Reduction of Oximes and Aliphatic Nitro Compounds to Imines for Further *in situ* Reactions: A Novel Synthesis of Pyrroles and Pyrrolin-2-ones

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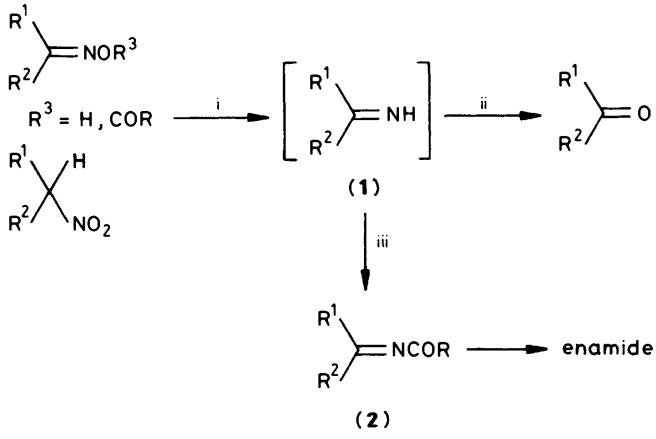
Tributylphosphine–diphenyl disulphide is a self-drying reagent capable of reducing ketoximes and secondary aliphatic nitro compounds to the corresponding imines under strictly anhydrous conditions at room temperature. The imine may be hydrolysed to a ketone, acetylated to give an enamide, reduced to an amine, or captured by hydrogen cyanide to produce an α-amino nitrile. In the case of 1,4-nitro ketones or esters, intramolecular cyclisation leads to pyrroles or pyrrolin-2-ones. Aldoximes and primary nitro compounds are converted into nitriles by the reagent. Hydroxamic acids are reduced to the corresponding amides.

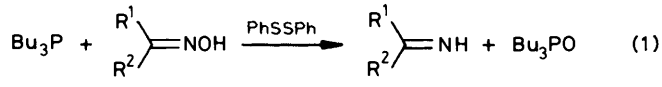
Reductive cleavage of oximes, oxime acetates, and nitro compounds with low-valent transition metal salts is a well established method for the obtention of the corresponding carbonyl derivatives.[1,2] The reduction is believed to proceed by way of the imine (**1**) which suffers a rapid hydrolysis in the usually aqueous and sometimes acidic medium (Scheme 1).



Scheme 1. *Reagents and reactions:* i, Reduction; ii, H_2O; iii, $(RCO)_2O$

The exceptional sensitivity of the unsubstituted imines to hydrolysis usually precludes their isolation and even trapping under such conditions. It is possible, in the case of oximes, to perform the reduction in the presence of a carboxylic acid anhydride which acts both as water scavenger and trap for the imine.[2] The initially produced *N*-acylimines (**2**) tautomerise under the reaction conditions to the more stable and useful enamides[3] (Scheme 1). Nevertheless, this modification is limited to the synthesis of enamides.

In two recent preliminary communications,[4] we described a novel and more general solution to this problem, applicable to both oximes and nitro compounds and which allows a much greater flexibility in the manipulation of the intermediate imine. We herein present this work in more detail along with additional examples and some mechanistic studies. Our conception, involving the use of tributylphosphine and diphenyl disulphide, is based on the strong affinity of trivalent phosphorus for oxygen and the relative weakness of the N–O bond [equation (1)].



(1)

The tributylphosphine–diphenyl disulphide reagent was introduced by Hata and co-workers[5] for the Mitsunobu-type transformation of primary or secondary alcohols into the corresponding phenyl thioethers (sulphides). It was subsequently shown to be also capable of converting aldehydes (but not ketones) into phenyl thioacetals and of effecting the opening of epoxides.[5]

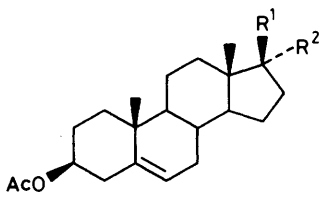
We have found that ketoximes and aliphatic and alicyclic secondary nitro compounds, when exposed to a mixture of tributylphosphine and diphenyl disulphide, undergo a totally different reaction resulting in a net deoxygenation to give the imine. Thus, addition of tributylphosphine to a mixture of diphenyl disulphide and oxime (**3**) at room temperature gave, *after an aqueous work-up*, pregnenolone acetate (**4**) in 90% yield. Steroid oximes (**5**), (**16**), and (**18**) behaved similarly affording the corresponding ketones (**6**), (**17**), and (**19**) in good yields (70—85%).

Combinations of phosphines and disulphides react rapidly and irreversibly with water.[6] The reagent is therefore self-drying and thereby protects the labile imine against premature hydrolysis by ensuring a rigorously anhydrous medium. Under such conditions, *in situ* capture of the imine is easily achieved leading to a variety of synthetically useful products.

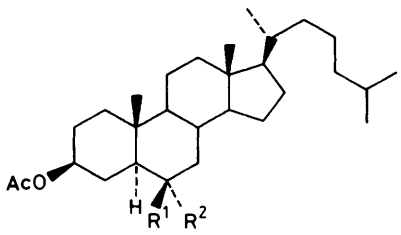
Thus, replacement of the aqueous work-up in the case of oxime (**3**) by addition of acetic anhydride and heating affords an excellent yield (94%) of the *NN*-diacetylenamine (**7**). Alternatively, the intermediate imine may be reduced to the amine using sodium cyanoborohydride and acetic acid. Amide (**9**) was thus obtained from oxime (**5**) in 93% yield after acetylation of amine (**8**) to facilitate isolation. Since oximes are generally prepared from the corresponding ketones, this process constitutes an overall reductive amination of even hindered ketones. These are usually recalcitrant substrates in the direct reductive amination employing sodium cyanoborohydride.[7] In addition, the compatibility, *a priori*, of a wide variety of reducing agents with the deoxygenation medium should allow better control of the stereochemical outcome in cases where this is important.[8]

The imine may also be intercepted with hydrogen cyanide. Sodium cyanide is simply added at the beginning of the reaction so as to be thoroughly dried by the reagent. Once the reaction is over, addition of acetic acid liberates the hydrogen cyanide, which reacts rapidly with the imine. By such a procedure, α-amino nitrile (**10**) was obtained directly in 88% yield from compound (**5**). α-Amino nitriles are important as immediate precursors of α-amino acids (the Strecker synthesis[9]).

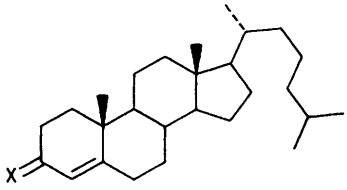
In instances where the imine is prone to dimerisation, trimerisation, *etc.* as is usually the case with low-molecular-weight imines, it is best to capture it as formed. This keeps imine



(3) R^1 = C(=NOH)Me, R^2 = H
(4) R^1 = COMe, R^2 = H
(5) R^1R^2 = NOH
(6) R^1R^2 = O
(7) R^1R^2 = =C(NAc$_2$)Me
(8) R^1 = NH_2, R^1 = H
(9) R^1 = NHAc, R^2 = H
(10) R^1 = NH_2, R^2 = CN
(11) R^1 = CH(=NOH), R^2 = H
(12) R^1 = CN, R^2 = H
(13) R^1 = C(=NSPh)Me, R^2 = H
(14) R^1R^2 = NSPh
(15) R^1 = CH_2NO_2, R^2 = H



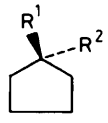
(16) R^1R^2 = NOH
(17) R^1R^2 = O



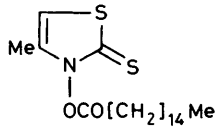
(18) X = NOH
(19) X = O

concentration low and suppresses self-condensation. For example, the oxime of cyclopentanone, compound (**20**), is cleanly converted into *N*-[1-(phenylthio)cyclopentyl]acetamide (**21**) (84%) by performing the reduction in the presence of *S*-phenyl thioacetate ($PhSCOCH_3$), a mild acetylating agent compatible with our reducing system. Compounds analogous to (**21**) have been used as substrates in radical cyclisation reactions induced by tributylstannane.[10]

We have found tributylphosphine–diphenyl disulphide to be, by far, the best combination. If the more electrophilic 2,2′-dipyridyl disulphide (**23**) is employed in the case of oxime (**3**) for instance, the reduction to the corresponding imine (84%) is very slow. Oxime (**5**), in contrast, reacts rapidly, but the product is the lactam (**25**) (89%), produced by a Beckmann rearrangement. Oximes at the 17-position of steriods are particularly prone to such rearrangements because of the strain inherent in the *trans*-



(20) R^1R^2 = NOH
(21) R^1 = NHCOMe, R^2 = SPh



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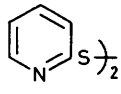

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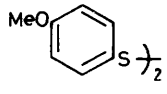

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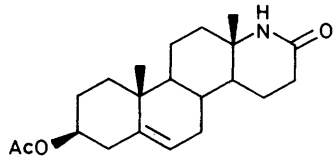


(25)

Aldoximes, in contrast to the ketoximes so far discussed, do not undergo the reduction. Instead, they suffer clean dehydration to nitriles as, for example, the conversion of (**11**) into (**12**) (85%).

fused *C,D* rings. If, in this case, the more electron-rich *p,p′*-dimethoxydiphenyl disulphide (**24**) is used, the major pathway is the reduction to imine but the reaction is again too slow for practical purposes. No reaction occurs if tributylphosphine is

replaced by triphenylphosphine or if either the phosphine or the disulphide is omitted.

As implicit in equation (1), the role of the disulphide is catalytic. Indeed, if allowance is made for its irreversible consumption when water is present, it may be recovered almost intact by quick elution (on silica) of the concentrated reaction mixture. Nevertheless, for reasons that will become apparent shortly, it is best to have more or less equimolar amounts in order to have an acceptable reaction time.

A further serendipitous finding of mechanistic and synthetic interest concerns the effect of a large excess of disulphide on the reaction course. Under such conditions, oxime (**3**) afforded a beautifully crystalline product identified as the *S*-phenyl thio-oxime (**13**) in yields of up to 60%. Oxime (**5**) behaved similarly to give compound (**14**) (50%). The same compound could be obtained (40%) by trapping the imine formed in the normal reduction with benzenesulphenyl chloride. Surprisingly, similar unsubstituted *S*-phenyl thio-oximes, especially those from hindered ketones, have been hitherto rather inaccessible.[11]

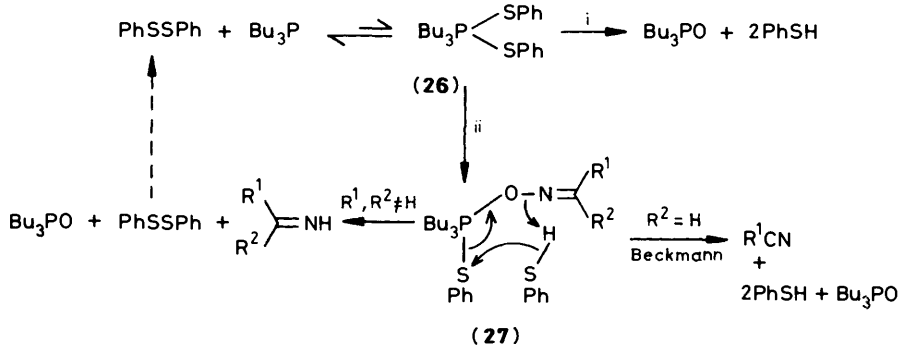
A mechanism in accord with the experimental observations presented so far is outlined in Scheme 2. Tributylphosphine and diphenyl disulphide react reversibly to generate small quantities of the reactive phosphorane (**26**). The equilibrium strongly favours the starting materials. Indeed, collapse of similar electrochemically produced phosphoranes by reductive elimination of disulphide is the basis of a recent method for the preparation of unsymmetrical disulphides.[12] Overman and co-workers[6] have reached similar conclusions following stopped-flow kinetic studies. Furthermore, the phosphorus n.m.r. spectrum of a mixture of tributylphosphine and diphenyl disulphide contains only two signals, attributed to starting phosphine and small amounts of tributylphosphine oxide impurity. No other signal, attributable to phosphorane (**26**), could be detected. On addition of water, the tributylphosphine signal disappears with a corresponding increase in the signal of the tributylphosphine oxide.

diphenyl disulphide which is thus regenerated. In accord with this proposed step is the significant increase in the reaction rate on deliberate addition of thiophenol. This further indicates that the fragmentation of intermediate (**27**) to give imine is slow and surely rate determining.

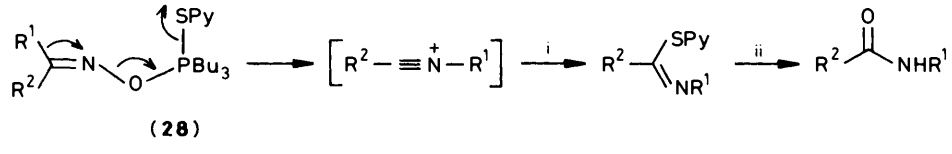
The equilibrium to give phosphoranes such as (**26**) was found by Overman and co-workers[6] to be very sensitive to the nature of the substituents on the disulphide, being strongly favoured by electron-withdrawing groups. Predictably, therefore, the formation of phosphorane (**28**) (Scheme 3) in the case of dipyridyl disulphide is relatively fast. This is confirmed by the rapid Beckmann rearrangement undergone by oxime (**5**) using this disulphide. When Beckmann rearrangement is not particularly easy however, collapse of intermediate (**28**) to give imine is slow. This may be ascribed to the lower '*S*-nucleophilicity'[13] of pyridine-2-thiol on the one hand and a modification in the polarisation of the P–S bond more propitious to a Beckmann rearrangement (flow of electrons in the opposite direction) on the other (Scheme 3).

In the case of more electron-rich disulphides (*e.g.*, *p,p'*-dimethoxydiphenyl disulphide) the formation of the corresponding phosphorane is disfavoured and probably rate determining. It appears therefore that diphenyl disulphide is a good compromise, allowing convenient reaction rates. Furthermore, it is evident from the above discussion that the dependence of the rate on disulphide concentration is complex. The unfavourable equilibrium to give phosphorane (**26**) and the slow collapse of intermediate (**27**) impose a minimum concentration of disulphide below which reactions are inconveniently slow. In addition allowance must be made for its irreversible consumption by traces of water present in the medium.

The formation of the *S*-phenyl thio-oxime (**30**) in the presence of excess of disulphide may be explained by the series of equilibria shown in Scheme 4. The imine reacts with the phosphorane (**26**) to give intermediate (**29**) which by reductive



Scheme 2. *Reagents:* i, H_2O; ii, $R^1R^2C{=}NOH$



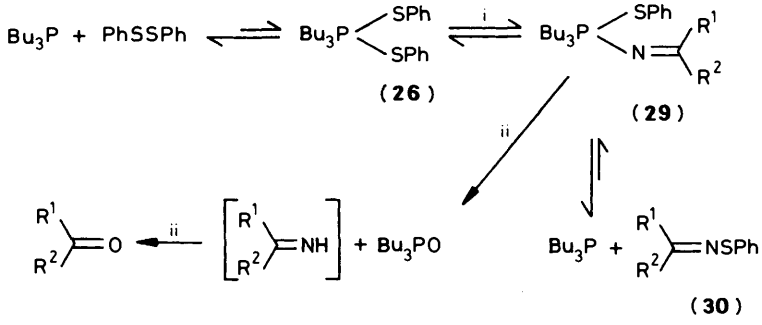
Scheme 3. *Reagents:* i, PyS^-; ii, H_2O

In the presence of oxime, the intermediate (**26**) reacts to give the pentavalent phosphorus complex (**27**) and thiophenol (Scheme 2). In the case of aldoximes (R^2 = H) a normal Beckmann fragmentation produces the nitrile. In contrast, the ketoxime-derived complex (**27**) suffers a thiophenol-induced fragmentation to give imine, tributylphosphine oxide, and elimination produces the thio-oxime (**30**) and tributylphosphine. Under the usual conditions the thio-oxime [*e.g.* (**13**)] is produced in small amounts, if at all. If at the end of the reduction a large excess of diphenyl disulphide is added, the quantity of thio-oxime increases dramatically (*ca.* 40%), in accord with a sulphenylation of the imine by the reagent (derived from the

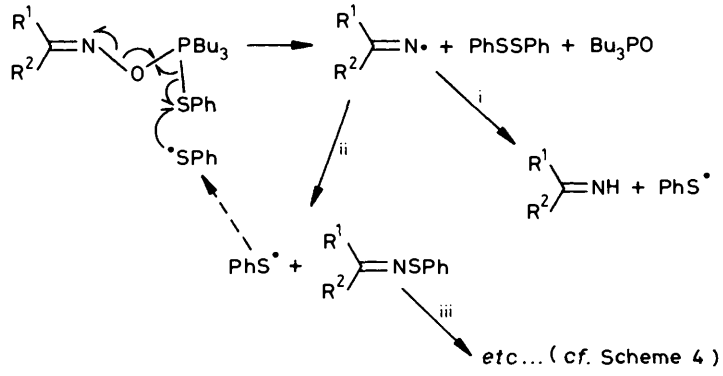
initial excess of tributylphosphine) as depicted in Scheme 4. Sulphenylation by diphenyl disulphide alone requires silver ion catalysis[11] and is therefore unlikely under the present conditions. Further in support of this mechanism is the observation that addition of thiophenol not only increases the rate of reduction but also results in a decrease in the amount of thio-oxime (**30**) produced. This is a consequence of the shift of the equilibrium in Scheme 4 towards phosphorane (**26**) caused by the thiophenol at the expense of intermediate (**29**).

reduction of oxime (**5**) was performed in refluxing pyridine, the major product was the lactam (**25**) (*via* Beckmann rearrangement) as would be expected under such vigorous conditions. The small amount of 17-oxo steroid produced, however, was of the natural ketone (**6**). None of the 13-epimer (**33**) could be detected. The iminyl radical is therefore an unlikely intermediate in the reduction.

Additional evidence against a radical mechanism was obtained by operating in the presence of thiohydroxamic ester



Scheme 4. *Reagents:* i, $R^1R^2C{=}NH$; ii, H_2O

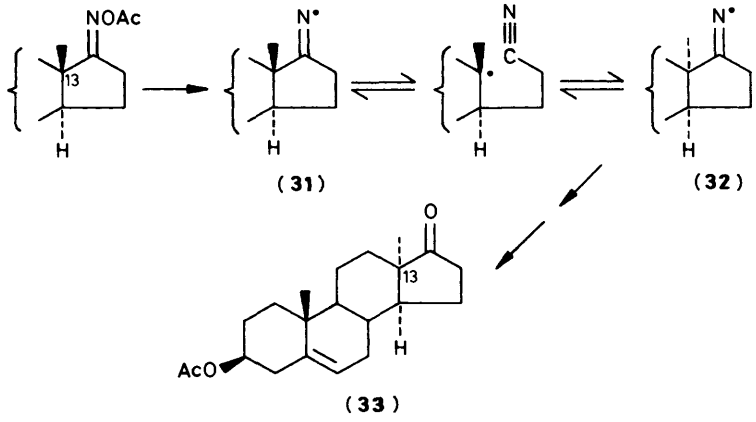


Scheme 5. *Reagents:* i, PhSH; ii, PhSSPh; iii, Bu_3P

Although a radical-chain mechanism involving iminyl radicals, a variant of which is presented in Scheme 5, would also account for the experimental data, it can be rejected as the major pathway of the reduction on the basis of the following observations. Iminyl radicals (**31**) at the 17-position of steroids are known to undergo ring opening followed by ring closure to give the more stable 13α-epimer (**32**) (Scheme 6). Indeed this is the best method for preparing 13-episteroids.[14] When the

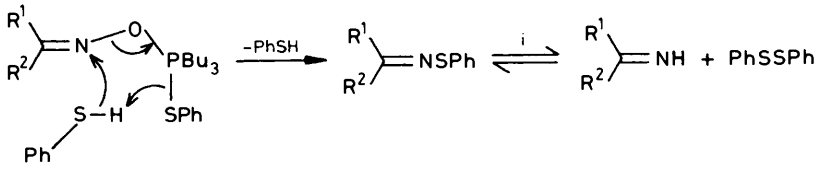
(**22**), known from other ongoing work to be a good trap for phenylthiyl radicals, giving products resulting from decarboxylation of the palmitic acid residue.[15] When the reduction was performed in the presence of compound (**22**), the reaction proceeded normally and no radical-derived products were observed. Finally the reduction did not appear to be significantly influenced by light or oxygen.

A third possible mechanism is the direct, Mitsunobu-type

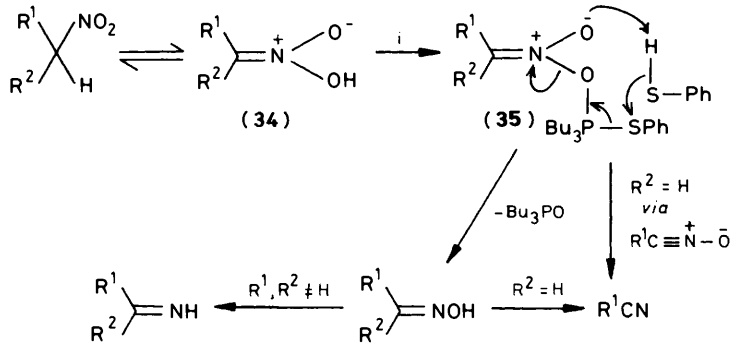


Scheme 6.

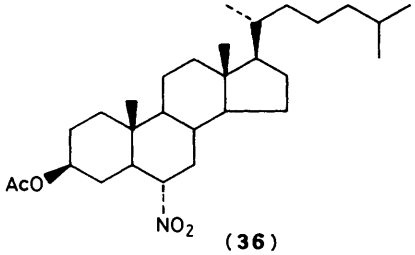
displacement of the oxygen by the thiol (Scheme 7). Despite its simplicity, this mechanism is not likely in view of the relative insensitivity of the reduction to steric hindrance in contrast to the other Mitsunobu-type reactions exhibited by the reagent. Furthermore, if such a mechanism is operating, it is difficult to understand the very slow reduction of oxime (**3**) when 2,2′-dipyridyl disulphide is used since the fragmentation in Scheme 7



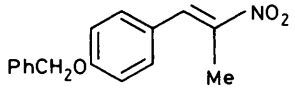
Scheme 7. *Reagents:* i, PhSH (Bu_3P catalysis)



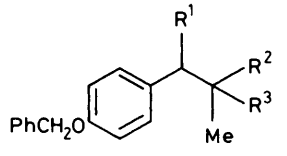
Scheme 8. *Reagent:* i, $Bu_3P(SPh)_2$



(**36**)



(**37**)



(**38**) $R^1 = R^2 = H$, $R^3 = NO_2$

(**39**) $R^1 = H$, $R^2R^3 = O$

(**40**) $R^1 = SPh$, $R^2 = H$, $R^3 = NO_2$

(**41**) $R^1 = SPh$, $R^2R^3 = O$

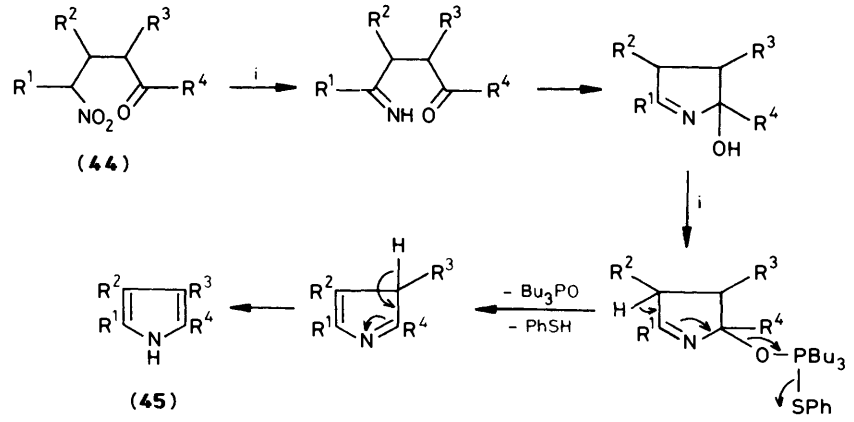
(**42**) $R^1 = H$, $R^2R^3 = NH$

(**43**) $R^1 = H$, $R^2 = NH_2$, $R^3 = CN$

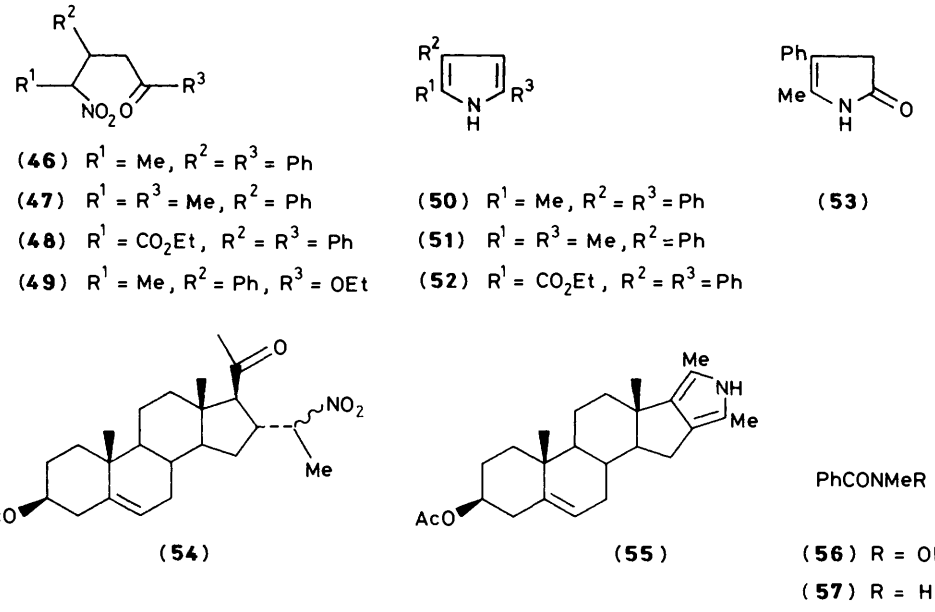
is analogous, as far as electronic flow is concerned, to that of the Beckmann rearrangement depicted in Scheme 3.

The reduction of nitro compounds probably follows a similar course (Scheme 8). The mildly basic tributylphosphine catalyses the formation of nitronate anion (**34**) which undergoes a dehydration in the case of a primary nitro group, giving ultimately the nitrile. In principle this transformation can proceed either through the aldoxime or by an initial dehydration to the corresponding nitrile oxide (Scheme 8). The latter reacts with the thiophenol thus produced before undergoing deoxygenation by the reagent, *i.e.* by the following sequence: (**35**) $\longrightarrow R^1C{\equiv}N^+{-}O^- \longrightarrow R^1C(SPh){=}NOH \longrightarrow R^1C(SPh){=}NH \longrightarrow R^1CN + PhSH$. Secondary nitro compounds lead to the imine conceivably through the ketoxime. Thus nitro steroid (**15**) afforded a quantitative yield of nitrile (**12**), whereas 6α-nitrocholestan-3β-yl acetate (**36**) gave the corresponding ketone (**17**) in 55% yield after aqueous work-up. Similarly, ketone (**39**) was produced in 82% yield from the nitropropane derivative (**38**). An interesting variant of this overall reductive Nef reaction is to expose a nitro-olefin, *e.g.* (**37**), to a mixture of thiophenol, diphenyl disulphide, and a little triethylamine in tetrahydrofuran (THF) to form *in situ* the Michael adduct (**40**). Addition of tributylphosphine effects the reduction to give directly the α-phenylthio ketone (**41**) in 75% yield. As in the case of ketoximes, the intermediate imine, *e.g.* (**42**), could be easily captured by hydrogen cyanide for example to produce the corresponding α-amino nitrile (**43**) (70%) in one step.

So far only external trapping agents have been employed. Clearly, if the imine could be trapped intramolecularly the reduction would lead to a variety of nitrogen heterocycles and the synthetic utility of this reduction considerably augmented. This conception is illustrated by the novel transformation of 1,4-nitro ketones (**44**) into pyrroles (**45**) (Scheme 9). As indicated in the Scheme, loss of a molecule of water is involved in one of the



Scheme 9. *Reagent:* i, Bu_3P, PhSSPh



When nitro ketone (**46**) was subjected to tributylphosphine and diphenyl disulphide in THF, a smooth reaction occurred to give the expected pyrrole (**50**) in 90% yield. Nitro ketones (**47**), (**48**), and (**54**) underwent a similar reduction and cyclisation to produce the corresponding pyrroles (**51**) (90%), (**52**) (65%), and (**55**) (85%) respectively. In the case of ester (**52**), replacing the THF with dichloromethane proved advantageous. In view of the ready availability of 1,4-nitro ketones by Michael addition to enones or by addition of enolates to nitro olefins,[1a] this method provides a simple and expedient access to a wide variety of pyrroles.[16,17]

If an ester group is used to capture the imine, *i.e.* (**44**; R^4 = OR), a pyrrolin-2-one is produced. Such compounds are important in the synthesis of bile pigments and 2,2′-bipyrroles.[16] Thus reductive cyclisation of nitro ester (**49**), obtained quantitatively by base-catalysed Michael addition of nitroethane onto ethyl cinnamate, afforded pyrrolinone (**53**) in 61% yield.

In addition to reducing ketoximes and secondary nitro compounds, we have also found the reagent to be capable of deoxygenating hydroxamic acids as illustrated by the transformation of *N*-methylbenzohydroxamic acid (**56**) into *N*-methylbenzamide (**57**) in 98% yield.

Experimental

M.p.s are uncorrected. Unless otherwise stated, n.m.r. data are for deuteriochloroform solutions with tetramethylsilane as internal standard. I.r. spectra are of neat liquids or of Nujol mulls in the case of solids. Rotations were determined in $CHCl_3$ at room temperature. Sodium sulphate was used as drying agent for organic layers.

General Procedure for the Reductive Cleavage of Oximes.—This is illustrated by the conversion of oxime (**16**) into ketone (**17**).

To a solution of oxime (**16**)[18] (200 mg) and diphenyl disulphide (200 mg) in dry THF (3 ml) under an inert atmosphere was added tributylphosphine (0.4 ml). After 30 min at room temperature, the reaction mixture was poured into 5% aqueous potassium carbonate, extracted with dichloromethane, and the organic layer was dried and concentrated. Chromatography of the residue on silica (dichloromethane) gave 6-oxo-5α-cholestan-3β-yl acetate (**17**) (169 mg, 85%) as a white crystalline solid, identical with authentic material.

20-(N,N-*Diacetylamino*)*pregna*-5,17(20)-*dien*-3β-*yl Acetate* (**7**).—Pregnenolone acetate oxime[2] (**3**) (150 mg) and diphenyl disulphide (150 mg) in pyridine (2 ml) were treated with tributylphosphine (0.5 ml) under nitrogen. After 0.5 h at room

temperature, the mixture was treated with acetic anhydride (2 ml) and was then heated at 100 °C for 3 h. The solvents were evaporated off under reduced pressure and the residue was heated with more acetic anhydride (5 ml) to reflux for 1.5 h. Removal of the excess of acetic anhydride under reduced pressure and chromatography of the residue [EtOAc–hexane (1:2)] gave compound (**7**) as a white crystalline solid (168 mg, 94%), identical with authentic material.[2]

17β-*Acetamidoandrost*-5-*en*-3β-*yl Acetate* (**9**).—Tributylphosphine (0.7 ml) was added to a solution of oxime (**5**) (345 mg) and diphenyl disulphide (250 mg) in dry THF (4 ml) under an inert atmosphere. After 2 h at room temperature, the mixture was treated with sodium cyanoborohydride (190 mg) followed by glacial acetic acid (0.5 ml) and, after a further 10 min, with acetic anhydride (0.5 ml). The resulting mixture was kept at room temperature for 49 h, the poured into 5% aqueous potassium carbonate, and the resulting precipitate was filtered through Celite. The solid was washed with water, then with dichloromethane, and the organic layer from the filtrate was dried, and concentrated under reduced pressure. The residue was purified by chromatography on silica [dichloromethane, then dichloromethane–methanol (95:5)] to give a semi-solid (*ca.* 450 mg). Trituration with hexane and careful decantation removed the remaining tributylphosphine oxide contaminant, leaving the title acetate as a white crystalline solid (349 mg, 93%), m.p. 294—299 °C (from acetone); $[\alpha]_D$ −100° (*c* 0.57) (lit.,[19] m.p. 296 °C; $[\alpha]_D$ −88°).

17β-*Amino*-17α-*cyanoandrost*-5-*en*-3β-*yl Acetate* (**10**).—To an ice-cooled mixture of oxime (**5**) (200 mg), diphenyl disulphide (200 mg), and sodium cyanide (300 mg) in dry THF (4 ml) under an inert atmosphere was added tributylphosphine (0.5 ml). After 1 h, acetic acid (1 ml) was added and the mixture was allowed to warm to room temperature overnight. It was then poured into 5% aqueous K_2CO_3, extracted with dichloromethane, and the extract was dried, and concentrated under reduced pressure. Purification of the residue by chromatography on silica [dichloromethane, then dichloromethane–ethyl acetate (1:1)] gave *aminonitrile* (**10**) as white crystals (183 mg, 88%), m.p. 149—152 °C (from methanol); $[\alpha]_D$ −91° (*c* 0.32); $\nu_{max.}$ 3 300, 2 200, and 1 735 cm^{-1}; δ_H 5.20 (1 H, br, 6-H), 4.50 (1 H, br, 3α-H), 2.00 (3 H, s, OAc), and 1.05 and 0.80 (6 H, 2 s, 10-and 13-Me); *m/z* 356 (M^+, weak), 296, and 269 (Found: C, 72.7; H, 9.1; N, 7.4. $C_{22}H_{32}N_2O_2 \cdot \frac{1}{2}MeOH$ requires C, 72.53; H, 9.22; N, 7.51%).

N-[1-(*Phenylthio*)*cyclopentyl*]*acetamide* (**21**).—To a water-cooled mixture of *S*-phenylthioacetate (4 g) and diphenyl disulphide (1.1 g) was added dropwise a solution of cyclopentanone oxime (**20**) (0.500 g) and tributylphosphine (2.2 g) in dry diethyl ether (5 ml) during 10—15 min with exclusion of moisture. After 1 h, the reaction mixture was concentrated under reduced pressure and directly purified by chromatography [first CH_2Cl_2–pentane (1:3), then CH_2Cl_2, and finally diethyl ether] to give the desired *amide* (**21**) as white crystals (0.990 g, 84%), m.p. 119—125 °C (partial decomp.) (from diethyl ether); $\nu_{max.}$ 3 260, 3 210, 3 070, 1 660, and 1 560 cm^{-1}; δ_H 7.5 (5 H, Ph), 6.92 (1 H, br s, N–*H*), 1.95 (3 H, s, MeCO), and 1.4—2.6 (8 H, $[CH_2]_4$; *m/z* 235 (M^+, weak), 126 (100%), 110, and 74 (Found: C, 66.1; H, 7.3; N, 6.2. $C_{13}H_{17}NOS$ requires C, 66.34; H, 7.28; N, 5.95%).

17-*Oxo*-D-*homo*-17a-*aza*-*androst*-5-*en*-3β-*yl Acetate* (**25**).—To a solution of oxime (**5**) (100 mg) and dipyridyl disulphide (75 mg) in dry pyridine (2 ml) under an inert atmosphere was added tributylphosphine (0.2 ml). After 30 min at room temperature, the mixture was poured into dil. hydrochloric acid and extracted with dichloromethane. The extract was dried, and concentrated, and the residue was purified by chromatography on silica (diethyl ether with a trace of methanol) to give pure lactam (**25**) (84 mg, 84%). The yield was slightly higher (89%) when dichloromethane was used instead of pyridine. The product had m.p. 295—298 °C (from methanol); $[\alpha]_D$ −79° (*c* 0.20) (lit.,[20] m.p. 292—295 °C; $[\alpha]_D$ −83°).

20-*Oxopregn*-5-*en*-3β-*yl Acetate* (**4**).—To a solution of the oxime (**3**) (80 mg) and dipyridyl disulphide (60 mg) in dry pyridine (2 ml) was added tributylphosphine (0.2 ml). The mixture was heated at 50 °C under nitrogen overnight, poured into dil. hydrochloric acid, and extracted into dichloromethane. The extract was washed with water, dried, and concentrated under reduced pressure. Purification of the residue by chromatography on silica (dichloromethane) gave pregnenolone acetate (**4**) as white crystals (64 mg, 84%), identical with authentic material.

17-(*Phenylthioimino*)*androst*-5-*en*-3β-*yl Acetate* (**14**).—To a solution of oxime (**5**) (100 mg) and diphenyl disulphide (200 mg) in pyridine (2 ml) under an inert atmosphere was added tributylphosphine (0.1 ml). After being stirred at room temperature for 30 min, the mixture was poured into water and extracted with dichloromethane–pentane (1:4). The extract was washed with water and dried. Concentration under reduced pressure and purification of the residue by preparative t.l.c. [dichloromethane–diethyl ether–pentant (1:1:6)] afforded the *sulphenimine* (**14**) (55 mg, 45%), m.p. 163—165 °C (from hexane); $[\alpha]_D$ = +81° (*c* 0.62); $\nu_{max.}$ 1 735, 1 630, 1 580, and 1 240 cm^{-1}; δ_H 7.1—7.7 (5 H, m, Ph), 5.30 (1 H, m, 6-H), 4.3—4.9 (1 H, br, 3α-H), 2.00 (3 H, s, OAc), and 1.05 and 0.90 (6 H, s 2, 10- and 13-Me) (Found: C, 73.9; H, 8.0; N, 3.1; S, 7.3. $C_{27}H_{35}NO_2S$ requires C, 74.10; H, 8.06; N, 3.20; S, 7.33%).

The same compound was also prepared as follows: tributylphosphine (0.4 ml) was added to a solution of the oxime (**5**) (200 mg) and diphenyl disulphide (110 mg) in dry pyridine (2 ml). After the mixture had been stirred at room temperature under an inert atmosphere for 30 min, 1M-benzenesulphenyl chloride in dichloromethane (0.6 ml) was added and the mixture was stirred for another 30 min. The mixture was poured into water, extracted with dichloromethane, and the extract was washed successively with dil. hydrochloric acid and water, and dried. Concentration, and chromatography of the residue on silica [dichloromethane–pentane (4:3)], gave the same sulphenimine (**14**) (104 mg, 43%).

20-(*Phenylthioimino*)*pregn*-5-*en*-3β-*yl Acetate* (**13**).—Tributylphosphine (100 mg) was added to 20-(hydroxyimino) pregn-5-en-3β-yl acetate (**3**) (150 mg) and diphenyl disulphide (150 mg) in dry pyridine (3 ml) under nitrogen. After being stirred for 40 min, the reaction mixture was poured into 5% aqueous K_2CO_3 solution, then extracted with dichloromethane, and the extract was dried (K_2CO_3). The solvent was evaporated with toluene under reduced pressure and the residue was chromatographed (SiO_2; eluant hexane–dichloromethane mixtures) to give the *title sulphenimine* (**13**) (108 mg, 58%), m.p. 159—162 °C (from methanol); $[\alpha]_D$ +57° (*c*, 1); $\nu_{max.}$ 1 725, 1 680, 1 245, and 740 cm^{-1}; δ_H 6.97—7.60 (5 H, br, Ph), 5.21—5.48 (1 H, br, 6-H), 4.19—4.90 (1 H, br, 3-H), 2.0 (6 H, s, acetate and 21-H_3), 1.0 (3 H, s, 10-Me), and 0.61 (3 H, s, 13-Me) (Found: C, 74.5; H, 8.4; N, 3.1; S, 7.0. $C_{29}H_{39}NO_2S$ requires C, 74.79; H, 8.44; N, 3.01; S, 6.88%).

17β-*Nitromethylandrost*-5-*en*-3β-*yl Acetate* (**15**).—17β-Nitromethylandrost-5-en-3β-ol[21] (500 mg) was added to a solution of acetic anhydride (1 ml) in diethyl ether (10 ml), followed by a few crystals of 4-(*NN*-dimethylamino)pyridine

(DMAP). The mixture was stirred at room temperature for 1 h, water (10 ml) was added, and the ether was evaporated off. The white solid was filtered off, washed with water, and dried to give the *title acetate* (**15**) (566 mg, 99%), m.p. 173—177 °C (from methanol); $[\alpha]_D$ −70° (*c* 1.0); $\nu_{max.}$ 1 725 and 1 550 cm^{-1}; δ_H 5.30 (1 H, br, 6-H), 4.1—4.6 (3 H, br m, 3α-H and 20-H), 1.95 (3 H, s, OAc), 1.0 (3 H, s, 10-Me), and 0.7 (3 H, s, 13-Me) (Found: C, 70.3; H, 8.8; N, 3.8. $C_{22}H_{33}NO_4$ requires C, 70.37; H, 8.86; N, 3.73%).

17β-*Cyanoandrost*-5-*en*-3β-*yl Acetate* (**12**).—A filtered solution of chromium(II) chloride [prepared by adding zinc powder (0.8 g) to a solution of $CrCl_3$-$6H_2O$ (1.5 g) in water (7.5 ml) and conc. hydrochloric acid (1.5 ml), and stirring for 10—15 min under an inert atmosphere] was added to a solution of the nitro steroid (**15**) (307 mg) in acetone (50 ml) under an inert atmosphere. After 2 min, water (*ca.* 100 ml) was added gradually and the white solid was filtered off and dried. The oxime (**11**) (148 mg, 50%; mixture of *E* and *Z* isomers) thus obtained was used directly without further purification.

A solution of the oxime (85 mg), diphenyl disulphide (100 mg), and tributylphosphine (0.13 ml) in dry THF was kept at room temperature for *ca.* 30 min with exclusion of moisture. The reaction mixture was concentrated and the residue was purified by chromatography on silica [dichloromethane–hexane (1:1), then dichloromethane] to give the corresponding nitrile (**12**) as a white crystalline solid (79 mg, 98%), m.p. 224—227 °C (from methanol–dichloromethane); $[\alpha]_D$ −19° (*c* 0.63) (lit.,[22] m.p. 223.5—224.5 °C; $[\alpha]_D$ −19.8°).

The same nitrile (**12**) (82 mg, 100%) was obtained from nitro steroid (**15**) (90 mg), diphenyl disulphide (110 mg), and tributylphosphine (0.3 ml) in dry pyridine (2 ml) and a reaction time of 2 h.

6-*Oxo*-5α-*cholestan*-3β-*yl Acetate* (**17**).—To a solution of 6α-nitrocholestan-3β-yl acetate[23] (**36**) (100 mg), diphenyl disulphide (200 mg), and N^2-t-butyl-N^1,N^1,N^3,N^3-tetramethylguanidine[24] (100 mg) in dry pyridine (3 ml) under an inert atmosphere was added tributylphosphine (0.25 ml). The mixture was heated at 60 °C overnight, cooled, poured into dil. hydrochloric acid, and extracted with dichloromethane. The extract was washed with water, dried, and concentrated under reduced pressure. Chromatography of the residue on silica (dichloromethane) gave ketone (**17**) as a white crystalline solid (52 mg, ~55%). A small amount (8%) of unchanged starting material was also recovered.

1-*Benzyloxy*-4-(2-*nitroprop*-1-*enyl*)*benzene* (**37**).—A solution of 4-benzyloxybenzaldehyde (3 g) and ethylenediamine (1 drop) in nitroethane (15 ml) was heated to reflux for 3—4 h. On cooling, yellow crystals of *compound* (**37**) were deposited, and were filtered off, washed with a little methanol, and dried (2.95 g, 77%), m.p. 143—145 °C (from ethanol); $\nu_{max.}$ 1 602, 1 520, and 1 500 cm^{-1}; δ_H 8.00 (1 H, br s), 7.40 (2 H, d, *J* 8 Hz), 7.35 (5 H, br s), 6.95 (2 H, d, *J* 8 Hz), 5.10 (2 H, s), and 2.45 (3 H, s) (Found: C, 71.5; H, 5.9; N, 5.1. $C_{16}H_{15}NO_3$ requires C, 71.36; H, 5.61; N, 5.07%).

1-*Benzyloxy*-4-(2-*nitropropyl*)*benzene* (**38**).—A mixture of the nitro-olefin (**37**) (0.90 g) and sodium borohydride (0.35 g) in propan-2-ol (10 ml) and THF (3 ml) was stirred for 24 h at room temperature. The reaction mixture was then poured into water (100 ml) containing a little acetic acid (2 ml), stirred for 20 min, and *compound* (**38**) was filtered off and dried (0.95 g, ~100%), m.p. 74—76 °C (from ethanol); $\nu_{max.}$ 1 540 cm^{-1}; δ_H 7.6 (5 H, br s), 7.2 (4 H, m), 5.15 (2 H, s), 4.8 (1 H, m), 3.1 (2 H, m), and 1.55 (3 H, d, *J* 6 Hz) (Found: C, 70.4; H, 6.4; N, 5.2. $C_{16}H_{17}NO_3$ requires C, 70.83; H, 6.32; N, 5.16%).

1-(4-*Benzyloxyphenyl*)*acetone* (**39**).—To a mixture of 1-benzyloxy-4-(2-nitropropyl)benzene (**38**) (202 mg) and diphenyl disulphide (400 mg) in THF (3 ml) was added tributylphosphine (0.7 ml). The mixture was kept at room temperature for 3 h under an inert atmosphere. Water (0.6 ml) was added and, after the mixture had been left overnight at room temperature, the solvents were evaporated off and the residue was purified by chromatography [dichloromethane–hexane (1:1), then dichloromethane] to give the ketone (**39**) as a white solid (149 mg, 82%), m.p. 53—55 °C (from methanol) (lit.,[25] reported as a low melting solid); $\nu_{max.}$ 1 710 cm^{-1}; δ_H 7.5 (5 H, br s), 7.1 (4 H, m), 5.05 (2 H, s), 3.60 (2 H, s), and 2.15 (3 H, s).

1-(4-*Benzyloxyphenyl*)-1-(*phenylthio*)*acetone* (**41**).—Triethylamine (4 drops) was added to a solution of nitro olefin (**37**) (130 mg), thiophenol (120 mg), and diphenyl disulphide (220 mg) in dry THF (4 ml) under an inert atmosphere. After *ca.* 20 min, tributylphosphine (0.5 ml) was added and the mixture was left overnight at room temperature. A few drops of water were added, the solvent was evaporated off, and the residue was purified by chromatography on silica [pentane–dichloromethane (2:1), then dichloromethane] to give *compound* (**41**) as an oil which slowly crystallised (128 mg, 76%), m.p. 67—69 °C (trituration with methanol); $\nu_{max.}$ 1 715, 1 602, 1 580, and 1 502 cm^{-1}; δ_H 6.6—7.2 (14 H, m), 4.85 (2 H, s), 4.75 (1 H, s), and 2.10 (3 H, s); *m/z* 348 (M^+), 305, and 239 (Found: C, 76.05; H, 5.7. $C_{22}H_{20}O_2S$ requires C, 75.84; H, 5.79%).

2-*Amino*-3-(4-*benzyloxyphenyl*)-2-*methylpropionitrile* (**43**).—To a mixture of the nitro derivative (**38**) (244 mg), diphenyl disulphide (400 mg), and sodium cyanide (200 mg) in dry THF (3 ml) was added tributylphosphine (0.7 ml), and the mixture was kept at room temperature for 3 h under an inert atmosphere. A solution of acetic acid (0.5 ml) in THF (0.5 ml) was added, and the mixture was stirred for 24 h then poured into 5% aqueous NaOH (50 ml) and extracted with dichloromethane. The extract was dried, and evaporated, and the residue was purified by chromatography (CH_2Cl_2, then diethyl ether) to give *compound* (**43**) as a white crystalline solid (172 mg, 70%), m.p. 82—86 °C (from diethyl ether); $\nu_{max.}$ 3 350, 2 200, and 1 605 cm^{-1}; δ_H 7.50 (5 H, br s), 7.4 and 7.05 (4 H, 2 d, *J* 9 Hz), 5.10 (2 H, s), 2.90 and 2.85 (2 H, 2 s), 1.75 (2 H, br s, N–H), and 1.55 (3 H, s); *m/z* 240 (M^+ − CN) (Found: C, 76.5; H, 6.8; N, 9.9. $C_{17}H_{18}N_2O$ requires C, 76.66; H, 6.81; N, 10.52%).

2-*Methyl*-3,5-*diphenylpyrrole* (**50**).—A solution of 4-nitro-1,3-diphenylpentan-1-one (**46**)[26] (283 mg) and diphenyl disulphide (440 mg) in dry THF (5 ml) was treated with tributylphosphine (1 ml) under an inert atmosphere. After 1 h at room temperature, the solvent was evaporated off and the residue was chromatographed on silica [dichloromethane–pentane (1:2)] to give the pyrrole (**50**) (210 mg, 90%), m.p. 71—72 °C (from CCl_4) [lit.,[27] 101—102 °C (!)]; $\nu_{max.}$ 3 360 and 1 605 cm^{-1}; δ_H 7.8 (1 H, br), 7.0—7.5 (10 H, m), 6.55 (1 H, d, *J* 3 Hz), and 2.30 (3 H, s); *m/z* 233 (M^+) (Found: C, 87.1; H, 6.3; N, 6.0. Calc. for $C_{17}H_{15}N$: C, 87.52; H, 6.00; N, 6.48%).

2,5-*Dimethyl*-3-*phenylpyrrole* (**51**).—To a solution of 5-nitro-4-phenylhexan-2-one (**47**)[28] (255 mg) and diphenyl disulphide (400 mg) in dry THF (2.5 ml) under an inert atmosphere was added tributylphosphine (0.9 ml). After 48 h at room temperature, the solvent was evaporated off and the residue was purified by chromatography [dichloromethane–pentane (1:4 to 3:2)] to give the pyrrole (**51**) as a white crystalline solid (177 mg, 90%), m.p. 80—81 °C (from CCl_4) (lit.,[27] 82—83 °C).

Ethyl 3,5-*Diphenylpyrrole*-2-*carboxylate* (**52**).—A solution of nitro keto ester (**48**)[26] (171 mg), diphenyl disulphide (250 mg), and tributylphosphine (0.5 ml) in dichloromethane (3 ml) was kept at room temperature under an inert atmosphere for 24 h. The reaction mixture was then heated to reflux for 24 h, then concentrated, and the residue was purified by chromatography on silica (dichloromethane–pentane gradient elution 3:7 ⟶ 8:2) to give the pyrrolecarboxylate (**52**) as a white crystalline solid (95 mg, 65%), m.p. 140—142 °C (sublimed) (lit.,[29] 140—144 °C).

2′,5′-*Dimethylandrost*-5-*eno*[16,17-c]*pyrrol*-3β-*yl Acetate* (**55**).—Tributylphosphine (0.5 ml) was added to a solution of nitro steroid (**54**)[30] (103 mg) and diphenyl disulphide (200 mg) in dry THF, and the mixture was kept under an inert atmosphere for 48 h. Concentration, and purification of the residue by chromatography on silica [dichloromethane–pentane (1:1) to remove the thiophenol and diphenyl disulphide, then diethyl ether–dichloromethane (5:95) to elute the product], gave the *pyrrole* (**55**) as yellowish crystals which easily oxidised in air, m.p. 205—211 °C (decomp.) (from ethanol); $[\alpha]_D$ −79° (*c* 0.44); $\nu_{max.}$ 3 450 and 1 725 cm^{-1}; δ_H 7.20 (1 H, br N–H), 5.5 (1 H, br, 6-H), 4.7 (1 H, br, 3α-H), 2.25 (6 H, s, 2′- and 5′-Me), 2.05 (3 H, s, OAc), and 1.10 and 1.00 (6 H, 2 s, 10-and 13-Me); *m/z* 381 (M^+) and 366 ($M^+ - 15$) (Found: C, 78.7; H, 9.25; N, 3.7. $C_{25}H_{35}NO_2$ requires C, 77.87; H, 9.44; N, 3.69%).

Ethyl 4-*Nitro*-3-*phenylpentanoate* (**49**).—A mixture of ethyl cinnamate (4 g), N^2-t-butyl-N^2,N^1,N^3,N^3-tetramethylguanidine[24] (1 ml), and nitroethane (10 ml) was heated to reflux for 30 min. After cooling, the solution was filtered through silica to remove the base. The silica was washed with diethyl ether and the combined washings and filtrate were concentrated under reduced pressure to give the crude product as a pale yellow oil (5.80 g, 100%; ~1:1 mixture of diastereoisomers). Bulb-to-bulb distillation (Kugelrohr; oven temperature 150 °C/0.5 mmHg) gave *ester* (**49**) as an oil (5.4 g, 95%), $\nu_{max.}$ 1 720 and 1 540 cm^{-1}; δ_H 7.5 (5 H, br s), 4.9 (1 H, m), 3.5—4.4 (3 H, m), 2.80 and 2.65 (2 H, 2 d, *J* ~8 Hz), 1.60 and 1.35 (3 H, 2 d, *J* ~7 Hz), and 1.15 and 1.05 (3 H, 2 t, *J* ~9 Hz) (Found: C, 62.3; H, 6.9; N, 5.65. $C_{13}H_{17}NO_4$ requires C, 62.14; H, 6.82; N, 5.57%).

5-*Methyl*-4-*phenyl*-1,3-*dihydropyrrol*-2-*one* (**53**).—Tributylphosphine (0.7 ml) was added to a solution of nitro ester (**49**) (265 mg) and diphenyl disulphide (250 mg) in dry THF (3 ml) under an inert atmosphere. The mixture was stirred at room temperature for 3 h, then heated to reflux for 48 h. Concentration under reduced pressure, followed by chromatography of the residue on silica (dichloromethane, then diethyl ether), gave *compound* (**53**) as relatively air-sensitive off-white crystals (111 mg, 61%), m.p. 115—135 °C (decomp.) (from ethyl acetate); $\nu_{max.}$ 2 200, 1 720, and 1 660 cm^{-1}; δ_H 9.80 (1 H, br, N–H), 7.60 (5 H, br s, Ph), 3.50 (2 H, q, *J* 2 Hz), and 2.25 (3 H, t, *J* 2 Hz); *m/z* 173 (M^+) (Found: C, 71.7; H, 6.4; N, 7.55. $C_{11}H_{11}NO \cdot \frac{1}{2}H_2O$ requires C, 72.49; H, 6.65; N, 7.69%).

N-*Methylbenzamide* (**57**).—A solution of *N*-methylbenzohydroxamic acid (**56**) (300 mg) and diphenyl disulphide (440 mg) in dichloromethane (3 ml) was treated with tributylphosphine (0.6 ml). An exothermic reaction took place. After 15 min, the solvent was evaporated off and the residue was purified by chromatography (dichloromethane, then ethyl acetate) to give *N*-methylbenzamide (**57**) as white crystals (264 mg, 98%), identical with authentic material.

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