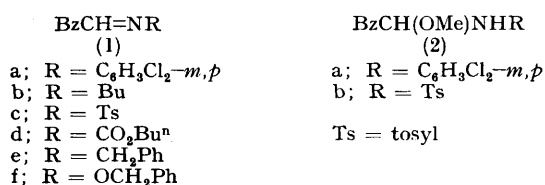# Removal of Toluene-p-sulphonyl Groups from Sulphonamides. Part 5.[1] Reactions of Phenylglyoxal Imines and some Tosylimines
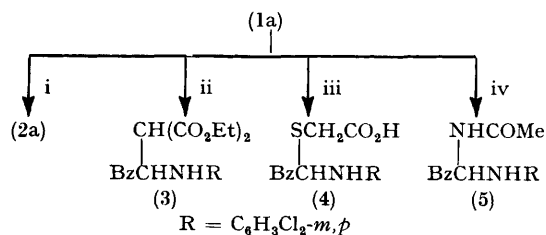
By **William R. McKay** and **George R. Proctor,*** Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL

Phenylglyoxal anil monomers have been shown to react with several nucleophilic reagents and the structures of the products have been elucidated. Various N-tosylarylimines also react with nucleophiles to give useful products. Phenacylimidates underwent [2 + 2]cycloadditions with diphenylketen; such reactions gave complex results with phenacylimines, but the latter reacted with conjugated dienes in the presence of BF_3 to give [2 + 4]cycloaddition products in good yield.

IT has been recognised for some time that the chromophore $R^1COCH=NR^2$ is quite reactive and it has been implicated as an intermediate in chemical reactions of various phenacylamine derivatives.[2-8] In the previous paper we described methods that allowed isolation of various phenylglyoxal imines as monomers. This, in turn, permits a systematic study of their chemistry which is presented in this paper.

BzCH=NR   BzCH(OMe)NHR
(1)   (2)

a; R = $C_6H_3Cl_2$–m,p   a; R = $C_6H_3Cl_2$–m,p
b; R = Bu   b; R = Ts
c; R = Ts
d; R = CO_2Bu^n Ts = tosyl
e; R = CH_2Ph
f; R = OCH_2Ph

Nucleophilic Addition.—(a) *Phenacylimines.* The anil (1a)[1] reacted with methanol to give the α-methoxyamino-ketone (2a). This lends credence to the belief that anils are intermediate in reactions between phenylglyoxal and arylamines in alcohols.[1,4,7,9] In a similar fashion, diethyl sodiomalonate, thioglycolic acid, and acetamide reacted with the same anil to give the expected products (3)—(5), respectively. These results (summarised in Scheme 1) indicate that several heterocyclics

(1a)

i	ii	iii	iv
(2a)	$CH(CO_2Et)_2$	SCH_2CO_2H	NHCOMe
	BzCHNHR	BzCHNHR	BzCHNHR
	(3)	(4)	(5)

R = $C_6H_3Cl_2$-m,p

SCHEME 1   *Reagents:* i, MeOH, heat; ii, $^-CH(CO_2Et)_2$, benzene, 25 °C; iii, $SHCH_2CO_2H$; iv, NH_2COMe, CH_2Cl_2, 25 °C, BF_3–Et_2O

might be available from the products; in particular, the syntheses of the thiazole derivatives form compounds like (4), which will be discussed below. Moreover, demonstration of the first two reactions in Scheme 1 sheds further light on the reaction of compound (6) with sodium methoxide in methanol, which we described previously.[2] Repetition of this reaction in the present work (diethyl malonate was omitted) gave, exclusively, the methoxyamine (8) which is probably formed by addition of
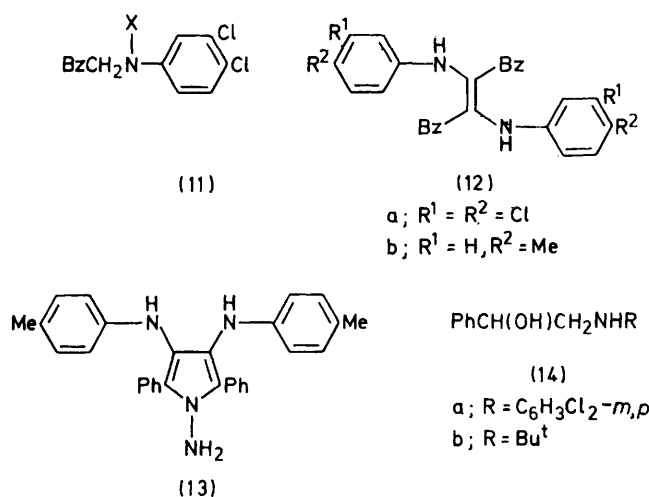
methanol to the imine (7), as shown in Scheme 2. It will be seen that Dieckman cyclisation precedes tosyl elimination, for which there is precedent.[9,10] Moreover, addition of malonate to the imine (7) described in our original work,[2] can now be explained plausibly as in
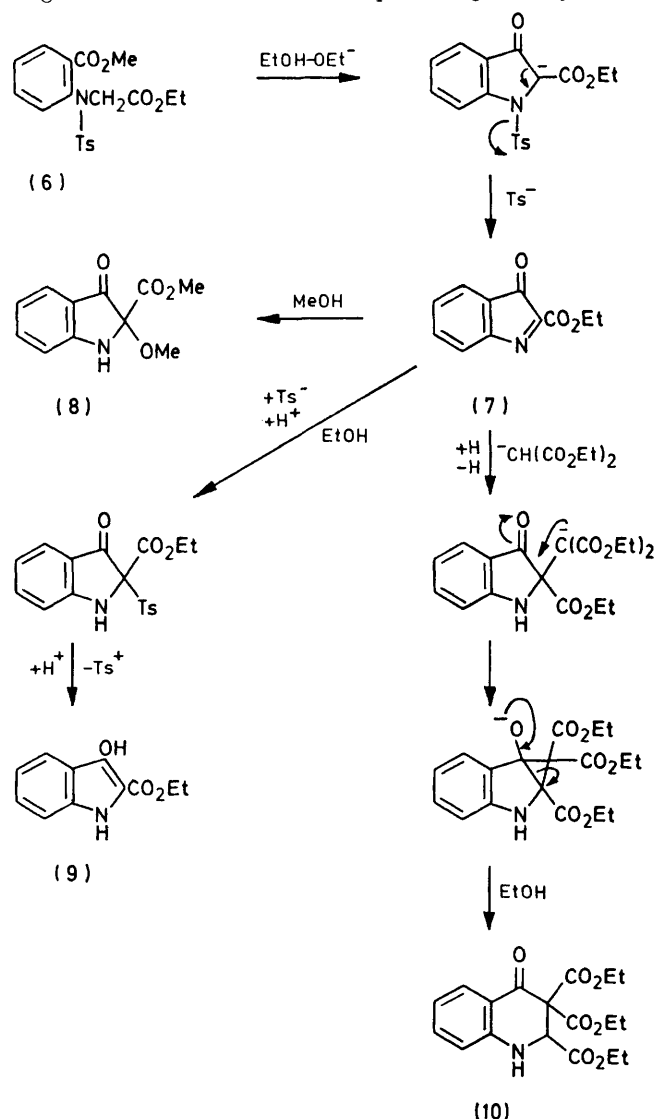
Ts = tosyl

SCHEME 2

Scheme 2, leading to the product (10). The formation of product (9), obtained in the original work, was difficult to explain[2], but could be presented (Scheme 2) as an artefact of toluene-p-sulphinate addition to the imine (7).[11] To support this, the imine (1a) was shown to react with toluene-p-sulphinic acid; although we were unable to elucidate the structure of the product, it contained CHClNO and S.
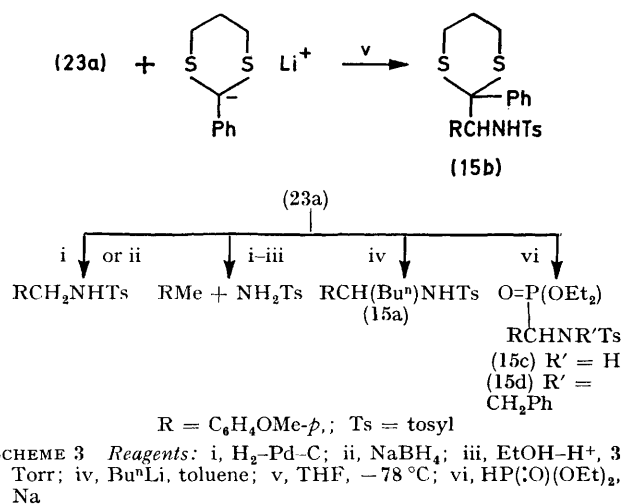
It was our belief that phenylglyoxal anil monomers were intermediates in the reaction of N-tosylphenacylamines (11; X = tosyl) with sodium methoxide in toluene, which gave the dimeric products (12). This is now supported by the fact that the monomer (1a) reacted with sodium methoxide to give the dimer (12a).


(11)   (12)

a; $R^1 = R^2 = Cl$
b; $R^1 = H, R^2 = Me$

(13)

$PhCH(OH)CH_2NHR$

(14)

a; $R = C_6H_3Cl_2$-m,p
b; $R = Bu^t$

The dimer (12a) reacted with hydrazine to give a substance, $C_{30}H_{28}N_4$, which, although its mass spectrum contained a strong ($M - 2$) peak, did not undergo dehydrogenation and is to be regarded, therefore, as the pyrrole (13) rather than the alternative dihydropyrazine.[11] Hydride reduction of the monomeric anil (1a) gave the same hydroxy-amine (14a) as that obtained by reduction of the corresponding phenacylamine (11; X = H).

The N-alkylimine (1b) did not react with refluxing methanol and, although it reacted with sodium methoxide in toluene, a multicomponent mixture was obtained. Hydride reduction, however, gave the expected, known[12] hydroxy-amine (14b) from the imine (1b).

(b) N-*Tosylimines*. Since several N-tosylimines are now[1] available, we have studied some of their reactions. As expected they are attacked by hydride, carbon, phosphorus, and sulphur nucleophiles. Some of these are illustrated in Scheme 3. It will be seen that these comprise useful methods for the syntheses of certain substituted benzylamines and α-amino-ketones. The reaction with diethyl phosphinate, which only proceeded in presence of sodium, gave a product (15c) which, after N-benzylation, reacted with sodium methoxide in methanol to give the imine (16). The latter did not prove reactive with methoxide nor did it undergo cycloaddition with dienes (see below). The only N-tosyl-

(15b)

(23a)

i or ii	i–iii	iv	vi
RCH_2NHTs	$RMe + NH_2Ts$	$RCH(Bu^n)NHTs$ (15a)	$O=P(OEt_2)$

$RCHNR'Ts$
(15c) R' = H
(15d) R' = CH_2Ph

$R = C_6H_4OMe$-p,; Ts = tosyl

SCHEME 3 *Reagents:* i, H_2–Pd–C; ii, $NaBH_4$; iii, $EtOH$–H^+, 3 Torr; iv, Bu^nLi, toluene; v, THF, -78 °C; vi, $HP(\colon O)(OEt)_2$, Na

imine that reacted with thioglycolic acid was the N-tosylimine (23c) which gave (17a), but only in the presence of benzoyl peroxide. The N-tosylimine (18a) is a useful


(16)

(17)

a; $R = C_6H_4NO_2$-p
b; $R = Bz$
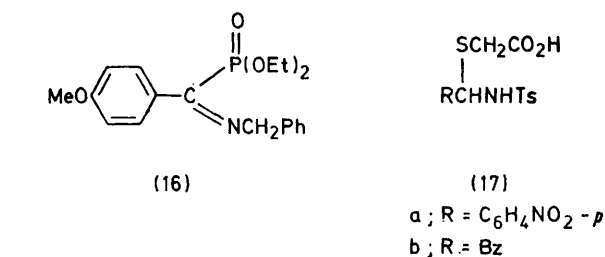
source of γ-phenylpropylamine derivatives; Scheme 4 illustrates an application of this idea. The glycine (19) has previously[13] been shown to cyclise to the azocinone derivative (20). Although the N-tosylimine (1c) was

(18a)   (18b)

(18c)   (18)

d; R = Et
e; R = H

(20)   (19)

Ts = tosyl
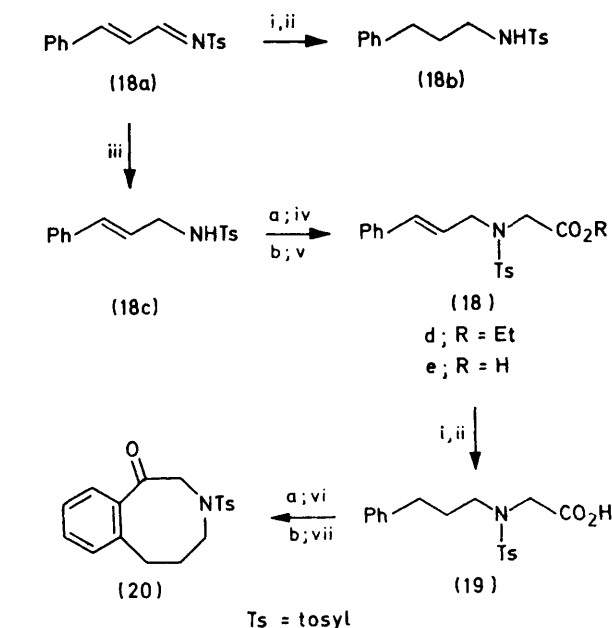
SCHEME 4 *Reagents:* i, Pd–C; ii, H_2; iii, $NaBH_4$; iv, $BrCH_2$-CO_2Et; v, $NaOH$–H_2O–MeOH; vi, $SOCl_2$; vii, $AlCl_3$

not isolated after the reaction of phenylglyoxal with toluene-*p*-sulphonamide in presence of BF_3–Et_2O,[1] its participation as an intermediate was inferred. Accordingly, the reaction was repeated in methanol and the imine was, indeed, trapped by the solvent to yield the methoxy-derivative (2b). Furthermore, inclusion of thioglycolic acid in the original recipe yielded an acidic adduct (17b) in 30% yield along with a neutral product (21) in 5% yield. The former could be converted into the latter with polyphosphoric acid. On the other hand, glycolic acid did not participate as the trapping agent.

During this work another very useful thiazolone synthesis was discovered; phenylglyoxal and thiourea reacted in the presence of BF_3–Et_2O to give 2-amino-4-phenylthiazolin-5-one (22) in 78% yield. Presumably, this result indicates that the nucleophilic sulphur atom in thiourea initiates the reaction rather than either of the


(21)

(22)

(23)

a; R^1 = H, R^2 = OMe
b; R^1 = OAc, R^2 = H
c; R^1 = H, R^2 = NO_2

(24)

Ts = tosyl
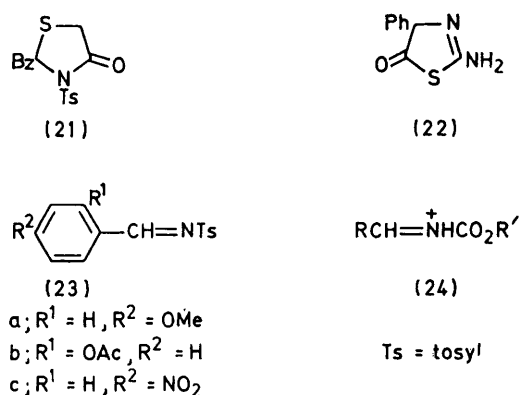
nitrogen atoms. This synthesis should complement known syntheses of thiazol-5-ones which generally involve thioamide cyclisations.[14,15]

Cycloadditions.—Previous studies have shown that the imines (1) only undergo cycloadditions with 1,3-dienes if they are doubly activated by electron-withdrawing groups (*e.g.* R = CO_2Bu^n)[16] or by salt formation [*e.g.* (24)].[17,18]

In the present study, *N*-arylimines (1; R = Aryl) failed to react with dienes even at 30 kbar pressure.* However, addition of a catalytic quantity of BF_3–Et_2O caused fairly rapid and efficient cycloaddition reactions, under mild conditions, with several dienes such as 2,3-dimethylbutadiene, cyclopentadiene, cyclohexa-1,3-diene, and cycloheptatriene (Scheme 5). In the last case, the structure was assigned by comparison with a known cycloheptatriene adduct.[19] The heterocyclic products thus obtained are novel and the methodology employed complements those[16,18] previously reported, in that it provides *N*-aryl compounds. We have been unable to react the *N*-alkylimines (1b) and (1e) with dienes even in the presence of an excess of BF_3–Et_2O. Efforts to employ other dienes such as 5-ethoxy-2-methyloxazole were unsuccessful; apparently poly-

* We thank Dr. C. Graham and Dr. R. Freer, Department of Geology, University of Edinburgh, for carrying out this reaction.

merisation of the dienes predominated. In our hands the literature preparation[20] for the oxazole required modifications and it was unexpectedly discovered that treatment of ethyl *N*-acetylglycinate with thionyl chloride in hot benzene gave a product, $C_6H_5Cl_2NO_2S$, which we believe is 4,5-dichloro-2-ethoxycarbonyl-thiazole (26), for which a tentative and speculative

(25a)

(25b)

(25c)

(25d)

R = $C_6H_3Cl_2$–*m,p*
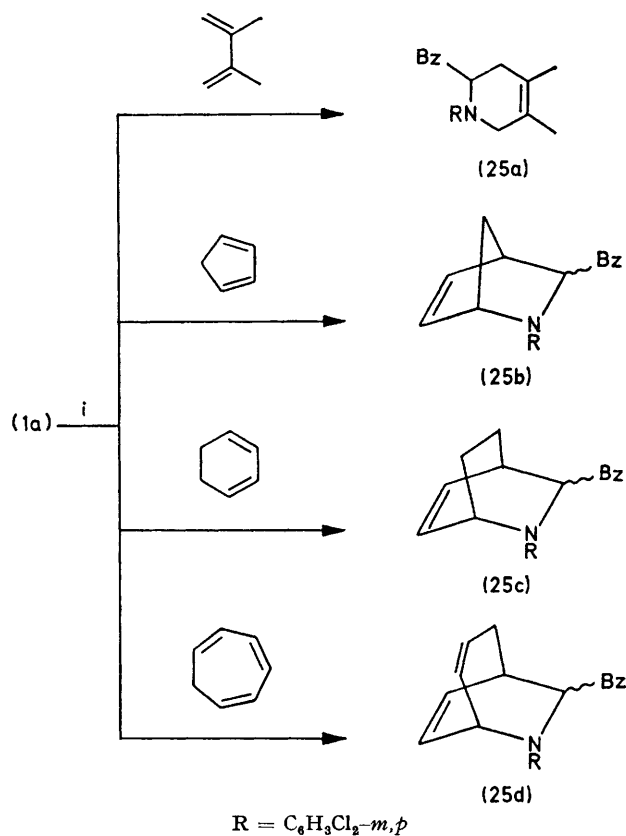
SCHEME 5 *Reagents:* i, BF_3, CH_2Cl_2, 25 °C

explanation is offered in Scheme 6. The latter is unsatisfactory and further work is required on the reaction of thionyl chloride with other *N*-acylamino-esters.

The cycloadduct obtained from dimethylbutadiene, (25a) (Scheme 5), was also obtained by allowing the α-methoxyamino-ketone (2a) to react with the diene in the presence of BF_3–E_2O; presumably an iminium ion [analogous to (24)] is involved. The latter modification means that the heterocyclic products (25) (Scheme 5) are easily available in two steps from the *N*-arylphenacyl-amines. *N*-Tosylimines (23) did not undergo cyclo-addition with 2,3-dimethylbutadiene or cyclohepta-triene in the presence of BF_3.

The comparative lack of reactivity found here for the *N*-alkylimines may be associated with electron-donating properties of the nitrogen substituent; benzyloxy-iminoacetophenone (1f) also failed to undergo cyclo-addition with dimethylbutadiene in the presence of BF_3 and was not attacked by sodium methoxide in methanol.

[2 + 2]Cycloadditions with imines are quite well

known.[21,22] The methoxyphenacylimines (*e.g.* 27) react with diphenylketen to give the azetidinones (28; R = alkyl or aryl), but other ketens (*N*-phthaloyl- or chloro-) were not fruitful. The anil (1a) gave an intractable mixture with diphenylketen, no reaction with phenylisothio-

SCHEME 6

cyanate, and the diarylurea (29) with phenyl isocyanate. The latter reaction, presumably, did proceed *via* the expected unstable [23] uretidinone (30), but hydrolysis of the

(27)

(28)

a ; R = C$_6$H$_3$Cl$_2$ -*m,p*

b ; R = Me

(29)

(30)

latter could not be suppressed, even by the rigorous drying of reagents. Repeated attempts to obtain useful addition reactions between phenacylimines (1) and several

enamines were unsuccessful. Thus, in this series of compounds, [4 + 2]cycloadditions appear to be more useful than [2 + 2]cycloadditions.
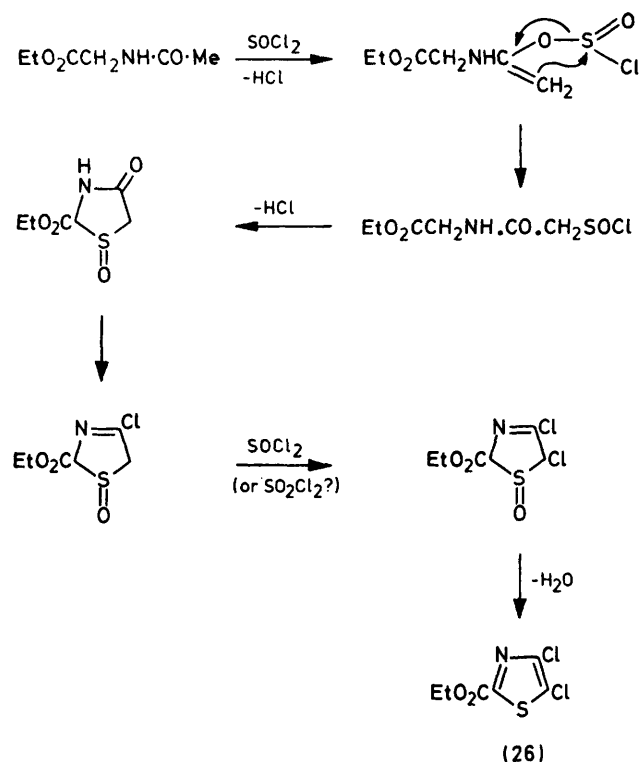
EXPERIMENTAL

Preparations of the following compounds are given in Supplementary Publication No. SUP 23074 (30 pp.),* which is the supplementary publication referred to throughout the Experimental section. i, 1-(3,4-*Dichlorophenyl*)-3-*phenylurea* (29); ii, 3-*benzoyl*-2-(3,4-*dichlorophenyl*)-2-*azabicyclo*[2.2.1]-*hept*-5-*ene* (25b); iii, 3-*benzoyl*-2-(3,4-*dichlorophenyl*)-2-*aza-bicyclo*[2.2.2]*oct*-5-*ene* (25c); iv, 9-*benzoyl*-8-(3,4-*dichloro-phenyl*)-8-*azabicyclo*[3.2.2]*nona*-2,6-*diene* (25d); and v, 1-*phenyl*-2-(*t*-*butylamino*)*ethanol* (14b). Details of the following reactions are also available in the supplementary publication. i, Reaction of phenylglyoxal and toluene-*p*-sulphonamide with glycolic acid in the presence of BF$_3$; ii, high-pressure reaction of the imine (1a) and cyclohepta-triene; iii, reactions of phenacylidene-t-butylamine (1b) with nucleophiles and dienes; iv, attempted reactions of the *O*-benzoyl-oxime (1f) with nucleophiles and dienes; and v, attempted cycloadditions of *N*-tosyl- and *N*-mesyl-imines with 2,3-dimethylbutadiene.

Methyl 2-*Methoxy*-3(2H)*oxo*-1H-*indole*-2-*carboxylate* (8). —To a solution of methyl *N*-ethoxycarbonylmethyl-*N*-tosyl-anthranilate [2] (6) (1.9 g, 5 mmol) in anhydrous methanol (20 cm^3) was added a solution of sodium methoxide (0.37 g, 7 mmol) in anhydrous methanol (20 cm^3) as drops during 5 min. The resultant green solution was stirred at room temperature for 3 h and then evaporated under reduced pressure. The residue was dissolved in chloroform and washed with water, and the organic layer was removed, dried (Na$_2$SO$_4$), and evaporated under reduced pressure to give the *product* (8) (0.65 g, 59%). Recrystallisation from chloroform–light petroleum (b.p. 60—80 °C) gave a green solid, m.p. 100 °C (Found: C, 59.8; H, 5.35; N, 6.35%; M^+, 221.0694. C$_{11}$H$_{11}$NO$_4$ requires C, 59.75; H, 5.0; N, 6.4%; *M*, 221.0688]; τ 2.4—3.3 (4 H, m, aromatic), 4.8 (1 H, br, exchangeable, NH), 6.25 (3 H, s, OMe), and 6.7 (3 H, s, OMe); ν$_{max.}$ (Nujol) 3 440 (NH), 1 750 (C=O, ester), and 1 720 cm^{-1} (C=O).

Reaction of Phenylglyoxal Hydrate and Toluene-p-sul-phonamide with Thioglycolic Acid in the Presence of Boron Trifluoride.—A solution of phenylglyoxal hydrate (6 g, 40 mmol) and toluene-*p*-sulphonamide (6 g, 35 mmol) in benzene (150 cm^3) was refluxed for 0.5 h on a Dean and Stark apparatus. Thioglycolic acid (10.4 g, 0.1 mol) was added, followed by BF$_3$–Et$_2$O (0.2 cm^3, 1.6 mmol) *via* a syringe, and the solution was refluxed for 16 h. The solution was then cooled and extracted successively with aqueous sodium hydrogencarbonate and 2M sodium hydroxide, and was finally washed with water. The organic layer was removed, dried (Na$_2$SO$_4$), and evaporated under reduced pressure to yield 2-*benzoyl*-3-*tosylthiazolidin*-4-*one* (21) (0.6 g, 5%) as a white solid, m.p. 190 °C (ether) (Found: C, 56.5; H, 4.4; N, 3.65%; M^+, 361.0451. C$_{17}$H$_{15}$NO$_4$S$_2$ requires C, 56.5; H, 4.2; N, 3.85%; M^+, 361.0442); τ 1.9—2.8 (9 H, m, aromatic), 3.5 (1 H, s, CH), 6.4—6.5 (2 H, d, CH$_2$), and 7.5 (3 H, s, Me); ν$_{max.}$ (Nujol) 1 720 (C=O, aryl) and 1 660 cm^{-1} (C=O).
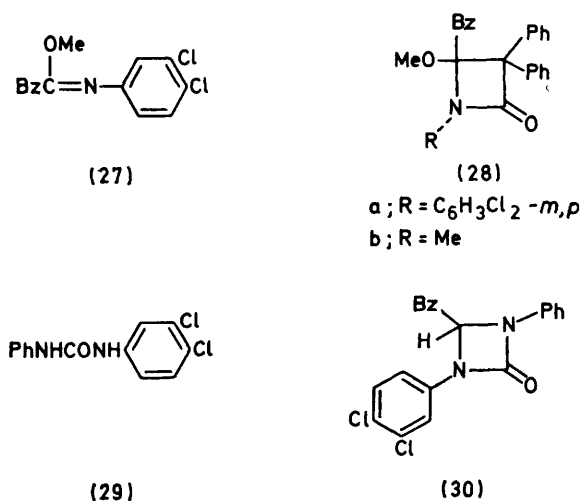
The sodium hydrogencarbonate extract was then acidified

with concentrated sulphuric acid and the liberated oil extracted with chloroform. The organic layer was removed, dried (Na$_2$SO$_4$), and the solvent removed under reduced pressure to yield an oil (8 g) which was triturated with benzene to give [(α-*tosylamino*)*phenacylthio*]*acetic acid acid* (17b) (4.5 g, 30%) as a white solid, m.p. 145 °C (benzene) (Found: C, 53.5; H, 4.25; N, 3.6. C$_{17}$H$_{17}$NO$_5$S$_2$ requires C, 53.8; H, 4.5; N, 3.7%); τ 1.7 (1 H, br, exchangeable, OH), 2.0—3.0 (9 H, m, aromatic; 1 H, m, exchangeable, NH), 3.8 (1 H, br, CH), 6.7 (2 H, d, CH$_2$), and 7.7 (3 H, s, Me); $\nu_{max.}$ (Nujol) 3 500—2 000 (br, OH, chelated), 3 300 (NH), and 1 680—1 700br cm^{-1} (2 × C=O).

Cyclisation of the Acid (17b) *to the Thiazolidinone* (21).—(a) *Using polyphosphoric acid.*—The acid (17b) (1 g, 2.6 mmol) and polyphosphoric acid (20 g) were heated at 100 °C for 10 h. The cooled solution was basified with 2M sodium hydroxide and extracted with chloroform. The organic phase was then removed, dried (Na$_2$SO$_4$), and evaporated under reduced pressure to give a red oil (0.3 g, 32%) which crystallised, on trituration with ether, to yield the product as a white solid, m.p. 190 °C, identical with (spectra and t.l.c.) the thiazolidinone (21).

Method (b) (using boron trifluoride–diethyl ether) is described in the supplementary publication.

3,4-*Dichloro*-N-(α-*methoxyphenacyl*)*aniline* (2a).—3,4-Dichloro-N-phenacylideneaniline[1] (1a) (0.556 g, 2 mmol) was dissolved in methanol (5 cm^3) and refluxed for 1 h. The solution was cooled and the resultant precipitate was filtered off to yield the product (2a) (0.5 g, 81%) which had spectral and analytical characteristics identical with an authentic sample.[1]

Diethyl α-[(3,4-*Dichloroanilino*)*phenacyl*]*malonate* (3).—To a suspension of diethyl sodiomalonate [1 mmol, obtained from sodium (0.023 g, 1 mmol) in ethanol (10 cm^3) and diethyl malonate (0.16 g, 1 mmol)] in anhydrous benzene (50 cm^3) was added, as drops during 0.5 h, a solution of the aniline (1a) (0.278 g, 1 mmol) in anhydrous benzene (20 cm^3). The resultant suspension was stirred for 16 h at 25 °C and poured into 2M HCl (20 cm^3). The organic phase was removed, dried (Na$_2$SO$_4$) and evaporated under reduced pressure to yield the *product* (3) (0.35 g, 79%) as a green oil which was distilled under reduced pressure, b.p. 200 °C at 0.01 Torr (Found: C, 57.8; H, 4.5; N, 3.0. C$_{21}$H$_{21}$Cl$_2$NO$_5$ requires C, 57.55; H, 4.85; N, 3.2%); τ 2.0—3.6 (8 H, m, aromatic), 4.5 (1 H, m, CH), 5.3 (1 H, d, NH), 5.6—6.0 (5 H, m, 2 × CH$_2$ + CH), and 8.6—8.9 (6 H, m, 2 × Me); $\nu_{max.}$ (film) 3 360 (NH), 1 720, and 1 680 cm^{-1} (2 × C=O).

[α-(3,4-*Dichloroanilino*)*phenacylthio*]*acetic Acid* (4).—To a solution of the aniline[1] (1a) (0.5 g, 1.8 mmol) in anhydrous chloroform (50 cm^3) was added thioglycolic acid (0.17 g, 0.13 cm^3, 1.85 mmol). The solution was refluxed for 16 h, then cooled, and the precipitated solid was filtered off to yield the *product* (4) (0.5 g, 74%) as white crystals, m.p. 129 °C (aqueous methanol) (Found: C, 52.35; H, 3.5; N, 3.8. C$_{16}$H$_{13}$Cl$_2$NO$_3$S requires C, 51.9; H, 3.55; N, 3.8%); τ[(CD$_3$)$_2$SO] 1.6—3.6 (8 H, m, aromatic; 1 H, m, CH; 2 H, m, exchangeable, OH + NH) and 6.7—6.8 (2 H, d, CH$_2$); $\nu_{max.}$ (Nujol) 3 290 (NH), 1 710, and 1 660 cm^{-1} (2 × C=O).

3,4-*Dichloro*-N-(α-*acetamidophenacyl*)*aniline* (5).—To a solution of the aniline[1] (1a) (0.278 g, 1 mmol) in anhydrous dichloromethane (20 cm^3) was added acetamide (0.06 g, 1 mmol) followed by BF$_3$·Et$_2$O (0.1 cm^3, 0.8 mmol) and the solution was stirred at 25 °C for 16 h. The resultant precipitate was filtered off to yield the *product* (5) (0.15 g,

44%) as a white solid, m.p. 180 °C [acetone–light petroleum (b.p. 60—80 °C)] (Found: C, 56.85; H, 4.25; N, 8.55%; M^+, 336.0462. C$_{16}$H$_{14}$Cl$_2$N$_2$O$_2$ requires C, 57.0; H, 4.2; N, 8.3%; M, 336.0432); τ[(CD$_3$)$_2$C=O] 1.8—3.0 (8 H, m, aromatic), 3.2 (1 H, m, CH), 3.9 (2 H, br, exchangeable, 2 × NH), and 7.3 (6 H, s, Me); $\nu_{max.}$ (Nujol) 3 400, 3 300 (2 × NH), and 1 690—1 650 cm^{-1} (2 × C=O).

2-(3,4-*Dichloroanilino*)-1-*phenylethanol* (14a).—To a solution of the aniline[1] (1a) (1 g, 3.6 mmol) in tetrahydrofuran (THF) (20 cm^3) was added sodium borohydride (0.5 g, 13 mmol) in portions during 2 h at 25 °C. The solution was diluted with ice–water–2M HCl (50 cm^3) and the liberated oil was extracted with chloroform. The organic phase was removed, dried (Na$_2$SO$_4$), and evaporated under reduced pressure to yield an oil which crystallised from ether–light petroleum (b.p. 60—80 °C) to give the *product* (14a) (0.9 g, 88%) as a white solid, m.p. 60 °C (ether) (Found: C, 59.4; H, 4.5; N, 5.05. C$_{14}$H$_{13}$Cl$_2$NO requires C, 59.6; H, 4.65; N, 4.95%); τ 2.6—3.7 (8 H, m, aromatic), 5.2 (1 H, m, CH), 5.9 (1 H, br, exchangeable, NH), 6.7 (2 H, m, CH$_2$), and 7.7 (1 H, br, exchangeable, OH); $\nu_{max.}$ (Nujol) 3 280 (OH) and 3 200 cm^{-1} (NH).

The amino-alcohol (14a) could also be obtained by reduction of 3,4-dichloro-N-phenacylaniline (11; X = H) with sodium borohydride in methanol.

Reaction of the Imine (1a) *with Sodium Methoxide.*—To a solution of the aniline[1] (1a) (0.556 g, 2 mmol) in anhydrous toluene (50 cm^3) was added sodium methoxide (0.54 g, 10 mmol) and the suspension was stirred for 20 h at 25 °C. Ice–water (50 cm^3) was added and the organic phase was separated off, dried (Na$_2$SO$_4$), and evaporated under reduced pressure to yield a red solid (0.55 g) which crystallised from acetone–light petroleum (b.p. 60—80 °C) to give a red powder, m.p. 210 °C which had identical spectral and analytical data with the previously obtained dimer (12a).[1]

1-*Amino*-2,5-*diphenyl*-3,4-*di*-(p-*toluidino*)*pyrrole* (13).—The dimer (12b) (0.134 g, 0.3 mmol) in ethanol (20 cm^3) which contained hydrazine hydrate (0.15 g, 1.5 mmol) was refluxed for 4 h. The solvent was removed under reduced pressure and the residue crystallised from chloroform–light petroleum (b.p. 60—80 °C) to give the *product* (13) (80 mg, 61%) as a green solid, m.p. 258—259 °C (Found: C, 80.6; H, 6.1; N, 12.4%; M^+, 444.2243. C$_{30}$H$_{28}$N$_4$ requires C, 81.1; H, 6.3; N, 12.6%; M, 444.2314); τ 2.4—3.8 (20 H, m, aromatic; 2 H, exchangeable, 2 × NH) 4.35 (2 H, s, exchangeable 2 × NH), and 7.9 (6 H, s, 2 × Me); $\nu_{max.}$ (Nujol) 3 260, 3 170, and 3 140 cm^{-1} (NH).

4-*Benzoyl*-1-(3,4-*dichlorophenyl*)-4-*methoxy*-3,3-*diphenylazetidin*-2-*one* (28a).—To a solution of the α-methoxyimine (27) 0.31 g, 0.10 mmol) in anhydrous acetonitrile (10 cm^3) was added a solution of diphenylketen[24] (0.2 g, 10 mmol) in anhydrous benzene (2 cm^3) and the resultant yellow solution was stirred for 24 h at 25 °C. The solvent was removed under reduced pressure and the solid crystallised from ether–light petroleum (b.p. 60—80 °C) to yield the *product* (28a) (0.3 g, 60%) as a white solid, m.p. 183 °C (Found: C, 69.2; H, 4.15; N, 2.75%; M^+, 501.0944. C$_{29}$H$_{21}$Cl$_2$NO$_3$ requires C, 69.3; H, 4.2; N, 2.8%; M, 501.0898); τ 2.0—3.1 (18 H, m, aromatic), and 7.0 (3 H, s, OMe); $\nu_{max.}$ (Nujol) 1 750 and 1 690 cm^{-1} (2 × C=O).

4-*Benzoyl*-4-*methoxy*-1-*methyl*-3,3-*diphenylazetidin*-2-*one* (28b) was prepared similarly as a solid (0.5 g, 48%), m.p. 170 °C (ether) (Found: C, 77.8; H, 5.35; N, 3.6%; M^+, 371.1519. C$_{24}$H$_{21}$NO$_3$ requires C, 77.6; H, 5.7; N, 3.75%; M, 371.1521); τ 2.2—3.2 (15 H, m, aromatic), 6.85 (3 H, s,

OMe), and 6.9 (3 H, s, NMe); $\nu_{max.}$ (Nujol) 1 740 and 1 650 cm^{-1} (2 × C=O).

2-Benzoyl-1-(3,4-dichlorophenyl)-4,5-dimethyl-1,2,3,6-tetrahydropyridine (25a).—To a solution of the imine (1a) (0.5 g, 1.8 mmol) and 2,3-dimethylbutadiene (0.164 g, 0.22 cm^3, 1.8 mmol) in anhydrous dichloromethane (25 cm^3) was added BF$_3$-Et$_2$O (0.025 cm^3, 0.2 mmol) and the resultant dark solution was stirred at 25 °C for 4 h. Ice–water (50 cm^3) was added and the organic phase was removed, dried (Na$_2$SO$_4$), and evaporated under reduced pressure to yield an oil which crystallised from methanol to give the *product* (25a) (0.35 g, 55%) as white crystals, m.p. 112 °C (Found: C, 66.8; H, 5.35; N, 4.15%; M^+, 359.0836. C$_{20}$H$_{19}$Cl$_2$NO requires C, 66.65; H, 5.3; N, 3.9%; M, 359.0844); τ 2.2—3.5 (8 H, m, aromatic), 4.65 (1 H, m, 2-H), 6.2 (2 H, s, 6-H), 7.2—7.7 (2 H, t, 3-H), and 8.3 and 8.4 (2 × 3 H, s, 4 and 5-Me); $\nu_{max.}$ (Nujol) 1 685 (C=O) and 1 580 cm^{-1} (C=C).

5-Ethoxy-2-methyloxazole.—To a solution of ethyl *N*-acetylglycinate [25] (10 g, 69 mmol) in alcohol-free chloroform (150 cm^3) was added phosphorus pentoxide (20 g, 0.14 mol) supported on Celite (10 g). The resulting suspension was stirred under reflux for 16 h, cooled, 2M sodium hydroxide (100 cm^3) added, and the suspension was stirred for 0.5 h at 0 °C. The suspension was filtered and the organic phase was removed, dried (Na$_2$SO$_4$), and evaporated under reduced pressure to yield an oily residue which was distilled under reduced pressure to give the product (4 g, 46%) as a pale yellow oil, b.p. 40 °C at 1 Torr (lit.,[21] 83 °C at 37 mmHg).

4,5-Dichloro-2-ethoxycarbonylthiazole (26).—A solution of ethyl *N*-acetylglycinate (4 g, 27.5 mmol) and thionyl chloride (16 g, 10.4 cm^3, 0.14 mol) in anhydrous benzene (30 cm^3) was refluxed for 0.5 h and then evaporated under reduced pressure. The resultant dark oil was distilled under reduced pressure to give the *product* (26) (2.5 g, 40%) as a yellow oil, b.p. 85 °C at 0.5 Torr (Found: C, 31.7; H, 2.4; N, 6.25%; M^+, 224.9418. C$_6$H$_5$Cl$_2$NO$_2$S requires C, 31.9; H, 2.2; N, 6.2%; M, 224.9422); τ 5.4—5.6 (2 H, q, CH$_2$) and 8.4—8.6 (3 H, t, Me); $\nu_{max.}$ (film) 1 740 cm^{-1} (C=O, ester); δ_C 181.469 (s, C=O), 158.958 (s, 2-C), 154.226 (s, 5-C), 147.132 (s, 4-C), 47.042 (t, CH$_2$), and 14.258 (q, Me) p.p.m.

The Tetrahydropyridine (25a).—To a solution of the α-methoxyamino-ketone (2a) (0.5 g 1.6 mmol) and 2,3-dimethylbutadiene (0.164 g, 0.22 cm^3, 1.8 mmol) in anhydrous dichloromethane (25 cm^3) was added BF$_3$-Et$_2$O (0.025 cm^3, 0.2 mmol) and the resultant solution was stirred at 25 °C for 16 h. Ice–water (50 cm^3) was added and the organic phase was removed, dried (Na$_2$SO$_4$), and evaporated under reduced pressure to yield an oil (0.5 g) which was purified by preparative t.l.c. on silica gel (eluant, chloroform) to give the *product* (25a) (0.2 g, 35%) as a white solid, m.p. 112 °C which had i.r. and ^{1}H n.m.r. spectral characteristics identical with an authentic sample.

α-Benzyloxyiminoacetophenone (1f).—To a suspension of sodium hydride (50% dispersion, 0.97 g, 20 mmol) in anhydrous benzene (150 cm^3) under an atmosphere of nitrogen was added isonitrosoacetophenone [1] (3 g, 20 mmol) in anhydrous THF (20 cm^3) and the resultant suspension was stirred under reflux for 6 h. The suspension was cooled and the precipitate filtered off to yield the sodium salt of isonitrosoacetophenone which was used without further purification. To a suspension of the sodium salt (1.7 g, 10 mmol) in anhydrous acetonitrile (50 cm^3) at 25 °C was added benzyl bromide (1.7 g, 10 mmol) and the resultant suspension was

refluxed for 2 h and stirred for 16 h at 25 °C. Filtration and evaporation (under reduced pressure) of the filtrate yielded an oil which was distilled under reduced pressure to yield the *product* (1f) (1.7 g, 71%) as a yellow liquid, b.p. 190—200 °C at 0.1 Torr (kugelrohr) (Found: C, 75.2; H, 5.5; N, 6.20. C$_{15}$H$_{13}$NO$_2$ requires C, 75.3; H, 5.45; N, 5.85%); τ 2.1—2.9 (10 H, m, aromatic), 2.2 (1 H, s, CH), and 4.8 (2 H, s, CH$_2$); $\nu_{max.}$ (film) 1 650 cm^{-1} (C=O).

3-Phenyl-N-tosylpropylamine (18b).—To a solution of the imine (18a) (5 g, 17.5 mmol) in ethyl acetate (200 cm^3) was added palladium-on-charcoal (10%, 0.5 g) and the suspension was hydrogenated at atmospheric pressure until uptake of hydrogen ceased (3 h). The catalyst was filtered off and the solvent evaporated off under reduced pressure to yield a gum (5.0 g) which crystallised from ether to give the product (4 g, 79%) as a white solid, m.p. 62 °C (lit.,[26] 66—67 °C).

3-Phenyl-N-tosylprop-2-enylamine (18c).—To a solution of the imine (18a) (5 g, 17.5 mmol) in methanol (150 cm^3) and THF (50 cm^3) at 25 °C was added sodium borohydride (2 g, 52 mmol) slowly with stirring. The solution was stirred for a further 2 h at 25 °C and then evaporated under reduced pressure. The residue was dissolved in chloroform and washed successively with hydrochloric acid (2M) and water. The organic phase was separated off, dried (Na$_2$-SO$_4$), and the solvent removed under reduced pressure to give a semi-crystalline residue which crystallised from dichloromethane–light petroleum (b.p. 60—80 °C) to yield the *product* (18c) (4 g, 82%) as crystals, m.p. 103—105 °C (Found: C, 66.55; H, 6.0; N, 4.75. C$_{16}$H$_{17}$NO$_2$S requires C, 66.9; H, 5.95; N, 4.9%); τ 2.2—3.0 (9 H, m, aromatic), 3.3—4.3 (2 H, m, 2 × CH), 4.8 (1 H, br, exchangeable, NH), 6.3 (2 H, t, CH$_2$), and 7.6 (3 H, s, Me); $\nu_{max.}$ (Nujol) 3 200 cm^{-1} (NH).

Ethyl N-(3-Phenylprop-2-enyl)-N-tosylglycinate (18d).—To a suspension of the sulphonamide (18c) (5 g, 17.4 mmol) in acetone (150 cm^3), which contained potassium carbonate (1.5 g, 11 mmol), under reflux was added ethyl bromoacetate (3 g, 18 mmol) in acetone (10 cm^3) and the resultant suspension was refluxed with stirring for 16 h. The suspension was then filtered off and the solvent removed under reduced pressure to yield an oily residue which was dissolved in chloroform and washed successively with sodium hydroxide (2M) and water. The organic phase was evaporated off, dried (Na$_2$SO$_4$), and the solvent removed under reduced pressure to yield a solid which crystallised from dichloromethane–light petroleum (b.p. 60—80 °C) to give the *product* (18d) (5 g, 77%) as a fawn solid, m.p. 100 °C (Found: C, 64.05; H, 6.3; N, 3.65. C$_{20}$H$_{23}$NO$_4$S requires C, 64.3; H, 6.2; N, 3.75%); τ 2.2—2.8 (9 H, m, aromatic), 3.3—4.0 (2 H, m, 2 × CH), 5.6—6.0 (6 H, m, 3 × CH$_2$), 7.6 (3 H, s, Me), and 8.8 (3 H, t, Me); $\nu_{max.}$ (Nujol) 1 750 cm^{-1} (C=O, ester).

N-(3-Phenylprop-2-enyl)-N-tosylglycine (18e).—To a solution of the *N*-tosylglycinate (18d) (3.73 g, 10 mmol) in methanol (100 cm^3) was added 2M sodium hydroxide (10 cm^3, 20 mmol). The solution was heated under reflux for 3 h, cooled, and diluted with water–chloroform. Separation of the aqueous extract was followed by acidification with concentrated sulphuric acid. After extraction with chloroform the organic extract was dried (Na$_2$SO$_4$) and evaporated under reduced pressure to yield a gummy solid (3.5 g, 94%) which crystallised from ether–light petroleum (b.p. 60—80 °C) to give the *product* (18e) as a white solid, m.p. 117—118 °C (Found: C, 62.85; H, 5.6; N, 3.9.

$C_{18}H_{19}NO_4S$ requires C, 62.6; H, 5.55; N, 4.05%); τ 1.0 (1 H, s, exchangeable, OH), 2.15—2.85 (9 H, m, aromatic), 3.3—4.0 (2 H, m, 2 × CH), 6.0, (4 H, 2 × s, 2 × CH$_2$), and 7.6 (3 H, s, Me); $\nu_{max.}$ (Nujol) 1 700 cm^{-1} (C=O, acid).

N-(3-*Phenylpropyl*)-N-*tosylglycine* (19).—To a solution of the tosylglycine (18e) (1 g, 2.9M) in ethanol (100 cm^3) was added 10% palladium-on-charcoal (0.1 g) and the suspension was hydrogenated at atmospheric pressure until the hydrogen uptake ceased (1 h). The catalyst was filtered off and the solvent evaporated off under reduced pressure to yield a gum which crystallised from ether to give the *product* (19) (0.8 g, 80%) as a white solid, m.p. 94 °C (Found: C, 62.2; H, 6.15; N, 4.2. $C_{18}H_{21}NO_4S$ requires C, 62.2; H, 6.1; N, 4.05%); τ 0.4 (1 H, s, exchangeable, OH), 2.3—3.1 (9 H, m, aromatic), 6.0 (2 H, s, CH$_2$), 6.8 (2 H, t, NCH$_2$), 7.45 (2 H, t, CH_2Ph), 7.65 (3 H, s, Me), and 8.2 (2 H, m, CH$_2$); $\nu_{max.}$ (Nujol) 1 700 cm^{-1} (C=O).

1-(p-*Methoxyphenyl*)-N-*tosylpentylamine* (15a).—To a solution of the N-tosylimine (23a) (0.436 g, 1.6 mmol) in anhydrous toluene (50 cm^3) under a nitrogen atmosphere at -78 °C was added n-butyl-lithium (1 cm^3, 1.6 mmol). The resultant dark solution was stirred at -78 °C for 6 h and then left to come to 25 °C overnight. Ice–water was added and the organic phase was separated off, dried (Na$_2$SO$_4$), and evaporated under reduced pressure to yield a solid which crystallised from dichloromethane–light petroleum, (b.p. 60—80 °C) as a white solid, m.p. 119 °C (Found: C, 65.85; H, 7.2; N, 4.3. $C_{19}H_{25}NO_3S$ requires C, 65.65; H, 7.25; N, 4.05%); τ 2.4—3.4 (8 H, m, aromatic), 4.65 (1 H, d, exchangeable, NH), 5.8 (1 H, m, NCH), 6.3 (3 H, s, OMe), 7.7 (3 H, s, tosyl-Me), 8.2—9.0 (6 H, m, 3 × CH$_2$), and 9.2 (3 H, t, CH$_2$Me); $\nu_{max.}$ (Nujol) 3 300 cm^{-1} (NH).

p-*Methoxy*-α-(2-*phenyl*-1,3-*dithian*-2-*yl*)-N-*tosylbenzyl-amine* (15b).—To a solution of 2-phenyl-1,3-dithiane [27] (0.313 g, 1.6 mmol) in anhydrous THF (10 cm^3) under a nitrogen atmosphere at -30 °C was added n-butyl-lithium (1 cm^3, 1.6 mmol) and the resultant dark green solution was stirred at -10 °C for 1 h. The solution was then cooled to -78 °C and treated with the N-tosylimine (23a) (1.6 mmol) in anhydrous THF (5 cm^3) *via* a syringe. The solution was warmed to 25 °C overnight and then diluted with ice–water and extracted with ethyl acetate. The organic phase was dried (Na$_2$SO$_4$) and evaporated under reduced pressure to yield a semi-crystalline residue which crystallised from dichloromethane–light petroleum (b.p. 60—80 °C) to give the *product* (15b) (0.55 g, 70%) as a white solid, m.p. 164 °C (Found: C, 62.0; H, 5.7; N, 2.8. $C_{25}H_{27}NO_3S_3$ requires C, 61.8; H, 5.6; N, 2.9%); τ 2.3—3.1 (8 H, m, aromatic), 3.55 (5 H, s, Ph), 4.5 (1 H, d, exchangeable, NH), 5.35 (1 H, d, CHN), 6.3 (3 H, s, OMe), 7.3—8.3 (6 H, m, 3 × CH$_2$), and 7.7 (3 H, s, Me); $\nu_{max.}$ (Nujol) 3 300 cm^{-1} (NH).

p-*Methoxy*-N-*tosylbenzylamine*.—To a solution of the N-tosylimine (23a) (1.445 g, 5 mmol) in ethyl acetate (70 cm^3) was added 10% palladium-on-charcoal (0.14 g) and the suspension was hydrogenated at atmospheric pressure until the hydrogen uptake ceased (2 h). The catalyst was filtered off and solvent removed under reduced pressure to yield the *product* (1.1 g, 75%) as a white solid, m.p. 117 °C (methanol) (Found: C, 62.0; H, 5.75; N, 4.6. $C_{13}H_{17}NO_3S$ requires C, 61.85; H, 6.0; N, 4.8%); τ 2.2—3.3 (8 H, m, aromatic), 5.0 (1 H, t, exchangeable, NH), 6.0 (2 H, d, CH$_2$), 6.25 (3 H, s, OMe), and 7.6 (3 H, s, tosyl-Me); $\nu_{max.}$ (Nujol) 3 200 cm^{-1} (NH).

Hydrogenation of the N-*Tosylimine* (23a) *at Elevated Pressure*.—The N-tosylimine (23a) (1.44 g, 5 mmol) and 10%

palladium-on-charcoal (0.14 g) in dioxan (100 cm^3) which contained concentrated hydrochloric acid (5 cm^3) were shaken with hydrogen at 40 lb in^{-2} for 15 h. The catalyst was filtered off and the solvent removed to give a semi-crystalline solid which was washed with 2M sodium hydr-oxide and extracted with chloroform. Concentration under reduced pressure of the dried (Na$_2$SO$_4$) extract yielded an oil (0.5 g) which was distilled under reduced pressure to yield p-methylanisole as an oil, b.p. 174 °C, identical with an authentic sample. Acidification of the basic aqueous phase with concentrated sulphuric acid produced a precipitate which was filtered off to isolate toluene-p-sulphonamide as a white solid (0.6 g, 70%), m.p. 140 °C (methanol), identical with an authentic sample.

2-*Hydroxy*-N-*tosylbenzylamine*.—To a solution of the N-tosylimine (23b) (1 g, 3.15 mmol) in ethanol (70 cm^3) and THF (10 cm^3) was added sodium borohydride (0.3 g, 25 mmol), slowly and with stirring, at 25 °C. The solution was then stirred for a further 16 h at 25 °C and then eva-porated under reduced pressure. The residue was dissolved in chloroform and washed successively with 2M hydrochloric acid and water. The organic phase was removed, dried (Na$_2$SO$_4$), and the solvent evaporated off under reduced pressure to yield a solid which was crystallised from di-chloromethane–light petroleum (b.p. 60—80 °C) to give the *product* (0.4 g, 46%) as white crystals, m.p. 110 °C (Found: C, 60.25; H, 5.45; N, 5.05. $C_{14}H_{15}NO_3S$ requires C, 60.65; H, 5.45; N, 5.05%); τ 2.1—3.4 (8 H, m, aro-matic), 4.6 (1 H, t, exchangeable, NH), 4.59 (1 H, s, ex-changeable, OH), 5.9 (2 H, d, CH$_2$), and 7.6 (3 H, s, Me); $\nu_{max.}$ (Nujol) 3 300 (OH) and 3 200 cm^{-1} (NH).

α-*Diethoxyphosphoryl*-p-*methoxy*-N-*tosylbenzylamine* (15c).—To a solution of the N-tosylimine (23a) (6 g, 21 mmol) in anhydrous benzene (70 cm^3) on a Dean and Stark apparatus was added diethyl phosphonate (3 g, 3 cm^3, 21.6 mmol) and sodium (0.06 g, 2.6 mmol). The resultant suspension was stirred under reflux for 3 d, then cooled and extracted with 2M sodium hydroxide. The basic aqueous extract was acidified with concentrated sulphuric acid and the liberated oil was extracted with chloroform. The organic phase was dried (Na$_2$SO$_4$) and the solvent removed under reduced pressure to yield the *product* (15c) (6.5 g, 76%) as a white solid, m.p. 114 °C [ether–light petroleum (b.p. 60—80 °C)] (Found: C, 53.6; H, 6.4; N, 3.2. $C_{19}H_{26}NO_6PS$ requires C, 53.4; H, 6.1; N, 3.3%); τ 2.4—3.5 (9 H, m, aromatic, 1 H exchangeable, NH), 5.0—5.4 (1 H, d of d, CH), 5.7 (4 H, m, CH_2Me), 6.3 (3 H, s, OMe), 7.7 (3 H, s, tosyl-Me), and 8.5—9.0 (6 H, d of t, 2 × MeCH$_2$); $\nu_{max.}$ (Nujol) 3 120 cm^{-1} (NH).

N-*Benzyl*-α-*diethoxyphosphoryl*-p-*methoxy*-N-*tosylbenzyl-amine* (15d).—To a solution of the sulphonamide (15c) (4.3 g, 10 mmol) in acetone (70 cm^3), which contained potassium carbonate (1.5 g, 10 mmol) and was under reflux, was added benzyl bromide (1.7 g, 10 mmol) in acetone (10 cm^3). The suspension was stirred under reflux for an additional 16 h, then filtered off and evaporated under reduced pressure to yield a residue which was dissolved in chloroform and washed with 2M sodium hydroxide and water. The organic phase was removed, dried (Na$_2$SO$_4$), and the solvent re-moved to yield an oil which crystallised from ether–light petroleum, (b.p. 60—80 °C) to give the *product* (15d) (4.1 g, 79%) as a white solid, m.p. 60 °C (Found: C, 60.15; H, 6.3; N, 2.6; $C_{26}H_{32}NO_6PS$ requires C, 60.3; H, 6.2; N, 2.7%); τ 2.4—3.3 (13 H, m, aromatic), 6.25—6.5 (1 H, 2 × s, CH), 5.1—5.6 (2 H, m, CH_2Ph), 5.8—4.2 (4 H, m, 2 ×

CH_2Me), 7.7 (3 H, s, tosyl-Me), 8.7—9.0 (6 H, d of t, 2 × MeCH$_2$), and 6.3 (3 H, s, OMe); $\nu_{max.}$ (Nujol) 1 220 cm^{-1} (P=O).

N-*Benzyl-α-diethylphosphoryl-p-methoxybenzylimine* (16).—To a solution of the N-benzylsulphonamide (15d) (2.5 g, 5.1 mmol) in anhydrous methanol (70 cm^3) was added a solution of sodium methoxide in methanol [prepared from sodium (0.23 g, 10 mmol) in anhydrous methanol (10 cm^3)]. The resultant solution was refluxed for 16 h and then cooled and evaporated under reduced pressure. The residue was dissolved in ethyl acetate and washed with water. The organic phase was dried (Na$_2$SO$_4$) and evaporated under reduced pressure to yield an oil which was distilled under reduced pressure to give the *product* (16) (1.5 g, 83%) as a pale green oil, b.p. 200 °C at 0.01 Torr (kugelrohr) (Found: C, 62.8; H, 6.5; N, 3.8%; M^+, 361.144. C$_{19}$H$_{24}$NO$_4$P requires C, 63.15; H, 6.7; N, 3.9%; M, 361.1443); τ 1.6—3.2 (9 H, m, aromatic), 5.0—5.2 (2 H, 2 × s, CH$_2$), 5.8—6.3 (4 H, m, 2 × CH$_2$), 6.2 (3 H, s, OMe), and 8.7—8.9 (6 H, t, 2 × Me); $\nu_{max.}$ (Nujol) 1 640 cm^{-1} (C=N).

[p-*Nitro-α-(N-tosylamino)benzylthio*]acetic *Acid* (17a).— To a solution of the N-tosylimine (23c) (6 g, 20 mmol) and thioglycolic acid (1.84 g, 20 mmol) in benzene (150 cm^3) was added benzoyl peroxide (50 mg) and the solution was re-fluxed for 48 h. The solution was cooled and the resultant precipitate was filtered off to isolate the *product* (17a) (6.6 g, 83%) as a white solid, m.p. 184 °C [acetone–light petroleum (b.p. 60—80 °C)] (Found: C, 48.65; H, 4.2; N, 6.85; C$_{16}$H$_{16}$N$_2$O$_6$S$_2$ requires C, 48.45; H, 4.05; N, 7.05%); τ 1.9—2.8 (10 H, m, 2 exchangeable, 8 aromatic + OH and NH), 4.1 (1 H, s, CH), 6.6 (2 H, d, s-CH$_2$), and 7.7 (3 H, s, Me); $\nu_{max.}$ (Nujol) 3 280 (NH) and 1 700 cm^{-1} (C=O).

2-*Amino-4-phenylthiazol*-5(4H)-*one* (22).—To a solution of phenylglyoxal hydrate (12 g, 80 mmol) and thiourea (4.8 g, 80 mmol) in toluene (100 cm^3) was added BF$_3$–Et$_2$O (0.25 cm^3, 0.288 g, 2 mmol) and the stirred solution was refluxed on a Dean and Stark apparatus for 16 h. The solution was then cooled and the precipitated solid was filtered off. Recrystallisation from ethanol gave the *product* (22) (12 g, 78%) as red crystals, m.p. 230 °C (Found: C, 56.0; H, 4.4; N, 14.3%; M^+, 192.0362. C$_9$H$_8$N$_2$OS requires C, 56.25; H, 4.2; N, 14.55%; M^+, 192.0357); τ\{[^{2}H$_6$]dimethyl sulphoxide\} 2.5—2.8 (5 H, m, aromatic), 4.6 (1H, s, CH), and 4.5—4.8 (2 H, s, NH$_2$, exchangeable); $\nu_{max.}$ (Nujol) 3 300—3 060 (NH$_2$) and 1 740 cm^{-1} (S–C=O).

REFERENCES

[1] Part 4, W. R. McKay and G. R. Proctor, preceding paper.
[2] E. D. Hannah, G. R. Proctor, and M. A. Rehman, *J. Chem. Soc. C,* 1967, 256.
[3] T. Bryce, G. R. Proctor, and M. A. Rehman, *J. Chem. Soc.,* 1965, 7105.
[4] G. R. Proctor and M. A. Rehman, *J. Chem. Soc. C,* 1967, 2696.
[5] E. Negishi and A. R. Day, *J. Org. Chem.,* 1965, **30**, 43.
[6] E. Fraser, W. Paterson, and G. R. Proctor, *J. Chem. Soc.,* 1963, 5107.
[7] G. Cavallini, E. Massarani, and D. Nardi, *J. Med. Pharm. Chem.,* 1960, **2**, 99.
[8] D. D. Berge and A. V. Kale, *Indian J. Chem.,* 1980, **19**, 150.
[9] H. McNab and D. M. Smith, *J. Chem. Soc., Perkin Trans. 1,* 1973, 1310.
[10] J. Machin, R. K. Mackie, H. McNab, G. A. Reed, A. J. G. Sagar, and D. M. Smith, *J. Chem. Soc., Perkin Trans. 1,* 1976, 394.
[11] D. M. Smith, personal communication.
[12] J. A. Deyrup and C. L. Moyer, *J. Org. Chem.,* 1969, **34**, 175.
[13] J. Schlademan and R. E. Partch, *J. Chem. Soc., Perkin Trans. 1,* 1972, 213.
[14] A. Cook, G. Harris, I. Heilbron, and G. Shaw, *J. Chem. Soc.,* 1948, 1056.
[15] C. Roussel, M. Chanon, and R. Barone, 'Heterocyclic Compounds,' ed. J. V. Metzger, J. Wiley, New York, 1979, part 2, p. 426.
[16] R. Albrecht and G. Kresze, *Chem. Ber.,* 1965, **98**, 1431.
[17] R. Merten and B. Muller, *Angew Chem.,* 1962, **74**, 866.
[18] G. R. Krow, C. Johnson, and M. Boyle, *Tetrahedron Lett.,* 1978, 1971.
[19] T. Tsuji, H. Ishitobi, and H. Tanida, *Bull. Chem. Soc. Jpn.,* 1971, **44**, 2447.
[20] N. D. Doktorova, *Tetrahedron,* 1969, **25**, 3529.
[21] P. G. Bird and W. J. Irwin, *J. Chem. Soc., Perkin Trans. 1,* 1973, 2664; A. K. Rose, S. G. Amin, J. C. Kapur, and M. S. Manhas, *J. Chem. Soc., Perkin Trans. 1,* 1976, 2193.
[22] T. Kamiya, M. Hashimoto, O. Nakaguchi, and T. Oku, *Tetrahedron,* 1979, **35**, 323.
[23] W. J. Hale and N. A. Lange, *J. Am. Chem. Soc.,* 1919, **41**, 379.
[24] E. C. Taylor, A. McKillop, and G. H. Hawks, *Org. Synth.,* 1972, **52**, 36.
[25] J. B. Wolff II and C. Niemann, *Biochemistry,* 1963, **2**, 493.
[26] P. S. Duckworth, *J. Chem. Soc.,* 1956, 1755.
[27] E. J. Corey, N. R. Jones, and D. Seebach, *J. Org. Chem.,* 1968, **33**, 300.