *	$C_{35}H_{39}N_3O_2$	C, 78.6; H, 7.35; N, 8.0 (C, 78.75; H, 7.35; N, 7.85)

* Crude sample dried for 6 h at room temperature and 0.1 mmHg.

TABLE 12

Reaction of the compounds (1c) with (A2) and (1a—c) with (A3)

Product	Physical aspect [yield (%)]	M.p. (°C)	Formula	Elemental analysis (%) Found (required)
(7c)	Red prisms [95]	150—151 [a]	$C_{30}H_{35}N_3O_3$	C, 74.4; H, 7.4; N, 8.75 (C, 74.2; H, 7.25; N, 8.65)
(8a)	Deep orange crystals [75]	79—80.5 [b]	$C_{27}H_{31}N_3O_2 \cdot H_2O$	C, 73.9; H, 7.6; N, 9.35 (C, 73.95; H, 7.35; N, 9.6)
(8b)	Deep orange crystals [60]	84—85 [b]	$C_{33}H_{35}N_3O_2$	C, 77.9; H, 7.0; N, 8.4 (C, 78.4; H, 7.0; N, 8.3)
(8c)	Red-orange crystals [97]	158—159 [a]	$C_{28}H_{31}N_3O_3$	C, 73.35; H, 6.95; N, 9.0 (C, 73.5; H, 6.85; N, 9.2)

[a] From acetonitrile. [b] Crude sample dried for 6 h at room temperature and 0.1 mmHg.

TABLE 13

Hydrolytic cleavage of the adducts (6a—c), (7a—c), and (8a—c)

Product	Physical aspect [yield (%)]	MeOH ml	H₂O ml	M.p. (°C)	Formula	Elemental analysis (%) Found (required)	I.r. ν(C=O) Lactam	Ketone	Amide
(9a)	White crystals [90]	5.0	3.3	166—167 [a]	$C_{23}H_{24}N_2O_4$	C, 70.55; H, 6.3; N, 7.3 (C, 70.39; H, 6.15; N, 7.15)	1 719bs	1 690s	1 649s
(9b)	White crystals [68]	38.4	25.6	134—136 [a]	$C_{31}H_{34}N_2O_5 \cdot 0.5H_2O$	C, 72.45; H, 6.3; N, 5.9 (C, 72.95; H, 6.1; N, 5.85)	1 710s	1 687s	1 630s
(9c)	White crystals [40]	3	12	183—184 [b]	$C_{22}H_{22}N_2O_4$	C, 69.45; H, 6.1; N, 7.5 (C, 69.80; H, 5.85; N, 7.4)	1 728s	1 679s	1 630w
(10a)	White crystals [82]	6	4	138—139 [b,c]	$C_{24}H_{26}N_2O_3$	C, 74.2; H, 6.95; N, 6.8 (C, 73.8; H, 6.7; N, 7.2)	1 704s	1 694s	1 638s
(10b)	White crystals [84]	18	12	125—127 [b,c]	$C_{30}H_{30}N_2O_3$	C, 77.35; H, 6.75; N, 5.4 (C, 77.2; H, 6.5; N, 6.0)	1 710s, 1 725s	1 680s	1 639s
(10c)	Pale yellow crystals [45]	8	6	180—181 [b,c]	$C_{23}H_{24}N_2O_3$	C, 73.0; H, 6.4; N, 7.5 (C, 73.4; H, 6.45; N, 7.45)	1 731s	1 689s	1 640s
(11a)	White crystals [86]	6	4	151—152 [b,c]	$C_{23}H_{24}N_2O_3$	C, 73.2; H, 6.5; N, 7.55 (C, 73.4; H, 6.45; N, 7.45)	1 719s	1 686s	1 643s
(11b)	White crystals [61]	19.6	11.2	152—153 [b]	$C_{29}H_{28}N_2O_3$	C, 77.05; H, 6.35; N, 6.2 (C, 76.95; H, 6.25; N, 6.2)	1 715s	1 681s	1 643s
(11c)	Pale yellow crystals [30]	8	6	177—178 [b]	$C_{22}H_{22}N_2O_3$	C, 72.4; H, 6.2; N, 7.9 (C, 72.9; H, 6.1; N, 7.75)	1 745s	1 702s	1 640s, 1 658s

[a] From ethanol. [b] From AcOEt. [c] Dried for 4 h at 100 °C and 0.1 mmHg.

(c) Freshly distilled enamine was added to a stirred and cooled suspension of (1) (1 mmol) in anhydrous diethyl ether (5.0 ml). Cooling and stirring was continued for the required time and the solution was directly hydrolysed as described below.

Methods, (1) : enamine ratios, reaction times, and properties of the isolated adducts are summarized in Table 9.

Hydrolytic Cleavage of the Adducts (2)—(4).—To a cooled and stirred suspension of the adducts (2c)—(4c) (1 mmol) in diethyl ether (4.0 ml), or to the above-mentioned solutions for (2a, b)—(4a, b), a cooled mixture of acetic acid (1.5 ml) and water (2.5 ml) was added. The emulsion was stirred and cooled for an additional 6 h and then maintained at 0 °C for 12 h. Solid sodium hydrogencarbonate was cautiously added with stirring to neutrality and the organic solvent was evaporated off at room temperature. The oily crystalline precipitate of (5) was filtered off, washed several

Hydrated (8a) and anhydrous (8b) decompose on heating in organic solvents and the crude samples must be stored at low temperature. (7c) and (8c) crystallize from acetonitrile and are stable at room temperature. If the reaction between (1c) and (A2) is performed using diethyl ether as solvent, (8c) precipitated as the hemihydrate [orange crystals, m.p. 135—136 °C; $\nu_{max.}$ 3 600, 3 480, 1 660, 1 625, and 1 585 cm^{-1} (Found: C, 72.55; H, 7.45; N, 8.55. $C_{30}H_{35}N_3O_3 \cdot 0.5H_2O$ requires C, 72.85; H, 7.35; N, 8.5%)]. The hemihydrate (8c) crystallizes from ethanol with one molecule of ethanol of crystallization [yellow-orange crystals, m.p. 125—126 °C; $\nu_{max.}$ 3 190, 1 661, 1 612, and 1 580 cm^{-1} (Found: C, 72.45; H, 7.65; N, 7.85. $C_{30}H_{35}N_3O_3 \cdot C_2H_5OH$ requires C, 72.3; H, 7.75; N, 7.9%)]. Anhydrous (8c) can be obtained from the solvated forms upon crystallization from acetonitrile. The properties of the zwitterionic adducts are in Table 12.

TABLE 14

N.m.r. data for the adducts (9)—(11)

| Adduct | Chemical shifts (δ) | | | | | | Coupling constants/Hz | |
	H_a	H_b	H_c, H_c	R	N-Substituents	Aromatic	J_{ab}	$J_{bc} + J_{bc}'$
(9a)	3.69(d)	4.96 *	2.68(m)	Me 3.24(s)	Morpholine 3.35—3.65(m)	6.7—8.25(m)	2.9	13.3
(9b)	3.78(d)	4.97 *	2.66(m)	CH$_2$Ph δ_A 4.85, δ_B 5.01 (J_{AB} —15.9)	3.1—3.7(m)	6.6—58.35(m)	2.6	13.9
(9c)	3.72(d)	4.94 *	2.70(m)	H 9.15(s)	3.15—3.7(m)	6.75—8.3(m)	2.9	13.3
(10a)	3.67(d)	4.96 *	2.74(m)	Me 3.25(s)	Piperidine 1.25—1.7(m) 3.2—3.6(m)	6.7—8.35(m)	3.3	13.3
(10b)	3.78(d)	4.99 *	2.75(m)	CH$_2$Ph δ_A 4.86, δ_B 5.04 (J_{AB} —15.3)	1.3—1.85(m) 3.05—3.65(m)	6.6—8.3(m)	3.3	13.3
(10c)	3.71(d)	4.93 *	2.72(m)	H 9.42(s)	1.1—1.8(m) 3.0—3.65(m)	6.7—8.4(m)	2.6	13.0
(11a)	3.69(d)	4.99 *	2.73(m)	Me 3.25(s)	Pyrrolidine 1.6—2.05(m) 3.15—3.6(m)	6.7—8.25(m)	3.0	13.3
(11b)	3.82(d)	5.02 *	2.77(m)	CH$_2$Ph δ_A 4.93, δ_B 5.03 (J_{AB} —15.3)	1.55—2.1(m) 3.1—3.65(m)	6.6—8.3(m)	3.0	13.3
(11c)	3.73(d)	4.97 *	2.66(m)	H 9.42(s)	1.6—2.0(m) 3.1—3.6(m)	6.7—8.35(m)	2.6	13.3

* Sextet.

times with water. dried under vacuum, and ground with di-isopropyl ether or ethanol. For (2a) and (3a), the oily residue had to be chromatographed [Kieselgel (Merck) 0.06—0.2; cyclohexane–ethyl acetate (70 : 30) as eluant]. Physical data for (5) are in Table 10.

Michael Adducts from Oxoindolinylidene Derivatives and Diaminoethylenes [(6a—c) *and* (7a, b)].—To a stirred and cooled suspension of (1) (1 mmol) in anhydrous diethyl ether (5.0 ml), was added the diaminoethylene. Cooling and stirring was continued for 2 h and the resulting precipitate was filtered off, washed with cold light petroleum and stored at low temperature. Reactant ratios and physical data for the adducts are in Table 11.

Zwitterionic Adducts from Oxoindolinylidene Derivatives and Diaminoethylenes [(7c) *and* (8d—c)].—To a stirred and cooled solution of (1) (1 mmol) in dry benzene [6.5 ml for (1c) and 4.0 ml for (1a and b)], the diaminoethylene (1 mmol) was slowly added. Cooling and stirring was continued for 1 h and the resulting coloured crystalline precipitate was filtered off and washed with dry benzene.

Hydrolytic Cleavage of the Adducts (6)—(8).—*General method.* Compound (6)—(8) (1 mmol) in methanol–water was heated on a steam-bath with occasional stirring for 45 min. The solution was cooled, and by scratching a crystalline precipitate was obtained which was filtered off. From the mother-liquors a second crop of product was some times obtained by evaporating the solvent.

Solvents, yields, m.p.s, elemental analyses, and i.r. spectra of the isolated amides (9)—(11) are summarized in Table 13, and their n.m.r. spectra are reported in Table 14.

Reaction of 1-*Acetyl*-3-*benzylidene*-2-*oxoindoline* (12) *with* (A2).—To a cooled and stirred suspension of (12) (1 mmol) in anhydrous diethyl ether (5.0 ml), was added freshly distilled 1,1-dipiperidinoethene (A2) (2 mmol). Cooling and stirring was continued for a further 6 h and by scratching a white crystalline precipitate was obtained. The crude (13) was dried for 3 h at room temperature at 0.5 mmHg, yield 66%, m.p. 114—115 °C; $\nu_{max.}$ 1 760, 1 710, and 1 625 cm^{-1} (C=O of lactam, C=O of acetyl and C=C of enamine respectively); δ 3.79 (1 H, d, *J* 3.3 Hz, H$_a$), 4.53 (1 H, dd,

H_b), and 3.13 (1 H, d, J 10.0 Hz, H_c) (Found: C, 75.8; H, 7.85; N, 9.25. $C_{29}H_{35}N_3O_2$ requires C, 76.1; H, 7.7; N, 9.2%).

Hydrolytic Cleavage of (13).—Compound 13 (1 mmol) in methanol–water (3 : 2, 10 ml) was heated on a steam-bath for 45 min. After cooling, colourless crystals of (14) separated in 85% yield, m.p. 168—170 °C (from AcOEt); $\nu_{max.}$ 3 200, 1 700, and 1 620 cm^{-1} (NH, C=O of lactam and C=O of amide respectively); δ 3.96 (2 H, m, H_a and H_b) and 2.8 (2 H, m, H_c and $H_{c'}$) (Found: C, 75.7; H, 6.8; N, 7.95. $C_{22}H_{24}N_2O_2$ requires C, 75.85; H, 6.95; N, 8.05%).

X-Ray Analysis.—Crystal data. (7c): $C_{30}H_{35}N_5O_3$, red crystals. Monoclinic, space group $P2_1/n$, $Z = 4$, $a = 16.550(4)$, $b = 17.335(6)$, $c = 9.127(2)$ Å, β = 98.7(1)°. The crystal used had dimensions 0.14 × 0.20 × 0.60 mm. A Philips PW 1100 four-circle diffractometer was used to record the intensities (room temperature, Cu-K_α radiation, λ = 1.541 8 Å, ω—2 θ scan technique). 4 028 independent reflections were collected up to 0 = 60° and processed according to the method of Davies and Gatehouse [26] to yield values of F_0 and σ (F_0). The structure was solved by direct methods (MULTAN); co-ordinates of hydrogen atoms were calculated on the basis of geometrical consider-ations and checked on a difference-Fourier map. They were inserted but not allowed to vary in the subsequent least-squares refinement, for which only the 2 794 reflections with $I > 3\sigma(I)$ were regarded as observed. The final R for the observed reflections was 6.4% (for all reflections R was 8.6%). Scattering factors for neutral atoms were those listed by Doyle and Turner,[27] and for hydrogen atoms those of Stewart *et al.*[28] Tables of least-squares planes, atomic fractional co-ordinates, anisotropic thermal parameters, and observed and calculated structure factors, are listed in Supplementary Publication No. SUP 22533 (30 pp.).*

[8/1661　*Received, 19th September*, 1978]

REFERENCES

[1] Part 22, G. Desimoni, C. Malaspina, P. P. Righetti, and G. Tacconi, *J. prakt. Chem.*, 1979, **321**, 43.

[2] G. Tacconi, A. Gamba Invernizzi, F. Marinone, and G. Desimoni, *Tetrahedron*, 1971, **27**, 561.

[3] G. Tacconi, A. Gamba Invernizzi, and G. Desimoni, *J.C.S. Perkin I*, 1976, 1872.

[4] G. Klopman, *J. Amer. Chem. Soc.*, 1968, **90**, 223.

[5] K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *J. Amer. Chem. Soc.*, 1973, **95**, 7301.

[6] F. P. Colonna, G. Distefano, S. Pignataro, G. Pitacco, and E. Valentin, *Chimica e Industia*, 1975, **57**, 209.

[7] L. N. Domelsmith and K. N. Houk, *Tetrahedron Letters*, 1977, 1981.

[8] (a) S. K. Malhotra and J. V. Pankstelis, in 'Enamines,' ed. A. G. Cook, Marcel Dekker, New York, 1969, pp. 46 and 179; (b) D. C. Cook and A. Lawson, *J.C.S. Perkin I*, 1974, 1112.

[9] Dipolar intermediates were isolated in (2 + 2) cycloadditions between olefins with donor and acceptor groups: R. Gomper, *Angew. Chem. Internat. Edn.*, 1969, **8**, 312.

[10] C. K. Johnson, ORTEP, Oak Ridge National Laboratory, Report ORNL-3794, 1965.

[11] G. Tacconi, A. Corsico Piccolini, P. P. Righetti, E. Selva, and G. Desimoni, *J.C.S. Perkin I*, 1976, 1248.

[12] A. Ducruix and C. Pascard-Billy, *Acta Cryst.*, 1974, **B30**, 1677.

[13] M. H. Koch, J. P. Declercq, G. Germain, and M. van Meerssche, *Acta Cryst.*, 1977, **B33**, 2945.

[14] J. P. Declerq, G. Germain, and M. van Meerssche, *Acta Cryst.*, 1977, **B33**, 2947.

[15] C. Humblet, M. Bailleux, G. Evrard, and F. Durant, *Acta Cryst.*, 1977, **B33**, 2949.

[16] G. Hite and B. M. Craven, *Acta Cryst.*, 1973, **B29**, 2929.

[17] H. Bock, G. Wagner, K. Wittel, J. Sauer, and D. Seebach, *Chem. Ber.*, 1974, **107**, 1869.

[18] G. Desimoni and G. Tacconi, *Chem. Rev.*, 1975, **75**, 651.

[19] R. Sustmann and H. Trill, *Angew. Chem. Internat. Edn.*, 1972, **11**, 838.

[20] A. Devaquet and L. Salem, *J. Amer. Chem. Soc.*, 1969, **91**, 3793.

[21] H. G. Lindwall and J. S. Maclennan, *J. Amer. Chem. Soc.*, 1932, **54**, 4739.

[22] T. Kato, H. Yamanaka, and H. Ichikawa, *Chem. Pharm. Bull. (Tokyo)*, 1969, **17**, 481.

[23] W. L. F. Armarego, *J. Chem. Soc. (C)*, 1969, 990.

[24] H. Baganz and L. Domaschke, *Chem. Ber.*, 1962, **95**, 2095.

[25] G. Opitz and F. Zimmermann, *Chem. Ber.*, 1964, **97**, 1270.

[26] J. E. Davies and B. M. Gatehouse, *Acta Cryst.*, 1973, **B29**, 1934.

[27] P. A. Doyle and P. S. Turner, *Acta Cryst.*, 1968, **A24**, 390.

[28] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1978, Index issue.