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SOME CHEMICAL TRANSFORMATIONS OF 4,5-DIHYDRO-5-METHYL-3H-SPIRO[BENZ-2-AZEPINE-3,1'-CYCLOHEXANE] N-OXIDE

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The oxidation and reduction of 4,5-dihydro-5-methyl-3H-spiro[benz-2-azepine-3,1'-cyclohexane] N-oxide, the reactions of this N-oxide with methylmagnesium iodide, the sodium salt of diethyl malonate, phenyl isocyanate, and its rearrangement by the action of acetic anhydride lead to N-hydroxy-1,2,3,4-tetrahydrobenz-2-azepines, benz-2-azepine-1-one, and its N-acetoxy derivative as well as isoxazolidino- and oxadiazolidino[3,2-a]benz-2-azepines spirofused with a cyclohexane ring.

Keywords: benz-2-azepines, isoxazolidino- and oxadiazolidino[3,2-*a*]benz-2-azepines, cyclic nitrones, reduction, nucleophilic addition, oxidation.

The properties and reactivity of acyclic nitrones have been studied rather extensively [1]. Cycloaddition is the best studied reaction of cyclic nitrones [2], while reactions with nucleophilic reagents have been studied less extensively [3]. Possessing a method for the synthesis of a benz-2-azepine nitrone, namely, 4,5-dihydro-5-methyl-3H-spiro[benz-2-azepine-3,1'-cyclohexane] N-oxide (**1**) [4], we carried out a systematic study of this compound. We have already studied the [3+2] cycloaddition of alkenes and diethylacetylenedicarboxylate [5-7] and the reaction of **1** with alkylmagnesium and arylmagnesium halides, nitromethane, and cyanide anion [8]. In the present work, we studied the reaction of nitrone **1** with nucleophiles, isocyanates, isothiocyanates, and acetic anhydride.

In contrast to benzylmagnesium and phenylmagnesium halides, isopropylmagnesium bromide reacts with nitrone **1** to give 1-isopropyl-5-methyl-4,5-dihydro-3H-spiro[benz-2-azepine-3,1'-cyclohexane], which is a benzazepine imine [8]. In an attempt to determine whether this reaction is common for alkylmagnesium halides and obtain a synthone [9] for use in the synthesis of 1-substituted and fused benzazepines, we carried out the reaction of nitrone **1** with methylmagnesium iodide. This reaction proceeds readily to give a 0.7:1 mixture of hydroxylamine **2** and imine **3** in 65% yield. This mixture was oxidized with hydrogen peroxide in the presence of sodium tungstenate to give the corresponding nitrone **4**. Nitrone **1** is reduced by the action of lithium aluminum hydride to the corresponding hydroxylamine **5**, which was characterized as O-carbamoyl derivative **6** [10].

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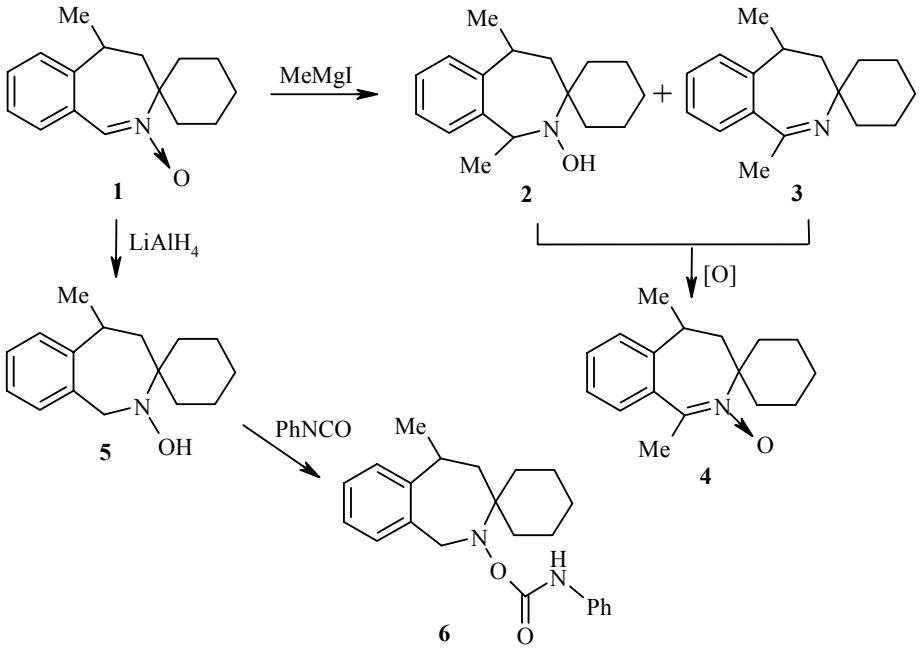
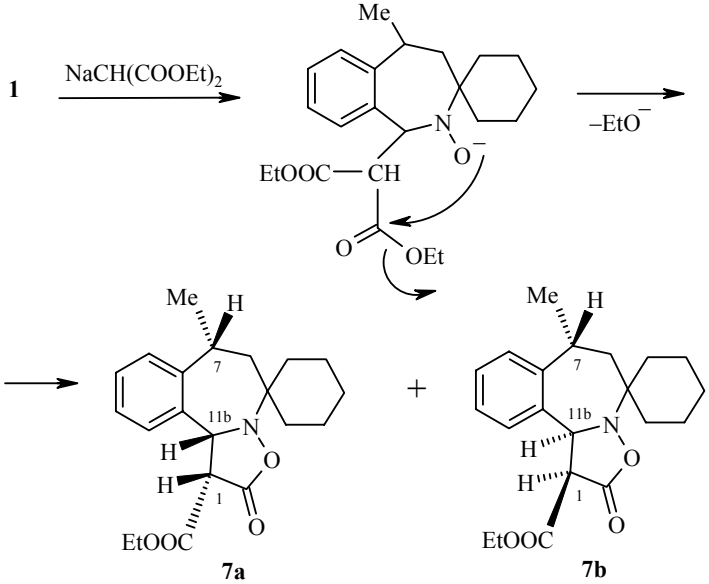


The reaction of the sodium derivative of diethyl malonate with nitrone **1** does not stop after addition [11], but rather proceeds with intramolecular nucleophilic substitution to give spiro[isoxazolidinobenz-2-azepine-5-cyclohexane] (**7**) formed as a mixture of diastereomers **7a** and **7b** differing in the arrangement of H-11b and the methyl group at C-7. ^{1}H NMR spectroscopy indicated a 1:0.8 ratio of **7a** and **7b**. A *cis* arrangement is found for H-11b and H-1 in both diastereomers.



The [3+2] cycloaddition of alkyl and aryl isocyanates and isothiocyanates to nitrones leads to 1,2,4-oxadiazolin-5-ones and 5-thiones [2]. The addition of phenyl isocyanate and phenyl isothiocyanate to nitrone **1** proceeds regiospecifically and stereoselectively to give mixtures of diastereomers of spiro[1,2,4-oxadiazolidinobenz-1-azepinecyclohexanes] **8** and **9** relative to the position of H-11b and the methyl group at C-7. ^{1}H NMR spectroscopy indicated that the ratio of isomers **8a** and **9a** with *trans* relationship of these groups

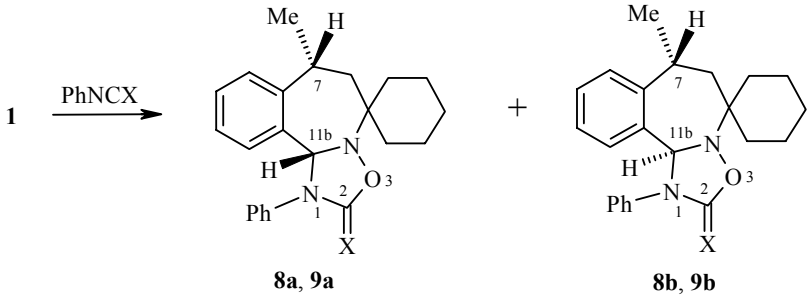
TABLE 1. ^{1}H NMR Spectra of Spiro[benzazepinecyclohexanes] **2-5, 10** and **11** in $CDCl_3$

Com-pound	Chemical shifts, δ, ppm (SSCC, *J*, Hz)						
	H-4a	H-4e	H-5	CH_3-5, d	H-cyclohex.	H-6–H-9	other signals
2	—	—	3.24 (m)	1.36 ($J_{5,Me}$ = 7.0)	0.9-2.45 (m, cyclohex. + CH_2-4)	7.05-7.50	1.60 (d, ^3J = 6.7, CH_3-1); 4.67 (q, ^3J = 6.7, H-1)
3	1.96 (dd, $J_{4a,4e}$ = 13.7, $J_{4a,5}$ = 12.5)	2.40 (dd, $J_{4a,4e}$ = 13.7, $J_{4e,5}$ = 5.8)	3.10 (m, $J_{5,Me}$ = 7.0, $J_{4e,5}$ = 5.8, $J_{4a,5}$ = 12.5)	1.30 ($J_{5,Me}$ = 7.0)	0.9-2.45	7.05-7.50	2.48 (s, CH_3-1)
4	1.97 (dd, $J_{4a,4e}$ = 13.7, $J_{4a,5}$ = 12.2)	2.40 (dd, $J_{4a,4e}$ = 13.7, $J_{4e,5}$ = 5.8)	3.11 (m, $J_{5,Me}$ = 7.0, $J_{4e,5}$ = 5.8, $J_{4a,5}$ = 12.2)	1.30 ($J_{5,Me}$ = 7.0)	1.0–2.4	7.1-7.45	2.48 (s, CH_3-1)
5	—	—	3.18 (m)	1.37 ($J_{5,Me}$ = 7.0)	1.2-2.0 (m, cyclohex. + CH_2-4)	7.35-7.05	4.47 (br. s, OH); 4.06 (d, $J_{A,B}$ = 14.7, 1A); 4.60 (d, $J_{A,B}$ = 14.7, 1B)
10	1.65 (dd, $J_{4a,4e}$ = 13.7, $J_{4a,5}$ = 11.6)	2.05 (dd, $J_{4a,4e}$ = 13.7, $J_{4e,5}$ = 5.8)	3.32 (m, $J_{5,Me}$ = 7.0, $J_{4e,5}$ = 5.8, $J_{4a,5}$ = 11.6)	1.36 ($J_{5,Me}$ = 7.0)	0.8-1.65	7.24 (dt, $J_{6,7}$ = 7.6, $J_{6,8}$ = 1.5, H-6); 7.30 (td, $J_{7,8}$ = $J_{8,9}$ = 7.6, $J_{6,8}$ = 1.5, H-8); 7.44 (td, $J_{6,7}$ = $J_{7,8}$ = 7.6, $J_{7,9}$=1.5, H-7); 7.67 (dd, $J_{8,9}$ = 7.6, $J_{7,9}$ = 1.5, H-9)	5.95 (br. s, NH)
11	1.64 (br. m)	2.22 (br. m)	3.81 (br. m)	1.38 ($J_{5,Me}$ = 7.0)	0.85-1.95	7.70-7.20	2.28 (3H, s, CH_3CO)

TABLE 2. ^{1}H NMR Spectra of Spiro[isoxazolidino- and Spiro[oxadiazolidinobenzazepinecyclohexanes] **7-9** in $CDCl_3$

Com-pound	Chemical shifts, δ, ppm (SSCC, *J*, Hz)								
	H-1, dd	H-6a, dd	H-6e	H-7, m	CH_3-7	H-cyclohex., m	H-arom.	H-11b	Other signals
7a	4.53 (^3J = 12.8)	2.29 ($J_{6a,6e}$ = 15.0)	—	3.23	1.42 (m)	1.0-2.1 (cyclohex. + H-6e)	6.8-7.4(H-6–H-9)	5.54 (dd, ^3J = 12.8)	1.40 (t, ^3J = 7.0, $\underline{CH_3}CH_2$); 4.41 (q, ^3J = 7.0, CH_2O)
7b	4.11 (^3J = 11.3)	2.25 ($J_{6a,6e}$ = 15.0)	—	3.33	1.41 (m)	1.0-2.1 (cyclohex. + H-6e)	6.8-7.4 (H-6–H-9)	5.62 (dd, ^3J = 11.3)	1.32 (t, ^3J = 7.0, $\underline{CH_3}CH_2$); 4.28 (q, ^3J = 7.0, CH_2O)
8a	—	1.35 ($J_{6a,6e}$ = 14.3, $J_{6a,7}$ = 13.4)	2.33 (d, $J_{6a,6e}$ = 14.3)	3.43 ($J_{7,Me}$ = 7.0, $J_{6a,7}$ = 13.4)	1.47 (d, $J_{7,Me}$ = 7.0)	1.2-2.5	6.9-7.4 (H-6–H-9 +Ph)	6.73 (s)	—
8b	—	—	2.17 (dd, $J_{6a,6e}$ = 14.3, $J_{6e,7}$ = 5.2)	3.50 ($J_{7,Me}$ = 7.0, $J_{6e,7}$ = 5.2)	1.45 (d, $J_{7,Me}$ = 7.0)	1.2-2.5 (cyclohex.+ H-6a)	6.9-7.4 (H-6–H-9 +Ph)	6.57 (s)	—
9a	—	1.90 ($J_{6a,6e}$ = 15.3, $J_{6a,7}$ = 10.7)	2.45 (dd, $J_{6a,6e}$ = 15.3, $J_{6e,7}$ = 2.8)	3.14 ($J_{7,Me}$ = 6.7, $J_{6a,7}$ = 10.7, $J_{6e,7}$ = 2.8)	1.43 (d, $J_{7,Me}$ = 6.7)	1.3-2.6	7.0-7.55 (H-6–H-9 +Ph)	7.96 (s)	—
9b	—	—	2.33 (dd, $J_{6a,6e}$ = 14.7, $J_{6e,7}$ ~0)	3.34 ($J_{7,Me}$ = 6.7, $J_{6e,7}$ ~0)	1.43 (d, $J_{7,Me}$ = 6.7)	1.3-2.6 (cyclohex. + H-6a)	7.0-7.55 (H-6–H-9 +Ph)	6.91 (s)	—

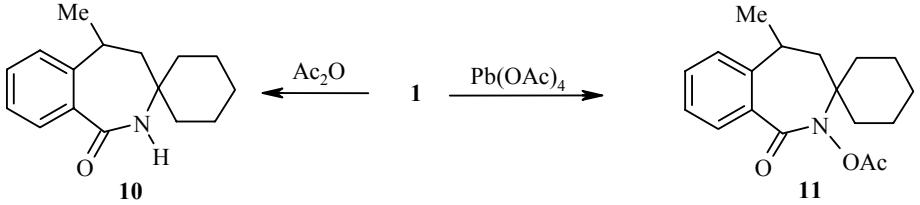
in the adducts with phenyl isocyanate (**8**) and phenyl isothiocyanate (**9**) to isomers **8b** and **9b** was 1.6:1 (**8a:8b**) and 7.1:1 (**9a:9b**). The arrangement of H-7 and H-11b in adducts **8a, 8b, 9a,** and **9b** was established using the homonuclear Overhauser effect. A pure sample of diastereomer **8a** was isolated in 57% yield upon crystallization of the reaction mixture from acetone.



8a, **9a** **8b**, **9b**

8 X = O; **9** X = S

The action of acid anhydrides, acid chlorides, PCl_3, PCl_5, $POCl_3$, and sodium ethylate on nitrones leads to their rearrangement to give amides [12]. Similarly, nitrone **1** is converted upon heating at reflux in acetic anhydride into benz-2-azepine-1-one (**10**) in 82% yield.



10 **11**

The lead tetraacetate oxidation of nitrone **1** gives the O-acetyl derivative of hydroxamic acid **11** in 90% yield. Manganese dioxide in benzene and potassium periodate in chloroform in the presence of crown ether do not oxidize nitrone **1**. The permanganate oxidation under phase-transfer conditions using TBAI and water–chloroform leads to the formation of a complex mixture.

The mass spectra of all these products show molecular ion peaks of different intensity, corresponding to their chemical formulas. The IR spectra of these compounds show stretching vibration bands of the corresponding functional groups.

The OH group stretching bands for hydroxylamines **2** and **5** are found at 3321 and 3222 cm^{-1}, respectively. The N→O stretching band in the spectrum of nitrone **4** is found at 1238 cm^{-1}, while the C=N stretching band is found at 1562 cm^{-1}. Three CO stretching bands are found in the mixture of isoxazolidinobenzazepines **7a** and **7b** (1788, 1768, and 1741 cm^{-1}), while only one CO stretching band is found in the spectrum of oxadiazolidinobenzazepine at 1738 cm^{-1}. The spectra of lactams **10** and **11** have N–C=O bands at 1641 and 1654 cm^{-1}, respectively, and also stretching bands for the NH group at 3270 and 3185 cm^{-1} (**10**) and ester group at 1754 cm^{-1} (**11**). The thione group in the spectrum of **9** is seen at 1221 cm^{-1}. The ^1H NMR spectra of fused benzazepinecyclohexanes **2-5, 10,** and **11** have signals for all the protons with chemical shifts and coupling constants corresponding to their position in the molecule. The methylene group signals for CH_2-4 in hydroxylamines **2** and **5** are overlapped by the cyclohexane ring signals. The CH_2-1 protons in the spectrum of **5** are not equivalent and appear as two doublets (4.06 and 4.60 ppm). The broadening of the signals in the spectrum of N-acetoxylactam **11** may be a consequence of conformational transitions of the hydrogenated azepine ring.

TABLE 3. Physical Data of the Products

Compound	Empirical formula	Found, % / Calculated, %			$[M]^+$	mp, °C*[2]	R_f	Yield, %
		C	H	N				
2	$C_{17}H_{25}NO$				259		0.51 (1:2)	65
3	$C_{17}H_{23}N$				241			
4	$C_{17}H_{23}NO$	79.60 / 79.38	9.03 / 8.95	5.30 / 5.45	257		0.12 (1:1)	52
5	$C_{16}H_{23}NO$	78.41 / 78.37	9.30 / 9.39	5.98 / 5.71	245	125.5-128	0.38 (1:1)	84
6	$C_{23}H_{28}N_2O_2$	75.73 / 75.82	7.82 / 7.69	7.85 / 7.69	364	141-142.5	0.73 (1:1)	77
7	$C_{21}H_{27}NO_4$	70.31 / 70.59	7.33 / 7.56	4.01 / 3.92	362	107-110	0.68 (1:1)	20
8	$C_{23}H_{26}N_2O_2$	76.11 / 76.24	7.02 / 7.18	7.91 / 7.73	362	199.5-204	0.70 (1:1)	96
9	$C_{23}H_{26}N_2OS$	73.18 / 73.02	6.74 / 6.88	7.57 / 7.41	378	125-127	0.56 (1:2)	96
10	$C_{16}H_{21}NO$	79.25 / 79.01	9.00 / 8.64	5.46 / 5.76	243	150-152	0.26 (1:1)	82
11	$C_{18}H_{23}NO_3$	71.88 / 71.76	7.53 / 7.64	4.49 / 4.65	301	88-90	0.57 (1:1)	90

* Elemental analysis not performed for compounds **2** and **3**.
*[2] Products **2-4** are oils.

The ^{1}H NMR spectra of spiro[isoxazolidino- and spiro[oxadiazolidinobenzazepinecyclohexanes] **7-9** given in Table 2 have two signals for H-1, H-6a, H-7, CH_3-7, and H-11b, which unequivocally indicates the formation of these compounds as two diastereomers. The $J_{7,6}$ coupling constant suggests that CH_3-7 in all the diastereomers occupies a pseudoequatorial position.

Thus, benzazepine nitrone **1** undergoes all the reactions characteristic for cyclic and acyclic nitrones to give 1-substituted and condensed spiro[benz-2-azepine-3-cyclohexanes].

EXPERIMENTAL

The IR spectra were taken on UR-20 and IR-75 spectrometers. The mass spectra were obtained on a Finnigan MAT Incos 50 mass spectrometer with direct inlet into the ion source. The ionizing voltage was 70 eV. The ^{1}H NMR spectra of ~2% solutions of the products in $CHCl_3$ were taken on a Bruker WP-200 spectrometer at 200 MHz and 30°C with TMS as the internal standard. Thin-layer chromatography was carried out on Silufol UV-254 plates with 1:1, 1:2, and 1:3 ethyl acetate–hexane as the eluent and detection with iodine vapor. Column chromatography was carried out using Woelm 32/64 silica gel and L 5/40 silica gel. The melting points were determined in glass capillaries and not corrected.

The physicochemical data of the products are given in Table 3.

2-Hydroxy-1,5-dimethyl-1,2,4,5-tetrahydro-3H-spiro[benz-2-azepine-3,1'-cyclohexane] (2) and 4,5-Dihydro-1,5-dimethyl-3H-spiro[benz-2-azepine-3,1'-cyclohexane] (3). A sample of nitrone **1** (1.00 g, 4 mmol) was added to a water-cooled solution of methylmagnesium iodide obtained from methyl iodide (0.5 ml, 8 mmol) and magnesium (0.28 g, 12 mmol) in absolute ether (30 ml) and heated at reflux for 1.5 h. The solution was monitored by thin-layer chromatography. Then, the solution was decomposed by adding saturated aqueous ammonium chloride and extracted with three 50-ml ether portions. The combined extracts were dried over $MgSO_4$. The residue after distilling off the solvent was passed through a silica gel layer with 1:5 hexane–ethyl

acetate as the eluent to give 0.68 g (65%) mixture of **2** and **3**. Product 2. IR spectrum in vaseline oil, ν, cm^{-1}: 3321 (OH), 1041 (N–O). Mass spectrum, *m/z* (I_{rel}, %): 259 $[M]^+$ (12), 244 (9), 243 (18), 242 (100), 226 (1), 216 (10), 211 (5), 200 (4), 188 (5), 172 (4), 157 (4), 148 (11), 147 (12), 146 (13), 145 (18), 131 (70), 130 (13), 129 (4), 128 (14), 117 (42), 116 (17), 115 (36), 114 (16), 105 (13), 103 (12), 98 (9), 91 (48), 77 (18), 55 (17), 41 (43). Product **3**: IR spectrum in vaseline oil, ν, cm^{-1}: 1641 (C=N). Mass spectrum, *m/z* (I_{rel}, %): 241 $[M]^+$ (20), 240 (100), 226 (6), 225 (14), 224 (11), 215 (18), 206 (6), 199 (12), 198 (42), 183 (13), 176 (5), 174 (8), 162 (25), 161 (11), 160 (14), 158 (19), 157 (17), 155 (11), 147 (12), 146 (99), 145 (49), 144 (73), 143 (30), 142 (13), 131 (11), 130 (25), 129 (37), 128 (56), 117 (16), 116 (16), 115 (58), 103 (38), 98 (1), 91 (46), 81 (17), 77 (55), 67 (20), 55 (26), 53 (29), 51 (23), 41 (35).

4,5-Dihydro-1,5-dimethyl-3H-spiro[benz-2-azepine-3,1'-cyclohexane] N-Oxide (4). A solution of mixture of **2** and **3** (0.86 g, 3.3 mmol), $Na_2WO_4 \cdot 2H_2O$ (0.11 g, 0.33 mmol), and 30% H_2O_2 (1 ml, 33 mmol) in acetone (20 ml) was heated at reflux for 8 h, poured into water (50 ml), and extracted with ether. The extract was washed with water and dried over $MgSO_4$. The residue after distilling off the solvent was subjected to chromatography on silica gel using 1:1 ethyl acetate–hexane as the eluent to give 0.44 g (52%) **4** as a thick yellow oil. IR spectrum in vaseline oil, ν, cm^{-1}: 1562 (C=N), 1238 (N→O). Mass spectrum, *m/z* (I_{rel}, %): 257 $[M]^+$ (13), 243 (11), 241 (6), 240 (48), 228 (10), 226 (12), 225 (14), 224 (8), 215 (10), 214 (6), 200 (23), 198 (18), 195 (5), 184 (13), 172 (8), 163 (33), 162 (20), 161 (31), 160 (16), 159 (17), 147 (44), 146 (100), 145 (70), 144 (43), 143 (30), 132 (14), 131 (34), 130 (34), 129 (40), 128 (37), 117 (18), 116 (13), 115 (38), 104 (14), 103 (30), 98 (13), 91 (39), 81 (22), 77 (34), 67 (22), 55 (26), 43 (53), 41 (47), 39 (27).

2-Hydroxy-5-methyl-1,2,4,5-tetrahydro-3H-spiro[benz-2-azepine-3,1'-cyclohexane] (5). A sample of lithium aluminum hydride (0.8 g, 2 mmol) was added to a suspension of nitrone **1** (0.50 g, 2 mmol) in absolute ether (20 ml) and heated at reflux for 1 h. A sample of 20% aqueous NaOH (0.5 ml) was added with water cooling and stirred until a precipitate formed. The ethereal layer was decanted and the precipitate was washed with two 20-ml ether portions. The combined ethereal extracts were dried over $MgSO_4$. The residue after distilling off ether was crystallized from hexane to give 0.42 g (84%) hydroxylamine **5** as white crystals. IR spectrum (KBr), ν, cm^{-1}: 3222 (OH), 1022 (N–O). Mass spectrum, *m/z* (I_{rel}, %): 245 $[M]^+$ (25), 229 (29), 228 (100), 226 (5), 214 (7), 202 (43), 200 (4), 186 (25), 172 (10), 158 (6), 156 (6), 143 (8), 141 (3), 132 (67), 131 (59), 130 (19), 129 (18), 118 (31), 117 (77), 115 (39), 105 (13), 103 (8), 98 (20), 91 (42), 77 (15), 55 (13), 41 (24).

5-Methyl-2-(N-phenylcarbamoyloxy)-1,2,4,5-tetrahydro-3H-spiro[benz-2-azepine-3,1'-cyclohexane] (6). A sample of phenyl isocyanate (0.26 ml, 2.4 mmol) was added to a solution of hydroxylamine **5** (0.30 g, 1.2 mmol) in absolute heptane (15 ml) and maintained for 0.5 h at 0°C. The crystalline precipitate was filtered off and washed on the filter with absolute heptane to give 0.34 g (77%) **6** as white crystals. IR spectrum (KBr), ν, cm^{-1}: 3388, 3281 (NH), 1741, 1708 (C=O), 1214 (C–O–N). Mass spectrum, *m/z* (I_{rel}, %): 364 $[M]^+$ (1), 245 [M^+ - PhNCO] (56), 228 (100), 212 (7), 202 (22), 186 (10), 172 (5), 158 (3), 143 (4), 132 (39), 119 [PhNCO] (17), 117 (34), 98 (9), 93 (15), 91 (30), 77 (12), 65 (11), 51 (3), 41 (12).

1-Ethoxycarbonyl-7-methyl-2-oxo-6,7-dihydro-5H-spiro{1,2-isoxazolidino[3,2-*a*]benz-2-azepine-5,1'-cyclohexane} (7). A sample of nitrone **1** (0.5 g, 2 mmol) was added to the sodium derivative of diethyl malonate obtained from sodium amide (0.31 g, 8 mmol) and diethyl malonate (1.21 ml, 8 mmol) in absolute benzene (25 ml). The mixture was heated at reflux for 12 h with monitoring by thin-layer chromatography. Then, ethanol (2 ml) and water (30 ml) were added. The mixture was extracted with benzene and the extract was dried over $MgSO_4$. Benzene was distilled off and the residue was purified by passing through alumina using 1:10 hexane–ethyl acetate as the eluent and then crystallization from hexane to give 0.14 g (20%) of a white crystalline mixture of diastereomers of **7**. IR spectrum (KBr), ν, cm^{-1}: 1788, 1768 (CO_2Et), 1741 (CO_2N). Mass spectrum, *m/z* (I_{rel}, %): 357 $[M]^+$ (5), 314 (24), 313 (10), 298 (4), 270 (6), 240 (7), 226 (32), 218 (13), 196 (4), 183 (5), 172 (10), 170 (9), 157 (8), 144 (48), 143 (100), 142 (47), 132 (17), 131 (22), 130 (36), 129 (52), 128 (50), 117 (26), 115 (36), 103 (12), 98 (75), 91 (140, 89 (16), 77 (18), 67 (20), 55 (39), 41 (60).

7-Methyl-2-oxo-1-phenyl-4,6,7,11b-tetrahydro-5H-spiro{1,2,4-oxadiazolidino[3,2-*a*]benz-2-azepine-5,1'-cyclohexane} (8). A sample of phenyl isocyanate (0.65 ml, 6 mmol) was added to a solution of nitrone **1** (0.5 g, 2 mmol) in absolute benzene (10 ml) and stirred for 2 h at 20°C with monitoring by thin-layer chromatography. Benzene was distilled off and the residue was crystallized from acetone to give 0.41 g (57%) **8a** as white crystals; mp 202-204°C (dec.).

Crystallization from hexane gave 0.69 g (96%) mixture of isomers **8a** and **8b** as white crystals; mp 199.5-204°C (dec.). IR spectrum (KBr), ν, cm^{-1}: 362 $[M]^+$ (2), 318 (3), 243 (23), 227 (24), 226 (100), 201 (5), 172 (9), 156 (3), 144 (11), 132 (25), 131 (45), 130 (31), 129 (15), 119 (59), 115 (16), 103 (7), 98 (8), 91 (39), 77 (32), 64 (17), 55 (12), 44 (23), 41 (21).

7-Methyl-1-phenyl-2-thioxo-4,6,7,11b-tetrahydro-5H-spiro{1,2,4-oxadiazolidino[3,2-*a*]benz-2-azepine-5,1'-cyclohexane} (9). A sample of phenyl isothiocyanate (0.36 ml, 3 mmol) was added to a solution of nitrone **1** (0.5 g, 2 mmol) in absolute benzene (15 ml) and stirred for 3 h at 20°C with monitoring by thin-layer chromatography. Benzene was distilled off and the residue was crystallized from 1:10 hexane–ethyl acetate to give 0.73 g (96%) mixture of isomers **9a** and **9b** as yellowish crystals. IR spectrum (KBr), ν, cm^{-1}: 1221 (C=S), 1048 (N–O). Mass spectrum, *m/z* (I_{rel}, %): 243 [M^+ - PhNCS] (5), 226 (30), 184 (4), 148 (4), 148 (4), 144 (3), 137 (11), 135 [PhNCS] (100), 132 (22), 131 (21), 130 (12), 117 (4), 116 (4), 115 (10), 104 (5), 103 (5), 91 (9), 77 (63), 63 (4), 55 (3), 51 (20), 41 (5), 39 (6).

5-Methyl-1-oxo-1,2,4,5-tetrahydro-3H-spiro[benz-2-azepine-3,1'-cyclohexane] (10). A sample of nitrone **1** (3.00 g, 12.3 mmol) in acetic anhydride (20 ml) was heated at reflux for 1 h. Excess acetic anhydride was distilled off in vacuum. The residue was made basic by adding ammonium hydroxide. The precipitate formed was filtered off, washed with water, and dried. Recrystallization from 1:10 hexane–ethyl acetate gave 2.45 g (82%) **10** as white crystals. IR spectrum (KBr), ν, cm^{-1}: 3270, 3185 (NH), 1641 (C=O), 1394 (NH). Mass spectrum, *m/z* (I_{rel}, %): 243 $[M]^+$ (50), 228 (18), 214 (7), 201 (12), 200 (100), 187 (10), 186 (8), 172 (22), 160 (8), 159 (17), 158 (9), 147 (74), 145 (13), 132 (10), 131 (57), 128 (13), 117 (15), 116 (8), 115 (20), 103 (44), 98 (27), 91 (20), 77 (43), 65 (10), 54 (19), 41 (53), 39 (30).

2-Acetoxy-5-methyl-1-oxo-1,2,4,5-tetrahydro-3H-spiro[benz-2-azepine-3,1'-cyclohexane] (11). A mixture of nitrone **1** (0.17 g, 0.7 mmol) and lead tetraacetate (0.31 g, 0.7 mmol) in absolute benzene (20 ml) was stirred for 4 h at room temperature. The reaction was monitored by thin-layer chromatography. The mixture was filtered and washed on the filter with absolute benzene. Benzene was distilled off and the residue was purified by passing through alumina using 1:1 hexane–ethyl acetate as the eluent to give 0.21 g of a light yellow oil. The crude product was crystallized from hexane to give 0.19 g (90%) **11** as white crystals. IR spectrum (KBr), ν, cm^{-1}: 1754 (CH_3CO_2), 1654 (CON). Mass spectrum, *m/z* (I_{rel}, %): 301 $[M]^+$ (2), 260 (18), 259 (100), 143 (15), 242 (79), 241 (18), 228 (17), 227 (80), 126 (11), 216 (38), 200 (8), 186 (5), 176 (15), 171 (9), 160 (20), 148 (26), 147 (86), 146 (90), 144 (5), 133 (28), 132 (29), 131 (50), 130 (11), 129 (15), 128 (19), 117 (24), 116 (11), 115 (28), 105 (16), 104 (45), 103 (43), 98 (7), 91 (27), 81 (35), 77 (38), 67 (13), 55 (26), 43 (95), 41 (41).

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