Removal of Toluene-*p*-sulphonyl Groups from Sulphonamides. Part 4.[1] Synthesis of Phenylglyoxal Imine Monomers

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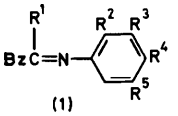
Syntheses and reactions of *N*-tosylphenacylamines with bases have been systematically examined. Monomeric *C*-methoxy-imines are available from some of these reactions. *C*-Methoxyphenacylarylamines, made by two routes, were converted into monomeric imines on treatment with noble-metal catalysts. The boron trifluoride-catalysed reactions of aryl aldehydes with sulphonamides provide a new and convenient route to *N*-sulphonylaryl-imines.

EARLIER attempts [2,3] to prepare the anils (1; R^1 = H) from phenylglyoxal resulted usually in isolation of the dimer (2),[4,5] the diamines (3),[6] the alkoxy-amines (4),[6] or more complex Michael-type adducts.[3] Participation of



(1)

All R^n=H, unless stated otherwise

a; R^1 = OMe, R^3 = R^4 = Cl

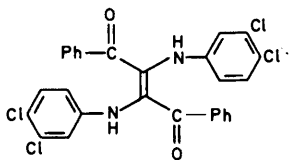
b; R^3 = R^4 = Cl

c; R^2 = R^5 = Cl

d; R^4 = Me

e; R^4 = Br

f; R^1 = R^4 = OMe



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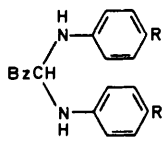
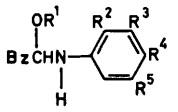


(3)

a; R = Br

b; R = Me



(4)

All R^n=H, unless stated otherwise

a; R^1 = Me, R^3 = R^4 = Cl

b; R^1 = Me, R^2 = R^5 = Cl

c; R^1 = Me, R^3 = R^5 = Cl

d; R^1 = Me, R^2 = R^4 = Cl

e; R^1 = Et, R^3 = R^4 = Cl

f; R^1 = R^4 = Me

g; R^1 = Me, R^4 = Br

h; R^1 = Me, R^4 = NO_2

(5)

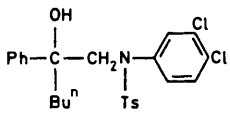
a; R = $C_6H_3Cl_2$-*m*,*p*

b; R = H

c; R = CH_2Ph

d; R = Me

e; R = Ac



(6)

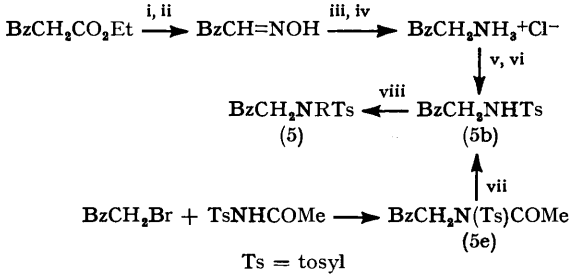
Ts = tosyl

phenylglyoxal anils has been inferred in several reactions,[1-6] but the only authentic monomers isolated contained blocking groups (1; R^1 = Ph) or were generated by mild base-induced elimination of the trifluoromethylsulphinyl anion from the appropriate phenacylsulphonamide.[7]

We felt it appropriate to reinvestigate systematically the reactions that would be expected to yield phenylglyoxalanils in an attempt to obtain the monomers. The reactivity of the latter could then, hopefully, be utilised selectively.

DISCUSSION

Elimination of the Tosyl Group from Sulphonamides.[8]— The required precursors (5; R = aryl) were, as before, made by the reaction of phenacyl bromide with *N*-tosylarylamines in the presence of potassium carbonate in acetone.[4] However, this approach proved inappropriate for *N*-alkyl compounds (5; R = alkyl) and an alternative method was developed (Scheme). Firstly, *N*-



SCHEME *Reagents:* i, NaOH; ii, HNO_2; iii, H_2–Pd–C; iv, EtOH–HCl; v, TsCl; vi, pyridine, 0 °C; vii, MeO^-; viii, RX–K_2CO_3–Me_2CO.

tosylphenacylamine (5b) was made, either from ethyl benzoylacetate [9-11] or, better, from *N*-acetyl-*N*-tosylphenacylamine (5e). Secondly, alkylation of *N*-tosylphenacylamine with alkyl halides in the presence of potassium carbonate in acetone gave the desired products (5c) and (5d).

It was convenient (see below) to study the 3,4-dichloroaniline (5a). Reaction with sodium methoxide in toluene gave the expected [4] dimer (2). Reactions with both sodium hydride in tetrahydrofuran (THF) [5] and lithium diisopropylamide in THF at −78 °C also yielded the same dimer, but reaction with n-butyl-lithium caused addition to the carbonyl group which gave the tertiary alcohol (6). Base-catalysed elimination from the *N*-alkyl compounds (5c) and (5d) gave toluene-*p*-sulphinic acid under a variety of conditions, but neither the imines (7c) and (7d) nor their artefacts, could be isolated. On the other hand, the methoxy-compounds (8a), (8b), and (8c) all underwent base-induced elimination to yield the monomers

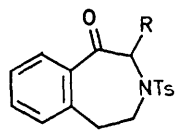
(1a), (1f), and (7a). The required *N*-tosylmethoxy-compounds (8) were made either from the α-haloketones (8; OMe = Br) with methanol or by reaction of α-bromo-α-methoxyacetophenone with the *N*-tosylamine

$BzC(R^1)=NR^2$ (7)	$BzCH(OMe)NRTs$ (8)
a; R^1 = OMe, R^2 = Me	a; R = $C_6H_3Cl_2$-*m*,*p*
b; R^1 = H, R^2 = Bu^t	b; R = C_6H_4OMe-*p*
c; R^1 = H, R^2 = Me	c; R = Me
d; R^1 = H, R^2 = CH_2Ph	d; R = $C_6H_4CO_2Me$-*o*
e; R^1 = H, R^2 = Pr^i	e; R = H

Ts = tosyl

(see Experimental section). Application of these procedures to the 3-benzazepinone derivative (9a) gave the cyclic methoxy-imine (10), but attempts to dehydrogenate (dichlorodicyanoquinodimethane, Pd–C, MnO_2, $BaMnO_4$) the latter were unsuccessful. Reaction of the dichloroaniline (5a) with sodium methoxide in methanol gave the amide of benzoylformic acid (11) possibly *via* the methoxy-amine (4a) which gives the same product (11) under the same treatment.

Thus, we conclude that tosyl elimination is a suitable



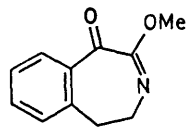
(9)

a; R = OMe

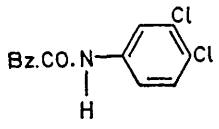
b; R = H

c; R = Br

Ts = tosyl



(10)



(11)

procedure for the synthesis of some methoxyphenylglyoxal imines, but is unsuitable for isolation of the monomers of the imines (1; R = H), despite claims to the contrary.[3,4,12]

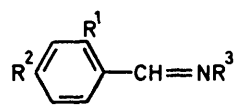
Condensation Reactions.—Reaction of phenylglyoxal and aniline in acetic acid gave complex results.[2,3,12] It has been stated [13,14] that reactions of phenylglyoxal with various substituted anilines in alcoholic solutions yielded the anil monomers (1; R = H), but in our hands [6] this type of reaction gave either compounds (3) or (4), apparently depending on the pK_a of the amine. The weaker bases tended to give products of type (4); this was attributed to trapping of the anil by alcohol. In the present work, we find that the slightly stronger bases (4-bromoaniline and 4-toluidine) react with phenylglyoxal in benzene to give the diamino-ketones (3), while the weaker base (4-nitroaniline) gave an intractable mixture. Interestingly, four dichloroanilines (2,4-; 2,5-; 3,4-; and 3,5-) all reacted with phenylglyoxal in methanol to give the corresponding methoxy-products (4a), (4b), (4c), and (4d), while 3,4-dichloroaniline and phenylglyoxal in ethanol gave the ethoxy-derivative (4e). The pK_a values of these amines vary from 3.0 (3,4-dichloro-) to 1.53 (2,5-dichloro-). Thus, the critical value of pK_a which governs the type of product obtained (3- or 4-) lies between 3.0 (3,4-dichloro-) and 3.8 (4-bromo-). Presumably, other factors may also be relevant since nucleophilicity does not necessarily parallel pK_a; however, it was convenient and instructive to use 3,4-dichloroaniline for further exploratory work.

Weakly basic substances, like amides, did not react with phenylglyoxal until the addition of a catalytic amount of boron trifluoride–diethyl ether, when they gave the bis-adducts (12a), (12b), (12c), and (12d). We

$BzCHR_2$ (12)	$R^1CHR^2_2$ (13)
a; R = NHCOMe	a; R^1 = CCl_3, R^2 = NHCOMe
b; R = $NHCO_2Et$	b; R^1 = Ph, R^2 = NHCOMe
c; R = NHTs	c; R^1 = Ph, R^2 = $NHCO_2Et$
d; R = $NHP(:O)(OEt)_2$	

Ts = tosyl

suppose this is caused by BF_3 activation of the aldehyde carbonyl group towards nucleophilic attack and that the imine thus formed, being doubly activated, reacts rapidly with a second molecule of amide. Even benzaldehyde [15] reacted with amides (urethane and acetamide) to give the bis-adducts (13b) and (13c). In



(14)

a; R^1 = R^2 = H, R^3 = Ts

b; R^1 = H, R^2 = NO_2, R^3 = SO_2Me

c; R^1 = H, R^2 = OMe, R^3 = SO_2Me

d; R^1 = H, R^2 = NO_2, R^3 = Ts

e; R^1 = H, R^2 = OMe, R^3 = Ts

f; R^1 = OAc, R^2 = H, R^3 = Ts

g; R^1 = OH, R^2 = H, R^3 = Ts

h; R^1 = CO_2Et, R^2 = H, R^3 = Ts

i; R^1 = R^2 = H, R^3 = SO_2Me

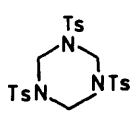
RCH=NTs

(15)

a; R = CH=CHPh

b; R = 2-furyl

c; R = Me_3C



(16)

Ts = tosyl

contrast, toluene-*p*-sulphonamide and methanesulphonamide reacted with benzaldehyde in the presence of BF_3 to give the *N*-sulphonylimines (14a) and (14i), respectively, in good yields; presumably the sulphonamide amino-group is too weakly nucleophilic to add to the imine. This is a more convenient synthesis than the only previous one [16] for *N*-sulphonylimines; it works

also for several other aryl aldehydes (see Experimental section), cinnamaldehyde, furfural, and pivaldehyde, but not for aliphatic aldehydes containing α-hydrogen atoms. The reaction with pyridine-3-carbaldehyde failed, possibly due to complexation of the heterocyclic nitrogen atom by BF_3: formaldehyde gave the triazine (16) for which there is precedent.[17]

Dehydrogenation.—Dehydrogenation of phenacylaniline (17d) gave adimeric product, explained by the assumption that the initially formed anil was trapped by Michael addition with the amino-group of the phenacylaniline molecule.[3] For this reason, it seemed profitable to

$BzCH_2NHR$
(17)

a; R = $C_6H_3Cl_2$-*m*,*p*
b; R = Bu^t
c; R = Pr^i
d; R = Ph

generate the anil in presence of alcohol as a trapping agent. Thus, the 3,4-dichloroaniline (17a) and manganese dioxide in methanol gave the same methoxy-aminoketone (4a) as that obtained by the condensation described above. Similarly, phenacyl-*p*-toluidine and *p*-bromo-*N*-phenacylaniline gave the corresponding methoxy-compounds (4f) and (4g) which were not available from condensation reactions in methanol. Dehydrogenation of these compounds with manganese dioxide (or with barium manganate [18]) in toluene was not successful, although previously a cyclic example was dehydrogenated thus.[19] In the latter case, models show that in all possible conformations, a *cis*-elimination of hydrogen atoms is possible whereas in the open-chain variants (4), there is a possibility for free rotation about the C–N bond which might make dehydrogenation less likely by a *cis*-mechanism.

Dehydrogenation of *N*-tosylphenacylamine (5b) with manganese dioxide, barium manganate, lead tetra-acetate, mercuric oxide, and mercuric acetate were uniformly unsuccessful. However, phenacyl-t-butylamine [obtained from phenacyl bromide with t-butylamine (6 mol equiv. at 0 °C)] reacted with barium manganate [18] in methanol to yield the imine (7b). This unexpected result could be explained by assuming that in *N*-alkylphenylglyoxal imines the enhanced electron-donating power of the nitrogen atom decreases the electrophilic attack on it by methanol. The structure of the imine (7b) was confirmed by spectroscopic means (see Experimental section), in particular by ^{13}C n.m.r. which showed the imine carbon at δ_C 154.8 p.p.m. as a doublet in the off-resonance decoupled spectrum. A similar result was obtained with the imine (7e), but this substance decomposed rapidly.

Demethanolation.—It has been claimed that heating substances such as the methoxy-amines (4; R = Me) caused loss of methanol and produced the imines.[20,21] In our hands the method failed with several substrates, but in connection with work in the previous section, we heated the methoxy-amine (4a) with 10% palladium-on-charcoal in benzene. This produced a new substance, elementary analysis and spectroscopy of which confirmed it as the long-sought anil (1a); again ^{13}C n.m.r. spectroscopy revealed a signal for the imine carbon atom at δ_C 158.7 p.p.m. (doublet), ^1H n.m.r. showed a singlet at δ 8.1 for the aldimine proton, and both mass spectroscopy and vapour pressure osmometry confirmed the molecular structure as $C_{14}H_9Cl_2NO$. In similar fashion the anils (1c), (1d), and (1e) were obtained, but the reaction failed for the 2- and 4-nitro-analogues Rhodium- or platinum-on-charcoal were equally effective reagents, but charcoal or ground glass had no effect.

To summarise, the present work shows that by selecting the appropriate starting materials and procedures, several phenylglyoxal imine monomers can be isolated. This has made possible a study of their chemistry which is described in the following paper.

EXPERIMENTAL

Preparations of the following compounds are given in Supplementary Publication No. SUP 23073 (30 pp.),* which is the supplementary publication referred to throughout the Experimantal section. i, *Diethyl* NN′-(*benzoylmethylene*)*dicarbamate* (12b); ii, NN′-(2,2,2-*trichloroethylene*)*diacetamide* (13a); iii, NN′-(*benzoylmethylene*)*ditoluene*-p-*sulphonamide* (12c); and iv, *bis*(N-*tosylbenzoylamine*)*mercury*. Details of the attempted demethanolation of the α-methoxyaminoketones (4a) and (4h) are also given in the supplementary publication.

3,4-*Dichloro*-N-*phenacyl*-N-*tosylaniline* (5a).—To a solution of 3,4-dichloro-*N*-tosylaniline [22] (5 g, 16 mmol) in dry acetone (80 cm^3) which contained potassium carbonate (1.1 g, 8M) was added phenacyl bromide (3.4 g, 17 mmol) and the resulting suspension was refluxed for 20 h. The solids were then filtered off and the filtrate was evaporated under reduced pressure. The residue was dissolved in chloroform and washed with 2M sodium hydroxide. The organic phase was separated off, dried (Na_2SO_4), and evaporated under reduced pressure to give a yellow solid. Recrystallisation from ethanol yielded the *product* (5a) (4.5 g, 65%) as a white solid, m.p. 128 °C (Found: C, 58.05; H, 3.9; N, 3.5; Cl, 16.35. $C_{21}H_{17}Cl_2NO_3S$ requires C, 57.9; H, 4.25; N, 3.2; Cl, 16.2%); τ 2.1—3.2 (12 H, m, aromatic), 5.1 (2 H, s, CH_2), and 7.65 (3 H, s, Me); $\nu_{max.}$ (Nujol) 1 695 cm^{-1} (C=O).

N-*Tosylphenacylamine* (5b).—To a solution of phenacylamine hydrochloride [10] (5 g, 30 mmol) in dry pyridine (50 cm^3) at 0 °C was added slowly with stirring toluene-*p*-sulphonyl chloride (5.5 g, 30 mmol). The mixture was stirred for a further 16 h at room temperature and then the solvent was removed under reduced pressure. The residue was poured into ice–water–2M HCl and the resultant precipitate was filtered off. Recrystallisation from methanol gave the product (5b) (8 g, 86%) as fawn crystals, m.p. 116 °C (lit.,[11] m.p. 116 °C).

N-*Benzyl*-N-*tosylphenacylamine* (5c).—To a solution of the amine (5b) (2.89 g, 10 mmol) in dry acetone (50 cm^3) containing potassium carbonate (0.7 g, 5 mmol) was added benzyl bromide (2 g, 11 mmol) and the resultant suspension

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 1*, 1979, Index Issue.

was refluxed for 20 h. The solids were filtered off and the filtrate was evaporated under reduced pressure; the residue was then dissolved in chloroform and washed with 2M sodium hydroxide. The organic phase was separated off, dried (Na_2SO_4), and evaporated under reduced pressure to yield a fawn solid. Recrystallisation from methanol gave the product (2.5 g, 64%) as crystals, m.p. 112—114 °C (lit.,[11] m.p. 114 °C).

N-*Methyl*-N-*tosylphenacylamine* (5d) was similarly prepared, using methyl iodide as alkylating agent, as a solid, m.p. 119 °C [methylene chloride–light petroleum (b.p. 60—80 °C)] (Found: C, 63.05; H, 5.7; N, 4.5; S, 10.4. $C_{16}H_{17}NO_3S$ requires C, 63.35; H, 5.6; N, 4.6; S, 10.55%); τ 2.1—2.9 (9 H, m, aromatic), 5.5 (2 H, s, CH_2), 7.2 (3 H, s, NMe), and 7.6 (3 H, s, Me); $\nu_{max.}$ (Nujol) 1 695 (C=O), 1 340, and 1 220 cm^{-1} (NSO_2).

N-*Acetyl*-N-*tosylphenacylamine* (5e).—A solution of the amine (5b) (1 g, 3.46 mmol) in acetic anhydride (2 cm^3), which contained a drop of concentrated sulphuric acid, was refluxed for 0.5 h. The cooled reaction mixture was then poured into ice–water–2M HCl and the resultant precipitate was filtered off. Recrystallisation from methanol gave the *product* (5e) (1 g, 85%) as a white solid, m.p. 120 °C (Found: C, 61.85; H, 5.25; N, 4.3. $C_{17}H_{17}NO_4S$ requires C, 61.7; H, 5.2; N, 4.25%); τ 2.1—2.8 (9 H, m, aromatic), 4.7 (2 H, s, CH_2), 7.6 (3 H, s, Ac), and 7.7 (3 H, s, Me); $\nu_{max.}$ (Nujol) 1 710 and 1 690 cm^{-1} (2 × C=O).

N-*Acetyltoluene*-p-*sulphonamide*.—To a stirred solution of toluene-*p*-sulphonamide (8.55 g, 50 mmol) in acetone (200 cm^3) was added potassium carbonate (14 g, 0.1 mol) and the suspension was refluxed for 0.5 h. Acetyl chloride (3.5 cm^3, 3.85 g, 5M) was added as drops and the solution was refluxed for 16 h with stirring. The reaction mixture was cooled, added to ice–water, and filtered. The filtrate was acidified with concentrated sulphuric acid and extracted with chloroform. The organic phase was dried (Na_2CO_4) and evaporated to yield the *product* (7.5 g, 70%). Recrystallisation from methylene chloride–light petroleum (b.p. 60—80 °C) gave a white solid, m.p. 108—110 °C (Found: C, 50.35; H, 5.2; N, 6.75. $C_9H_{11}NO_3S$ requires C, 50.7; H, 5.2; N, 6.55%); τ 1.5 (1 H, br, exchangeable, NH), 2.0—2.8 (4 H, m, aromatic), 7.6 (3 H, s, Me), and 7.9 (3 H, s, Ac); $\nu_{max.}$ (Nujol) 3 400 (NH) and 1 715 cm^{-1} (C=O).

N-*Acetyl*-N-*tosylphenacylamine* (5e).—To a solution of *N*-acetyltoluene-*p*-sulphonamide (1 g, 4.36 mmol) in acetone (70 cm^3) was added triethylamine (1 cm^3, 1 g, 10 mmol) and phenacyl bromide (0.867 g, 5.36 mmol). The solution was refluxed for 24 h and then cooled and evaporated under reduced pressure. The residue was taken up in chloroform and washed with 2M sodium hydroxide. The organic phase was separated off, dried (Na_2SO_4), and evaporated under reduced pressure to give a semi-crystalline solid (1 g, 73%). Recrystallisation from methanol yielded the product (5e) as a fawn solid, m.p. 120 °C, which was identified by mixed m.p. and by comparison of the i.r. spectrum with that of authentic sample.

Reaction of the Phenacylamine (5e) *with Sodium Methoxide*.—To a solution of the phenacylamine (5e) (1 g, 3 mmol) in anhydrous toluene (100 cm^3) under nitrogen, was added sodium methoxide (0.97 g, 18 mmol). After 1 h a black gum precipitated which was added to ice–water. The organic layer was then separated off, dried (Na_2SO_4), and evaporated under reduced pressure to yield a white solid (0.7 g). Recrystallisation from methanol gave *N*-tosylphenacylamine (5b), m.p. 116 °C (identified by comparison of m.p. and i.r. and ^1H n.m.r. spectra with those of an authentic sample).

Reaction of the Dichloroaniline (5a) *with Bases in Aprotic Solvents*.—(a) *Sodium methoxide in toluene*. To the *N*-tosylamino-ketone (5a) (1 g, 2.3 mmol) in anhydrous toluene (100 cm^3) was added sodium methoxide (0.74 g, 0.138 mol). The solution turned deep red and was stirred for 20 h. Water was then added and the organic phase was separated off, dried (Na_2SO_4), and evaporated under reduced pressure to give a red oil (0.5 g) which crystallised from acetone–light petroleum (b.p. 60—80 °C) to yield 1,2-*dibenzoyl*-1,2-*di*-(3,4-*dichloroanilino*)*ethylene* (2) as a red powder, m.p. 210 °C (Found: C, 60.9; H, 3.4; N, 5.0%; M^+, 556.0070. $C_{28}H_{18}Cl_4N_2O_2$ requires C, 60.4; H, 3.24; N, 5.05%; *M*, 556.0093); $\nu_{max.}$ (Nujol) 3 350 (NH) and 1 630 cm^3 (C=O).

Methods (b) [sodium hydride in tetrahydrofuran (THF)] and (c) (lithium di-isopropylamide in THF) are given in the supplementary publication.

(d) *n-Butyl-lithium in toluene*. To a solution of the *N*-tosylamino-ketone (5a) (0.868 g, 2 mmol) in anhydrous toluene (80 cm^3) at −60 °C under a nitrogen atmosphere was added, *via* a syringe, 1.6M n-butyl-lithium (1.25 cm^3, 2 mmol). The dark solution was stirred at −60 °C for 2 h, then brought to room temperature overnight. Water was added to the organic phase which was then separated off, dried (Na_2SO_4), and evaporated under reduced pressure to give a gum (0.8 g) which crystallised from ether–light petroleum (b.p. 60—80 °C) to yield the 1-(3,4-*dichloro*-*N*-*tosylanilino*)-2-*phenylhexan*-2-*ol* (6) as a white solid, m.p. 120 °C (Found: C, 60.75; H, 5.5; N, 2.8. $C_{25}H_{27}Cl_2NO_3S$ requires C, 60.9; H, 5.5; N, 2.85%); τ 2.5—3.6 (12 H, m, aromatic), 5.9—6.6 (2 H, d of d, CH_2), 6.7 (1 H, br, exchangeable, OH), 7.6 (3 H, s, Me), and 8.1—9.4 (9 H, m, Bu^n); $\nu_{max.}$ (Nujol) 3 510 cm^{-1} (OH).

N-(*Diethoxyphosphoryl*)*toluene*-p-*sulphonamide*.—To a stirred solution of toluene-*p*-sulphonamide (3.4 g, 20 mmol) in acetone (100 cm^3) was added potassium carbonate (5.5 g, 40 mmol) and the suspension was refluxed for 15 min. After the addition of drops of diethyl chlorophosphate (2.8 g, 20 mmol), the suspension was refluxed with stirring for 16 h. The reaction mixture was cooled and added to ice–water and was then filtered off. The filtrate was acidified with concentrated sulphuric acid and extracted with chloroform. The organic phase was dried (Na_2SO_4) and evaporated under reduced pressure to yield the *product* (3.2 g, 58%), m.p. 76 °C [ether–light petroleum (b.p. 60—80 °C)] (Found: C, 43.0; H, 6.05; N, 4.75. $C_{11}H_{18}NO_5PS$ requires C, 43.0; H, 5.9; N, 4.5%); τ 1.6 (1 H, br, exchangeable, NH), 2.1—2.8 (4 H, m, aromatic), 5.7—6.2 (4 H, m, 2 × CH_2), 7.6 (3 H, s, tosyl-Me), and 8.75 (6 H, t, 2 × Me); $\nu_{max.}$ (Nujol) 3 320 (NH) and 1 240 cm^{-1} (P=O).

3,4-*Dichloro*-N-(α-*methoxyphenacyl*)-N-*tosylaniline* (8a).—To a solution of the 3,4-dichloroaniline (5a) (1 g, 2.3 mmol) in anhydrous chloroform–carbon tetrachloride (100 cm^3, 1 : 10) was added *N*-bromosuccinimide (0.41 g, 2.3 mmol) and a few crystals of benzoyl peroxide. The solution obtained was refluxed over a 150 W lamp for 6 h and then cooled to room temperature. The precipitated succinimide was filtered off and the solvent was evaporated off under reduced pressure to yield an oily residue which was refluxed in dry methanol (10 cm^3) for 5 min and then left to cool. The precipitated *product* (0.8 g, 75%) was filtered off. Recrystallisation from methanol gave a white solid, m.p. 115 °C (Found: C, 57.0; H, 4.15; N, 2.9; S, 6.7. $C_{22}H_{19}Cl_2NO_4S$ requires C, 56.9; H, 4.15; N, 3.0; S, 6.9%); τ 2.1—3.4 (12 H, m, aromatic), 3.5 (1 H, s, CH) 6.5 (3 H, s,

OMe), and 7.6 (3 H, s, Me); $\nu_{max.}$ (Nujol) 1 700 (C=O) and 1 080 cm^{-1} (C–O).

N-(α-*Methoxyphenacyl*)-N-*tosyl*-p-*anisidine* (8b) and N-(α-*methoxyphenacyl*)-N-*tosylmethylamine* (8c) were prepared similarly (see the supplementary publication).

α-*Bromo*-α-*methoxyacetophenone*.[23]—To stirred acetyl bromide (22 cm^3, 0.3 mol) was added the dimethyl acetal of phenylglyoxal [23] (42 g, 0.234 mol) and the solution was refluxed for 15 min. The excess of acetyl bromide and other volatiles was removed under reduced pressure and the residue was vacuum distilled to yield the product (49 g, 91%) as a pale yellow oil, b.p. 125 °C at 0.4 Torr (lit.,[23] b.p. 90 °C at 0.12 Torr).

3,4-*Dichloro*-N-(α-*methoxyphenacyl*)-N-*tosylaniline* (8a).—To a solution of 3,4-dichloro-*N*-tosylaniline (3.15 g, 10 mmol) in acetone (70 cm^3) containing potassium carbonate (0.7 g, 5 mmol) was added α-bromo-α-methoxyacetophenone (2.3 g, 10 mmol) in acetone (10 ml). After the solution had been refluxed for 24 h the solids were filtered off and the filtrate was evaporated. The residue was taken up in chloroform and washed with 2M sodium hydroxide. The organic phase was separated off, dried (Na_2SO_4) and the solvent was removed under reduced pressure to yield the product (8a) (2.6 g, 56%). Recrystallisation from methanol gave white crystals, m.p. 115 °C (identical by m.p. and i.r. and ^1H n.m.r. spectra with an authentic sample of the product).

Methyl N-(α-*methoxyphenacyl*)-N-*tosylanthranilate* (8d) was prepared similarly (see the supplementary publication).

Methyl N-(3,4-*Dichlorophenyl*)*benzoylcarboximidate* (1a).—To a solution of the *N*-tosylamino-ketone (8a) (1 g, 2.16 mmol) in anhydrous methanol (50 cm^3) was added sodium methoxide (0.234 g, 4.32 mmol) in anhydrous methanol (10 cm^3). The solution was refluxed for 3 h and then stirred at room temperature overnight. The solvent was evaporated off under reduced pressure and the residue was taken up in chloroform and washed with water. The organic phase was separated, dried (Na_2SO_4), and the solvent was evaporated off under reduced pressure to yield an oil (0.5 g, 75%) which was distilled under reduced pressure to give the *product* (1a) as a green liquid, b.p. 200 °C at 0.4 Torr (kugelrohr) (Found: C, 58.35; H, 3.7; Cl, 23.0; N, 5.05%; M^+, 309.0134. $C_{15}H_{11}Cl_2NO_2$ requires C, 58.5; H, 3.6; Cl, 23.0; N, 4.55%; *M*, 309.0137); τ 2.3—3.6 (8 H, m, aromatic) and 6.1 (3 H, s, OMe;) $\nu_{max.}$ (film) 1 670 (C=O) and 1 600 cm^{-1} (C=N).

Methyl N-*Methylbenzoylcarboximidate* (7a).—To a suspension of sodium hydride (50% dispersion; 0.15 g, 3 mmol) in anhydrous benzene (20 cm^3) under an atmosphere of nitrogen was added a solution of the amino-ketone (8c) (1 g, 3 mmol) in anhydrous benzene (20 cm^3) during 15 min. The solution was then stirred at room temperature for 20 h and poured into water. The organic phase was separated off, dried (Na_2SO_4), and the solvent was evaporated off under reduced pressure to yield an oil (0.47 g, 88%) which was distilled under reduced pressure to give the product as a lemon liquid, b.p. 130 °C at 0.5 Torr (kugelrohr) (Found: C, 67.35; H, 6.5; N, 7.9%; M^+, 177.0751. $C_{10}H_{11}NO_2$ requires C, 67.8; H, 6.25; N, 7.9%; *M*, 177.0790); τ 2.1—2.6 (5 H, m, aromatic), 6.2 (3 H, s, OMe), and 7.0 (3 H, s, Me); $\nu_{max.}$ (film) 1 675 (C=O) and 1 600 cm^{-1} (C=N).

2-*Methoxy*-N-*tosyl*-2,3,4,5-*tetrahydro*-3-*benzazepin*-1-*one* [24] (9a).—To a solution of the *N*-tosylbenzazepinone (9b) (4.7 g, 14.9 mmol) in anhydrous chloroform (50 cm^3) was added bromine (0.8 cm^3, 2.48 g, 30 mmol) in anhydrous chloroform (10 cm^3). The solution was stirred for 2 h at room temperature and then evaporated under reduced pressure to yield the α-bromo-*N*-tosylbenzazepinone (9c) (5.9 g, quantitative) as a brown solid, m.p. 95 °C (lit.,[24] 95—96 °C). Methanol (20 cm^3) was added to the α-bromo-*N*-tosylbenzazepinone (9c) (5.9 g) and the solution was refluxed for 2 h. The solution was cooled and the resultant precipitate was filtered off to give the product (9a) (4 g, 80%) as a fawn solid, m.p. 103 °C (lit.,[24] 103—104 °C).

2-*Methoxy*-4,5-*dihydro*-3-*benzazepin*-1-*one* (10).—To a solution of the *N*-tosylbenzazepinone (9a) 2.5 g, 7.24 mmol) in anhydrous toluene (70 cm^3) under an atmosphere of nitrogen was added sodium methoxide (0.6 g, 11 mmol) and the suspension was stirred for 20 h at room temperature. Water was then added and the organic layer was separated, dried (Na_2SO_4), and evaporated under reduced pressure to yield an oil which was distilled under reduced pressure to give the *product* as a green liquid (75%), b.p. 150 °C at 0.01 Torr (kugelrohr) (Found: C, 70.2; H, 6.1; N, 7.15%; *M*, 189.0773. $C_{11}H_{11}NO_2$ requires C, 69.8; H, 5.85; N, 7.4%; *M*, 189.0790); τ 2.0—2.8 (4 H, m, aromatic), 6.2 (3 H, s, OMe), and 6.2—6.8 (4 H, d of t, 2 × CH_2); $\nu_{max.}$ (film) 1 660 (C=O) and 1 690 cm^{-1} (C=N).

N-(*Benzoylcarbonyl*)-3,4-*dichloroaniline* (11).—To a solution of the dichloroaniline (5a) (1 g, 2.3 mmol) in anhydrous methanol–dichloromethane (50 cm^3 1 : 1) was added a solution of sodium methoxide (0.74 g, 13.8 mmol) in anhydrous methanol (20 cm^3). The solution was stirred at room temperature for 7 h, refluxed for 1 h, and then evaporated under reduced pressure. The residue was dissolved in chloroform and washed with water. The organic phase was separated off, dried (Na_2SO_4), and the solvent evaporated off under reduced pressure to yield the *product* (11) (0.51 g, 75%) which crystallised from chloroform–light petroleum (b.p. 40—60 °C) as a white solid, m.p. 160 °C (Found: C, 57.4; H, 2.95; Cl, 24.2; N, 5.35. $C_{14}H_9Cl_2NO_2$ requires C, 57.2; H, 3.1; Cl, 24.1; N, 4.75%); τ 1.1. (1 H, br, exchangeable, NH) and 1.6—2.8 (8 H, m, aromatic); $\nu_{max.}$ (Nujol) 3 340 (NH), and 1 685 and 1 660 cm^{-1} (2 × C=O).

NN′-(*Benzoylmethylene*)*di*-p-*bromoaniline* (3a).—A solution of phenylglyoxal hydrate [25] (1.52 g, 10 mmol) in benzene (70 cm^3) was refluxed for 0.5 h on a Dean and Stark apparatus. To this solution was added *p*-bromoaniline (1.72 g, 10 mmol) and reflux was continued for 4 h. The solvent volume was then halved by evaporation under reduced pressure and the precipitated *product* (3a) (1.3 g, 56%) was filtered off. Recrystallisation from chloroform–light petroleum (b.p. 60—80 °C) gave a yellow solid, m.p. 145 °C (lit.,[6] 145 °C).

NN′-(*Benzoylmethylene*)*di*-p-*toluidine* (3b) was prepared similarly, as a yellow solid (2.5 g, 75%), m.p. 107 °C [chloroform–light petroleum (b.p., 60—80 °C)] (lit.,[6] 107 °C).

3,4-*Dichloro*-N-(α-*methoxyphenacyl*)*aniline* (4a).—To a solution of phenylglyoxal hydrate (15.2 g, 0.1 mol) in methanol (100 cm^3) at 50 °C was added 3,4-dichloroaniline (16.2 g, 0.1 mol). The resultant solution was refluxed for 16 h and filtered off white still hot. The precipitate produced from the cooled filtrate was filtered off to yield the *product* (4a) (22 g, 69%) as fawn crystals, m.p. 110 °C (methanol) (Found: C, 58.45; H, 4.35; Cl, 23.3; N, 4.5%; M^+, 309.0309. $C_{15}H_{13}Cl_2NO_2$ requires C, 58.05; H, 4.2; Cl, 22.85; N, 4.5%; *M*, 309.0323); τ 1.8—3.4 (8 H, m, aromatic), 4.1 (1 H, d, CH), 4.3 (1 H, d, exchangeable, NH), and 7.0 (3 H, s, OMe); $\nu_{max.}$ (Nujol) 3 360 (NH) and 1 670 cm^{-1} (C=O).

2,5-*Dichloro*-N-(α-*methoxyphenacyl*)*aniline* (4b), 3,5-*di*-

chloro-N-(α-*methoxyphenacyl*)*aniline* (4c), and 2,4-*dichloro*-N-(α-*methoxyphenacyl*)*aniline* (4d) were prepared similarly (see Supplementary publication).

3,4-*Dichloro*-N-(α-*ethoxyphenacyl*)*aniline* (4e).—To a solution of phenylglyoxal hydrate (1.52 g, 10 mmol) in ethanol (50 cm^3) was added 3,4-dichloroaniline (1.62 g, 10 mmol) and the solution was refluxed for 16 h. After reduction of the solvent volume by half the solution was cooled to precipitate the *product* (4e) (2.3 g, 72%) which was filtered off as a white solid, m.p. 89 °C (Found: C, 59.6; H, 4.8; N, 4.35. $C_{16}H_{15}Cl_2NO_2$ requires C, 59.3; H, 4.65; N, 4.3%); τ 1.7—3.3 (8 H, m, aromatic), 4.0 (1 H, d, CH), 4.3 (1 H, d, exchangeable, NH), 6.3—7.0 (2 H, m, CH_2), and 9.0 (3 H, t, Me); $\nu_{max.}$ (Nujol) 3 280 (NH) and 1 680 cm^{-1} (C=O).

NN′-(*Benzoylmethylene*)*diacetamide* (12a).—A solution of phenylglyoxal hydrate (6 g, 40 mmol) in benzene (50 cm^3) which contained acetamide (2.4 g, 40 mmol) was refluxed for 0.5 h on a Dean and Stark apparatus. To this solution was added (*via* a syringe) boron trifluoride–diethyl ether (0.1 cm^3, 0.8 mmol) and the solution was refluxed for 16 h. The precipitated solid was filtered off and recrystallised from acetone–light petroleum (b.p. 60—80 °C) to yield the *product* (12a) (3.3 g, 70%) as a white powder, m.p. 210 °C (Found: C, 61.1; H, 6.15; N, 11.7. $C_{12}H_{14}N_2O_3$ requires C, 61.55; H, 6.05; N, 11.95%); τ[$(CD_3)_2CO$] 1.9—2.9 (5 H, m, aromatic and 2 H, m, exchangeable 2 × NH), 4.4 (1 H, m, CH), and 7.3 (6 H, s, 2 × Me); $\nu_{max.}$ (Nujol) 3 300 (NH) and 1 660 cm^{-1} (C=O).

Tetraethyl NN′-(*Benzoylmethylene*)*diphosphoramidate* (12d).—A solution of phenylglyoxal (1.52 g, 10 mmol) and diethyl phosphoramidate [26] (1.5 g, 10 mmol) in benzene (70 cm^3) was refluxed for 0.5 h on a Dean and Stark apparatus. To this solution was added (*via* a syringe) BF_3–Et_2O (0.1 cm^3, 0.8 mmol) and the mixture was then refluxed for 16 h. The solution was cooled and filtered off to a yield the *product* (12d) (0.4 g, 20%). Recrystallisation from chloroform–light petroleum (b.p., 60—80 ° C) gave a fawn solid, mp. 140 °C (Found: C, 45.2; H, 6.55; N, 6.8. $C_{16}H_{28}N_2O_7P_2$ requires C, 45.5; H, 6.75; N, 6.65%); τ 1.8—2.6 (5 H, m, aromatic), 4.1 (1 H, t, CH), 5.6—5.9 (2 H, br, exchangeable, 2 × NH), 4.0 (4 H, q, 2 × CH_2), and 8.8 (6 H, t, 2 × Me); $\nu_{max.}$ (Nujol) 3 120 (NH) and 1 690 cm^{-1} (C=O).

N-*Benzylidenetoluene*-p-*sulphonamide* (14a).—To a refluxing solution of benzaldehyde (11 g, 0.1 mmol) and toluene-*p*-sulphonamide (17 g, 0.1 mol) in benzene (300 cm^3) on a Dean and Stark apparatus was added (*via* a syringe) BF_3–Et_2O (0.2 cm^3 1.6 mmol). The mixture was refluxed until the theoretical amount of water (1.8 cm^3, 0.1 mol) had been collected (4 h). The solution was then cooled and extracted with 2M sodium hydroxide and washed with water. The organic phase was separated off, dried (Na_2SO_4), and the solvent was evaporated off under reduced pressure to yield a solid which crystallised from dichloromethane–light petroleum (b.p. 60—80 °C) to give the *product* (14a) (19.5 g, 75%) as a white solid, m.p. 104 °C (lit.,[27] 104 °C) (Found: C, 65.25; H, 5.15; N, 5.6; S, 12.35%; M^+, 259.0673. Calc. for $C_{14}H_{13}NSO_2$: C, 64.85; H, 5.05; N, 5.4; S, 12.35%; *M*, 259.0667); τ 1.1 (1 H, s, CH), 2.1—2.9 (9 H, m, aromatic), and 7.6 (3 H, s, Me); $\nu_{max.}$ (Nujol) 1 600 cm^{-1} (C=N).

N-(p-*Nitrobenzylidene*)*methanesulphonamide* (14b).—To a refluxing solution of *p*-nitrobenzaldehyde (1.5 g, 10 mmol) and methanesulphonamide [28] (0.95 g, 10 mmol) in benzene (70 cm^3) on a Dean and Stark apparatus was added (*via* a syringe) trifluoroborate (0.1 cm^3, 0.8 mmol). Reflux was continued for 16 h and the solution was then cooled and extracted with 2M sodium hydroxide and washed with water. The organic phase was separated, dried (Na_2SO_4), and evaporated under reduced pressure to yield a solid which crystallised from chloroform–light petroleum (b.p., 60—80 °C) to give the *product* (14b) (2 g, 87%) as pale yellow crystals, m.p. 166 °C (Found: C, 41.85; H, 3.3; N, 12.0. $C_8H_8N_2O_4S$ requires C, 42.1; H, 3.55; N, 12.25%); τ 0.9 (1 H, s, CH), 1.4—1.9 (4 H, m, aromatic), and 6.8 (3 H, s, Me); $\nu_{max.}$ (Nujol) 1 600 cm^{-1} (C=N).

N-(p-*Methoxybenzylidene*)*methanesulphonamide* (14c) and N-(α-*methoxyphenacyl*)*toluene*-p-*sulphonamide* (8e) were prepared similarly (see supplementary publication).

3,4-*Dichloro*-N-*phenacylaniline* (17a).—To a solution of 3,4-dichloroaniline (9.72 g, 60 mmol) in ethanol (75 cm^3) at room temperature was added phenacyl bromide (5.97 g, 30 mmol) with stirring. After 2 h at room temperature the precipitate was filtered off to yield the *product* (17a) (4 g, 50%) as a fawn solid, m.p. 158 °C (ethanol) (Found: C, 60.0; H, 4.0; Cl, 25.35; N, 5.5. $C_{14}H_{11}Cl_2NO$ requires C, 60.0; H, 3.9; Cl, 25.35; N, 5.0%); τ 2.0—3.6 (8 H, m, aromatic), 5.1 (1 H, m, exchangeable NH), and 5.5 (2 H, d, CH_2); $\nu_{max.}$ (Nujol) 3 380 (NH) and 1 680 cm^{-1}.

N-*Phenacyl*-*t*-*butylamine Hydrochloride* (17b).—To a solution of t-butylamine (33.5 g, 50 cm^3, 0.43 mol) in ether (80 cm^3) and benzene (30 cm^3) at 25 °C was added a solution of phenacyl chloride (12 g, 80 mmol) in benzene (50 cm^3) as drops during 0.5 h. The solution was refluxed with stirring for 20 h and then cooled to 0 °C. The solids were filtered off and the solvent was evaporated off under reduced pressure to yield a residue which was dissolved in ether (100 cm^3) and benzene (100 cm^3) and cooled to 0 °C. Dry hydrogen chloride was then introduced into the solution until it was acidic. The resultant precipitate was filtered off to yield the *product* (17b) (15 g, 82%) as a white solid, m.p. 206 °C (ethanolic hydrogen chloride) (Found: C, 63.3; H, 7.8; N, 6.15. $C_{12}H_{18}ClNO$ requires C, 63.3; H, 7.95; N, 6.15%); τ[$(CD_3)_2SO$] 0.9 (2 H, br, exchangeable, NH), 1.9—2.7 (5 H, m, aromatic), 5.4 (2 H, m, CH_2), and 8.6 (9 H, s, 3 × Me); $\nu_{max.}$ (Nujol) 1 675 cm^{-1} (C=O).

N-*Phenacylisopropylamine Hydrochloride* (17c).—To a stirred solution of isopropylamine (3.45 g, 5.1 cm^3, 60 mmol) in ether (15 cm^3) and benzene (5 cm^3) at 0 °C was added phenacyl bromide (1.99 g, 10 mmol) in benzene (20 cm^3) as drops during 0.75 h. The resultant solution was stirred at 0 °C for 2 h then filtered off, and the filtrate was evaporated under reduced pressure to yield an oily residue which was dissolved in benzene (50 cm^3) and cooled to 0 °C. Dry hydrogen chloride was introduced into the solution until it was acidic. The resultant precipitate was filtered off to yield the *product* (17c) (1 g, 45%) as a white solid, m.p. 190 °C (isopropanolic hydrogen chloride) (Found: C, 61.8; H, 7.7; N, 6.75. $C_{11}H_{16}ClNO$ requires C, 61.5; H, 7.55; N, 6.55%); τ [$(CD_3)_2SO$] 0.9 (1 H, br, exchangeable, NH), 2.0—3.0 (5 H, m, aromatic), 5.4 (2 H, m, CH_2), 7.6 (2 H, m, CH), and 8.7 (6 H, d, 2 × Me); $\nu_{max.}$ (Nujol) 1 675 cm^{-1} (C=O).

N-(α-*Methoxyphenacyl*)-p-*toluidine* (4f).—To a solution of *N*-phenacyl-*p*-toluidine [4] (1 g, 44 mmol) in chloroform (50 cm^3) and methanol (50 cm^3) was added active manganese dioxide (1 g). The reaction mixture was refluxed with stirring for 24 h whereupon the solids were filtered off and the solvent was evaporated off under reduced pressure. The residue was triturated with methanol, and cooled. The resultant solid was filtered off to yield the *product* (4f) (0.5 g,

45%) as a yellow solid, m.p. 78 °C (methanol) (Found: C, 75.45; H, 6.55; N, 5.7%; M^+, 255.1263; $C_{16}H_{17}NO_2$ requires C, 75.25; H, 6.7; N, 5.5%; *M*, 255.12259); τ 1.8—3.3 (9 H, m, aromatic), 4.1 (1 H, d, CH), 4.7 (1 H, d, exchangeable, NH), 7.0 (3 H, s, OMe), and 7.8 (3 H, s, Me); $\nu_{max.}$ (Nujol) 3 400 (NH) and 1 680 cm^{-1} (C=O).

Similarly, p-*bromo*-N-(α-*methoxyphenacyl*)*aniline* (4g) was prepared as a fawn solid (0.55 g, 50%), m.p. 90 °C (methanol) (Found: C, 56.05; H, 4.35; Br, 25.3; N, 4.25. $C_{15}H_{14}BrNO_2$ requires C, 56.25; H, 4.35; Br, 24.95; N, 4.4%); τ 1.8—3.3 (9 H, m, aromatic), 4.1 (1 H, d, CH), 4.5 (1 H, d, exchangeable, NH), and 7.0 (3 H, s, OMe); $\nu_{max.}$ (Nujol) 3 400 (NH) and 1 680 cm^{-1} (C=O).

N-*Phenacylidene-t-butylamine* (7b).—A suspension of phenacyl-t-butylamine hydrochloride (1 g, 44 mmol) in benzene (50 cm^3) was shaken with aqueous sodium hydrogencarbonate (50 cm^3) and the organic phase was separated off and dried (Na_2SO_4). The solids were filtered off to leave a pale yellow solution to which barium manganate (2 g, 8 mmol) was added. The resultant suspension was stirred at 25 °C for 24 h. The solids were filtered off and the solvent was evaporated off under reduced pressure to give an oil which was distilled under reduced pressure to yield the *product* (7b) (0.4 g, 48%) as a pale green liquid, b.p. 100—120 °C at 0.02 Torr (kugelrohr) (Found: C, 76.2; H, 8.05; N, 7.1; M^+, 189.1140; osmometer, 211. $C_{12}H_{15}NO$ requires C, 76.15; H, 8.0; N, 7.4%; *M*, 189.1154); τ 1.7—2.6 (5 H, m, aromatic), 2.0 (1 H, s, CH), and 8.7 (9 H, s, 3 × Me; $\nu_{max.}$ (film) 1 660 (C=O) and 1 600 cm^{-1} (C=N); δ_C 196.389 (s, C=O), 154.832 (d, CH=N), and 53.208 (s, CMe_3) p.p.m.

The butylamine (7b) (0.4 g, 48%) was also obtained when methanol (50 cm^3) was included in the above dehydrogenation experiment.

3,4-*Dichloro*-N-*phenacylideneaniline* (1b).—To a solution of the α-methoxyamino-ketone (4a) (10 g, 32 mmol) in anhydrous benzene (150 cm^3) was added 10% palladium-on-charcoal (1 g) and the suspension was stirred under reflux for 20 h on a Dean and Stark apparatus. The mixture was cooled, the catalyst filtered off, and the solvent evaporated off under reduced pressure to give a residue which crystallised from dichloromethane–light petroleum (b.p. 60—80 °C) to yield the *product* (1b) (6.5 g, 73%) as a yellow solid, m.p. 100 °C [Found: C, 60.7; H, 3.5; Cl, 25.7; N, 5.0%; *m/e*, 278.9953; osmometer (toluene), 289. $C_{14}H_9Cl_2NO$ requires C, 60.45; H, 3.25; Cl, 25.5; N, 5.05%; *M*, 279.0032]; τ 1.8—3.1 (8 H, m, aromatic) and 1.9 (1 H, s, CH); $\nu_{max.}$ (Nujol) 1 650 (C=O) and 1 600 cm^{-1} (C=N); δ_C 190.322 (s, C=O) and 158.773 p.p.m. (d, CH=N).

The dichloroaniline (1b) was also prepared as described above except that the catalyst used was either 5% platinum-on-charcoal (1 g) or 5% rhodium-on-charcoal (1 g).

2,5-*Dichloro*-N-*phenacylideneaniline* (1c).—To a solution of the α-methoxyamino-ketone (4b) (1.0 g, 3.2 mmol) in anhydrous benzene (70 cm^3) was added 10% palladium-on-charcoal (0.1 g) and the suspension was stirred under reflux for 20 h on a Dean and Stark apparatus. The solution was cooled, the catalyst filtered off, and the solvent evaporated off under reduced pressure to give a semi-crystalline residue which crystallised from dichloromethone–light petroleum (b.p., 60—80 °C) to yield the *product* (1c) (0.8 g, 94%) as a yellow solid, m.p. 114 °C (Found: C, 60.0; H, 3.7; Cl, 25.85; N, 5.15. $C_{14}H_9Cl_2NO$ requires C, 60.45; H, 3.25; Cl, 25.5; N, 5.05%); τ 1.6—3.0 (8 H, m, aromatic) and 2.0 (1 H, s, CH); $\nu_{max.}$ (Nujol) 1 650 (C=O) and 1 595 cm^{-1} (C=N).

N-*Phenacylidene*-p-*toluidine* (1d) and *bromo*-N-4-*phenacylideneaniline* (1e) were prepared similarly (see supplementary publication).

Action of Palladium-on-charcoal on N-(α-*Methoxyphenacyl*)*toluene*-p-*sulphonamide* (8e).—To a solution of the α-methoxyamino-ketone (8e) (0.1 g, 0.3 mmol in anhydrous benzene (70 cm^3) was added 10% palladium-on-charcoal (0.1 g) and the suspension was stirred under reflux on a Dean and Stark apparatus in an atmosphere of dry nitrogen for 16 h. The solution was cooled, the catalyst filtered off, and the solvent evaporated off under reduced pressure to give a semi-crystalline residue which crystallised from chloroform–light petroleum (b.p., 60—80 °C) to yield the bis(toluene-*p*-sulphonate) (12c) (80 mg) as a white solid, m.p. 196 °C which was identical (spectra and analysis) with an authentic sample.

N-(p-*Nitrobenzylidene*)*toluene*-p-*sulphonamide* (14d).—To a solution of *p*-nitrobenzaldehyde (1.5 g, 10 mmol) and toluene-*p*-sulphonamide (1.7 g, 10 mmol) in benzene (70 cm^3) under reflux on a Dean and Stark apparatus was added (*via* a syringe) BF_3–Et_2O (0.05 cm^3, 0.4 mmol). Reflux was continued for 16 h and the solution was then cooled and washed with 2M sodium hydroxide. The organic phase was separated, dried (Na_2SO_4), and the solvent was evaporated off under reduced pressure to yield a solid which crystallised from chloroform–light petroleum (b.p., 60—80 °C) to give the *product* (14d) (2.0 g, 66%) as a yellow solid, m.p. 204 °C (lit.,[27] m.p. 206—207 °C).

N-(p-*Methoxybenzylidene*)*toluene*-p-*sulphonamide* (14e), N-(o-*acetoxybenzylidene*)*toluene*-p-*sulphonamide* (14f), N-(o-*hydroxybenzylidene*)*toluene*-p-*sulphonamide* (14g), N-(o-*ethoxycarbonylbenzylidene*)*toluene*-p-*sulphonamide* (14h), N-(trans-3-*phenylprop*-2-*enylidene*)*toluene*-p-*sulphonamide* (15a), and N-(*furfurylidene*)*toluene*-p-*sulphonamide* (15b) were prepared similarly (see supplementary publication).

N-(2,2-*Dimethylpropylidene*)*toluene*-p-*sulphonamide* (15c).—To a solution of trimethylacetaldehyde (0.861 g, 10 mmol) and toluene-*p*-sulphonamide (1.7 g, 10 mmol) in anhydrous benzene (70 cm^3) under reflux, which contained molecular sieves (4A, 1 g), was added (*via* a syringe) BF_3–Et_2O (0.1 cm^3, 1.6 mmol). Reflux was continued for 16 h and the solution was then cooled, filtered off, and extracted with 2M sodium hydroxide (20 cm^3). The organic phase was separated off, dried (Na_2SO_4), and the solvent was evaporated off to yield the *product* (15c) (1.5 g, 63%) which crystallised from dichloromethane–light petroleum (b.p., 60—80 °C) as a white solid, m.p. 90 °C (Found: C, 59.85; H, 7.35; N, 6.15%; M^+, 239.0980. $C_{12}H_{17}NO_2S$ requires C, 60.25; H, 7.15; N, 5.85%; *M*, 239.0980); τ 1.55 (1 H, s, CH), 2.1—2.8 (4 H, d of d, aromatic), 7.6 (3 H, s, Me), and 8.9 (9 H, s, 3 × Me); $\nu_{max.}$ (Nujol) 1 600 cm^{-1} (C=N).

Perhydro-1,3,5-*tri*(*toluene*-p-*sulphonyl*)-1,3,5-*triazine* (16).—To a solution of toluene-*p*-sulphonamide (1.7 g, 10 mmol) in anhydrous benzene (70 cm^3), which contained BF_3–Et_2O (0.1 cm^3, 1.6 mmol) and was under reflux on a Dean and Stark apparatus was added paraformaldehyde (0.5 g, 16.6 mmol) during a few minutes. The solution was then refluxed for 4 h, cooled, and extracted with 2M sodium hydroxide. The organic phase was separated off, dried (Na_2SO_4), and the solvent was evaporated off under reduced pressure to yield a solid which crystallised from chloroform–light petroleum (b.p., 60—80 °C), m.p. 182 °C (Found: C, 52.25; H, 5.0; N, 7.75%; M^+, 549.1029. $C_{24}H_{27}N_3O_6S_3$ requires C, 52.45; H, 4.95; N, 7.65%; *M*, 549.1062); τ 2.3—2.8 (12 H, d of d, aromatic), 5.45 (6 H, s, 3 × CH_2),

and 7.6 (9 H, s, 3 × Me); $\nu_{max.}$ (Nujol) 1 170 cm^{-1} (SO_2N).

We thank the S.R.C. for a C.A.S.E. studentship, Drs. K. Godfrey and P. Meyers (Reckitt and Colman) for helpful discussion, and Mr. A. Sneddon for technical assistance.

[1/071 *Received*, 19*th January*, 1981]

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