Selective Reduction of αβ-Olefinic Amides and Lactams by Magnesium and Methanol

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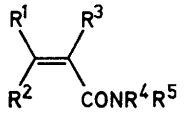
αβ-Olefinic amides with various substitution patterns at the carbon–carbon double bond and at nitrogen are all reduced to the corresponding saturated amides by magnesium and methanol. The same reducing system reduces *N*-benzyl-8-azabicyclo[4.3.0]nona-1(6),3-dien-7-ones at the conjugated double bond to give mixtures of the *cis*- and *trans*-dihydro-derivatives; the isolated, non-conjugated double bond is not reduced, even in the 3,4-diphenyl-substituted compound. Magnesium and methanol reduces quinolin-2(1*H*)-ones to their 3,4-dihydro-derivatives, and 5,6,7,8-tetrahydroquinolin-2(1*H*)-one to a mixture of two dihydro-derivatives.

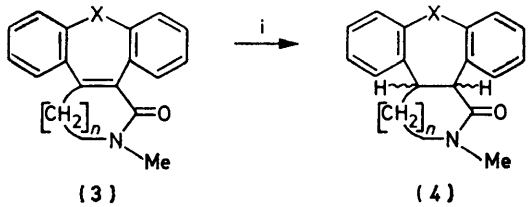
In connection with our work on the synthesis of systems which are models for the reduced isoindolone unit present in the cytochalasans,[1] we required a method for the monomolecular reduction of the carbon–carbon double bond in αβ-olefinic lactams which would not simultaneously reduce non-conjugated olefinic bonds elsewhere in the molecule. With the exception of heterogeneous catalytic hydrogenation, which would not show the desired chemoselectivity, no general method for the monomolecular reduction of simple αβ-olefinic amides (1) to the corresponding saturated amides (2) has hitherto been reported, although there are scattered accounts in the literature of the use for this purpose of lithium aluminium hydride,[2] titanium(III) chloride,[3] sodium hydrogen telluride,[4] sodium hydrido-octacarbonyldiferrate,[5] zinc and acetic acid in the presence of cob(I)alamin or heptamethyl cob(I)yrinate,[6] and the combination of carbon monoxide and water in the presence of hexarhodium hexadecacarbonyl.[7] We have sought to find a general reducing system for the transformation of (1) into (2) which would be independent of the nature of R^1, R^2, R^3, R^4, or R^5, and now report that magnesium and methanol is a very satisfactory system for this purpose. Since the publication of a preliminary report on part of this work [8] our attention has been drawn to a patent [9] on the use of magnesium and methanol for the reduction of olefinic lactams of type (3) to a mixture of the *cis*- and *trans*-forms of the lactams (4) (Scheme 1).



(1)

$R^1R^2CH—CHR^3CONR^4R^5$

(2)



(3) (4)

X = O or S; *n* = 0 or 1

SCHEME 1 *Reagents:* i, Mg, MeOH

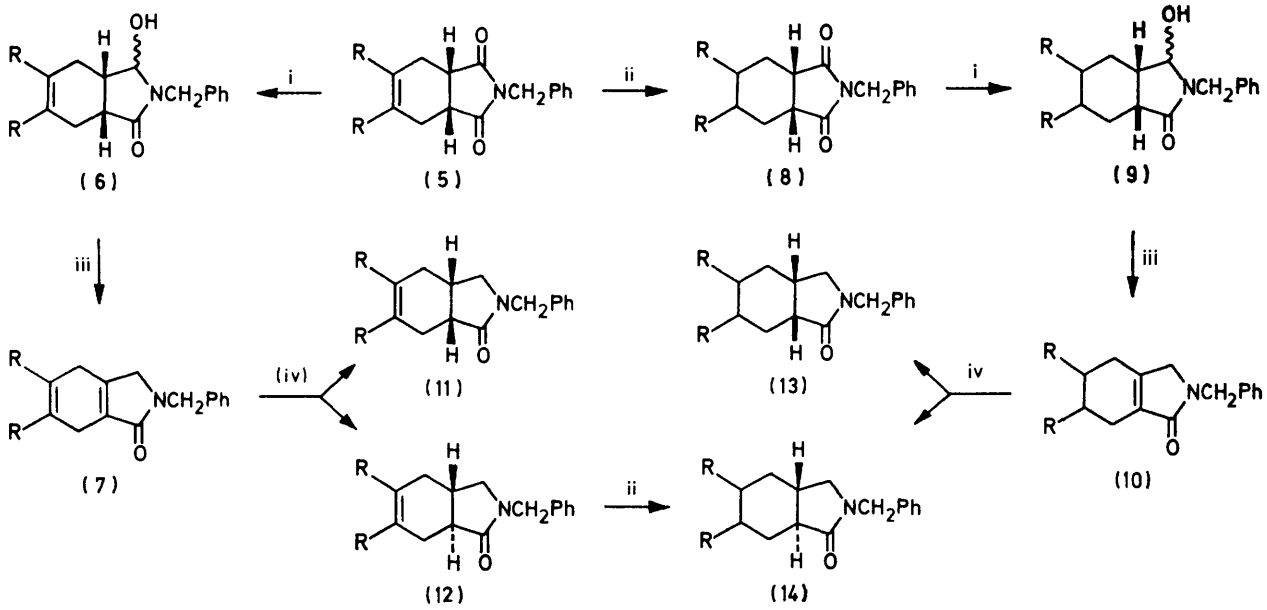
We were encouraged to try magnesium and methanol as the reducing system by recent reports [10] that, with one exception,[11] this combination can bring about the reduction of the conjugated double bond in αβ-olefinic nitriles, and that unconjugated double bonds elsewhere in the nitrile remain unchanged. The system had earlier been shown to reduce two αβ-olefinic ketones to the corresponding saturated alcohols [12] and to reduce a conjugated Schiff base to the saturated amine.[13] In the one case where magnesium and methanol did not reduce an αβ-olefinic nitrile to the saturated nitrile the product was a ββ-linked dihydrodimer,[11] but we have not observed coupling of this sort in the reduction of any simple αβ-olefinic amides, although the reductive dimerisation of such compounds has been observed in electrochemical reductions [14] and reductions using potassium amalgam.[15] The results of our reductions of simple conjugated amides (1) are given in Table 1. Amides in which the carbon–carbon double bond was mono- (entry 1), di- (entries 2, 4, 5, 6, and 7), and tri- (entries 3, 8, and 9) substituted were all successfully reduced, and the reaction worked for various substitution patterns at nitrogen (*cf.* entries 5, 6, and 7). The reaction is extremely simple to carry out, though it should be noted that after the amide (1) has been added to the magnesium covered by methanol, there is an induction period of from a few minutes to several hours before a vigorous exothermic reaction occurs, at which point it is necessary to control the reaction by external cooling.

TABLE 1

Reduction of αβ-olefinic amides (1)

	Conjugated amide (1)					Isolated yield of amide (2) (%)
	R^1	R^2	R^3	R^4	R^5	
1	H	H	H	H	Ph	54
2	Me	H	H	H	Ph	77
3	Me	Me	H	H	Ph	65
4	H	H	Me	H	Ph	78
5	Ph	H	H	H	H	50
6	Ph	H	H	Et	Et	83
7	Ph	H	H	H	Ph	72
8	Ph	Me	H	H	Ph	74
9	Ph	H	Me	H	Ph	92

We then investigated the magnesium–methanol reduction of the bicyclic lactam (10; R = H), which has a tetra-substituted olefinic bond. It was prepared from



SCHEME 2 *Reagents:* i, $NaBH_4$, HCl, 0 °C; ii, Pd–C, H_2; iii, $C_7H_7SO_3H$, reflux in MeOH; iv, Mg, MeOH
All work was carried out with racemic materials: only one enantiomer is shown in displayed formulae.

the imide (8; R = H) by the route shown in Scheme 2. A similar route to more highly substituted derivatives of (6) and (7) has been described recently [16] and we had earlier reported [1] that the acid-catalysed dehydration of the tertiary benzylic alcohols related to (9) likewise gives the product in which the double bond is conjugated with the carbonyl group and endocyclic to both rings. Reduction of (10; R = H) with magnesium and methanol, unlike all the reductions of simple αβ-olefinic amides (1) did not go to completion; about 25% of the starting material remained. Two products were obtained, in the ratio 1 : 6, which were separated on a small scale by sequential thin layer and liquid chromatography. The minor product was identified spectroscopically as the *trans*-isomer (14; R = H) (see below) and was subsequently shown to be identical with the product of the catalytic hydrogenation of (12; R = H). The major product had spectroscopic properties entirely consistent with its formulation as the other expected reduction product, the *cis*-isomer (13; R = H). An attempt to prepare (10; R = H) by the selective reduction of the non-conjugated double bond in (7; R = H) using hydrogen and a palladium–carbon catalyst was unsatisfactory, as disproportionation took place and the desired product was accompanied by the related phthalimidine.[17] Such palladium-catalysed disproportionation of a dihydroaromatic system (7; R = H) is well precedented,[18] although we had previously reduced the 9-benzyl-substituted derivative of (7; R = H) to the tetrahydroaromatic compound using a palladium catalyst without any sign of disproportionation.[1] We next investigated the three bicyclic lactams (7; R = H, Me, or Ph) containing two carbon–carbon double bonds, one conjugated with the lactam carbonyl group, but the other isolated, in order to assess the chemical selectivity of the magnesium–methanol reduction. The three lactams were prepared (Scheme 2) from the corresponding *N*-benzylimides (5; R = H, Me, or Ph) by the route used for the preparation of (10; R = H); the hitherto unreported imide (5; R = Ph) was prepared by the cycloaddition of 2,3-diphenylbuta-1,3-diene to *N*-benzylmaleimide. The results of the reductions of the lactams (7; R = H, Me, or Ph) are given in Table 2. The

TABLE 2

Reduction of bicyclic lactams (7)

Substituent R	Isolated yield of (11) (%)	Isolated yield of (12) (%)	Recovered starting material (%)
H	12	3	71
Me	49	12	22
Ph	72	11	14

desired selectivity was achieved, but the reactions, as in the case of (10; R = H) did not go to completion, and in the case of (7; R = H) only a disappointingly low yield of the reduction products could be obtained. It has recently been reported [19] that *E*- and *Z*-stilbene and some heterocyclic systems containing a stilbene-type double bond are reduced by magnesium and methanol, so that it is of considerable interest that in the case of (7; R = Ph) the conjugated αβ-olefinic lactam bond is selectively reduced in the presence of the stilbene-type system, which is unaffected.

The ^1H n.m.r. spectra of the products (13 and 14; R = H) and (11 and 12; R = H, Me, or Ph) were in good agreement with the proposed constitutions in terms of the chemical shifts and integrated intensities. Evidence for the selective reduction of the conjugated, tetrasubstituted carbon–carbon bonds in (7; R = H, Me, or Ph) is provided by a comparative analysis of the appro-

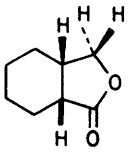
priate ^{13}C chemical shifts of the starting materials and reduction products (see Table 3). On reduction of the conjugated double bonds the chemical shifts of the carbonyl carbon atoms, as expected,[20] moved downfield by *ca.* 5 p.p.m. and the signals due to the α- and β-carbon atoms of the conjugated double bond at *ca.* 130 and *ca.*

TABLE 3

^{13}C Chemical shifts (p.p.m.) of *N*-benzyl-8-azabicyclo-[4.3.0]nonan-7-one derivatives

Compound	C-1	C-6	C-3 and C-4		C-7
(7; R = H)	147.0	129.3	122.4	124.5	171.1
(11; R = H)	29.2	39.7	125.3	126.3	176.3
(7; R = Me)	147.3	130.0	121.4	123.6	171.1
(11; R = Me)	33.6	40.8	124.6	125.6	176.4
(12); R = Me)	32.0	35.5	125.3	125.8	175.5
(7; R = Ph)	146.7	129.7	130.6	132.8	170.7
(11; R = Ph)	29.8	31.8	134.4	136.1	176.0
(12; R = Ph)	32.3	36.0	134.8	135.1	175.0

147 p.p.m. respectively, were replaced by signals due to the two new saturated carbon atoms at C-1 and C-6; signals due to the other two olefinic carbon atoms remained, but were shifted downfield by a few p.p.m. The stereochemistry at the ring junction in the reduced products could be deduced from a consideration of those proton–proton coupling constants which it was possible to extract from the ^1H n.m.r. spectra, in relation to the dihedral angles in the preferred conformations which could be measured from Dreiding models of the structures. Assignment of the stereochemistry at the ring junctions in the analogous *cis*- and *trans*-saturated lactones (15) and (16) had already been made on the



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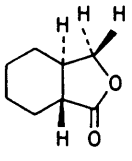

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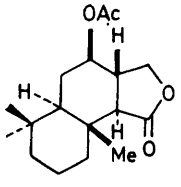


(17)

basis of similar considerations [21] and the close correspondence of the coupling constants of (15) and (16) with those of one or other of the reduction products from (10; R = H) (see Table 4) permitted the unambiguous

TABLE 4

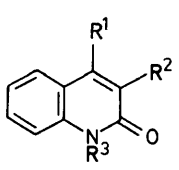
Proton–proton coupling constants in Hz for 8-oxa- and 8-benzyl-8-azabicyclo[4.3.0]nonan-7-ones

Compound	Ring-junction stereochemistry	Coupling constants [a] 1—9α	1—9β	9α, 9β
(13; R = H)	*cis*	2	6	10
(15)	*cis*	1.3	4.8	8.8
(14; R = H)	*trans*	10	5	10
(16)	*trans*	10.6	6.2	8.2

[a] Values for (15) and (16) are from ref. 21.

identification of the *cis*- and *trans*-isomers (13 and 14; R = H). We were only able to measure the value of $J_{1,6}$ for the *cis*-isomer (13; R = H) which had a value of 5 Hz. The *trans*-isomer (14; R = H) would be expected to have a somewhat higher value of $J_{1,6}$ than that, on the basis of the angle between H-1 and H-6, which from models is *ca.* 170°, on the relative values observed [22] for $J_{1,6}$ in a series of *cis*- and *trans*-8-oxabicyclo[4.3.0]-nonane-7,9-diones [*cis*, 7—8 Hz; *trans* 13 Hz], and in view of the value of 8.5 Hz for the coupling constant recorded [23] for the protons at the junction of the five- and six-membered rings in the tricyclic lactone (17). The benzylic methylene protons in (13; R = H) were markedly non-equivalent (Δδ 0.16 p.p.m.), whereas in (14; R = H) they were equivalent. The same behaviour was observed in the unsaturated lactams (11 and 12; R = H, Me, or Ph) where the compounds which we deduce to have *cis*-fused rings, have non-equivalent benzylic methylene protons (11; R = H, Δδ 0.18; R = Me, Δδ 0.37; R = Ph, Δδ 0.70 p.p.m.) whereas in the other, *trans*-fused, series (12; R = H, Me, or Ph) there is little or no non-equivalence (Δδ ≃ 0). The *trans*-fused unsaturated lactams (12) have a rigid molecular structure, in which the six-membered ring adopts a half-chair conformation. For one of the two products from the reductions of (7; R = H, Me, or Ph) an analysis of the absorptions in the ^1H n.m.r. spectra due to the 9α- and 9β-protons shows that in each case the geminal constant has a value of 10 Hz and the vicinal coupling constants with H-1 have values of 5 and 10 Hz. These vicinal coupling constants are only compatible with $J_{1,9\beta}$ and $J_{1,9\alpha}$ respectively in the *trans*-fused products (12; R = H, Me, or Ph) for which the corresponding dihedral angles are *ca.* 150° and *ca.* 20°. These assignments are supported by the appearance of the signals due to the benzylic methylene protons, and by the close general similarity of the coupling constants to those for the analogous compounds with a saturated six-membered ring, (14; R = H) and (16) shown in Table 4. For the other reduction products, which must be (12; R = H, Me, or Ph) less information could be obtained from the ^1H n.m.r. spectra, owing to overlapping peaks, but in two cases a vicinal coupling constant of 3 Hz was observed for a coupling of H-1 with one of the H-9 methylene protons, which taken with values in all three cases for the coupling between H-1 and the other H-9 methylene proton in the range 6—8 Hz and for $J_{9\alpha,9\beta}$ of 10 Hz is entirely compatible with a *cis*-fused structure. A general similarity in the appearance of the signals due to the benzylic methylene protons and of the coupling constants to those for the analogous compounds with a saturated six-membered ring (13; R = H) and (15) is again evident.

We have also applied the magnesium–methanol reduction to quinolin-2(1*H*)-one and some related compounds. Quinolin-2(1*H*)-one (18; $R^1 = R^2 = R^3 = H$)



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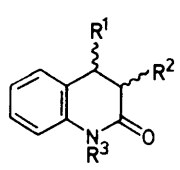
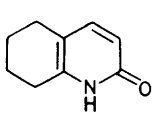


(19)

has been reduced previously [24] to the dihydro-derivative (19; $R^1 = R^2 = R^3 = H$), using sodium amalgam, but a high-melting byproduct was also formed which was believed to be a dihydro-dimer. Similarly, the reduction of *N*-methylquinolin-2(1*H*)-one (18; $R^1 = R^2 = H$, $R^3 = Me$) with a sodium–lead alloy gave the dihydro-derivative (19; $R^1 = R^2 = H$, $R^3 = Me$) together with substantial amounts of a dihydrodimer.[25] Other *N*-substituted pyridin-2(1*H*)-ones have been reduced to dihydro-derivatives by sodium amalgam,[26] calcium, lithium, or sodium in liquid ammonia,[27] lithium aluminium hydride,[27,28] and by heterogeneous catalytic hydrogenation.[29]

The reduction of quinolin-2(1*H*)-one (18; $R^1 = R^2 = R^3 = H$) by magnesium and methanol gave a 30% yield of 3,4-dihydroquinolin-2(1*H*)-one (19; $R^1 = R^2 = R^3 = H$), accompanied by a large amount of material, m.p. 300 °C, insoluble in the usual solvents employed for measuring ^1H n.m.r. spectra, giving a parent ion peak at *m/e* 292, which is presumed to be a dihydro-dimer (M_R 292). The reduction of 4-methylquinolin-2(1*H*)-one, (18; $R^1 = Me$, $R^2 = R^3 = H$) to (19; $R^1 = Me$, $R^2 = R^3 = H$) went in higher yield (55%), but again a high-melting solid which had a parent ion peak corresponding to a dihydro-dimer, at *m/e* 320, was also formed. The reduction of 3,4-dimethylquinolin-2(1*H*)-one (18; $R^1 = R^2 = Me$, $R^3 = H$) gave a 95% yield of a mixture of the *cis*- and *trans*-forms of the dihydro-derivative (19; $R^1 = R^2 = Me$, $R^3 = H$), and no dihydro-dimer was detected. The *cis*- and *trans*-forms were readily separated by preparative medium pressure liquid chromatography (m.p.l.c.) and had m.p.s in agreement with those reported earlier [26a] for the products obtained by the reduction of (18; $R^1 = R^2 = Me$, $R^3 = H$) by sodium amalgam. We could not establish the relative stereochemistries of the methyl groups in these two isomers from their ^1H n.m.r. spectra as there was little difference between the values of $J_{3,4}$ (3.5 and 4.5 Hz). We hoped that a distinction might be made by a synthesis of the *cis*-form by catalytic hydrogenation of 3,4-dimethylquinol-2(1*H*)-one, but attempts to achieve this using conditions successful with quinolin-2(1*H*)-ones less substituted at the 3- and 4-positions,[29a] and under which quinolin-2(1*H*)-one was reduced to 3,4-dihydroquinolin-2(1*H*)-one, were unavailing; the benzene ring appeared to be more easily reduced than the tetrasubstituted double bond when more vigorous conditions were used.

We finally investigated the magnesium–methanol reduction of 5,6,7,8-tetrahydroquinolin-2(1*H*)-one (20).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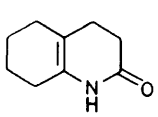
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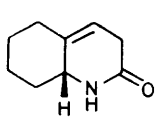
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Two products were formed, which were separated by column chromatography. The major product, isolated in 35% yield, was 3,4,5,6,7,8-hexahydroquinolin-2(1*H*)-one [30] (21). The other product, isolated in 15% yield, was shown to be the isomer, 3,5,6,7,8,8a-hexahydroquinolin-2(1*H*)-one (22), on the basis of the microanalytical data, the parent ion peak at *m/e* 151 in the mass spectrum, and the ^1H n.m.r. spectrum which showed *inter alia*, a single vinyl proton at δ 4.9, a two-proton singlet due to the C-3 methylene protons at δ 2.75, and a broad multiplet at δ 3.42 due to H-8a.

Since sodium borohydride reduces 3-benzylideneoxindoles to the corresponding benzyloxindoles,[31] and as conjugate reductions of αβ-olefinic carbonyl compounds by sodium borohydride are favoured by carrying out the reductions in pyridine [32] we attempted to reduce two representative simple amides (1; $R^1 = R^5 = Ph$, $R^2 = R^3 = R^4 = H$) and (1; $R^1 = R^2 = Me$, $R^3 = R^4 = H$, $R^5 = Ph$) with sodium borohydride using both propan-2-ol and pyridine separately as solvents, but in all four experiments the amides were recovered unchanged. We take this opportunity to record that these two amides can be reduced by transfer hydrogenation from tributylammonium formate in the presence of palladium–charcoal,[33] although reduction with magnesium and methanol is a superior method.

EXPERIMENTAL

^1H N.m.r. spectra were recorded on a Perkin-Elmer R34 (220 MHz) instrument and ^{13}C n.m.r. spectra on a JEOL PFT 100 (25.15 MHz) instrument for solutions in $CDCl_3$ with Me_4Si as internal standard. I.r. spectra were measured on a Perkin-Elmer 157G spectrophotometer. Mass spectra were recorded on an AEI MS 12 instrument. H.p.l.c. was performed on an apparatus consisting of a Waters Associates model 6000 pump, with a Waters differential refractometer, a Cecil 212 u.v. spectrophotometer, and a Waters V6K injector. Columns used were 25 × 0.4 cm for analytical work and 25 × 1 cm for preparative work, packed with 5μ and 11μ silica gel respectively. M.p.l.c. was performed on Jobling columns with a 2.5 × 25 cm pre-column and a 2.5 × 100 cm main column, packed with 60μ silica gel (Kieselgel) with a Metering Pumps Ltd. pump, a Cecil 202 u.v. spectrophotometer, and a Chemlab 270 fraction collector. Preparative t.l.c. was carried out on glass plates (20 × 30 cm) coated with silica gel (1 mm thickness, Merck Kieselgel G), using light petroleum–ether (3 : 7 v/v) as the developing solvent unless otherwise stated. Light petroleum refers to the fraction having b.p. 60—80 °C. Solutions in organic solvents were dried with anhydrous magnesium sulphate. Solvents were evaporated on a Büchi Rotavapor rotary evaporator. M.p.s were determined on a Kofler hot-stage apparatus.

Starting Materials and Reference Compounds.—(E)-α-*Methylcinnamanilide* was prepared from the acid,[34] m.p. 79—80 °C (lit.,[34] 77—78 °C), *via* the acid chloride,[35] m.p. 48—50 °C (lit.,[35] 50 °C), which reacted with aniline in refluxing acetone containing suspended anhydrous potassium carbonate,[36] and after crystallisation from ethanol and then light petroleum had m.p. 97—98 °C, $\nu_{max.}$ 3 400 (NH), 1 660 (CO), and 1 620 cm^{-1} (C=C), *m/e* 237 ($M^{\cdot+}$), 145 ($M^{\cdot+}$ − NHPh), and 117 ($M^{\cdot+}$ − CONHPh), δ_H 2.14 (3 H, s, Me), 7.01—7.68 (11 H, complex 2 × Ph + PhC*H*=), and 7.86 (1 H, s, NH) (Found: C, 81.1; H, 6.5; N, 5.8. $C_{16}H_{15}NO$ requires C, 81.0; H, 6.4; N, 5.9%). Cinnamamide,

hydrocinnamamide, *NN*-diethylcinnamamide, *NN*-diethylhydrocinnamamide, cinnamanilide, hydrocinnamanilide, acrylanilide, crotonanilide, and 3,3-dimethylacrylanilide were likewise made from the corresponding acids *via* the acid chlorides, using literature procedures. (*E*)-β-Methylcinnamanilide and methacrylanilide were more conveniently prepared from ethyl (*E*)-β-methylcinnamate [37] and methyl methacrylate, respectively, by the Bodroux reaction [38] with anilinomagnesium iodide. 4-Methyl-, 3,4-dimethyl- and 5,6,7,8-tetrahydroquinolin-2(1*H*)-ones were prepared by literature methods.[39-41] *N*-Benzyl-*cis*-1,2,3,6-tetrahydrophthalimide, *N*-benzyl-*cis*-hexahydrophthalimide, and *N*-benzylmaleimide were prepared as described previously.[1] All the known compounds listed here had m.p.s * in agreement with published values, and were fully characterised by i.r. and ^{1}H n.m.r. spectroscopy.

N-*Benzyl*-4,5-*diphenyl*-cis-1,2,3,6-*tetrahydrophthalimide*.—Benzil (51.87 g, 0.247 mol) in sodium-dried ether (800 ml) was added dropwise to a freshly prepared solution of methylmagnesium iodide (1.235 mol) in ether, and the solution was then heated under reflux overnight. The usual acidic work-up gave colourless prisms (42 g, 70%), $\nu_{max.}$ 3 350 and 3 470 (OH) cm^{-1}, of 2,3-diphenylbutane-2,3-diol, shown by ^{1}H n.m.r. spectroscopy, δ_H 1.66 and 1.75 (s, 2 × Me), 2.85br (s, OH), and 7.5 (s, Ph), to be a mixture of the (±)- and *meso*-forms in the ratio 1 : 4.[42] Dehydration of this mixture with potassium hydrogensulphate [43] gave 2,3-diphenylbuta-1,3-diene (68%), m.p. 48—55 °C (lit.,[43] 50—51 °C), δ_H 5.47 (2 H, d, J_{AB} 1 Hz, 2 × PhC=CH_AH_B), 5.68 (2 H, d, J_{AB} 1 Hz, 2 × PhC=CH$_A$H$_B$), and 7.2—7.8 (10 H, m, 2 × Ph), and 3,3-diphenylbutan-2-one,[44] $\nu_{max.}$ 1 710 cm^{-1} (CO), δ_H 1.35 (3 H, s, *Me*Ph$_2$C), 2.08 (3 H, *s*, *Me*CO), and 7.37br (10 H, s, 2 × Ph), which were separated by fractional distillation, followed by m.p.l.c. *N*-Benzylmaleimide (12.5 g, 67 mmol) and 2,3-diphenylbuta-1,3-diene (14 g, 67 mmol) were heated under reflux in benzene (300 ml) for 48 h. Evaporation of the benzene and crystallisation from aqueous ethanol and then light petroleum–benzene afforded N-*benzyl*-4,5-*diphenyl*-cis-1,2,3,6-*tetrahydrophthalimide* (22.0 g, 81%), m.p. 106—107 °C, $\nu_{max.}$ 1 770 and 1 700 cm^{-1}, *m/e* 393 ($M^{\bullet+}$) and 302 ($M^{\bullet+}$ − CH$_2$Ph), δ_H 2.64 (2 H, m, J_{AB} 15 Hz, 2 × =CPhCH_AH_B), 3.00 (2 H, m, bridgehead protons), 3.04 (2 H, d, J_{AB} 15 Hz, 2 × =CPhCH$_A$H$_B$), 4.64 (2 H, *s*, NCH_2Ph), and 6.55—7.44 (15 H, complex, 3 × Ph) (Found: C, 82.3; H, 5.9; N, 3.75. $C_{27}H_{23}NO_2$ requires C, 82.4; H, 5.9; N, 3.6%).

N-*Benzyl*-8-*azabicyclo*[4.3.0]*non*-1(6)-*en*-7-*ones*.—(*a*) Sodium borohydride (1.75 g, 46 mmol) was added to *N*-benzyl-*cis*-hexahydrophthalimide (4.03 g, 16.6 mmol) in ethanol (200 ml) at 0 °C, and the mixture was stirred at 0 °C for 4 h, with addition of 2M-hydrochloric acid (2—3 drops) every 0.25 h. The mixture was then poured into water (500 ml) and extracted with chloroform (2 × 100 ml), the extracts were combined and dried, and the solvent was evaporated off. From five such experiments an oil (18.2 g, 88%) was obtained, which slowly solidified to give a mixture of the two isomers of *cis*-*N*-benzyl-9-hydroxy-8-azabicyclo-[4.3.0]nonan-7-one (9; R = H), $\nu_{max.}$ 3 330 (OH) and 1 670 cm^{-1} (CO), δ_H 1.1—2.46 (complex, ring and bridgehead protons), 4.05 (d, J_{AB} 15 Hz, NCH_AH$_B$Ph, minor isomer) 4.15 (d, J_{AB} 15 Hz, NCH_AH$_B$Ph, major isomer), 4.50 [m, C*H*(OH), minor isomer], 4.80 (d, J_{AB} 15 Hz, NCH$_A$$H_B$Ph, major isomer), 4.89 (d, J_{AB} 15 Hz, NCH$_A$$H_B$Ph, minor isomer), 5.00 [m, C*H*(OH), major isomer], 5.14 (d, CH(O*H*), major isomer], 5.54 [d, CH(O*H*), minor isomer], and 7.1—7.42 (m, Ph). The mixture was used for the next step without separation or purification.

(*b*) A mixture of the isomers of *cis*-*N*-benzyl-9-hydroxy-8-azabicyclo[4.3.0]nonan-7-one (18.0 g, 73 mmol) and toluene-*p*-sulphonic acid (5 g, 29 mmol) in toluene (600 ml) was heated under reflux for 24 h. The mixture was then cooled, and shaken with water (500 ml). The organic layer was separated, washed with water (500 ml), and dried and the solvent was evaporated. The resultant oil slowly solidified. Crystallisation from light petroleum then gave N-*benzyl*-8-*azabicyclo*[4.3.0]*non*-1(6)-*en*-7-*one* (10; R = H) (12.2 g, 73%), m.p. 80—81 °C, $\nu_{max.}$ 1 670 cm^{-1} (CO), *m/e* 227 ($M^{\bullet+}$) and 136 ($M^{\bullet+}$ − CH$_2$Ph), δ_H 1.56—1.8 (4 H, m, CH$_2$CH_2-CH_2CH$_2$), 2.1—2.3 (4 H, m, 2 × CH$_2$C=C), 3.62 (2 H, s, =CCH$_2$N), 4.6 (2 H, s, NCH_2Ph), and 7.1—7.4 (5 H, m, Ph), δ_C 20.4, 22.1, and 24.2 (C-3, C-4, C-2, and C-5 with overlapping), 46.0 and 52.6 (C-9 and NCH$_2$Ph), 127.3 (*p*), 128.0 (m), 131.6 (C-6), 137.8 (*ipso*), 138.5 (*o*), 150.1 (C-1), and 171.7 (CO) (Found: C, 79.1; H, 7.5; N, 6.0. $C_{15}H_{17}NO$ requires C, 79.3; H, 7.5; N, 6.2%).

Similarly prepared were N-*benzyl*-8-*azabicyclo*[4.3.0]*nona*-1(6),3-*dien*-7-*one* (7; R = H) (55%), m.p. 81—82 °C (from light petroleum–benzene), $\nu_{max.}$ 1 665 cm^{-1} (CO), *m/e* 225 ($M^{\bullet+}$) and 134 ($M^{\bullet+}$ − CH$_2$Ph), δ_H 2.83 (4 H, s, =CCH_2CH=CHCH_2C=), 3.6 (2 H, s, CH_2NCH$_2$Ph), 4.56 (2 H, s, NCH_2Ph), 5.71 (1 H, d, J_{AB} 10 Hz, CH_A=CH$_B$), 5.87 (1 H, d, J_{AB} 10 Hz, CH$_A$=CH_B), and 7.07—7.35 (5 H, m, Ph) (Found: C, 79.7; H, 6.8(5); N, 6.5. $C_{15}H_{15}NO$ requires C, 79.8; H, 6.7; N, 6.2%); N-*benzyl*-4,5-*dimethyl*-8-*azabicyclo*[4.3.0]*nona*-1(6),3-*dien*-7-*one* (7; R = Me) (50%), m.p. 130—132 °C (from light petroleum–benzene), $\nu_{max.}$ 1 660 cm^{-1} (CO), *m/e* 253 ($M^{\bullet+}$), 238 ($M^{\bullet+}$ − Me), and 162 ($M^{\bullet+}$ − CH$_2$Ph), δ_H 1.68 and 1.72 (each 3 H, s, 3 × Me), 2.8 (4 H, s, 2 × =CCH_2-C=), 3.65 (2 H, s, =CCH_2N), 4.6 (2 H, s, NCH_2Ph), and 7.1—7.4 (5 H, m, Ph) (Found: C, 80.4; H, 7.6; N, 5.4. C_{17}-$H_{19}NO$ requires C, 80.6; H, 7.6; N, 5.5%); and N-*benzyl*-4,5-*diphenyl*-8-*azabicyclo*[4.3.0]*nona*-1(6),3-*dien*-7-*one* (7; R = Ph) (50%), m.p. 180—181 °C (from light petroleum–benzene), $\nu_{max.}$ 1 680 cm^{-1} (CO), *m/e* 377 ($M^{\bullet+}$), 300 ($M^{\bullet+}$ − Ph) and 286 ($M^{\bullet+}$ − CH$_2$Ph), δ_H 3.3 (4 H, complex, 2 × =C−CH_2−C=), 3.6 (2 H, s, =CCH_2N), 4.7 (2 H, s, NCH_2Ph), and 6.93—7.46 (15 H, complex, 3 × Ph) (Found: C, 85.6; H, 5.9; N, 3.9. $C_{27}H_{23}NO$ requires C, 85.9; H, 6.1; N, 3.7%). The more significant ^{13}C n.m.r. chemical shifts for (7; R = H, Me, and Ph) are included in Table 3.

Disproportionation of N-*Benzyl*-8-*azabicyclo*[4.3.0]*nona*-1(6),3-*dien*-7-*one* (7; R = H).—*N*-Benzyl-8-azabicyclo-[4.3.0]nona-1(6),3-dien-7-one (0.5 g) was dissolved in methanol (25 ml), 10% palladium–charcoal (0.1 g) was added and the mixture was maintained under 1 atm of hydrogen at room temperature for 28 h. Filtration and evaporation of the solvent then gave a mixture (analytical t.l.c.) which was separated by preparative t.l.c., using ethyl acetate–light petroleum (1 : 1 v/v) as the solvent system, to give *N*-benzyl-8-azabicyclo[4.3.0]non-1(6)-en-7-one (0.1 g), m.p. 79—80 °C, identical (^{1}H n.m.r., i.r., and mass spectra) with the material described above, and *N*-benzylphthalimidine (0.2 g), m.p. 89—90 °C (from light petroleum) (lit.,[17] 89—90 °C), δ_H 4.25 (2 H, s, CH$_2$N), 4.8 (2 H, s, NCH_2Ph), and 7.17—7.98 (9 H, complex, aromatic protons).

General Procedures for Reductions with Magnesium and Methanol.—The compound to be reduced (96 mmol) and clean dry magnesium turnings (12.8 g, 0.533 mol) were

* B.p. in the case of *NN*-diethylhydrocinnamamide, a liquid.

covered by methanol (160 ml) and stirred at room temperature in an apparatus fitted with a double-surface reflux condenser. After an induction period a very vigorous exothermic reaction ensued, which was controlled by immersing the reaction flask in an ice-bath. The resultant slurry was then stirred at room temperature for several hours. The product was isolated in one of two ways. In method A, 6M-hydrochloric acid (250 ml) was added dropwise over 1 h, and the resultant solution was then extracted with ether (3 × 200 ml). The combined ethereal extracts were then washed with water (250 ml) and dried, and the solvent was evaporated off. In method B, at the end of the reaction the methanol was evaporated off and ice–water (200 ml) was added to the residual white solid. The resulting suspension was then treated with 50% aqueous acetic acid (*ca.* 150 ml) added with vigorous stirring at 0 °C until a clear solution was obtained. The solution was extracted with ether (3 × 200 ml) and the combined extracts were washed with water (250 ml) and dried. Evaporation of the solvent gave the crude product, which was dried (KOH) *in vacuo* overnight (to remove traces of acetic acid).

The crude products were purified by crystallisation or chromatography, and, in the case of compounds previously reported, were identified by their m.p.s, which were in agreement with published values, in a few cases by direct comparison with authentic samples, and in all cases by their ^{1}H n.m.r. and i.r. spectra.

(E)-α-*Methylhydrocinnamanilide*.—Reduction of (*E*)-α-methylcinnamanilide by the general procedure, and isolation by method A gave E-α-*methylhydrocinnamanilide* (92%) as white needles, m.p. 127—128 °C (from light petroleum–benzene), $\nu_{max.}$ 3 250 (NH) and 1 650 cm^{-1} (CO), *m/e* 239 ($M^{\bullet+}$), δ_H 1.2 (3 H, d, *J* 7 Hz, Me) 2.5—2.8 (2 H, m, PhCH_2-CHMe), 2.9—3.1 (1 H, m, PhCH_2C*H*Me), and 6.98—7.6 (11 H, complex, 2 × Ph + NH) (Found: C, 80.1; H, 6.9; N, 5.7. $C_{16}H_{17}NO$ requires C, 80.3; H, 7.2; N, 5.8(5)%).

Reduction of Simple αβ-Olefinic Amides.—The other simple amides were similarly reduced, and the products were isolated by method A, except for cinnamamide and crotonanilide where the products were obtained in better yield by isolation using method B. Yields are given in Table 1.

Reduction of Bicyclic Lactams (*Scheme* 2).—(*a*) Reduction of *N*-benzyl-8-azabicyclo[4.3.0]nona-1(6),3-dien-7-one (7; R = H) (2.16 g) and isolation by method A gave an oil (1.95 g). Preparative t.l.c. on a part of this (1.7 g) gave two oily fractions, and a considerable amount of a solid (1.2 g, 71%) which was identified spectroscopically (^{1}H n.m.r., i.r.) as recovered starting material. One oily fraction (0.05 g, 3%) solidified on standing and on crystallisation from light petroleum afforded white plates of N-*benzyl*-trans-8-*azabicyclo*[4.3.0]*non*-3-*en*-7-*one* (12; R = H), m.p. 71—73 °C, $\nu_{max.}$ 1 690 cm^{-1} (CO), *m/e* 227 ($M^{\bullet+}$) and 136 ($M^{\bullet+}$ − CH_2Ph), δ_H 1.86—2.6 (6 H, complex, bridgehead and allylic protons), 2.94 (1 H, m, $J_{AX} = J_{AB}$ = 10 Hz, $CH_XCH_AH_BNCH_2Ph$), 3.25 (1 H, m, J_{BX} 5, J_{AB} 10 Hz, $CH_XCH_AH_BNCH_2Ph$), 4.46 (2 H, s, NCH_2Ph), 5.63—5.85 (2 H, m, CH=CH), and 7.1—7.4 (5 H, m, Ph) (Found: C, 79.3; H, 7.7; N, 6.35. $C_{15}H_{17}NO$ requires C, 79.3; H, 7.5; N, 6.2%). The second oily fraction (0.2 g, 12%) was purified by bulb–tube distillation to give N-*benzyl*-cis-8-*azabicyclo*[4.3.0]*non*-3-*en*-7-*one* (11; R = H) as an oil, $\nu_{max.}$ 1 680 cm^{-1} (CO), *m/e* 227 ($M^{\bullet+}$) and 136 ($M^{\bullet+}$ − CH_2Ph) δ_H 1.63—1.82 (1 H, m, =CC*H*). 2.03—2.6 (4 H, complex, remaining allylic protons + a bridgehead proton), 2.68 (1 H, m, CHCO), 2.8 (1 H, m, J_{AX} 3, J_{AB} 10 Hz, $CH_XCH_AH_BNCH_2Ph$), 3.35 (1 H, m, J_{BX} 6, J_{AB} 10 Hz, $CH_XCH_AH_BNCH_2Ph$), 4.40 (1 H, d, J_{AB} 15 Hz, NCH_AH_BPh), 4.58 (1 H, d, J_{AB} 15 Hz, NCH_AH_BPh), 5.64—5.9 (2 H, m, CH=CH), and 7.14—7.4 (5 H, m, Ph) (Found: C, 79.2; H, 7.6; N, 6.1. $C_{15}H_{17}NO$ requires C, 79.3; H, 7.5; N, 6.2%).

Hydrogenation of *N*-benzyl-*trans*-8-azabicyclo[4.3.0]non-3-en-7-one (12; R = H) (0.12 g, 53 mmol) in ethyl acetate (20 ml) with 10% palladium–charcoal (20 mg) at room temperature and atmospheric pressure gave the reduced product, which was purified by bulb–tube distillation to give N-*benzyl*-trans-8-*azabicyclo*[4.3.0]*nonan*-7-*one* (14; R = H) as an oil, $\nu_{max.}$ 1 675 cm^{-1} (CO), *m/e* 229 ($M^{\bullet+}$) and 138 ($M^{\bullet+}$ − CH_2Ph), δ_H 1.0—1.45 (4 H, complex, ring protons), 1.6—2.34 (6 H, complex, remaining ring protons + bridgehead protons), 2.86 (1 H, m, $J_{AX} = J_{AB}$ = 10 Hz, $CH_XCH_AH_BNCH_2Ph$), 3.11 (1 H, m, J_{BX} 5, J_{AB} 10 Hz, $CH_XCH_AH_BNCH_2Ph$), 4.44 (2 H, s, NCH_2Ph), and 7.16—7.4 (5 H, m, Ph) (Found: C, 78.2; H, 8.2; N, 5.8. $C_{15}H_{19}NO$ requires C, 78.6; H, 8.35; N, 6.1%).

(*b*) Reduction of *N*-benzyl-8-azabicyclo[4.3.0]non-1(6)-en-7-one (10; R = H) (2.18 g) and isolation by method A gave an oil (2.0 g) which was shown (h.p.l.c.) to contain *ca.* 25% of starting material. The products were separated from this by preparative t.l.c. H.p.l.c. showed that two products were present in the ratio 1 : 6 (peak areas). Small quantities of each of the pure products were separated by preparative h.p.l.c. *N*-Benzyl-*trans*-8-azabicyclo[4.3.0]-nonan-7-one (14; R = H) was identified by spectroscopic comparison with the sample from (a). N-*Benzyl*-cis-8-*azabicyclo*[4.3.0]*nonan*-7-*one* (13; R = H) was obtained as an oil, $\nu_{max.}$ 1 680 cm^{-1} (CO), *m/e* 229 ($M^{\bullet+}$) and 138 ($M^{\bullet+}$ − CH_2Ph), δ_H 1.0—1.75 (7 H, complex, ring protons), 2.05 (1 H, m, ring proton), 2.24 (1 H, m, C*H*CH_2N), 2.48 (1 H, m, *J* 5 Hz, CHCO), 2.72 (1 H, m, J_{AX} 2, J_{AB} 10 Hz, $CH_XCH_ANCH_2Ph$), 3.2 (1 H, m, J_{BX} 6, J_{AB} 10 Hz, $CH_XCH_AH_BNCH_2Ph$), 4.36 (1 H, d, J_{AB} 15 Hz, NCH_AH_BPh), 4.52 (1 H, d, J_{AB} 15 Hz, NCH_AH_BPh), and 7.04—7.4 (5 H, m, Ph) (Found: C, 78.4; H, 8.5; N, 5.8. $C_{15}H_{19}NO$ requires C, 78.6; H, 8.35; N, 6.1%).

(*c*) Reduction of *N*-benzyl-3,4-dimethyl-8-azabicyclo-[4.3.0]nona-1(6),3-dien-7-one (7; R = Me) (1.42 g) and isolation by method A gave a semi-solid mixture. Preparative t.l.c. gave two oily products and a solid (0.38 g, 22%) which was identified spectroscopically (^{1}H n.m.r., i.r.) as recovered starting material. One oily product (0.2 g, 12%) solidified on standing, and on crystallisation from light petroleum afforded white needles of N-*benzyl*-trans-3,4-*dimethyl*-8-*azabicyclo*[4.3.0]*non*-3-*en*-7-*one* (12; R = Me), m.p. 101—102 °C, $\nu_{max.}$ 1 675 cm^{-1} (CO), *m/e* 255 ($M^{\bullet+}$), 240 ($M^{\bullet+}$ − Me), and 164 ($M^{\bullet+}$ − CH_2Ph), δ_H 1.63 and 1.66 (each 3 H, s, 2 × Me), 1.82—2.45 (6 H, complex, ring and bridgehead protons), 2.94 (1 H, m, $J_{AX} = J_{AB}$ = 10 Hz, $CH_XCH_AH_BNCH_2Ph$), 3.24 (1 H, m, J_{BX} 5, J_{AB} 10 Hz, $CH_XCH_AH_BNCH_2Ph$), 4.45 (2 H, s, NCH_2Ph), and 7.17—7.43 (5 H, m, Ph) (Found: C, 80.0; H, 8.1; N, 5.3. $C_{17}H_{21}NO$ requires C, 79.9; H, 8.3; N, 5.5%). Bulb–tube distillation of the other product (0.84 g, 49%) gave N-*benzyl*-cis-3,4-*dimethyl*-8-*azabicyclo*[4.3.0]*non*-3-*en*-7-*one* (11; R = Me) as an oil, $\nu_{max.}$ 1 675 cm^{-1} (CO), *m/e* 255 ($M^{\bullet+}$), 240 ($M^{\bullet+}$ − Me), and 164 ($M^{\bullet+}$ − CH_2Ph), δ_H 1.47—1.8 (7 H, complex, 2 × Me + 1 ring proton), 1.9—2.55 (4 H, *c*, remaining ring protons + H-1), 2.58—2.75 (2 H, complex, H-6 + $CH_XCH_AH_BNCH_2Ph$, J_{AX} 3, J_{AB} 10 Hz), 3.3 (1 H, *m*, J_{BX} 7, J_{AB} 10 Hz, $CH_XCH_AH_BNCH_2Ph$), 4.23 (1 H, d, J_{AB} 15 Hz, NCH_AH_BPh), 4.6 (1 H, d, J_{AB} 15 Hz, NCH_AH_B-

Ph), and 7.08—7.4 (5 H, m, Ph) (Found: C, 79.7; H, 8.4; N, 5.4. $C_{17}H_{21}NO$ requires C, 80.0; H, 8.3; N, 5.5%).

(*d*) Reduction of *N*-benzyl-3,4-diphenyl-8-azabicyclo-[4.3.0]nona-1(6),3-dien-7-one (7; R = Ph) (2.26 g) and isolation by method A gave a solid (2.1 g). Preparative t.l.c. on a part of this material (1.8 g) gave a solid (1.3 g, 72%) which on crystallisation from ethanol afforded white plates of *N-benzyl*-cis-3,4-*diphenyl*-8-*azabicyclo*[4.3.0]*non*-3-*en*-7-*one* (11; R = Ph), m.p. 145—146 °C, $\nu_{max.}$ 1 665 cm^{-1} (CO) δ_H 2.28—2.4 (1 H, m, ring proton), 2.5—3.15 (6 H, complex, bridgehead and ring protons + $CH_XCH_AH_BNCH_2$-Ph), 3.37 (1 H, m, J_{BX} 8, J_{AB} 10 Hz, $CH_XCH_AH_BNCH_2Ph$), 4.1 (1 H, d, J_{AB} 15 Hz, NCH_AH_BPh), 4.8 (1 H, d, J_{AB} 15 Hz, NCH_AH_BPh), and 6.4—7.3 (15 H, complex, 3 × Ph) (Found: C, 85.2; H, 6.5; N, 3.6. $C_{27}H_{25}NO$ requires C, 85.45; H, 6.6; N, 3.7%), a second solid (0.2 g, 11%), which on crystallisation gave pale yellow plates of N-*benzyl*-trans-3,4-*diphenyl*-8-*azabicyclo*[4.3.0]*non*-3-*en*-7-*one* (12; R = Ph), m.p. 165—166 °C, $\nu_{max.}$ 1 680 cm^{-1} (CO), *m/e* 379 ($M^{\cdot+}$), 302 ($M^{\cdot+}$ − Ph) and 288 ($M^{\cdot+}$ − CH_2Ph), δ_H 2.16—2.95 (6 H, complex, ring and bridgehead protons), 3.02 (1 H, m, $J_{AX} = J_{AB}$ = 10 Hz, $CH_XCH_AH_BNCH_2Ph$), 3.34 (1 H, m, J_{BX} 5, J_{AB} 10 Hz, $CH_XCH_AH_BNCH_2Ph$), 4.48 (1 H, d, J_{AB} 15 Hz, NCH_AH_BPh), 4.54 (1 H, d, J_{AB} 15 Hz, NCH_AH_BPh), and 6.87—7.4 (15 H, complex, 3 × Ph) (Found: C, 85.5; H, 6.6; N, 3.8. $C_{27}H_{25}NO$ requires C, 85.45; H, 6.6; N, 3.7%) and a third solid (0.25 g, 14%) identified spectroscopically (^{1}H n.m.r., i.r.) as recovered starting material.

Reduction of Quinolin-2(1H)-*ones*.—(*a*) Reduction of quinolin-2(1*H*)-one (1.39 g), isolation by method B, and extraction of the products with hot methanol left a white solid (0.6 g), m.p. 300 °C (lit.,[24] 300 °C), *m/e* 292 ($M^{\cdot+}$) and 146 ($M/2^{\cdot+}$), presumed to be a dihydrodimer.[24] Concentration of the methanol extract gave a second product, which, after crystallisation from methanol (charcoal), gave 3,4-dihydroquinolin-2(1*H*)-one (0.32 g, 30%), m.p. 163—164 °C (lit.,[24] 163 °C), identical with material obtained in 89% yield by the hydrogenation of quinolin-2(1*H*)-one (0.5 g) in methanol (50 ml) with a W2 Raney nickel catalyst [45] (0.125 g) in a stirred autoclave at 140 °C under 85 atm. of hydrogen for 5 h, $\nu_{max.}$ 3 150 (NH) and 1 680 cm^{-1} (CO), δ_H 2.62 (2 H, t, *J* 6 Hz, CH_2CH_2CO), 2.95 (2 H, t, *J* 6 Hz, CH_2CH_2CO), 6.6—7.3 (4 H, complex, aromatic protons), and 9.54br (1 H, s, NH).

(*b*) Reduction of 4-methylquinolin-2(1*H*)-one (1.52 g) and isolation by method B left an ether-insoluble white solid which after drying ($CaCl_2$) *in vacuo* gave a solid (0.45 g), m.p. >300 °C, *m/e* 320 ($M^{\cdot+}$) and 160 ($M/2^{\cdot+}$) presumed to be a dihydro-dimer. The ether-soluble material on crystallisation from water gave white needles of 4-methyl-3,4-dihydroquinolin-2(1*H*)-one (0.85 g. 55%), m.p. 97—98 °C (lit.,[46] 98 °C), $\nu_{max.}$ 3 170 (NH) and 1 670 cm^{-1} (CO), δ_H 1.3 (3 H, d, *J* 6 Hz, *Me*), 2.4 (1 H, q, J_{AB} 15, J_{AX} 6 Hz, $CH_XMeCH_AH_B$), 2.74 (1 H, q, J_{AB} 15, J_{BX} 6 Hz, $CH_XMeCH_AH_B$), 3.1 (1 H, m, *J* 6 Hz, $CH_XMeCH_AH_B$), 6.8—7.24 (4H, complex, aromatic protons), and 9.89br (1 H, s, NH).

(*c*) Reduction of 3,4-dimethylquinolin-2(1*H*)-one (1.66 g) and isolation by method A gave a crude mixture of products (1.59 g, 95%) which was separated by preparative m.p.l.c. into two fractions. Crystallisation of the first of these from light petroleum–benzene, and then ethanol, gave the low-melting isomer of 3,4-dimethyl-3,4-dihydroquinolin-2(1*H*)-one, m.p. 118—120 °C (lit.,[26a] 117 °C), $\nu_{max.}$ 3 150 (NH) and 1 680 cm^{-1} (CO), δ_H 1.15 and 1.20 (each 3 H, d, *J* 7 and 6 Hz respectively, 2 × Me), 2.75 (1 H, m, J_{AB} 4.5 Hz CH_BMeCH_AMeCO), 3.0 [1 H, m, J_{AB} 4.5 Hz, $CH_B(Me)CH_AMeCO$], 6.84—7.23 (4 H, m, aromatic protons), and 9.35br (1 H, s, NH) (Found: C, 75.3; H, 7.5; N, 7.8. Calc. for $C_{11}H_{11}NO$: C, 75.4; H, 7.5; N, 8.0%). Crystallisation of the second fraction from light petroleum–benzene, and then ethanol, gave the high-melting isomer, m.p. 126—127.5 °C (lit.,[26a] 127—128 °C), $\nu_{max.}$ 3 200 (NH) and 1 675 cm^{-1} (CO), δ_H 1.20 and 1.24 (each 3 H, d, *J* 7 and 6 Hz respectively, 2 × Me), 2.5 [1 H, m, J_{AB} 3.5 Hz, $CH_B(Me)CH_AMeCO$], 2.75 [1 H, m, J_{AB} 3.5 Hz, $CH_B(Me)CH_AMeCO$], 6.9—7.25 (4 H, complex, aromatic protons), and 10.5br (1 H, s, NH) (Found: C, 75.7; H, 7.6; N, 7.8%).

(*d*) Reduction of 5,6,7,8-tetrahydroquinolin-2(1*H*)-one (20) (1.43 g) and isolation by method A gave an oil which was separated into three solid components by column chromatography on silica gel using light petroleum–ethyl acetate (3 : 7 v/v) as the eluting solvent. The first fraction to be eluted crystallised from ethanol to give white needles of 3,4,5,6,7,8-hexahydroquinolin-2(1*H*)-one (21) (0.5 g, 34%), m.p. 140.5—141.5 °C (lit.,[30] 143—144 °C), $\nu_{max.}$ 3 160 (NH) and 1 655 cm^{-1} (CO); δ_H 1.63br and 1.96br (each 4 H, m, $=C[CH_2]_4C=$), 2.17 (2 H, t, *J* 7 Hz, CH_2CH_2CO), 2.45 (2 H, t, *J* 7 Hz, CH_2CH_2CO), and 7.5br (1 H, s, NH). The second fraction on crystallisation from water, gave white needles of 3,5,6,7,8,8a-*hexahydroquinolin*-2(1H)-*one* (22) (0.22 g, 15%), m.p. 136—138 °C, $\nu_{max.}$ 3 180 (NH) and 1 670 cm^{-1} (CO), *m/e* 151 ($M^{\cdot+}$), δ_H 0.78—2.5 (8 H, complex, $=C[CH_2]_4$), 2.75 (2 H, s, CH_2CO), 3.42br (1 H, m, CH_2CHNH), 4.9 (1 H, s, $=CHCH_2$-CO), and 8.5br (1 H, s, NH) (Found: C, 71.7; H, 8.85; N, 9.2. $C_9H_{13}NO$ requires C, 71.5; H, 8.7; N, 9.3%). Starting material (0.2 g), identified spectroscopically (^{1}H n.m.r. and i.r.) was also recovered.

Reduction of Simple Amides by Catalytic Hydrogen Transfer.—(*a*) Cinnamanilide (1.12 g, 5 mmol), tributylamine (1.7 ml, 7.25 mmol), formic acid (0.2 ml, 5.5 mmol), and 10% palladium–charcoal (0.052 g) were heated at 100 °C for 1 h with stirring. The mixture was then cooled and filtered to remove the catalyst, which was washed with dichloromethane (25 ml). The filtrate was combined with the washings, dichloromethane (50 ml) was added, and the resultant solution was washed with 10% sulphuric acid (8 × 25 ml) and water (2 × 50 ml) and dried, and the solvent evaporated. Crystallisation of the residue from light petroleum gave white needles of slightly impure hydrocinnamanilide (0.5 g, 44%), m.p. 94—97 °C (lit.,[47] 96—97 °C), shown spectroscopically (^{1}H n.m.r., i.r.) to be essentially identical with an authentic sample.

(*b*) A similar reduction of 3,3-dimethylacrylanilide (1.75 g) gave pale yellow needles (0.75 g) with a wide m.p. range, shown by ^{1}H n.m.r. spectroscopy to be a mixture of 3,3-dimethylacrylanilide and isovaleranilide in the ratio 1.4 : 1, by comparison with the spectra of authentic samples.

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