SYNTHESIS OF 2,5-DIAZA-3-OXATETRACYCLO[7.3.1.1^{7,11}.0^{2,6}]TETRADECAN-4-ONE AND -THIONE DERIVATIVES BY 1,3-DIPOLAR CYCLOADDITION REACTION OF HOMOADAMANTANE-INCORPORATED NITRONES WITH ISOCYANATES AND ISOTHIOCYANATES (1)

Yang Yu, Masatomi Ohno, Shoji Eguchi*

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

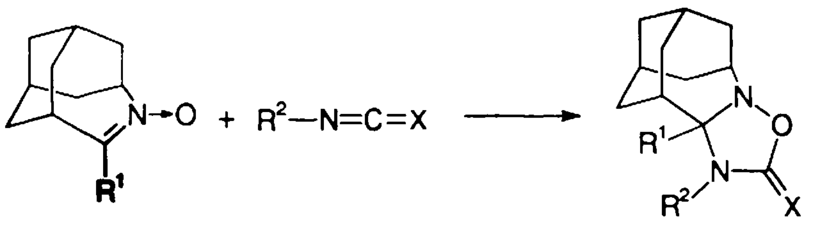
Abstract: The 1,3-dipolar cycloaddition reaction of homoadamantane-incorporated nitrones 1 and 2 with various isocyanates and isothiocyanates afforded 1,2,4-oxadiazolidinones and 1,2,4-oxadiazolidinethiones in title as a 1:1 cycloadduct. Considerable retardation of the cycloaddition due to a steric effect was observed in the nitrone 2 having a 5-Me substituent and some cycloadducts were readily decomposed via the retro-1,3-dipolar cycloaddition.

Introduction

We have recently reported synthesis of homoadamantane-incorporated nitrones 1 and 2, and their cycloaddition reactions with C≡C and C≡N triple bond functions as a useful method for synthesis of novel homoadamantane-fused nitrogen heterocycles (2-4). For example, In the reactions with acetylenic compounds, the initial cycloadducts of 2 rearranged readily to give homoadamantane-fused pyrroles (2), and the 1,3-dipolar cycloaddition with nitrile compounds provided a general and efficient route to 2,3-dihydro-1,2,4-oxadiazole derivatives which are difficult to prepare by other routes (3, 4). Nitrones are known to cycloadd across the C=N double bond of isocyanates and isothiocyanates, affording oxadiazolidinones and oxadiazolidinethiones (5, 6), but these adducts decompose often under the reaction conditions (7). From our continued interest in the synthetic application of the unique nitrones 1 and 2, we investigated the cycloaddition reaction of 1 and 2 with isocyanates and isothiocyanates as readily available and stable heterocumulenes. These results are reported herein. The nitrone unit embedded within the rigid polycyclic framework have proved to be valuable probes for the cycloaddition reactivity and steric effects as a seminal example of such compounds.

Results and Discussion

Readily available phenyl, methyl, cyclohexyl and trimethylsilyl isocyanates 3a–d, and the corresponding isothiocyanates 4a–d were employed as the 1,3-dipolarophiles. The cycloaddition reactions were carried out using 2.0 equivalents of the dipolarophiles in toluene or without solvent for unreactive isothiocyanates. As a general trend, the cycloaddition occurred rapidly at 0–25°C except for the reaction of 2 with phenyl isothiocyanate 4a, which did not proceed at all even under more severe conditions. These results are summarized in Scheme 1 and Table. Typically, the reaction of nitrone 1 with phenyl isocyanate 3a proceeded very rapidly even at 0°C for 40 min to afford a solid product 5a in 82% yield, which was characterized as the corresponding 1:1 cycloadduct, 1,2,4-oxadiazolidin-5-one by the spectral and analytical data. The reaction of nitrone 2 with 3a proceeded similarly and the formation of adduct 7a was evidenced by TLC analysis, ^{1}H NMR and MS spectral data of the crude product (see Experimental). However, the adduct was not stable on both preparative TLC and column chromatography (alumina), decomposing to starting nitrone 2 and side products derived from 3a. Much lower dipolarophilicity of isothiocyanates was observed in the reaction of nitrone 2, especially with phenyl isothiocyanate 4a. Even the reaction in neat at 100°C for 6 days did not produce any product; the reaction of 2 with cyclohexyl isothiocyanates 4c without a solvent at 25°C for 4 h afforded the cycloadduct 8c as evidenced by TLC analysis, however,



1: R^1 = H
2: R^1 = Me

3a: R^2 = Ph, X = O
3b: R^2 = Me, X = O
3c: R^2 = cyclohexyl, X = O
3d: R^2 = Me_3Si, X = O
4a: R^2 = Ph, X =S
4b: R^2 = Me, X = S
4c: R^2 = cyclohexyl, X = S
4d: R^2 = Me_3Si, X = S

5a: R^1 = H, R^2 = Ph, X = O
5b: R^1 = H, R^2 = Me, X = O
5c: R^1 = H, R^2 = cyclohexyl, X = O
5d: R^1 = H, R^2 = Me_3Si, X = O
6a: R^1 = H, R^2 = Ph, X = S
6b: R^1 = H, R^2 = Me, X = S
6c: R^1 = H, R^2 = cyclohexyl, X = S
7a: R^1 = Me, R^2 = Ph, X = O
7b: R^1 = Me, R^2 = Me, X = O
7c: R^1 = Me, R^2 = cyclohexyl, X = O
7d: R^1 = Me, R^2 = Me_3Si , X = O
8a: R^1 = Me, R^2 = Ph, X = S
8b: R^1 = Me, R^2 = Me, X = S
8c: R^1 = Me, R^2 = cyclohexyl, X = S

Scheme 1

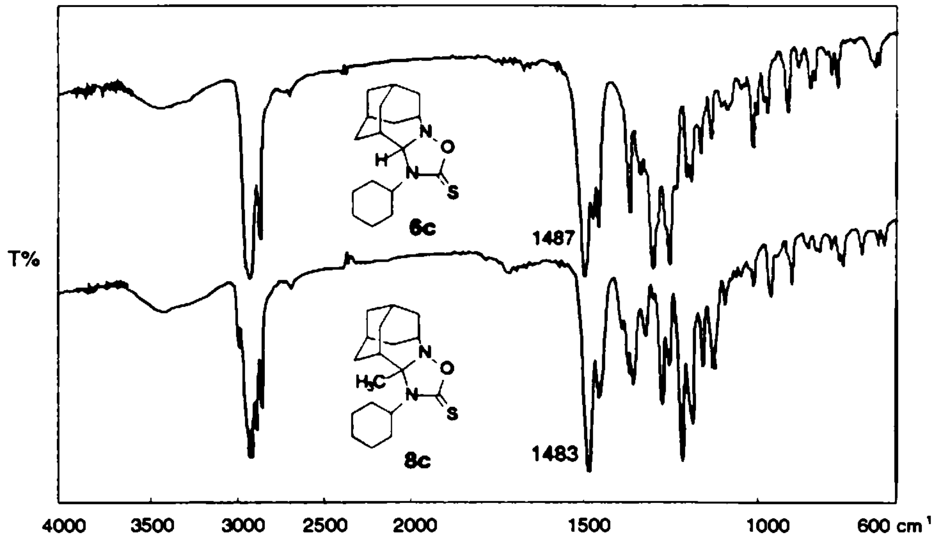
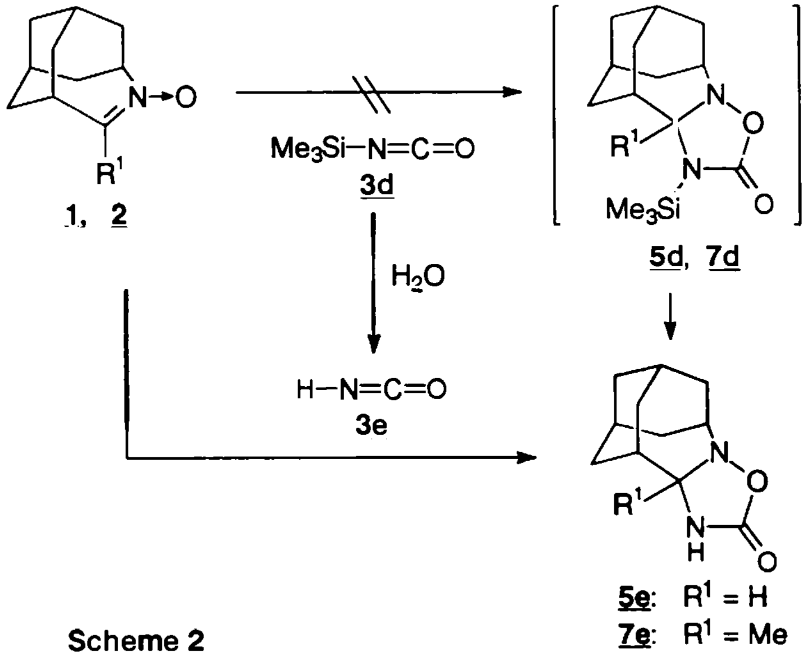


Fig. 1

attempted isolation of the adduct by chromatography (silica gel, hexane/AcOEt 3:1) was not successful due to facile decomposition of the adduct. Fortunately we found that addition of acetone to the reaction mixture precipitated crystalline product 8c, which was characterized as the corresponding 1:1-cycloadduct, 1,2,4-oxadiazolidine-5-thione derivative by IR spectral comparison with 6c (Fig 1), and ^{1}H NMR and analytical data. In the MS (EI) spectrum, M$^+$ ion peak was not observed by facile retrocycloaddition. Since most of the isocyanates exhibited high reactivity in 1,3-cycloaddition with 1 and 2 as above, the reactions of 1 and 2 with trimethylsilyl isocyanate 3d were carried out similarly expecting formation of the corresponding adducts 5d and 7d. However, the products separated by preparative TLC (silica gel) were desilylated 5e (70%) and 7e (78%), respectively. One possible explanation for isolation of 5e and 7e is the desilylation of the initial adducts 5d and 7d during the purification. However, in the same reactions carried out in a sealed glass vessel under exclusion of the moisture,



Scheme 2

the cycloaddition did not proceed at all. Furthermore, the reactions at 80°C for 12 h gave only intractable mixtures. These facts indicate that trimethylsilyl isocyanate 3d was hydrolyzed to isocyanic acid 3e by moisture, and thus formed 3e underwent the rapid cycloaddition with 1 and 2 to yield the adduct 5e and 7e as explained in Scheme 2. On the other hand, the similar type of reaction with trimethylsilyl isothiocyanate 4d was not observed but afforded only intractable complex mixtures. Other reactions of 1 and 2 with an acyl isocyanate such as benzoyl isocyanate were also examined but gave no major compounds worthy of separation.

In summary, novel 4-azahomoadamantane-fused 1,2,4-oxadiazolidin-5-ones 5a-c,e and 7b,c,e, and 1,2,4-oxadiazolidin-5-thiones 6a-c and 8b,c were prepared by cycloaddition of 1 and 2 with isocyanates and isothiocyanates (Table).

Table : 1,3-Dipolar Cycloaddition of Nitrones 1, 2 with Isocyanates 3 and Isothiocyanates 4

	Reactants[a]		Reaction Conditions			Product[b]	
Entry	Nitrone	Iso(thio)cyanate	Temp.(°C)	Time	Solvent	No.	Yield (%)
1	1	3a	0	40 min	toluene	5a	82
2	1	4a	25	1.0 h	toluene	6a	61
3	2	3a	0	5 min	toluene	7a	-[c]
4	2	4a	100	6 days	none	8a	0
5	1	3b	25	1.0 h	toluene	5b	72
6	1	4b	25	3.0 h	toluene	6b	84
7	2	3b	25	1.0 h	toluene	7b	89
8	2	4b	25	3.0 h	toluene	8b	99
9	1	3c	25	1.0 h	toluene	5c	60
10	1	4c	25	3.0 h	toluene	6c	64
11	2	3c	25	2.0 h	toluene	7c	77
12	2	4c	25	4.0 h	none	8c	86
13	1	3d	25	2.0 h	toluene	5e	70
14	2	3d	25	2.0 h	toluene	7e	78

a) A 2.0 equiv. of Iso(thio)cyanate was used except for entries 4 and 12.

b) Isolated yield.

c) The crude product was obtained but it decomposed on preparative TLC.

Experimental

Melting points were taken on Yanagimoto micro melting point apparatus and are uncorrected. Infrared spectra were measured on Jasco FT/IR 5300 spectrometer. ^1H and ^{13}C NMR spectra were obtained on a Varian GEMINI 200 instrument at 200 MHz for ^1H NMR and at 50 MHz for ^{13}C NMR with $CDCl_3$ as solvent. Chemical shifts are reported in part per million (ppm) relative to $(CH_3)_4Si$ as the internal standard and coupling constant are in Hertz. Microelemental analyses were performed on PERKIN-ELMER 2400S CHN Elemental Analyzer. Mass spectra (EI and CI) were measured on a JEOL JMS-AX505H GC mass spectrometer and ESCO EMD-05B mass spectrometer at 70 eV. All the reactions were monitored by TLC (Merck Aluminiumoxid 60 F_{254})

Typical Procedure for the 1,3-Dipolar Cycloaddition of Nitrones with Iso(thio)cyanates:

An appropriate nitrone (0.30 mmol) and an iso(thio)cyanate (0.6 mmol) dissolved in dry toluene (1.0 mL) were stirred in a 5 ml reaction vessel and allowed to react at room temperature for 1 h (or the conditions given as in the Table). The reaction was completed at the disappearance of the nitrones on TLC (alumina, CH_2Cl_2/CH_3OH, 40:1). After removal of the solvent under reduced pressure, the crude products were purified by preparative TLC (siiica gel or alumina) to give the cycloadduct. The yields were listed in the Table.

5-Phenyl-2,5-diaza-3-oxatetracyclo$[7.3.1.1^{7,11}.0^{2,6}]$tetradecan-4-one 5a

Separation of the reaction mixture obtained from 1 and 3a on TLC (alumina, CH_2Cl_2/hexane 2:1, *Rf* 0.35) gave 5a as a colorless solid. m. p. 136–138°C; IR(KBr)ν(cm^{-1}) 2920, 2855, 1748 (s), 1597, 1502, 1450, 1408, 1354, 1304, 1225, 1155, 1007, 954, 752, 693; ^1H NMR ($CDCl_3$) δ 7.21–7.46 (m, 5H), 5.81 (d, J = 3.6 Hz, 1H), 3.83 (m, 1H), 1.50–2.31 (m, 13H); MS m/e (%) 284 (M^+, 4), 240 (25), 165 (38), 149 (23), 135 (45), 119 (100); Anal. Calcd for $C_{17}H_{20}N_2O_2$ (284.35): C 71.81, H 7.09, N 9.85; Found: C 71.76, H 7.08, N 9.91.

5-Phenyl-2,5-diaza-3-oxatetracyclo$[7.3.1.1^{7,11}.0^{2,6}]$tetradecane-4-thione 6a

Separation of the reaction mixture obtained from 1 and 4a on TLC (alumina, CH_2Cl_2/hexane 2:1, *Rf* 0.60) gave 6a as colorless solid. m. p. 142–144°C; IR(KBr)ν(cm^{-1}) 2917, 2851, 1595, 1497 (s), 1472 (s), 1445 (s), 1356, 1296, 1277, 1194, 1117, 777, 747, 694; ^1H NMR ($CDCl_3$) δ 7.35–7.50 (m, 5H), 5.79 (d, J = 3.2 Hz, 1H), 3.96 (m, 1H), 1.50–2.18 (m, 13H); MS m/e (%) 300 (M^+, 2), 240 (8), 239 (16) 165 (15), 149 (39), 135 (100), 119 (98); Anal. Calcd for $C_{17}H_{20}N_2OS$ (300.41): C 67.97, H 6.71, N 9.32; Found: C 67.64, H 6.65, N 9.48.

6-Methyl-5-phenyl-2,5-diaza-3-oxatetracyclo$[7.3.1.1^{7,11}.0^{2,6}]$tetradecan-4-one 7a

The reaction of 2 and 3a was completed at 0°C within 5 min, while monitored by TLC (alumina, CH_2Cl_2/CH_3OH 40:1). However, the product decomposed during separation on TLC (alumina, CH_2Cl_2/hexane 2:1 or silica gel, EtOAc/hexane 1:3). Thus the crude product was analyzed without further purification; IR(neat)ν(cm^{-1}) 2917, 2855, 1753 (s), 1597, 1499, 1441, 1375, 1350, 1219, 1148, 1042, 750, 696; ^{1}H NMR ($CDCl_3$) δ 7.06–7.47 (m, 5H), 3.77 (m, 1H), 1.73 (s, 3H), 1.56–2.23 (m, 13H); MS (EI at 20 eV) m/e (%) 298 (M^+, 1), 283 (6), 254 (4), 239 (1), 179 (100), 162 (99), 149 (62).

5-Methyl-2,5-diaza-3-oxatetracyclo[7.3.1.1^{7,11}.0^{2,6}]tetradecan-4-one 5b

Separation of the reaction mixture obtained from 1 and 3b on TLC (alumina, CH_2Cl_2/hexane 2:1, *Rf* 0.23) gave 5b as a waxy solid. m. p. 57–59°C; IR(KBr)ν(cm^{-1}) 2913, 2851, 1748 (s), 1429, 1410, 1288, 1144, 1116, 1053, 1028, 949, 932, 760, 745, 679, 660; ^{1}H NMR ($CDCl_3$) δ 5.00 (d, J = 4.0 Hz, 1H), 3.71 (m, 1H), 2.78 (s, 3H), 1.55–2.20 (m, 13H); MS m/e (%) 222 (M^+, 15), 178 (50), 165 (37), 149 (10), 148 (13), 135 (100); Anal. Calcd for $C_{12}H_{18}N_2O_2$ (222.29): C 64.84, H 8.16, N 12.60; Found: C 64.86, H 8.15, N 12.58.

5-Methyl-2,5-diaza-3-oxatetracyclo[7.3.1.1^{7,11}.0^{2,6}]tetradecane-4-thione 6b

Separation of the reaction mixture obtained from 1 and **4b** on TLC (alumina, $CHCl_3$/hexane 3:1, *Rf* 0.52) gave 6b as a colorless solid. m. p. 113–115°C; IR(KBr)ν(cm^{-1}) 2915, 2847, 1655, 1528 (s), 1443, 1404, 1362, 1294, 1184, 1130, 1051, 949, 932, 750, 633; ^{1}H NMR ($CDCl_3$) δ 5.16 (d, J = 3.8 Hz, 1H), 3.86 (m, 1H), 3.10 (s, 3H), 1.51–2.29 (m, 13H); MS m/e (%) 238 (M^+, 11), 178 (40), 165 (21), 148 (56), 135 (45), 122 (17), 80 (100); Anal. Calcd for $C_{12}H_{18}N_2OS$ (238.35): C 60.47, H 7.61, N 11.75; Found: C 60.16, H 7.52, N 12.03.

5,6-Dimethyl-2,5-diaza-3-oxatetracyclo[7.3.1.1^{7,11}.0^{2,6}]tetradecan-4-one 7b

Separation of the reaction mixture obtained from 2 and 3b on TLC (alumina, CH_2Cl_2/hexane 2:1, *Rf* 0.35) gave 7b as a colorless solid. m. p. 99–102°C; IR(KBr)ν(cm^{-1}) 2917, 2849, 1748 (s), 1425, 1398, 1378, 1349, 1277, 1134, 1073, 986, 951, 764, 664; ^{1}H NMR ($CDCl_3$) δ 3.63 (m, 1H), 2.77 (s, 3H), 1.57–2.11 (m, 13H), 1.51 (s, 3H); MS m/e (%) 236 (M^+, 8), 221 (100), 192 (9), 179 (43), 162 (38), 149 (21); Anal. Calcd for $C_{13}H_{20}N_2O_2$ (236.31): C 66.07, H 8.53, N 11.85; Found: C 66.07, H 8.52, N 11.85.

5,6-Dimethyl-2,5-diaza-3-oxatetracyclo[7.3.1.1^{7,11}.0^{2,6}]tetradecane-4-thione 8b

Separation of the reaction mixture obtained from 2 and **4b** on TLC (alumina, $CHCl_3$/hexane 3:1, *Rf* 0.65) gave 8**b** as a colorless solid. m. p. 121–123°C; IR(KBr)ν(cm^{-1}) 2920, 2853, 1508 (s), 1441, 1404, 1360, 1279 (s), 1240, 1167, 1109, 1064, 952, 885, 793, 639; ^{1}H NMR ($CDCl_3$) δ 3.78 (m, 1H), 3.07 (s, 3H), 1.57–2.17 (m, 13H), 1.52 (s, 3H); MS m/e (%) 252 (M^+, 8), 237 (8), 179 (100), 163 (64), 162 (56), 149 (18); Anal. Calcd for $C_{13}H_{20}N_2OS$ (252.37): C 61.87, H 7.99, N 11.10; Found: C 61.76, H 7.99, N 11.11.

5-Cyclohexyl-2,5-diaza-3-oxatetracyclo[7.3.1.1^{7,11}.0^{2,6}]tetradecan-4-one 5c

Separation of the reaction mixture obtained from 1 and 3c on TLC (alumina, $CHCl_3$/hexane 3:1, *Rf* 0.40) gave 5c as a colorless solid. m. p. 128–131°C; IR(KBr)ν(cm^{-1}) 2924, 2853, 1738 (s), 1445, 1393, 1360, 1250, 1206, 1125, 995, 953, 752; ^{1}H NMR ($CDCl_3$) δ 5.14 (d, J = 3.2 Hz, 1H), 3.71 (m, 1H), 3.12 (tt, J = 11.9 and 3.8 Hz, 1H), 1.02–2.25 (m, 23H); MS m/e (%) 290 (M^+, 3), 247 (3), 246

(10), 245 (4), 231 (2), 217 (5), 204 (9), 203 (41), 191 (4) 190 (3), 189 (4), 177 (2), 176 (3), 175 (3), 166 (4), 165 (26), 164 (25), 148 (100); Anal. Calcd for $C_{17}H_{26}N_2O_2$ (290.40): C 70.31, H 9.02, N 9.65; Found: C 70.60, H 8.96, N 9.42.

5-Cyclohexyl-2,5-diaza-3-oxatetracyclo[7.3.1.1^{7,11}.0^{2,6}]tetradecane-4-thione 6c

Separation of the reaction mixture obtained from 1 and 4c on TLC (alumina, CHCl$_3$/hexane 3:1, *Rf* 0.64) gave 6c as a colorless solid. m. p. 154-156°C; IR(KBr)ν(cm^{-1}) 2919, 2853, 1487 (s), 1445, 1393, 1360, 1292, 1244, 1177, 997, 897, 831, 752; ^{1}H NMR (CDCl$_3$) δ 5.29 (d, J = 2.2 Hz, 1H), 4.14 (tt, J = 12.0 and 3.7 Hz, 1H), 3.91 (m, 1H), 1.00-2.34 (m, 23H); MS m/e (%) 306 (M$^+$, 5), 247 (4), 246 (15), 245 (6), 231 (3), 216 (6), 204 (10), 203 (46), 191 (4) 190 (3), 189 (4), 177 (3), 176 (4), 175 (3), 166 (12), 165 (67), 164 (38), 150 (15), 149 (100) 148 (16), 141 (54), 137 (25), 136 (12), 135 (55), 122 (26); Anal. Calcd for $C_{17}H_{26}N_2OS$ (306.47): C 66.63, H 8.55, N 9.14; Found: C 66.71, H 8.62, N 9.19.

5-Cyclohexyl-6-methyl-2,5-diaza-3-oxatetracyclo[7.3.1.1^{7,11}.0^{2,6}]tetradecan-4-one 7c

Separation of the reaction mixture obtained from 2 and 3c on TLC (alumina, CHCl$_3$/hexane 3:1, *Rf* 0.36) gave 7c as a colorless solid. m. p. 158-160°C; IR(KBr)ν(cm^{-1}) 2922, 2853, 1748 (s), 1445, 1414, 1370, 1348, 1312, 1238, 1206, 1123, 1086, 995, 955, 928, 893, 718; ^{1}H NMR (CDCl$_3$) δ 3.61 (m, 1H), 2.65 (tt, J = 11.8 and 3.4 Hz, 1H), 1.15-2.52 (m, 23H), 1.56 (s, 3H); MS m/e (%) 304 (M$^+$, 14), 300 (6), 221 (19), 207 (11), 179 (100), 163 (17), 162 (48); Anal. Calcd for $C_{17}H_{26}N_2O_2$ (304.43): C 71.02, H 9.27, N 9.20; Found: C 70.89, H 9.30, N 9.29.

5-Cyclohexyl-6-methyl-2,5-diaza-3-oxatetracyclo[7.3.1.1^{7,11}.0^{2,6}]tetradecane-4-thione 8c

A solution of 2 in cyclohexyl isothiocyanate 4c (0.5 ml) was stirred at r. t. for 3 h. After the disappearance of the nitrone monitored by TLC (alumina, CH$_2$Cl$_2$/CH$_3$OH, 40:1), acetone (2 ml) was added to the reaction mixture which was cooled at 0°C overnight. Filtration of the solid product and recrystallization from acetone gave the cycloadduct as a colorless crystal. Yield 58%, m. p. 105-107°C, IR(KBr)ν(cm^{-1}) 2922, 2853, 1483 (s), 1453, 1368, 1354, 1271, 1246, 1213, 1184, 1152, 1119, 951, 893; ^{1}H NMR (CDCl$_3$) δ 3.76 (m, 1H), 3.69 (m, 1H), 1.20-2.25 (m, 23H), 1.59 (s, 3H) (8); MS m/e (%) 179 (100), 162 (93), 141 (74), 93 (35), 83 (78) (9); Anal. Calcd for $C_{18}H_{28}N_2OS$ (320.49): C 67.46, H 8.81, N 8.74; Found: C 67.16, H 8.80, N 8.71.

2,5-Diaza-3-oxatetracyclo[7.3.1.1^{7,11}.0^{2,6}]tetradecan-4-one 5e

Separation of the reaction mixture obtained from 1 and 3d on TLC (silica gel, EtOAc *Rf* 0.48) gave 5e as a colorless solid. m. p. 171-174°C; IR(KBr)ν(cm^{-1}) 3050, 2913, 2851, 1748 (s), 1429, 1410, 1288, 1144, 1116, 1053, 1028, 949, 932, 760, 745, 679, 660; ^{1}H NMR (CDCl$_3$) δ 6.58 (br s, 1H), 5.39 (d, J = 3.8 Hz, 1H), 3.71 (m, 1H), 1.54-2.15 (m, 13H); MS m/e (%) 208 (M$^+$, 8), 164 (63), 163 (23), 149 (39), 148 (22), 135 (100); Anal. Calcd for $C_{11}H_{16}N_2O_2$ (208.26): C 63.44, H 7.74, N 13.45; Found: C 63.77, H 7.74, N 13.11.

6-Methyl-2,5-diaza-3-oxatetracyclo[7.3.1.1^{7,11}.0^{2,6}]tetradecan-4-one 7e

Separation of the reaction mixture obtained from **2** and **3d** on TLC (silica gel, EtOAc *Rf* 0.58) gave 7e as a colorless solid. m. p. 138–141°C, IR(KBr)ν(cm^{-1}) 3246, 2920, 2855, 1752 (s), 1439, 1412, 1368, 1335, 1236, 1136, 990, 949; ^{1}H NMR (CDCl$_3$) δ 6.64 (br s, 1H), 3.63 (m, 1H), 1.54–2.28 (m, 13H), 1.61 (s, 3H); MS m/e (%) 222 (M$^+$, 4), 207 (18), 180 (21), 179 (100), 163 (23), 162 (63), 149 (20); Anal. Calcd for $C_{11}H_{16}N_2O_2$ (222.29): C 64.82, H 8.17, N 12.61; Found: C 64.67, H 8.10, N 12.58.

Acknowledgments

Support by a Grant-in-Aid for Scientific Research (No. 04403017) from the Ministry of Education, Science and Culture of Japan is gratefully acknowledged.

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(8) Compound 8c underwent cycloreversion partly in CDCl$_3$

(9) The M$^+$ ion could not be observed due to facile cycloreversion under MS (EI and CI) measurements

Received February 25, 1995