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A MILD PROCEDURE FOR THE REDUCTION OF ALIPHATIC NITRO COMPOUNDS TO OXIMES

Derek H.R. Barton*, Isabel Fernandez, Caroline S. Richard and Samir Z. Zard

Institut de Chimie des Substances Naturelles, C.N.R.S.
91190 Gif-sur-Yvette

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Abstract - Aliphatic nitro compounds react with carbon disulphide in the presence of triethylamine to give the corresponding oximes in moderate to good yields.

Reduction plays a primordial role in the exceptionally rich chemistry of the nitro group.[1,2] Yet, partial reduction to the corresponding oxime or oxime derivative has attracted comparatively little attention as reflected by the limited number of reagents capable of effecting this transormation. Earlier methods relied on deoxygenation with diethyl chlorophosphite[3] or the controlled reduction of the corresponding nitronic acids with hydrogen sulphide, hydrogen iodide or sodium thiosulphate.[1,4] The decomposition of appropriate nitronic esters has also been reported to afford oximes.[1] More recently trimethyl phosphite was shown to deoxygenate silyl nitronates giving rise to the corresponding silylated oximes.[2] A more practical method, involving reduction with chromous chloride was introduced by Hanson[5] and co-workers some years ago. The reaction is almost instantaneous and usually stops at the oxime stage, although further hydrolysis due to the aqueous acidic medium has sometimes been encountered. Other low valent transition metals[6] (e.g. Ti^{III}) also reduce the nitro group but the putative intermediate oxime is not easily intercepted under the usual reaction conditions. β-Nitrostyrene was recently reported to give phenylacetaldehyde oxime on exposure to formic acid and palladium.[7a] With sodium phosphinate as hydrogen donor and Raney nickel catalyst, however, nitroolefins give the corresponding ketones or aldehydes.[7b] Sodium stannite appears to be a more general reagent for obtaining oximes from nitroalkenes.[7c]

In the course of related studies we have found that, under certain conditions, this conversion may be realised using carbon disulphide. This reagent is known to deoxygenate nitrones and amine oxides[8], but the few scattered reactions reported with nitro compounds indicate a rather complex behaviour. Thus nitro-methane produces, after alkylation of the intermediate, thioketene acetal derivatives.[9] In contrast nitroaromatics[10] and nitrocyclohexane[11] are converted into isothiocyanates directly.

We envisaged that in situ formed nitronates could perhaps be reduced in a more controlled manner. As a first model, we prepared the tetralin derivative 1 by the ethylenediamine catalysed condensation[12] of nitromethane with α-tetralone. Exposure of a solution of 1 in carbon disulphide in the presence of the hindered guanidine[13] base 4 resulted in the rapid disappearance of the starting material. The expected oxime 2 was indeed produced but only in low yield (23%) wih the major product being the α,β-unsaturated nitrile 3 (62%). This unfavourable ratio could be improved to 45:20 by using only one equivalent of

* Present Address : Dept. of Chemistry, Texas A & M University, College Station, Texas 77843

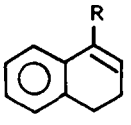
carbon disulphide. Evidently, the oxime was reacting further at a rate comparable to its formation. In view of the similar acidities of nitroalkanes (pK_a 8-9) and oximes (pK_a ~10-11),[14] the choice of the strong guanidine base was perhaps not appropriate. A weaker base should exhibit a better selectivity.

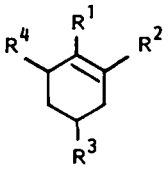
In keeping with this reasoning, the use of triethylamine produced a significant improvement in the yield (~65%) albeit after a longer reaction time. A cursory examination of the experimental factors revealed acetonitrile as the best solvent and 0-20°C as a convenient reaction temperature, although the yield in this particular example was not much altered.

The most reactive and highest yielding substrates were those with an allylic nitro group (Table, entries 1-8). Other nitro derivatives reacted more slowly with a consequent decrease in the yield of oxime (Table, entries 9-11). Long reaction times were particularly detrimental to non-allylic primary nitro compounds due to extensive formation of nitrile especially when acetonitrile is used as solvent (hence the use of dichloromethane in the case of 19 and 21, Table, entries 9, 10). For example, the nitrosteroid 19 afforded the corresponding nitrile 25 in 83% yield after prolonged contact with the reagent. Finally, the reduction did not appear to be significantly influenced by light.

Table

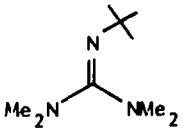
Entry	Nitro derivative	Reaction solvent	Reaction Time (hours)	Oxime (Yield %)
1	1	CH_3CN	5	2 (66)
2	5	"	1.5	6 (64)
3	7	"	4	8 (72)
4	9	"	2	10 (77)
5	11	"	1	12 (85)
6	13	"	1.5	14 (83)
7	15	"	60	16 (63)
8	17	"	0.5	18 (59)
9	19	CH_2Cl_2	75	20 (38)
10	21	CH_2Cl_2	72	22 (29)
11	23	CH_3CN	84	24 (53)





1 R = $-CH_2NO_2$
2 R = -CH=NOH
3 R = CN

5 $R^1 = CH_2NO_2$; R^2 = Me; $R^3 = R^4$ = H
6 R^1 = CH=NOH; R^2 = Me; $R^3 = R^4$ = H
7 $R^1 = CH_2NO_2$; $R^2 = R^3$ = H; R^4 = Me
8 R^1 = CH=NOH; $R^2 = R^3$ = H; R^4 = Me
9 $R^1 = CH_2NO_2$; $R^2 = R^4$ = Me; R^3 = H
10 R^1 = CH=NOH; $R^2 = R^4$ = Me; R^3 = H
11 $R^1 = CH_2NO_2$; $R^2 = R^4$ = H; R^3 = t-Bu
12 R^1 = CH=NOH; $R^2 = R^4$ = H; R^3 = t-Bu
15 $R^1 = CH(NO_2)CH_2CH_2CO_2Me$; $R^2 = R^4$ = H; R^3 = t-Bu-
16 $R^1 = C(=NOH)-CH_2CH_2CO_2Me$; $R^2 = R^4$ = H; R^3 = t-Bu-



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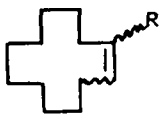
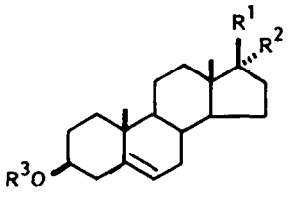
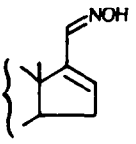


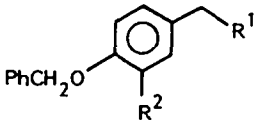




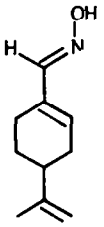
13 R = CH_2NO_2
14 R = CH=NOH
(E)

17 $R^1 = R^2 = =CHNO_2$; R^3 = Ac
19 $R^1 = CH_2NO_2$; R^2 = H, R^3 = Ac
20 R^1 = CH=NOH; R^2 = H, R^3 = Ac
25 R^1 = CN; R^2 = H, R^3 = Ac

18



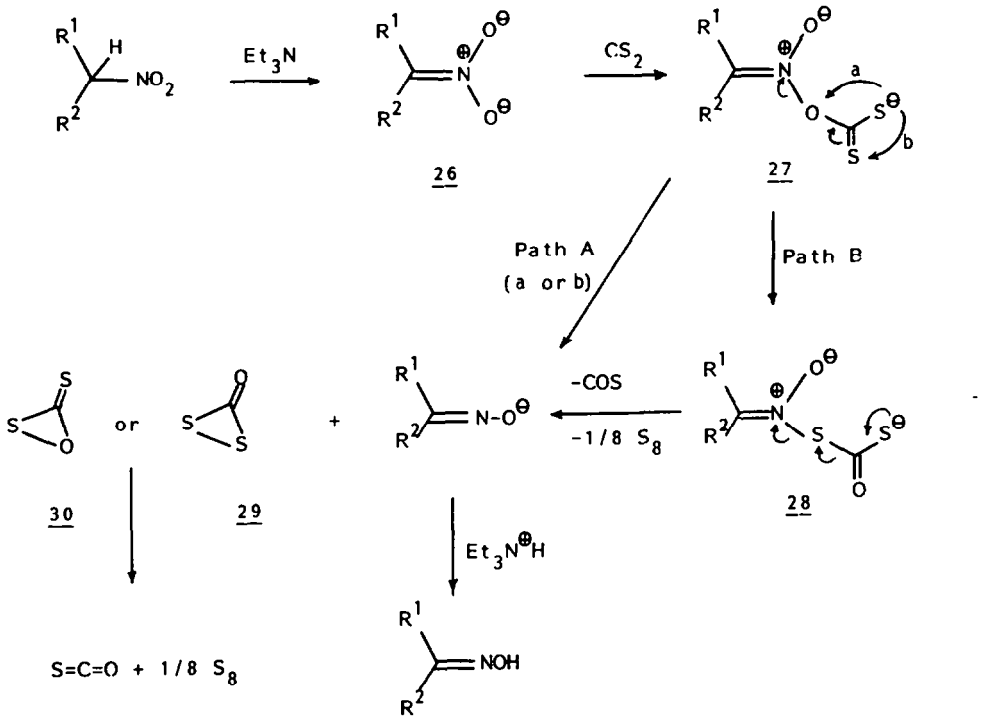
21 $R^1 = CH_2NO_2$; R^2 = OMe
22 R^1 = CH=NOH; R^2 = OMe
23 $R^1 = -\overset{Me}{\underset{|}{C}}HNO_2$; R^2 = H
24 $R^1 = -\overset{Me}{\underset{|}{C}}=NOH$; R^2 = H



33

The mechanism of this reduction is not clear at present. Addition of the nitronate 26 to carbon disulphide would lead to a xanthate 27 (Scheme 1). This first intermediate could in principle evolve along various pathways. Thus, by analogy with the mechanism postulated for the deoxygenation of amine oxides,[8,15] a fragmentation would lead to the oxime with loss of a reactive species 29 and/or 30 (Scheme 1, path A). However, when the reduction was carried out in the presence of a large excess of cyclohexene, no cyclohexene episulphide could be detected. In the case of amine oxides, the formation of episulphide was construed as evidence for the existence of such reactive intermediates.[15] In the absence of alkene, 29 and/or 30 undergo extrusion of sulphur to give carbon oxysulphide. In our system, we have observed both sulphur and carbon oxysulphide. The latter has a characteristic intense band at 2045 cm^{-1}.[8]

Alternatively, the first intermediate 28 may first rearrange to 28 which subsequently suffers a fragmentation, concerted or otherwise, to produce oxime, carbon oxysulphide and sulphur (Scheme 1, path B). Similar rearrangements of thiocarbonyl derivatives of oximes have been reported previously by Hudson and co-workers.[16] Obviously, other variants cannot, at this point be excluded.

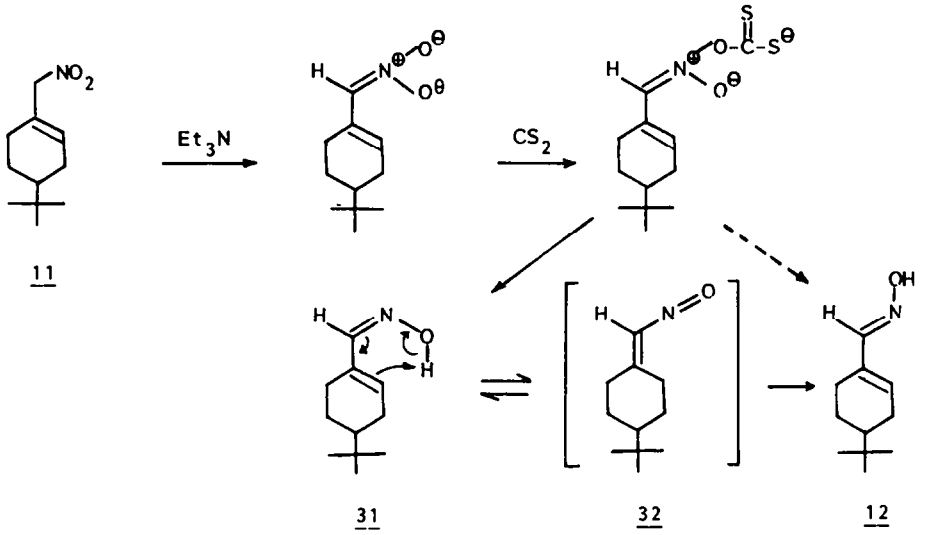


Scheme 1

A further observation of some mechanistic relevance was made while examining substrates with a primary allylic nitro group. We noted by thin layer chromatography the rapid formation of an intermediate which was gradually converted into the ultimate α,β-unsaturated aldoxime. This last transformation was strongly accelerated by heat and by acid. Using compound 11 as a model, we monitored the reaction by NMR spectroscopy. The singlet (2H) at 4.85 ppm and the multiplet at 5.90 ppm corresponding to the methylene and olefine protons respectively were soon replaced by a singlet at 6.85 ppm and a multiplet at 6.40 ppm. These in turn eventually gave way to a singlet at 7.72 ppm and a multiplet at 6.05 ppm belonging to the final oxime 12. The NMR spectrum of the intermediate is therefore quite similar to that of the final oxime 12. Eventually, after several attempts, we succeeded in isolating this unstable substance in almost pure form. The spectral and microanalytical data were indeed very close to those of 12 and, moreover, it was converted to the latter on standing in solution. Clearly the most reasonable structure for this intermediate would be 31, the geometrical isomer of aldoxime 12. By comparing the respective NMR spectra in DMSO-d_6, and especially the difference in the chemical shifts of the oxime group protons ( ), we were able to confirm the relative stereochemistry of each.[17,18] Thus, for 12, the difference is of ~3.0 ppm, diagnostic of E-aldoximes.

It seems therefore that the reduction produces the less stable oxime first by removing the least hindered and most accessible oxygen in the nitronate with retention of configuration at the nitrogen centre (Scheme 2). The ensuing isomerisation presumably occurs by a 1,5 hydrogen shift to the reactive vinyl nitroso intermediate 32 followed by an ionic tautomerisation to the thermodynamically more stable oxime 12. Worthy of note is that α,β-unsaturated Z-aldoximes related to 31 are apparently unknown species and previous attempts to prepare them have been thwarted by the exceptionally facile isomerisation process.

Ordinary oximes require much harsher reaction conditions to undergo inversion at nitrogen.[14] The mechanistic aspects of these observations are clearly deserving of further attention.



Scheme 2

Although, from a preparative standpoint, the reduction works best with allylic nitro compounds, the corresponding oximes produced are not devoid of interest. For example, the cyclohexene derivatives 6, 8, 10 and 12 are close analogs of perillartine 33, better known as Perilla Sugar, a substance 2000 times sweeter than sugar.[18] In conjunction with the efficient ethylene diamine mediated condensation of nitromethane with ketones,[12] this reduction allows a convenient access to this class of compounds.

Experimental

Melting points are uncorrected. Unless otherwise stated, NMR data are for deuteriochloroform solutions with tetramethylsilane as internal standard. I.R. spectra are of dichloromethane solutions unless stated to the contrary. Starting nitro derivatives 17, 19 and 23 were available from previous work.[12,19] Compound 21 may be prepared by the method described by McDonald and Martin.[21] Optical rotations were obtained for chloroform solutions.

1-Nitromethyl-3,4-dihydronaphthalene 1 (In collaboration with Dr. R.-M. Bergé-Lurion).

A mixture of α-tetralone (15 ml), ethylenediamine (0.37 ml) and nitromethane (170 ml) was heated to reflux under an inert atmosphere for 50 hours. The excess nitromethane was distilled off and the brown residue purified by chromatography on silica (hexane:-dichloromethane 4:1) to give a yellowish low melting solid (m.p. 30°C); ν_{max} : 1550 cm^{-1}; δ_H: 7.18 (4H, m), 6.30 (1H, t, J = 4.5 Hz), 5.25 (s, 2H), 2.20-3.00 (4H, m); m/z: 189 (M^+) (Found: C, 69.97; H, 5.77; N, 7.18. Calc. for $C_{11}H_{11}NO_2$: C, 69.80; H, 5.86; N, 7.43%).

6-Methyl-1-nitromethylcyclohexene 5 and 2-Methyl-1-nitromethylcyclohexene 7.

2-Methylcyclohexanone (10 g), nitromethane (100 ml) and ethylenediamine (0.4 ml) were heated to reflux under an inert atmosphere for 24 hours. The reaction mixture was then concentrated and the residue purified by chromatography on silica (pentane:dichloromethane 9:1) to give 7 as a colourless liquid (9 g, 65%); ν_{max} (neat): 1535 cm^{-1}; δ_H: 5.85 (1H, broad t), 5.00 (1H, d, J = 13 Hz), 4.65 (1H, d, J = 13 Hz), 1.05 (3H, d, J = 7 Hz) (Found: C, 61.85; H, 8.28; N, 8.93. Calc. for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.02%).

If chromatography is preceded by bulb to bulb distillation of the residue (200°C oven temperature, 5 mmHg), isomerisation of the double bond takes place to give 5; ν_{max} (neat): 1555 cm^{-1}; δ_H: 5.05 (2H, s); 1.85 (3H, s), 1.3-2.5 (8H, m) (Found: C, 61.94; H, 8.35; N, 9.09. Calc. for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.02%).

2,6-Dimethyl-1-nitromethylcyclohexene 9.

A mixture of 2,6-dimethyl cyclohexanone (5 g), nitromethane (35 ml) and ethylenediamine (0.15 ml) was heated to reflux for 44 hours under an inert atmosphere. The reaction mixture was concentrated and the residue purified by chromatography on silica (pentane:dichloromethane 9:1) to give a colourless liquid (4.3 g, 65%); $\nu_{max.}$ (neat): 1540 cm^{-1}; δ_H: 4.95 (2H, broad s), 1.75 (3h, s), 1.05 (3H, d, J = 7 Hz) (Found: C, 63.61; H, 8.65; N, 8.34. Calc. for $C_9H_{15}NO_2$: C, 63.88; H, 8.93; N, 8.28%).

4-t-Butyl-1-nitromethylcyclohexene 11.

A mixture of 4-t-butyl cyclohexanone (10 g), nitromethane (100 ml) and ethylenediamine (0.6 ml) was heated to reflux under an innert atmosphsere for 3 hours. Concentration and purification of the residue by chromatography on silica (pentane:dichloromethane 9:1) gave a colourless oil (8.05 g, 63%); $\nu_{max.}$ (neat): 1550 cm^{-1}; δ_H: 5.90 (1H, broad t), 4.85 (2H, s), 0.95 (9H, s) (Found: C, 67.31; H, 9.24; N, 7.13. Calc. for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10%).

1-Nitromethylcyclododecene 13.

This compound was obtained as an unseparable mixture of cis- and trans-isomers (3:8 by NMR, the major presumably the trans- by analogy with cyclododecene[20]) in about 70% yield by an identical procedure to that of 5; $\nu_{max.}$ (neat): 1555 cm^{-1}; δ_H (of major isomer): 5.55 (1H, broad t), 4.80 (2H, s), 1.9-2.4 (4H, m), 0.8-1.8 (16H) (Found: C, 69.15; H, 10.39; N, 6.48. Calc. $C_{13}H_{23}NO_2$: C, 69.29; H, 10.28; N, 6.22%).

Methyl 4-(4-t-butyl-cyclohexen-1-yl)-4-nitrobutanoate 15.

A solution of nitro derivative 11 (1 g) in a mixture of methyl acrylate (8 ml) and methanol (25 ml) containing potassium fluoride (0.75 g) was heated to reflux for 2 hours. The reaction mixture was then concentrated and the residue purified by chromatography on silica (pentane:dichloromethane 1:1) to give the addition product 15 as a white solid (1.17 g, 81%); m.p. 35-39°C (methanol); $\nu_{max.}$: 1730, 1540 cm^{-1}; δ_H: 5.90 (1H, broad), 4.90 (1H, m), 3.75 (3H, s), 0.9 (9H, s) (Found: C, 63.49; H, 8.86; N, 4.69. Calc. for $C_{15}H_{25}NO_4$: C, 63.57; H, 8.89; N, 4.94%).

General Procedure for the Reduction using Triethylamine.

To a solution of the nitro derivative (1 mmole) in acetonitrile (3 ml) is added triethylamine (10 mmole) followed by carbon disulphide (1.5-3 mmoles). The mixture is stirred at room temperature for the specified time (table), concentrated under reduced pressure and the residue purified by chromatography on silica.

3,4-Dihydro-1-naphthaldehyde Oxime 2.

This oxime was eluted with pentane:dichloromethane (1:4); m.p. 75-77°C; $\nu_{max.}$: 3350, 3300 and 1620 cm^{-1}; δ_H (80 MHz): 8.35 (1H, broad s), 8.05 (1H, s), 7.76 (1H, m), 7.05-7.33 (3H, m), 6.38 (1H, t, J = 4.5 Hz), 2.20-2.90 (4H, m); m/z= 173 (M^+) (Found: C, 75.99; H, 6.21; N, 8.06. Calc. for $C_{11}H_{11}NO$: C, 76.25; H, 6.40; N, 8.12%).

2-Methyl-cyclohexene-1-carboxaldehyde Oxime 6.

This oxime was eluted with dichloromethane; m.p. 135°C (hexane-dichloromethane); $\nu_{max.}$: 3575, 3250 and 1640 cm^{-1}; δ_H: 9.30 (1H, broad s), 8.45 (1H, s), 2.00-2.58 (4H, m), 1.90 (3H, s), 1.45-1.84 (4H, m); m/z: 139 (M^+) (Found: C, 69.06; H, 9.23; N, 9.90. Calc. for $C_8H_{13}NO$: C, 69.02; H, 9.41; N, 10.06%).

6-Methyl-cyclohexene-1-carboxaldehyde Oxime 8.

This oxime was eluted with dichloromethane; m.p. 83-84°C (pentane-dichloromethane); δ_H: 9.10 (1H, s), 7.50 (1H, s), 5.90 (1H, t, J = 3 Hz), 1.4-3.0 (7H, m), 1.20 (3H, d, J = 7 Hz); m/z: 139 (M^+) (Found: C, 68.83; H, 9.57; N, 9.99. Calc. for $C_8H_{13}NO$: C, 69.02; H, 9.41; N, 10.06%).

2,6-Dimethyl-cyclohexene-1-carboxaldehyde Oxime 10.

This oxime was eluted with dichloromethane; m.p. 90-91°C (pentane-dichloromethane); $\nu_{max.}$: 3575, 3300 and 1635 cm^{-1}; δ_H: 9.17 (1H, broad), 8.15 (1H, s), 1.00-3.00 (10H, m), 1.80 (3H, s), 1.10 (3H, d, J = 8 Hz); m/z: 153 (M^+) (Found: C, 70.45; H, 9.91; N, 8.92. Calc. for $C_9H_{15}NO$: C, 70.54; H, 9.87; N, 9.14%).

4-t-Butyl-cyclohexene-carboxaldehyde Oxime 12.

This oxime was eluted with dichloromethane; m.p.: 132-133°C (pentane:dichloromethane); $\nu_{max.}$ (nujol): 3250, 1640 cm^{-1}; δ_H: 8.70 (1H, broad s), 7.72 (1H, s), 6.05 (1H, m), 1.0-3.0 (7H, m), 0.90 (9H, s); m/z: 181 (M^+) (Found: C, 73.03; H, 10.07; N, 7.73. Calc. for $C_{11}H_{19}NO$: C, 72.88; H, 10.56; N, 7.72%).

Cyclododecene-1-carboxaldehyde Oxime 14.

This oxime was isolated (elution with pentane:ether 9:1) as two geometrical isomers 14a (17%) and 14b (66%) with respect to the ring unsaturation. Since in cyclododecene itself, the trans isomer is slightly more stable than the cis (~1 Kcal)[20], we have assigned the trans stereochemistry to the major isomer 14b. This compound had a m.p. of 111-112°C (pentane-dichloromethane); ν_{max} (nujol): 3250, 1630 cm^{-1}; δ_H: 8.70 (1H, s), 7.60 (1H, s), 5.70 (1H, t, J = 8 Hz), 2.0-2.7 (4H, m), 1.0-2.0 (16H, m); m/z: 209 (M^+) (Found: C, 74.40; H, 11.11; N, 6.58. Calc. for $C_{13}H_{23}NO$: C, 74.58; H, 11.07; N, 6.69%).

The minor isomer 14a had a m.p. of 48-50°C (pentane-dichloromethane). The spectral data was identical except for the NMR spectrum which showed the following signals : δ_H: 8.35 (1H, s), 8.0 (1H, s), 5.7 (1H, t, J = 8 Hz), 2.0-2.5 (4H, m), 1.0-2.0 (16H, m).

Methyl-4-(4-t-butyl cyclohexen-1-yl)-4-oximinobutanoate 16.

This oxime was eluted with pentane:ether (4:1); m.p.: 91-93.5°C (hexane); ν_{max} : 3350, 1740 cm^{-1}; δ_H: 9.6 (1H, broad s), 6.3 (1H, m), 3.7 (3H, s), 1.0-3.3 (11 H, m), 0.95 (9H, s); m/z: 267 (M^+) (Found: C, 67.37; H, 9.34; N, 5.30. Calc. for $C_{15}H_{25}NO_3$: C, 67.38; H, 9.42; N, 5.24%).

3β-Acetoxy-androsta-5,16-diene-17β-carboxaldehyde Oxime 18.

In this case, the nitrolefin 17 was left in contact with the triethylamine overnight (to induce partial migration to the Δ^{16} isomer) prior to the addition of carbon disulphide. The oxime 18 was eluted with dichloromethane; m.p. 183-185°C (methanol); $[\alpha]_D$ = -45.6° (c=1); ν_{max} (nujol): 3450, 1720 cm^{-1}; δ_H: 7.55 (1H, s), 5.85 (1H, m), 5.25 (1H, m), 4.45 (1H, m), 2.00 (3H, s), 1.05 (3H, s), 0.95 (3H, s) (Found: C, 73.51; H, 8.82; N, 4.04. Calc. for $C_{22}H_{31}NO_3$: C, 73.92; H, 8.74; N, 3.92%).

3β-Acetoxy-androst-5-ene-17β-carboxaldehyde Oxime 20.

This oxime was eluted with pentane:ethylacetate (4:1). Nitrile 25 (28%) and some starting material 19 (20%) were also recovered. The oxime 20 was recrystallised from methanol; m.p. 184-185°C; $[\alpha]_D$ = -64° (c = 0.6); ν_{max} (nujol) 3350, 1700 cm^{-1}; δ_H (80 MHz): 7.40 (1H, d, J = 7 Hz), 5.32 (1H, m), 4.60 (1H, m), 2.05 (3H, s), 1.05 (3H, s), 0.70 (3H, s); m/z: 359 (M^+), 299 (M^+-AcOH) (Found: C, 73.54; H, 8.97; N, 3.68. Calc. for $C_{22}H_{33}NO_3$: C, 73.50; H, 9.25; N, 3.89%).

(4-Benzyloxy-3-methoxyphenyl)-acetaldehyde Oxime 22.

This oxime was eluted with dichloromethane:ether (9:1); m.p.: 112-115°C (hexane:dichloromethane); ν_{max} : 3575, 3300 cm^{-1}; δ_H: 8.20 (1H, broad s), 7.2-7.7 (5H, m), 6.5-7.0 (3H, m), 5.15 (2H, s), 3.86 (3H, s), 3.65 (1H, d, J = 5.5 Hz), 3.45 (1H, d, J = 6.5 Hz); (the protons adjacent to the oxime are not equivalent because of restricted rotation and appear as two doublets. If the spectrum is recorded in DMSO-d_6 only one doublet is observed); m/z: 271 (M^+) (Found: C, 70.73; H, 6.40; N, 5.27. Calc. for $C_{16}H_{17}NO_3$: C, 70.82; H, 6.40; N, 5.16%).

1-(4-Benzyloxyphenyl)-2-oximinopropane 24.

This oxime was eluted with dichloromethane; m.p. 80-83°C (sublimed); ν_{max} (nujol): 3350, 1610 cm^{-1}; δ_H (80 MHz): 8.5 (1H, broad), 7.35 (5H, broad s), 7.12 (2H, d, J = 9 Hz), 6.85 (2H, d, J = 9 Hz), 5.00 (2H, s), 3.65 and 3.40 (2H, two broad s in ~1:2 ratio), 1.80 (3H, s); m/z= 255 (M^+) (Found: C, 75.27; H, 6.60; N, 5.54. Calc. for $C_{16}H_{17}NO_2$: C, 75.26; H, 6.71; N, 5.48%).

3β-Acetoxy-androst-5-ene-17β-carbonitrile 25.

A solution of the nitrosteroid 19 (104 mg) in acetonitrile (3 ml) containing triethylamine (0.5 ml) and carbon disulphide (0.4 ml) was kept at room temperature for 36 hours. Concentration of the reaction mixture and purification of the residue by chromatography on silica[16] (pentane:ether 2:1) gave the nitrile 25 (81 mg, 86%) identical to authentic material.

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