Enamine Chemistry. Part XI.[1] Reaction of αβ-Unsaturated Acids and Acid Chlorides with Imines. Synthesis of 2-Oxotetrahydropyridines and 2-Oxo-octahydroquinolines

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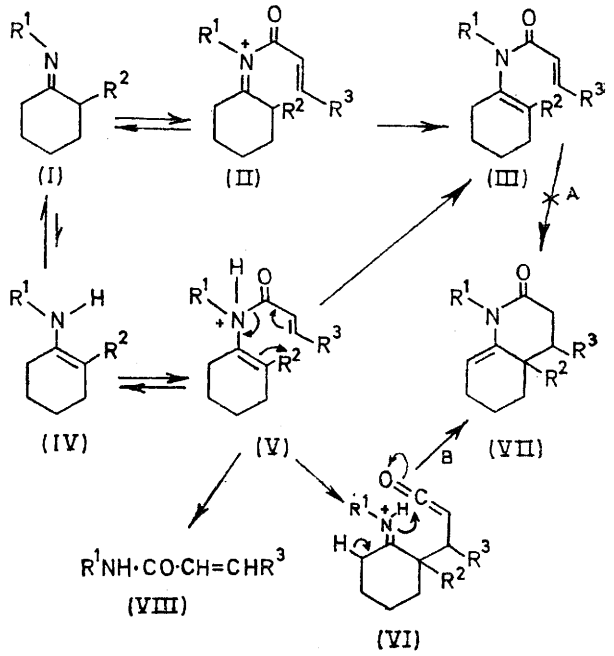
2-Oxotetrahydropyridines and 2-oxo-octahydroquinolines have been isolated from the reaction of acryloyl chloride with imines, together with the enamide and, in some cases, the amide. Crotonoyl and cinnamoyl chlorides give mixtures consisting mainly of the enamides. 2-Oxotetrahydropyridines and 2-oxo-octahydroquinolines have also been isolated from the reaction of acrylic acid with imines. The mechanisms of these reactions are discussed.

In continuation of our investigation into the reactions of αβ-unsaturated acid chlorides with enamines[2] and dienamines,[3] their reaction with imines has now been studied. The reaction of imines with aliphatic and aromatic acylating agents has previously been reported to result in the formation of *N*-acylated[4] and *C*-acylated[5] products. The latter presumably arise through the intermediacy of the enamine tautomer and, although spectroscopic studies[6,7a] indicate that the equilibrium is virtually completely in favour of the imine form for simple aldehydes and ketones, this imine–enamine tautomerism has been clearly demonstrated in reactions which involve the enamine form with a variety of electrophilic reagents at the α-position to the original carbonyl function (C-β of the enamine).[7] In their reaction with αβ-unsaturated acid chlorides we have found no evidence for the *C*-acylation of imines, the products isolated being the enamide and, in some cases, the amide, formed by *N*-acylation of the imine or enamine tautomer, and heterocyclic compounds formed from the enamine tautomer.

The imine (I; $R^1 = C_6H_{11}$, $R^2 = Me$) was treated with acryloyl chloride at low temperatures, and then briefly heated in the presence of triethylamine [method (A)] to give a mixture of the enamide (IX; $R^1 = C_6H_{11}$, $R^2 = Me$, $R^3 = H$), the amide (VIII; $R^1 = C_6H_{11}$, $R^3 = H$), and the oxoquinoline (VII; $R^1 = C_6H_{11}$, $R^2 = Me$, $R^3 = H$). The structure of the oxoquinoline followed from the ^1H n.m.r. spectrum which showed the methyl group as a singlet, an olefinic proton, as a triplet, and the absence of an NH signal, indicative of cyclisation as in (VII) or (X; $R = C_6H_{11}$). Structure (X) was ruled out by the i.r. spectrum which showed no carbonyl stretching absorption in the 1720 $cm.^{-1}$ region. The yield of the quinolone was increased (to 38%) by carrying out the addition of the acryloyl chloride to the imine in boiling benzene in the absence of triethylamine [method (B)], conditions previously shown[2a] to give optimum yields of 1-methylbicyclo[3,3,1]nonane-2,9-dione in the corresponding reaction with the morpholine enamine of 2-methylcyclohexanone. Under these conditions the reaction of acryloyl chloride with the *N*-phenylimine (I; $R^1 = Ph$, $R^2 = Me$) and the *N*-benzylimine (I; $R^1 = PhCH_2$, $R^2 = H$), gave the quinolones (VII; $R^1 = Ph$, $R^2 = Me$, $R^3 = H$) and (XI; $R = PhCH_2$) respectively, but in lower yield. The acyclic ketone imine (XIII; $R^1 = PhCH_2$, $R^2 = Et$) gave a heterocyclic product shown to be a mixture of the endocyclic and exocyclic double-bond isomers [(XIV) and (XV)]. Further confirmation for these structures follows from the u.v. spectra (Experimental section) since enaminoketones [such as (XII) or (XVI)] are known to absorb at considerably longer wavelength (290—354 mμ).[2b,8]



SCHEME

[1] Part X, N. F. Firrell, P. W. Hickmott, and B. J. Hopkins, *J. Chem. Soc.* (*B*), 1971, 351.

[2] (*a*) P. W. Hickmott and J. R. Hargreaves, *Tetrahedron*, 1967, **23**, 3151; (*b*) J. R. Hargreaves, P. W. Hickmott, and B. J. Hopkins, *J. Chem. Soc.* (*C*), 1968, 2599; *ibid.*, 1969, 592; (*c*) P. W. Hickmott and B. J. Hopkins, *ibid.*, 1968, 2918.

[3] N. F. Firrell and P. W. Hickmott, *J. Chem. Soc.* (*C*), 1968, 2320; N. F. Firrell, P. W. Hickmott, and B. J. Hopkins, *ibid.*, 1970, 1477; P. W. Hickmott, B. J. Hopkins, and C. T. Yoxall, *Tetrahedron Letters*, 1970, 2519.

[4] H. Breederveld, *Rec. Trav. chim.*, 1960, **79**, 401; J. P. Chupp and E. R. Weiss, *J. Org. Chem.*, 1968, **33**, 2357.

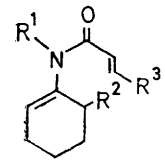
[5] U.S.P. 2,418,173/1947; B.P. 638,091/1950.

[6] B. Witkop, *J. Amer. Chem. Soc.*, 1956, **78**, 2873.

[7] (*a*) G. Bianchetti, P. Dalla Croce, D. Pocar, and G. G. Gallo, *Rendiconti dell'Istituto Lombardo di Scienze e Lettere* [*Sezione*] *A*, 1965, **99**, 296; G. Bianchetti, P. Dalla Croce, and D. Pocar, *Tetrahedron Letters*, 1965, 2043; R. W. Layer, *Chem. Rev.*, 1963, **63**, 489; (*b*) G. Bianchetti, P. Dalla Croce, D. Pocar, and E. Vigevani, *Gazzetta*, 1967, **97**, 289; G. Bianchetti, D. Pocar, P. Dalla Croce, and R. Stradi, *ibid.*, 1967, **97**, 304.

[8] G. H. Alt and A. J. Speziale, *J. Org. Chem.*, 1965, **30**, 1407.

In the case of crotonoyl and cinnamoyl chlorides, heterocyclic compounds have not been isolated and the reaction mixtures were less complex, consisting mainly of the amides (VIII) or the enamides (III) (Table 2).



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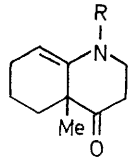

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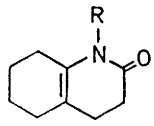

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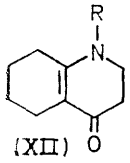

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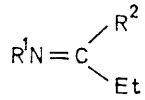

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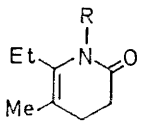

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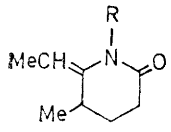

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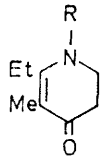

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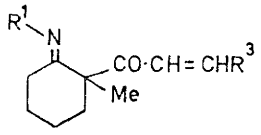
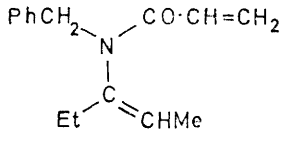


(XVII)



(XVIII)

No evidence for the formation of any *C*-acylated compounds has been obtained, although the high τ values of the singlet signals for the MeC= group in the enamides derived from *N*-(2-methylcyclohexylidene)benzylamine (τ 8·76—8·8) compared to those from other *N*-(2-methylcyclohexylidene)amines (τ 8·43—8·47) (Table 2) led us to suspect *C*-acylated structures (XVII; $R^1 = PhCH_2$, R^3 = H, Me, or Ph) for these products at first. However hydrolysis with concentrated hydrochloric acid gave the corresponding amide [*i.e.* (VIII; $R^1 = PhCH_2$, R^1 = Me)] confirming the structures as enamides (III; $R^1 = PhCH_2$, R^2 = Me, R^3 = H, Me, or Ph). The high τ values associated with the MeC= group must therefore be attributed to shielding by the benzyl group.

The structures of the enamides are interesting in that unlike tertiary enamines, the more substituted double-bond structures (III) are favoured. Although mixtures of structurally isomeric enamides [(III) and (IX)] were obtained, in some cases, only that derived from acryloyl chloride and *N*-(2-methylcyclohexylidene)cyclohexylamine was isolated completely in the less-substituted double-bond form (IX) and this too rearranged to (III) when heated in benzene in the presence of toluene-*p*-sulphonic acid. This difference in behaviour between enamides and tertiary enamines must be due to preferential orbital interaction of the nitrogen lone-pair with the carbonyl group rather than the carbon–carbon double-bond, and is reflected in the low τ-value (4·55) of the C-β olefinic proton in (IX; $R^1 = C_6H_{11}$, R^2 = Me, R^3 = H) (Table 2). This results in decreased stabilisation of the less substituted form of the enamide (IX) and a reduction in the steric interactions, which destabilise tetrasubstituted enamines [$A^{(1,3)}$ strain],[9] in the more substituted form of the enamide (III) by allowing the acylamino-group to twist out of the plane of the cyclohexene ring.

The formation of the heterocyclic compounds has been shown not to occur by ring closure of the enamide (Path A) (Scheme) since all attempts to initiate this cyclisation by the action of heat, mineral acids, or alkylating agents, on the enamides (III; $R^1 = C_6H_{11}$, R^2 = H, R^3 = Ph) or (III; $R^1 = C_6H_{11}$, R^2 = Me, R^3 = H) have been unsuccessful.* Of the remaining alternatives the mechanistic sequence which we favour involves *N*-acylation of the enamine tautomer followed by a [3,3]sigmatropic rearrangement, as we have previously postulated in the corresponding reaction of acryloyl chloride with tertiary enamines,[2] to give the keten intermediate (VI) and hence the heterocycle (VII) (Path B).

The fact that the enamide (III) failed to rearrange even under strongly acidic conditions does not invalidate the proposed mechanism [Path B, (IV) ⟶ (V) ⟶ (VI) ⟶ (VII), in Scheme] since it is likely that there are stereoelectronic factors operating which favour a [3,3]-sigmatropic rearrangement in the *N*-protonated enamide (V), when formed by *N*-acylation of the enamine tautomer (IV), which are absent in (V) formed by protonation of (III).† These would arise as a result of dipole–dipole interactions between the approaching molecules, thus causing all the orbitals involved in the rearrangement process to be lined up and ' ready to go.' Fission of the newly formed or partially formed C–N bond between the acid chloride and the enamine would then be favoured, or at least able to compete favourably, over fission of the N–H bond [to give the enamide (V) ⟶ (III)]. In (V) formed by protonation of (III) it is unlikely that the C–N acid chloride–enamine bond and the *p*-orbitals of the acid chloride double-bond would be lined up with the *p*-orbitals of the enamine carbon–carbon double-bond at the moment of protonation. An unfavourable stereoelectronic factor then operates against the rearrange-

* Photochemical cyclisation of αβ-unsaturated enamides to give 2-oxo-octahydroquinolines has recently been reported (I. Ninomiya, T. Naito, and S. Higuchi, *Chem. Comm.*, 1970, 1662).

† The failure of (III) to rearrange cannot be attributed solely to preferred *O*- (or *C*-) protonation of the enamide. Although i.r. spectral evidence has been interpreted in favour of *O*-protonation of amides (D. Cook, *Canad. J. Chem.*, 1962, **40**, 2362) there is evidence for the simultaneous existence of *O*- and *N*-protonated amides in strong acid solution (G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, 1970, **70**, 561), and similar considerations must apply to enamides.

[9] F. Johnson, *Chem. Rev.*, 1968, **68**, 375.

ment process and favours fission of the weakest bond (N–H) or fission of bonds not governed by such stringent stereoelectronic requirements, such as the C–N enamine bond [to give the amide (V) ⟶ (VIII)].[2c]

Acrylic acid has also been found to condense with imines [*i.e.* (I; $R^1 = C_6H_{11}$, R^2 = Me) and (XIII; $R^1 = PhCH_2$, R^2 = Et)] to give the same heterocyclic product as that obtained in the corresponding reaction with acryloyl chloride, but in somewhat lower yield. It seems probable that the enamine tautomer of the imine is again involved in this reaction, the acid behaving as an electrophilic olefin as has been previously suggested in the corresponding reaction with β-aminocrotonic esters.[10]

EXPERIMENTAL

The u.v. and i.r. spectra were measured with Unicam SP 800A and Perkin-Elmer 257 spectrophotometers respectively, and the n.m.r. and mass spectra with Varian A60 and A.E.I. MS 12 instruments.

Preparation of Imines.—A mixture of the ketone, primary amine (slight excess), and toluene-*p*-sulphonic acid (catalytic amount) was heated under reflux in benzene for the time stated (Table 1); the water was removed initially by means of a Dean and Stark separator followed by a molecular sieve. The solvent was evaporated off and the residue was distilled until free from unchanged ketone. Preparative and spectral data are summarised in Table 1.

Reaction of αβ-Unsaturated Acid Chlorides with Enamines.—*Method A.* The αβ-unsaturated acid chloride (0·01 mole) in dry benzene (20 ml.) was added gradually during 30—45 min. to the imine (0·01 mole) stirred and cooled (ice–salt) in dry benzene (50 ml.). An excess of triethylamine (0·02 mole) was added to the mixture which was then allowed to rise to room temperature slowly; it was then heated under reflux for 30 min., cooled, and filtered. The filtrate was evaporated and the residue was purified by preparative t.l.c. on silica with 5% acetone in benzene as the solvent system unless stated otherwise.

Method B. The αβ-unsaturated acid chloride (0·01 mole) in dry benzene (25 ml.) was added to the imine (0·01 mole) in boiling dry benzene (50 ml.) during 1 hr., and the mixture was heated under reflux for 48 hr. or until evolution of hydrogen chloride had ceased. The solvent was removed *in vacuo* and the residual oil was purified as in method A.

Preparative and spectral data for the enamides obtained pure by Methods A or B are summarised in Table 2.

(a) *Reactions of* N-(2-*Methylcyclohexylidene*)*cyclohexylamine.*—(i) *With acryloyl chloride.* The residue from method A was purified by preparative t.l.c. on silica (acetone–ethyl acetate–benzene, 5 : 5 : 90). This resulted in the separation of three distinct bands which were removed, extracted with acetone, and evaporated. The first band (from the solvent front) gave the *enamide* (IX; $R^1 = C_6H_{11}$, R^2 = Me, R^3 = H) (Table 2) and the second gave 1-*cyclohexyl*-4a-*methyl*-2-*oxo*-$\Delta^{8,8a}$-*octahydroquinoline* (VII; $R^1 = C_6H_{11}$, R^2 = Me, R^3 = H) in 26% yield [(Found: N, 5·4%; M^+ *m/e* 247·1936. $C_{16}H_{25}NO$ requires N, 5·7%; M^+ *m/e* 247·1936), $\lambda_{max.}$ (MeOH) 232 mμ (ε 9000); ν (film) 1670 and 1640 cm.; τ (CCl_4) 8·92 (s, Me), 8·9—7·5 (complex, methylene envelope), 6·3 (m, N·CH), 4·75 (t, CH=)]. The final band was impure but contained the amide (VIII; $R^1 = C_6H_{11}$, R^3 = H) [(M^+ *m/e* 153. $C_9H_{15}NO$ requires: M^+ *m/e* 153), ν (film) 3300 (NH), 1660, and 1625 cm.$^{-1}$; τ (CCl_4) 2·75br (NH), 3·8 and 4·5 (m, CH_2=CH·CO), and 6·3 (m, N·CH)].

Addition of the acid chloride at high temperatures (method B) gave a cleaner reaction with less material left on the base line of the silica plate. The yield of enamide was reduced and that of the oxoquinoline (VII; $R^1 = C_6H_{11}$, R^2 = Me, R^3 = H) increased to 38%.

(ii) *Crotonoyl chloride.* The residues from methods A and B purified on alumina (3% acetone in benzene), gave the *enamide* (III; $R^1 = C_6H_{11}$, $R^2 = R^3$ = Me) (Table 2) as the second band from the solvent front. The third band gave the amide (VIII; $R^1 = C_6H_{11}$, R^3 = Me) [(Found: N, 7·9%; M^+ *m/e* 167. $C_{10}H_{17}NO$ requires N, 8·3%; M^+ *m/e* 167), ν (Nujol) 3300 (NH), 1670, and 1630 cm.$^{-1}$; τ ($CDCl_3$) 9·0—7·85 (methylene envelope), 8·16 (dd, *J* 1·5 and 7 Hz), 4·15 (dm, *J* 1·5 and 15 Hz, =CH·CO), and 3·13 (dq, *J* 7 and 15 Hz) (CH_3CH=)].

(iii) *Cinnamoyl chloride.* Method A gave the *enamide* (III; $R^1 = C_6H_{11}$, R^2 = Me, R^3 = Ph) (Table 2).

(b) *Reaction of* N-*Cyclohexylidenebenzylamine with Acryloyl Chloride.*—The residue from method B gave two main bands by preparative t.l.c. on silica (acetone–ethyl acetate–benzene, 4 : 3 : 93). The first was not obtained sufficiently pure for analysis but consisted mainly of the enamide (III; $R^1 = PhCH_2$, $R^2 = R^3$ = H) [M^+ *m/e* 241; ν (film) 1660 and 1620 cm.$^{-1}$; τ (CCl_4) 8·7—7·8 (complex, methylene envelope), 5·35 (CH_2N), 4·5 (m, =CH·CO and ring CH=), 3·6 (m, CH_2=), and 2·75 (C_6H_5)]. The second band gave 1-*benzyl*-2-*oxo*-$\Delta^{4a,8a}$-*octahydroquinoline* (XI; R = $PhCH_2$) in 12% yield [(Found: N, 5·7%; M^+ *m/e* 241. $C_{16}H_{19}NO$ requires N, 5·8%; M^+ *m/e* 241), $\lambda_{max.}$ (MeOH) 215 (ε 7650) and 230sh mμ (4900), ν (film) 1665 and 1645 cm^{-1}; τ (CCl_4) 8·7—7·3 (complex, methylene envelope), 5·16 (s, $PhCH_2$), and 2·75 (s, C_6H_5)].

(c) *Reactions of* N-(2-*Methylcyclohexylidene*)*benzylamine.*—(i) *With acryloyl chloride.* The residue from method B gave two main bands by preparative t.l.c. on silica (acetone–ethyl acetate–benzene, 5 : 5 : 90). The first consisted of the *enamide* (III; $R^1 = PhCH_2$, R^2 = Me, R^3 = H) (Table 2) and the second band gave 1-*benzyl*-4a-*methyl*-2-*oxo*-$\Delta^{8,8a}$-*octahydroquinoline* (VII; $R^1 = PhCH_2$, R^2 = Me, R^3 = H) in 22% yield [(Found: N, 5·0%; M^+ *m/e* 255. $C_{17}H_{21}NO$ requires N, 5·5%; M^+ *m/e* 255); ν (film) 1670 and 1645 cm.$^{-1}$; τ (CCl_4) 8·86 (s, CH_3), 8·6—7·3 (methylene envelope), 5·35 and 4·9 (both d, *J* 15·5, PhCH_2), 5·05 (overlaid t, ring CH=), and 2·8 (C_6H_5)].

(ii) *With crotonoyl chloride.* Only the *enamide* (III; $R^1 = PhCH_2$, $R^2 = R^3$ = Me) (Table 2) was isolated in a pure state.

A sample of the enamide (0·1 g.) was heated under reflux with concentrated hydrochloric acid for 4 hr.; the mixture was cooled, extracted with ether, and the aqueous layer made alkaline with 4N-sodium hydroxide solution. Ether extraction gave *N*-benzylcrotonamide (0·04 g., 61·5%), m.p. 110° (from benzene–light petroleum). The i.r. and ^{1}H n.m.r. spectra were identical with those of authentic material.

(iii) *With cinnamoyl chloride.* Method B gave a small amount of *N*-benzylcinnamamide [ν (Nujol) 3270 (NH), 1655, and 1615 cm.$^{-1}$; τ ($CDCl_3$) 5·4 (d, *J* 6 Hz) (PhCH_2N), 3·52 (d, *J* 16 Hz, =CH·CO), 2·62 (m, C_6H_5), 2·26 (d, *J*

[10] G. Schroll, P. Klemmensen, and S.-O. Lawesson, *Arkiv Kemi*, 1967, **26**, 317.

TABLE 1

Imines: synthesis and spectra

Compd.	Time (hr.)	Yield (%)	B.p.	M^+ (*m/e*)	Relevant spectral data: $\nu(CCl_4)$ ($cm.^{-1}$)	Relevant spectral data: ^1H N.m.r. (τ)
(I; R^1 = Ph, R^2 = H)	72	79	140—144°/15 mm	173	1658 1598	2·5—3·4 (C_6H_5), 7·4—8·5 (C_6H_{10}) *
(I; R^1 = Ph, R^2 = Me)	72	68	144—148/16 mm	187	1660 1598	2·5—3·4 (C_6H_5), 7·3—8·7 (C_6H_9), 8·77 (d, CH_3) *
(I; R^1 = $PhCH_2$, R^2 = Me)	48	40	120—135/0·7 mm	201	1660 1607	2·75 (C_6H_5), 5·48 (CH_2), 7·0—8·8 (C_6H_9), 8·9 (d, CH_3) †
(I; R^1 = C_6H_{11}, R^2 = Me)	72	67		193	1656	6·6—8·8 (C_6H_{11},C_6H_9), 8·91 (d, CH_3) *
(I; R^1 = R^2 = Me)	§	49	68—72/18 mm	125	1663	6·83 (CH_3N=), 7·1—8·9 (C_6H_9), 8·92 (d, CH_3) *
(XIII; R^1 = $PhCH_2$, R^2 = Me)	48	20	74—80/0·7 mm	161	1663 1603	2·74 (C_6H_5), 5·6 (CH_2N), 7·72 (qm, CH_2), 8·23 (CH_3C=), 8·94 (t, CH_3) †
(XIII; R^1 = Bu^n, R^2 = Me)	48	28	42—44/15 mm	127	1660	6·79 (t, CH_2N), 7·6—8·8 (three CH_2), 8·55 (CH_3C=), 8·92 and 9·04 (overlaid t, two CH_3) ‡
(XIII; R^1 = $PhCH_2$, R^2 = Et)	48	63	134/20 mm	175	1663 1605	2·73 (C_6H_5), 5·5 (CH_2N), 7·5—8·0 (two CH_2), 8·9 and 8·98 (overlaid t, two CH_3) †

* In $CDCl_3$. † In CCl_4. ‡ In C_6D_6. § Prepared as described in U.S.P. 2,700,681; B.P. 702,985.

TABLE 2

Enamides: synthesis and spectra

Compound	Method	Yield (%)	M.p.(°)	Analysis (%) Found N	Analysis (%) Reqd. N	M^+ (*m/e*)	Relevant spectral data: $\nu_{max.}$ (cm^{-1})	Relevant spectral data: ^1H N.m.r. (τ)
(III; R^1 = R^3 = Ph, R^2 = H)	A	60	79—81	4·5	4·6	303	1660 * 1618 1599	1·88 (d, *J* 16 Hz, R^3CH=), 2·5—3·1 (two C_6H_5), 3·16 (d, *J* 16 Hz, COCH=), 4·41 (t, CH=), 7·7—8·9 (C_6H_8) †
(III; R^1 = C_6H_{11}, R^2 = R^3 = Me)	A	30	Oil	5·2	5·4	261	1660 ‡ 1620	3·2 (dq, *J* 7 and 15 Hz, CH_3·CH=), 4·13 (dm, *J* 1·5 and 15 Hz, =CH·CO), 6·0 (m, N·CH), 7·7—9·0 (m, C_6H_{10} and C_6H_8), 8·17 (dd, *J* 1·5 and 7 Hz, CH_3·CH=-CH), 8·47 (s, CH_3·C=) §
(III; R^1 = C_6H_{11}, R^2 = Me, R^3 = Ph)	A	50	Oil	4·2	4·3	323	1653 * 1610	2·42 (d, *J* 16 Hz, PhCH=), 2·65 (m, C_6H_5), 3·48 (d, *J* 16 Hz,=CH·CO), 6·0 (m, N·CH), 7·7—8·9 (C_6H_{10} and C_6H_8), 8·43 (s, CH_3·C=) §
(IX; R^1 = C_6H_{11}, R^2 = Me, R^3 = H)	A B	27 10	Oil	5·4	5·7	247	1655 ‡ 1615	3·67 (m, CH_2=), 4·55 (m, =CH·CO, ring CH=), 6·0 (m, N·CH), 7·4—8·9 (C_6H_7 and C_6H_{10}), 8·97, (d, *J* 7 Hz, CH_3·CH) §
(III; R^1 = $PhCH_2$, R^2 = Me, R^3 = H)	B	21	Oil	5·5	5·5	255	1655 ‡ 1620	2·7 (C_6H_5), 3·63 (m, CH_2=), 4·45 (m, =CH·CO), 5·37 (s, $PhCH_2$), 7·8—8·6 (methylene envelope), 8·8 (s, CH_3C=) §
(III; R^1 = $PhCH_2$, R^2 = R^3 = Me)	B	43	Oil	5·45	5·2	269	1670 ‡ 1630	2·65 (C_6H_5), 2·95 (dq, *J* 7 and 15 Hz, =CH·CO), 3·92 (dm, *J* 1·5 and 15 Hz, CH_3CH=), 5·32 (s, $PhCH_2$), 7·8—8·6 (methylene envelope), 8·15, (dd, *J* 1·5 and 7 Hz, CH_3·CH=), 8·76 (s, CH_3C=) ¶
(III; R^1 = $PhCH_2$, R^2 = Me, R^3 = Ph)	B	44	Oil	4·17	4·23	331	1650 † 1610	2·15 (d, *J* 16 Hz, PhCH=), 2·55 (m, C_6H_5), 3·25 (d, *J* 16 Hz, =CH·-CO), 5·22 (s, $PhCH_2N$·), 7·7—8·6 (methylene envelope), 8·7 (s, CH_3C=) ¶
(III; R^1 = R^2 = Me, R^3 = Ph)	B	38	86	5·5	5·4	255	1660 * 1620	2·36 (d, *J* 16 Hz, PhCH=), 2·6 (m, C_6H_5), 3·4 (d, *J* 16 Hz, =CH·CO), 6·98 (s, CH_3·N), 7·7—8·4 [·(CH_2)·$_4$], 8·42 (s, CH_3C=) §
(XVIII)	B	14	Oil	6·0	6·1	229	1660 ‡ 1620	2·75 (s, C_6H_5), 3·56 (m, CH_2=), 4·45 (m, =CHCO), 4·95 (q, *J* 7 Hz, CH_3CH=), 5·32 (s, $PhCH_2$), 7·73 (q, *J* 7 Hz, CH_3CH_2), 8·38 (d, *J* 7 Hz, CH_3CH=), 9·02 (t, *J* 7 Hz, CH_3CH_2) §

* Nujol. † C_6D_6. ‡ Film. § CCl_4. ¶ $CDCl_3$.

16 Hz, PhC*H*=)] and the *enamide* (III; R^1 = $PhCH_2$, R^2 = Me, R^3 = Ph) (Table 2).

(d) *Reaction of* N-(2-*Methylcyclohexylidene*)*aniline with Acryloyl Chloride.* Method B gave three fractions. The first gave the enamide as a mixture of isomers [(III) and (IX), R^1 = Ph, R^2 = Me, R^3 = H)] (28%) [M^+ *m/e* 241; ν (film) 1670, 1620, and 1600 cm.$^{-1}$; τ (CCl_4) 8·98 (d, *J* 7, CH_3CH), 8·35 (s, CH_3·C=), 8·5—7·5 (methylene envelope), 4·4 (m, =CH·CO and ring CH=), 3·6 (m, CH_2=), and 2·72 (C_6H_5)]. The second fraction was an unidentified oil, and the third fraction consisted of 4a-*methyl*-2-*oxo*-1-*phenyl*-$\Delta^{8,8a}$-*octahydroquinoline* (VII; R^1 = Ph, R^2 = Me, R^3 = H) (11%), m.p. 136—137° (from benzene–light petroleum) [(Found: C, 79·5; H, 7·7; N, 5·7%; M^+ *m/e* 241. $C_{16}H_{19}NO$ requires C, 79·5; H, 7·9; N, 5·8%; M^+ *m/e* 241), $\lambda_{max.}$ (MeOH) 240 mμ (ε 8950); ν (Nujol) 1670 and 1650 cm.$^{-1}$; τ (CCl_4) 8·7 (s, CH_3), 8·5—7·3 (methylene envelope), 5·63 (t, CH=), and 3·1—2·5 (m, C_6H_5)].

(e) *Reaction of* N-*Cyclohexylideneaniline with Cinnamoyl Chloride.*—Method A gave the *enamide* (III; R^1 = R^3 = Ph, R^2 = H) (Table 2).

A sample of the enamide (0·5 g.) was heated under reflux with concentrated hydrochloric acid (20 ml.) for 8 hr. The crystals which separated from the cool mixture were recrystallised from aqueous ethanol to give cinnamanilide (48%), m.p. 150° (M^+ *m/e* 223). The i.r. and ^{1}H n.m.r. spectra were identical with those of authentic material.

(f) *Reactions of* N-(2-*Methylcyclohexylidene*)*methylamine.*—(i) *With acryloyl chloride.* Methods A and B gave an inseparable mixture consisting of the two isomeric enamides [(III) and (IX), R^1 = R^2 = Me, R^3 = H] [ν (film) 1650br and 1620sh cm.$^{-1}$; τ (CCl_4) 8·98 (d, *J* 7 Hz, CH_3CH), 8·45 (s, CH_3C=), 8·7—7·4 (methylene envelope), 6·98 and 6·93 (s, CH_3N of two isomers), 4·45 (m, =CH·CO and ring CH=) and 3·65 (m, CH_2=)] and the 2-oxo-octahydroquinoline (VII; R^1 = R^2 = Me, R^3 = H) [τ (CCl_4) 8·97 (s, CH_3), 8·7—7·4 (methylene envelope), 7·03 (s, CH_3N), and 5·0 (t, CH=)].

(ii) *With cinnamoyl chloride.* Method B gave the *enamide* (III; R^1 = R^2 = Me, R^3 = Ph) (Table 2).

(g) *Reaction of* N-(3-*Pentylidene*)*benzylamine with Acryloyl Chloride.*—Method B gave two main bands consisting of the *enamide* (XVIII) (Table 2) and an inseparable mixture of 1-*benzyl*-6-*ethyl*-5-*methyl*-2-*oxo*-1,2,3,4-*tetrahydropyridine* (XIV) and 1-*benzyl*-6-*ethylidene*-5-*methyl*-2-*oxo*-*piperidine* (XV) (ratio 3 : 1) in 35% yield [(Found: N, 5·9%; M^+ *m/e* 229·1463. $C_{15}H_{19}NO$ requires N, 6·1%; M^+ *m/e* 229·1467), $\lambda_{max.}$ (MeOH) 215 (ε 7700) and 235sh mμ (5000); ν (film) 1670 and 1650sh cm^{-1}; τ (CCl_4) for (XIV): 9·05 (t, *J* 7 Hz, CH_3CH_2), 8·25 (s, CH_3C=), 8·1—7·3 (methylene envelope), 5·14 (s, $PhCH_2$), and 2·8 (s, C_6H_5) for (XV): 8·92 (d, *J* 7 Hz, CH_3CH), 8·4 (d, *J* 7 Hz, CH_3CH=), and 5·22 (overlaid q, CH=)].

Attempted Rearrangements of Enamides.—N-(1-*Cyclohexen*-1-*yl*)*cinnamanilide.* (i) A solution of the enamide (1 g.) and a catalytic amount of toluene-*p*-sulphonic acid in dry toluene (50 ml.) was heated under reflux for 17 days. Samples were removed periodically and examined by t.l.c. for the possible formation of the rearranged heterocyclic product, but without success. After 17 days the solvent was evaporated off and the residue was purified by preparative t.l.c. on silica (5% acetone in benzene) to give unchanged enamide (25%) and cinnamanilide (28% yield), m.p. 150° (from aqueous ethanol) (Found: C, 80·2; H, 6·1; N, 6·1. Calc. for $C_{15}H_{13}NO$: C, 80·7; H, 5·8; N, 6·3%). The i.r. and ^{1}H n.m.r. spectra were identical with those of authentic material.

(ii) A solution of the enamide (0·5 g.) and a catalytic amount of toluene-*p*-sulphonic acid in ethylene glycol (25 ml) was heated under reflux for 14 days. The solvent was removed *in vacuo* and the black residue was purified by preparative t.l.c. on silica (30% ethyl acetate in benzene) to give β-*hydroxyethyl cinnamate* (45% yield) as an oil (M^+ *m/e* 192·0789. $C_{11}H_{12}O_3$ requires M^+ *m/e* 192·0786), ν (film) 1710 and 1640 cm.$^{-1}$; τ (CCl_4) 6·8 (s, HO, exchangeable), 6·19 (m) and 5·72 (m, CH_2CH_2), 3·62 (d, *J* 16 Hz, =CH·CO), 2·6 (m, C_6H_5), and 2·33 (d, *J* 16 Hz, Ph·C*H*=).

(iii) A mixture of the enamide (1 g.), methyl toluene-*p*-sulphonate (0·62 g.) and an excess of dry potassium carbonate in dry mesitylene was heated under reflux for 5 hr. The mixture was cooled, filtered, and the filtrate was evaporated to give unchanged enamide (83% recovery).

N-*Cyclohexyl*-N-(6-*methylcyclohex*-1-*enyl*)*acrylamide.*—(i) A solution of the enamide and a catalytic amount of toluene-*p*-sulphonic acid in dry toluene was heated under reflux for 15 days. The solvent was evaporated off and the residue was purified by preparative t.l.c. on silica (3% acetone in benzene) to give the isomeric enamide, N-*cyclohexyl*-N-(2-*methylcyclohex*-1-*enylacrylamide* (44%) (Found: M^+ *m/e* 247. $C_{16}H_{25}NO$ requires: M^+ *m/e* 247), ν (film) 1655 and 1618 cm.$^{-1}$; τ (C_6D_6) 9·2—7·6 (complex methylene envelope), 8·55 (s, CH_3C=) 5·7br (N·CH), 4·6 (m, 1H), and 3·5 (m, 2H, CH_2=CH·CO).

(ii) Treatment of the enamide with methyl toluene-*p*-sulphonate, as above, or treatment with polyphosphoric acid for 4 hr. at 150—160°, resulted in the isolation only of unchanged starting material.

Reactions of Acrylic Acid.—(i) *With* N-(2-*methylcyclohexylidene*)*cyclohexylamine.* A solution of acrylic acid (0·05 mole) and the imine (0·05 mole) in chlorobenzene (100 ml.) was heated under reflux for 22 hr. The solvent was removed *in vacuo* and the residue was purified by preparative t.l.c. on silica (5% acetone in benzene) to give 1-cyclohexyl-4a-methyl-2-oxo-$\Delta^{8,8a}$-octahydroquinoline (28%), identical with the product derived from experiment (a) (i).

(ii) *With* N-(3-*pentylidene*)*benzylamine.* The imine was treated with acrylic acid as above to give the same mixture of 2-oxotetrahydropyridine and 2-oxopiperidine (25%) as obtained in the corresponding reaction with acryloyl chloride.

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