Base-promoted Reactions of β-Enaminones with 2-Bromo-2-methylpropanamides. Formation of 2-Ketonyloxazolidin-4-ones and Cyclohexanespiro-oxazolidin-4-ones

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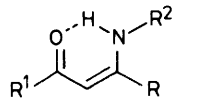
Representative β-enaminones (1) and (2) react with *N*-alkyl-2-bromo-2-methylpropanamides (**4a**), (**4b**), and (**4c**) in the presence of NaH, to afford oxazolidin-4-ones (**5**) and (**6**) or spiro-oxazolidinone derivatives (**7**) and (**8**). The formation of an imidazolidin-4-one derivative (**9**) from 2-bromo-2-methylpropanilide (**4c**) is ascribed to the presence of an intermediate α-lactam (**15**). The behaviour of a spiro-oxazolidinone derivative on hydrolysis, reduction, and thiation is described.

During an investigation of base-promoted reactions of 2-halogenoamides, we noticed that the character of the halogenated carbon (primary, secondary, or tertiary) and of the substituent at the nitrogen atom influenced the product distribution. In particular, 2-bromo-2-methylpropanamides react regioselectively, yielding oxazolidinone derivatives or related compounds, through self cyclo-condensations or cross cyclo-condensations with other amide moieties.[1]

Since β-enaminones are vinylogous amides, we studied the behaviour of representative enaminones towards the 2-bromoamides.

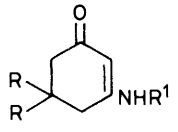
Common halides are known to alkylate β-enaminones at one of five different sites (oxygen, nitrogen or one of three carbon atoms), depending on the reagents and the experimental conditions.[2]

We found that sodium hydride promoted reactions between the enaminones (**1**) and (**2**) and the 2-bromo-2-methylpropanamides (**4a**), (**4b**), and (**4c**), regioselectively affording oxazolidin-4-one and spiro-oxazolidinone derivatives; the influence of the relevant parameters on the product distribution has been studied.



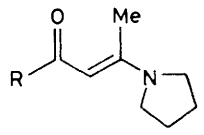
(1)

R	R^1	R^2
a; Me,	Me,	CH_2Ph
b; Me,	Ph,	CH_2Ph
c; Ph,	Me,	CH_2Ph



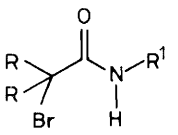
(2)

R	R^1
a; Me	CH_2Ph
b; Me	Ph
c; H	CH_2Ph



(3)

R
a; Me
b; Ph



(4)

R	R^1
a; Me,	CH_2Ph
b; Me,	Me
c; Me,	Ph
d; H,	CH_2Ph

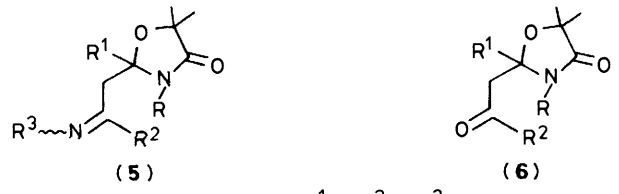
Results

Reactions of Enaminones with 2-Bromo-2-methylpropanamides.—Protic enaminones (**1a—c**) and (**2a—c**) derived from acyclic or cyclic β-diketones react with 2-bromo-2-methylpropanamides (**4a**) and (**4b**), yielding the imino-oxazolidinone or iminospiro-oxazolidinone derivatives (**5**) and (**7**) as primary products. These products have been isolated or demonstrated spectroscopically in few cases, *e.g.* (**5a**) and (**7a**). The imino-oxazolidinone derivatives (**5**) and (**7**) are easily converted into the stable ketonyloxazolidinone (**6**) and the ketonylspiro-oxazolidinone derivatives (**8**) by straightforward hydrolysis with dilute acid or elution on a silica-gel column. When the enaminone (**1b**) was allowed to react with 2-bromo-2-methylpropananilide (**4c**), a by-product was obtained along with the oxazolidinone derivative (**6e**). Its spectral features show it to be the 2-methyl-2-phenacylimidazolidinone derivative (**9**) [equation (1)] in which the carboxanilide moiety has been rearranged with respect to the parent 2-halogenoanilide (**4c**).

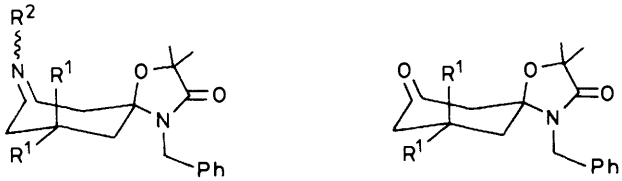
No cross-condensations were observed under the same experimental conditions, *i.e.* (i) on treatment of the aprotic enaminones (**3a**) and (**3b**) with 2-bromo-2-methylpropanamide (**4a**) or (ii) on treatment of the enaminone (**1b**) with *N*-benzyl-2-bromoacetamide (**4d**). Instead, independent self-condensations of the halogenoamide occurred in each case, affording the previously described products.[3]

Chemical Behaviour of a Spiro-oxazolidinone Derivative (*Scheme* 1).—The spiro-oxazolidinone (**8a**) is stable under strongly hydrolytic conditions, as expected for a hindered amide.[4] With $NaBH_4$, it undergoes regiospecific reduction of the carbocyclic ketone group, affording the corresponding secondary alcohol (**10**) (Scheme 1). The hydroxy-cyclohexanespiro-oxazolidinone derivative (**10**) was obtained as a mixture of two diastereoisomers in the ratio 4:1. The stereoselectivity must be ascribed to complexation of the reducing agent by the oxazolidinone oxygen, as suggested by a molecular model of (**10**). Such complexation would favour the axial delivery of hydrogen to give predominantly the equatorial alcohol.† On treatment with $LiAlH_4$ or with BH_3–Me_2SO,[5] reduction at both carbonyls takes place with concurrent ring cleavage of the heterocyclic ring; a dihydroxy tertiary amine derivative (**11**) was obtained, whose structure was established by ^1H n.m.r. spectroscopy. It was obtained as a single isomer for which we propose the indicated *cis*-diequatorial stereochemistry. Finally, on reaction of compound (**8a**) with

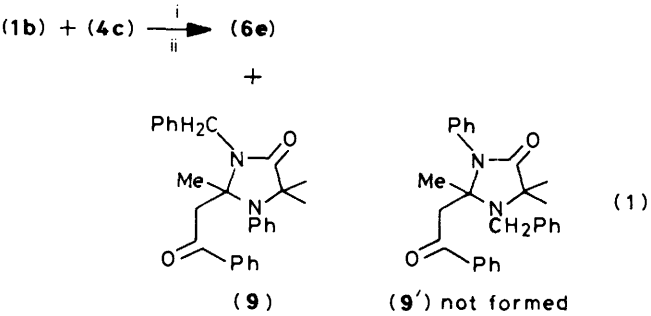
† We acknowledge the helpful comments of a referee about the stereochemistry of the reduction.



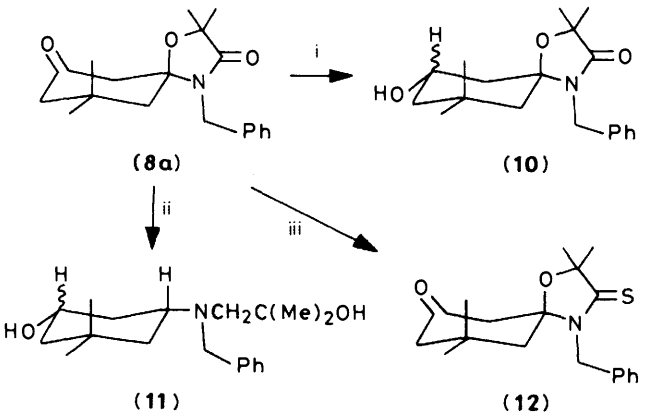
	R	R^1	R^2	R^3
a;	CH_2Ph,	Me,	Me,	CH_2Ph
b;	CH_2Ph,	Ph,	Me	
c;	CH_2Ph,	Me,	Ph	
d;	Me,	Ph,	Me	
e;	Ph,	Ph,	Me	



	R^1	R^2
a;	Me,	Ph
b;	H	

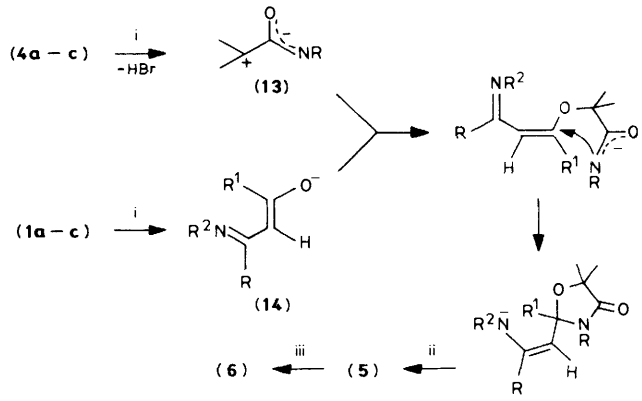


Reagents: i, NaH; ii, SiO_2

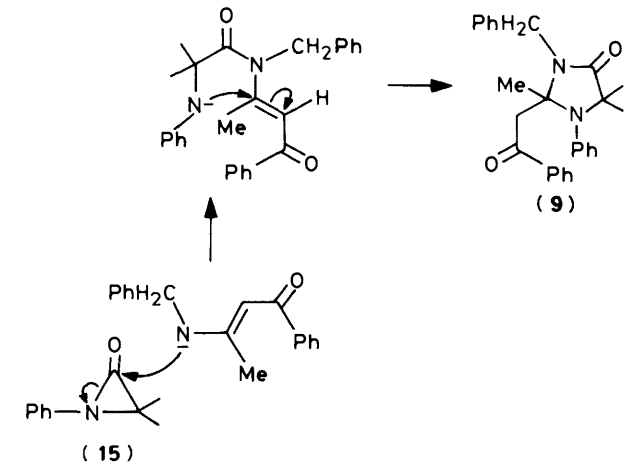


Scheme 1. *Reagents:* i, $NaBH_4$; ii, $LiAlH_4$ or BH_3–Me_2SO; iii, Lawesson's reagent.

Lawesson's reagent,[6] only the amide carbonyl undergoes thiation, thus giving access to the spiro-4-thioxo-oxazolidine derivative (**12**).



Scheme 2. *Reagents:* i, NaH; ii, H^+; iii, H^+, H_2O



Scheme 3.

Discussion

The formation of oxazolidinone derivatives can be rationalized by the mechanism outlined in Scheme 2 for an acyclic enaminone.

The key step is assumed to consist of the *O*-alkylation of the β-enaminone conjugated anion (**14**) by the zwitterion (**13**); (**13**) was previously postulated as a possible intermediate in the base-promoted reactions of 2-halogenoamides.[7,8] According to the Hard/Soft Acid/Base (HSAB) rules,[9] the hard positive site of (**13**) is expected to alkylate the hard site (oxygen) of the enaminone anion (S_N1-like transition state); a Michael-type attack by the amide nitrogen on the α,β-unsaturated imine leads to the cyclization product (**5**). The proposed mechanism is consistent with the finding that *N*-benzyl-2-bromoacetamide, which is unable to react by an S_N1-type mechanism, follows an independent reaction path.

The demonstration of the formation of the imidazolidin-4-one (**9**) from the enaminone (**1b**) and 2-bromo-2-methylpropananilide (**4c**), rules out two alternative isomeric structures: (i) the imine precursor (**5**) of (**6e**), and (ii) the 2-methyl-2-phenacylimidazolidin-4-one (**9′**). The formation of (**9**) stresses the fact that no cyclo-condensation onto the carbon–nitrogen bond of the parent enaminone, which is unexpected by HSAB considerations, is observed. We propose that the imidazolidinone (**9**) arises through the dehalogenation of the halogenoanilide anion of (**4c**) to a transient α-lactam (**15**) (Scheme 3);[8] attack of the soft site of the enaminone anion (nitrogen) on the carbonyl of the lactam (**15**), a soft–soft interaction, would finally lead to the product (**9**).

The failure of an aprotic enaminone, such as (**3a**) or (**3b**), to yield a condensation product with a 2-bromo-2-methylpropanamide emphasizes the importance of deprotonation as a prerequisite for the regiospecific cyclo-condensation onto the enaminone carbonyl. Protic enaminones, on the other hand, undergo such cyclo-condensations irrespective of the nature of the adjacent group (R^1 = Me or Ph) and of the acyclic or cyclic structure of the molecule.

In conclusion, in the cyclo-condensations here reported, the β-enaminone behaves as a regioselectively masked β-diketone.[10] Parallel investigations on the base-catalysed reactions of 2-halogenoamides with ketones and β-diketones are in progress.

Experimental

For reagent and experimental details, see ref. 3. T.l.c. was performed on 0.25-mm silica-gel plates (Merck); R_F1 and R_F2 refer to the systems ethyl acetate–toluene (1:1) and chloroform–methanol (4:1), respectively. Compounds were visualized on t.l.c. with u.v. light or brown spots with I_2–NaN_3.

All ^1H n.m.r. signals are singlets, unless stated otherwise.

Preparation of the β-Enaminones.—4-Benzylaminopent-3-en-2-one (**1a**), 3-benzylamino-1-phenyl-but-2-ene-1-one (**1b**), 3-benzylamino- and 3-phenylamino-5,5-dimethylcyclohex-2-enone (**2a**) and (**2b**), and 3-benzylaminocyclohex-2-enone (**2c**) were prepared from benzylamine or aniline and the pertinent β-diketone.[2]

1-Benzylamino-1-phenylbut-1-en-3-one (**1c**). This was prepared according to the Eschenmoser procedure,[11] as follows. A sample of *N*-benzylbenzamide (1.8 g, 8.8 mmol) in anhydrous benzene (45 ml) was treated with Lawesson's reagent[6] (1.78 g, 4.4 mmol). The reaction mixture was refluxed for 5 h and then concentrated; the crude solid was purified using a column of neutral alumina and ethyl acetate–toluene (1:1) as eluant. The fractions with R_F1 0.7 gave yellow crystals (1.53 g, 77%) of *N*-benzylthiobenzamide, m.p. 82—83 °C; δ($CDCl_3$) 4.9 (2 H, d, *J* 6 Hz, CH_2), 7.3 (8 H, m, Ar), and 7.6—7.7 (3 H, m, Ar, NH). Bromoacetone (0.54 ml, 4.5 mmol) was added to a solution of *N*-benzylthiobenzamide (0.8 g, 3.5 mmol) in tetrahydrofuran (THF) (15 ml). The reaction mixture was stirred at room temperature for 24 h and concentrated under reduced pressure. The resulting oil (1.54 g) was dissolved in dry chloroform and treated with triethylamine (0.49 ml, 3.5 mmol) and triphenylphosphine (1.83 g, 7 mmol). The mixture was refluxed for 24 h and concentrated; the crude product was purified using a column of silica (ethyl acetate–toluene, 1:1). The *enaminone* (**1c**) was obtained as a colourless oil (1.54 g, 42%); δ($CDCl_3$) 2.1 (3 H, Me), 4.35 (2 H, d, *J* 6 Hz, CH_2), 5.15 (1 H, CH), 7.3—7.45 (10 H, m, Ar), and 11.1 (1 H, NH) (Found: C, 80.9; H, 6.7; N, 5.7. $C_{17}H_{17}NO$ requires C, 81.24; H, 6.82; N, 5.57%).

General Procedure for the Reactions of the β-Enaminones with 2-Bromoamides.—A sample of the β-enaminone was added to a suspension of NaH in anhydrous THF, with stirring and in a slow stream of nitrogen. After stirring for 30 min and occasional mild warming to favour the elimination of hydrogen, a solution of the bromoamide in THF was added during *ca.* 2 h. When the halogenoamide had completely reacted (t.l.c.) (3—5 h), the suspension was centrifuged and the solution was concentrated under reduced pressure. ^1H N.m.r. spectroscopic analysis indicated the presence of the products (**5**) and (**7**) in all cases. The crude product was worked up as follows: (a) extraction of compound (**5**) or (**7**) with hot n-hexane; (b) column chromatography on silica gel with ethyl acetate–toluene (1:1); or (c) treatment with 1M-HCl (1 equiv.) in EtOH at 20 °C for 0.5 h. Procedures (b) and (c) afforded the hydrolysed products (**6**) and (**8**). A detailed procedure and the products obtained are as follows.

3-Benzyl-2-(2-benzyliminopropyl)-2,5,5-trimethyloxazolidin-4-one (**5a**) *and 2-acetonyl-3-benzyl-2,5,5-trimethyloxazolidin-4-one* (**6a**). 4-Benzylaminopent-3-en-2-one (**1a**) (380 mg, 2 mmol) was added to a suspension of NaH (108 mg, 4.4 mmol) in THF (5 ml). The suspension was refluxed for 15 min and then allowed to reach 20 °C; it was then treated, during *ca.* 2 h with stirring, with *N*-benzyl-2-bromo-2-methylpropanamide (**4a**) (512 mg, 2 mmol) in THF (5 ml). Stirring was continued for 1 h, then the mixture was centrifuged and the resulting solution taken to dryness.

(a) The thick oil was worked up with n-hexane (3 × 10 ml) to yield the imine (**5a**) as an oil (545 mg, 66%); δ(CCl_4) 1.14 (3 H, Me), 1.28 (3 H, Me), 1.36 (3 H, Me), 1.90 (3 H, Me), 2.53 (2 H, CH_2), 4.30—4.68 (2 H, AB *J* 16 Hz, CH_2), 4.38 (2 H, CH_2), and 7.10—7.28 (10 H, m, 2 Ph). Prompt hydrolysis both on alumina and silica gel converted (**5a**) into (**6a**); accordingly, an analytically pure sample of (**5a**) could not be obtained.

(b) Chromatography on silica or even on alumina afforded (**6a**) as a colourless oil (78%); $\nu_{max.}$(liquid film) 1 700 cm^{-1} (br, CO); δ(CCl_4) 1.27 (3 H, Me), 1.37 (6 H, 2 Me), 2.00 (3 H, Me), 2.56 (2 H, CH_2), 4.36—4.53 (2 H, AB, *J* 15.3 Hz, CH_2N), and 7.20—7.29 (5 H, m, Ph) (Found: C, 69.8; H, 7.7; N, 5.1. $C_{16}H_{21}NO_3$ requires C, 69.52; H, 7.61; N, 5.17%)

2-Acetonyl-3-benzyl-5,5-dimethyl-2-phenyloxazolidin-4-one (**6b**). This was obtained by treating (**1b**) with (**4a**) and purifying it on silica [method (b)]; a colourless *oil* (73%); $\nu_{max.}$(liquid film) 1 700br cm^{-1} (CO); δ($CDCl_3$) 1.52, 1.58 (6 H, 2 Me), 1.83 (3 H, Me), 2.82, 3.13 (2 H, AB, *J* 15 Hz, CH_2), 3.93, 4.73 (2 H, AB, *J* 16 Hz, CH_2N), and 7.15—7.6 (10 H, 2 Ph) (Found: C, 74.5; H, 7.0; N, 4.25. $C_{21}H_{23}NO_3$ requires C, 74.75; H, 6.87; N, 4.15%)

3-Benzyl-2,5,5-trimethyl-2-phenacyloxazolidin-4-one (**6c**). This was obtained from (**1c**) and (**4a**) and worked up as for (**6b**); a colourless *oil* (55%), $\nu_{max.}$(liquid film) 1 700br cm^{-1} (CO); δ($CDCl_3$) 1.2 (3 H, Me), 1.4 (6 H, 2 Me), 3.12, 3.32 (2 H, AB, *J* 14 Hz, CH_2), 4.52, 4.78 (2 H, AB, *J* 16 Hz, CH_2N), and 7.3—8.0 (10 H, 2 Ph) (Found: C, 74.5; H, 6.9; N, 4.2. $C_{21}H_{23}NO_3$ requires C, 74.75; H, 6.87; N, 4.15%)

2-Acetonyl-3,5,5-trimethyl-2-phenyloxazolidin-4-one (**6d**). This was obtained as for (**6b**) from compounds (**1b**) and (**4b**); the crude oil was purified according to method (b) to give *colourless crystals*, m.p. 129—132 °C (from diethyl ether) (44%), R_F1 0.35; $\nu_{max.}$(KBr) 1 720 and 1 690 cm^{-1} (CO); δ($CDCl_3$) 1.33 (3 H, Me), 1.43 (3 H, Me), 2.18 (3 H, MeCO), 2.9 (3 H, MeN), 2.95—3.5 (2 H, AB, *J* 15 Hz, CH_2), and 7.35 (5 H, Ph) (Found: C, 68.7; H, 7.5; N, 5.3. $C_{15}H_{19}NO_3$ requires C, 68.94; H, 7.33; N, 5.36%).

2-Acetonyl-5,5-dimethyl-2,3-diphenyloxazolidin-4-one (**6e**) *and 3-Benzyl-2,5,5-trimethyl-1-phenyl-2-phenacylimidazolidin-4-one* (**9**). These were obtained from (**1b**) and (**4c**). Work-up [method (b)] of the crude oil afforded: (i) the *oxazolidinone* (**6e**) (25%) as colourless crystals, m.p. 112—115 °C, R_F1 0.35; $\nu_{max.}$(KBr) 1 730 and 1 715 cm^{-1} (CO); δ($CDCl_3$) 1.6, 1.63 (6 H, 2 Me), 2.05 (3 H, MeCO), 3.16, 3.45 (2 H, AB, *J* 16 Hz, CH_2), 6.9—7.1 (2 H, m, Ar), and 7.3—7.4 (8 H, m, Ar) (Found: C, 74.6; H, 6.6; N, 4.6. $C_{20}H_{21}NO_3$ requires C, 74.28; H, 6.55; N, 4.33%); and (ii) the *imidazolidinone* (**9**) (18%) as a colourless oil, R_F1 0.5; $\nu_{max.}$ ($CHCl_3$) 1 705 and 1 700 cm^{-1} (CO); δ($CDCl_3$) 1.22 (3 H, Me), 1.41 (6 H, 2 Me), 3.1, 3.33 (2 H, AB, *J* 15 Hz, CH_2), 4.5, 4.8 (2 H, AB, *J* 18 Hz, CH_2N), and 7.3—8.0 (15 H, m, 3 Ph) (Found: C, 78.2; H, 7.0; N, 6.6. $C_{27}H_{28}N_2O_2$ requires C, 78.61; H, 6.84; N, 6.79%)

3′-Benzyl-5,5,5′,5′-tetramethyl-3-phenyliminocyclohexane-spiro-2′-oxazolidin-4′-one (**7a**). This was obtained from (**2b**) and (**4a**) as for (**5a**) [method (a)]. The crude solid was recrystallized from chloroform–light petroleum as colourless *crystals* (72%), m.p. 124—128 °C, R_F2 0.7. The ^1H n.m.r. spectra of the crude

and recrystallized product showed two compounds, in a ratio of *ca.* 1:1, probably C=N isomers; δ($CDCl_3$) 0.9, 1.0, 1.01, 1.15, 1.24, 1.42, 1.45, 1.53 (24 H, 4 Me, 4 Me), 1.8—2.7 (12 H, m, 6 CH_2), 4.31, 4.66 (2 H, AB, *J* 17 Hz, CH_2N), 4.40, 4.50 (2 H, AB, *J* 16 Hz, CH_2N), 6.6—6.8 (4 H, m, Ar), and 7.2—7.5 (16 H, m, Ar) (Found: C, 76.5; H, 7.7; N, 6.9. $C_{25}H_{30}N_2O_2$ requires C, 76.88; H, 7.74; N, 7.17%).

3'-Benzyl-5,5,5',5'-tetramethylcyclohexanespiro-2'-oxazolidine-3,4'-dione (**8a**). This was obtained from (**2a**) and (**4a**), treating the crude oil according to method (c), or by hydrolysis of compound (**7a**); colourless *crystals* (75%), m.p. 138—140 °C; $\nu_{max.}$(KBr) 1 720, 1 680 cm^{-1} (CO); δ($CDCl_3$) 1.02, 1.10 (6 H, 2 Me), 1.41, 1.42 (6 H, 2 Me), 1.6—2.8 (6 H, m, 3 CH_2), 4.42, 4.70 (2 H, AB, *J* 16 Hz, CH_2N), and 7.3 (5 H, Ph) (Found: C, 72.2; H, 8.0; N, 4.5. $C_{19}H_{25}NO_3$ requires C, 72.34; H, 7.98; N, 4.44%).

3'-Benzyl-5',5'-dimethylcyclohexanespiro-2'-oxazolidine-3,4'-dione (**8b**). This was prepared from (**2c**) and (**4a**) by method (c), as colourless *crystals* (57%), m.p. 103—105 °C, R_F1 0.5; $\nu_{max.}$ (KBr) 1 725, 1 690 cm^{-1} (CO); δ($CDCl_3$) 1.42 (3 H, Me), 1.44 (3 H, Me), 1.8—2.7 (6 H, m, 3 CH_2) 4.5, 4.6 (2 H, AB, *J* 17 Hz, CH_2), and 7.3 (5 H, Ph) (Found: C, 71.3; H, 7.3; N, 4.8. $C_{17}H_{21}NO_3$ requires C, 71.05; H, 7.36; N, 4.87%).

Behaviour of Compound (**8a**) *with Acids and Bases.*—A solution of compound (**8a**) (0.158 g, 0.5 mmol) in EtOH (3 ml) and 6M-HCl (1 ml) was refluxed for 4 h; on concentration, the starting material was recovered unchanged. Analogous treatment with 6M-NaOH in EtOH similarly gave unchanged (**8a**).

3'-Benzyl-3-hydroxy-5,5,5',5'-tetramethylcyclohexanespiro-2'-oxazolidine-3,4'-dione (**10**).—To a stirred suspension of $NaBH_4$ (0.114 g, 3 mmol) in THF (5 ml), a solution of (**8a**) (0.315 g, 1 mmol) in THF (5 ml) was added during 0.5 h. The reaction mixture was stirred at room temperature for 12 h, until all the (**8a**) had reacted (t.l.c.). The mixture was taken up with water (0.5 ml) and diethyl ether (20 ml); the ether solution was dried (Na_2SO_4) and concentrated under reduced pressure, to yield a colourless oil (309 mg, 97%). Trituration with light petroleum (b.p. 40—60 °C) gave colourless *crystals* (0.244 g, 77%), m.p. 136—138 °C (from Et_2O–light petroleum), R_F1 0.5; $\nu_{max.}$(KBr) 3 560, 3 460 (OH), and 1 690 (CO) cm^{-1}. The ^1H n.m.r. spectrum showed these crystals to be a mixture of two diastereoisomers, but they could not be separated through either t.l.c. or fractional crystallization. *Major diastereoisomer* (80%): δ($CDCl_3$) 0.85 (3 H, Me), 1.25 (3 H, Me), 1.45 (3 H, Me), 1.48 (3 H, Me), 1.5—2.2 (6 H, m, 3 CH_2), 3.45 (1 H, OH; exchanges with D_2O in a few min), 4.15 (1 H, m, CH), 4.35, 4.6 (2 H, AB, *J* 16 Hz, CH_2N), and 7.3 (5 H, C_6H_5); *minor diastereoisomer* (20%): δ($CDCl_3$) 1.05 (3 H, Me), 1.3 (3 H, Me), 1.39 (3 H, Me), 1.40 (3 H, Me), and 4.37, 4.47 (2 H, AB, *J* 17 Hz, CH_2N).

Other signals (OH, CH_2, CH, and phenyl) were hidden under the corresponding signals of the major isomer, as shown by integration (Found: C, 72.0; H, 8.7; N, 4.5. $C_{19}H_{27}NO_3$ requires C, 71.89; H, 8.57; N, 4.41%).

3-[N-Benzyl-N-(3-hydroxy-5,5-dimethylcyclohexyl)amino]-2-methylpropan-2-ol (**11**).—(A) *Reduction of compound* (**8a**) *with* $LiAlH_4$. A solution of (**8a**) (0.315 g, 1 mmol) in THF (5 ml) was added to a stirred suspension of $LiAlH_4$ (0.38 g, 10 mmol) in THF (10 ml). The mixture was refluxed for 2 h, allowed to cool, diluted with diethyl ether (30 ml) and 1M-NaOH (0.5 ml), shaken and filtered. The organic solution was dried (Na_2SO_4) and concentrated. The resulting oil was purified through a column of Sephadex LH 20, eluting with $CHCl_3$. The oil (0.220 g, 73%) was triturated with light petroleum to give colourless *crystals*, m.p. 87—88 °C, R_F2 0.8; $\nu_{max.}$($CHCl_3$) 3 610, 3 420 (OH) cm^{-1}; δ($CDCl_3$) 0.93 (3 H, Me), 1.04 (3 H, Me), 1.1 (6 H, 2 Me), 1.2—2.1 (6 H, m, 3 CH_2), 2.5 (2 H, CH_2N), 3.15 (1 H, m, CH), 2.8—3.5 (2 H, br, 2 OH, exchange with D_2O in few min), 3.75 (2 H, CH_2N), 4.2 (1 H, m, CH), and 7.3 (5 H, Ph) (Found: C, 74.6; H, 10.3; N, 4.5. $C_{19}H_{31}NO_2$ requires C, 74.71; H, 10.23; N, 4.59%).

(B) *Reduction of compound* (**8a**) *with the* $\overline{BH_3}$–$\overline{Me_2SO}$ *complex.* A sample of the BH_3–Me_2SO complex[5] (0.315 ml, 3 mmol) was added to a solution of compound (**8a**) (0.315 g, 1 mmol). The reaction mixture was refluxed under N_2 for 0.5 h and concentrated under reduced pressure. 1M-HCl (10 ml) was then added and the mixture stirred at room temperature for 0.5 h, extracted with diethyl ether (30 ml), dried and concentrated to give a solid (0.266 g, 87%): the m.p. and i.r. and ^1H n.m.r. spectra were identical with those indicated for compound (**11**). The product was obtained by both procedures (A) and (B) and had the characteristics of a single compound; no diastereoisomers could be found in the reaction mixture.

3'-Benzyl-5,5,5',5'-tetramethyl-3-oxocyclohexanespiro-2'-oxazolidine-4'-thione (**12**).—A solution of (**8a**) (1.26 g, 4 mmol) in toluene (50 ml) was heated at reflux for 7 h with Lawesson's reagent[6] (0.808 g, 2 mmol). Concentration to dryness gave a residue which was purified on a column of neutral alumina; elution with AcOEt–toluene (1:1) and concentration gave yellow crystals (0.795 g, 60%), m.p. 126—128 °C (recrystallized from diethyl ether–light petroleum), R_F1 0.8, colourless with I_2–NaN_3; $\nu_{max.}$(KBr) 1 715 (CO), 1 470 cm^{-1}; δ($CDCl_3$) 0.92 (3 H, Me), 0.98 (3 H, Me), 1.5 (6 H, 2 Me), 1.9—2.7 (6 H, m, 3 CH_2), 4.8, 5.15 (2 H, AB, *J* 16 Hz, CH_2N), and 7.3 (5 H, Ph) (Found: C, 68.8; H, 7.6; N, 4.2; S, 9.7. $C_{19}H_{25}NO_2S$ requires C, 68.84; H, 7.60; N, 4.22; S, 9.67%).

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