Thermal Cycloaddition Reactions of Thiocarbonyl Compounds. Part 2.[1] 1,3-Dipolar Cycloaddition Reactions of Adamantanethione with Nitrile Oxides, Nitrilimines, and Diazoalkanes

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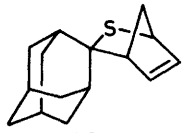
1,3-Dipolar cycloaddition of adamantanethione (**1**) with nitrile oxides, nitrilimines, and diazoalkanes occurred smoothly to afford regioselective cycloadducts, adamantane-2-spiro-5'-(1',4',2'-oxathiazolines) (**4a—f**), adamantane-2-spiro-2'-(1',3',4'-thiadiazolines) (**11a—d**), and (**21b**), respectively in high yields. These results are discussed on the basis of FMO and steric effects.

The 1,3-dipolar cycloaddition reaction is well known as one of the most useful methods for the synthesis of 5-membered heterocycles[2] and is also of considerable theoretical interest. Numerous studies based on quantum theoretical calculations have been reported[3] and mechanistic aspects have been discussed at length.[4] However, relatively few reports are available on cycloaddition reactions involving a thiocarbonyl group.[2,5-7] In this paper, we report a convenient regiospecific synthesis of adamantane-2-spiro-thiaheterocycles by cycloaddition of nitrile oxides,[8,9] nitrilimines,[10] and diazolalkanes[11] to adamantanethione (**1**).

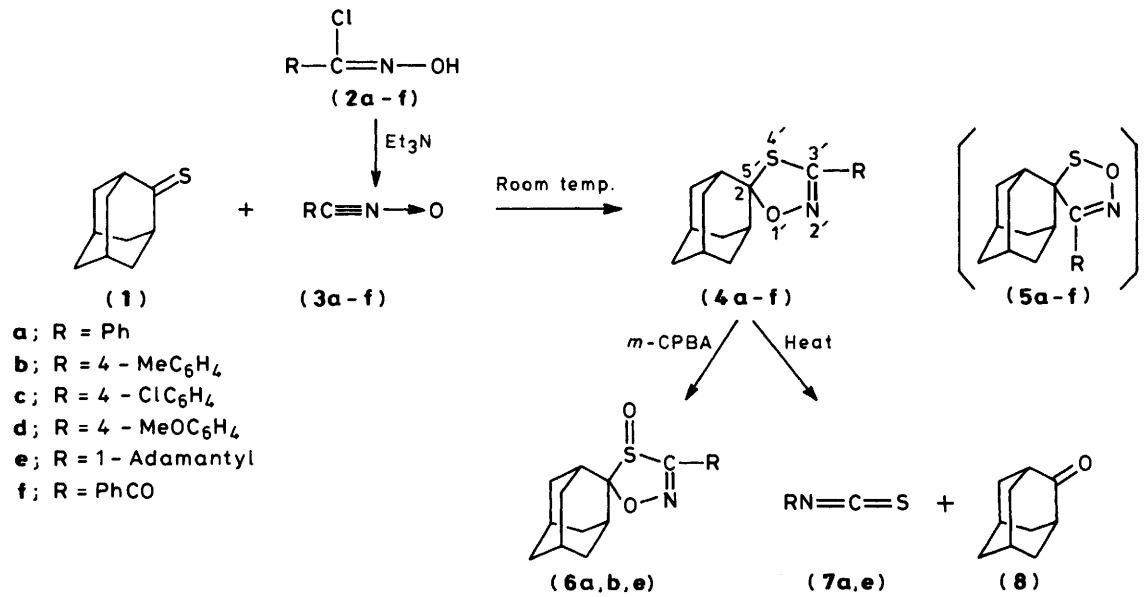
Results and Discussion

1,3-*Dipolar Cycloaddition of Adamantanethione* (**1**) *with Nitrile Oxides.*—The reaction of (**1**)[12] with benzonitrile oxide (**3a**) generated *in situ* from benzohydroximoyl chloride (**2a**) and triethylamine in ether[13] occurred smoothly at room temperature to afford the cycloadduct (**4a**) in 85% yield after chromatography (Scheme 1). The adduct (**4a**) was characterized as 3-phenyladamantane-2-spiro-5'-(1',4',2'-oxathiazoline) on the basis of its elemental analysis and spectral data (Table 4). The mass spectral molecular ion at *m/z* 285 (50%) as well as fragment ions at *m/z* 166 (38%, adamantanethione) and 150 (56%, adamantanone) supported structure (**4a**) rather than its isomer (**5a**). Characteristic signals in the ^{13}C n.m.r. spectrum at δ 156.3 (s, C-3') and 112.3 (s, C-2) were compatible with structure (**4a**). The spiro-carbon in (**5a**) was expected to appear at higher field (*ca.* 70—75 p.p.m.) in parallel with the chemical shifts of the spiro-carbon of Diels-Alder adducts of (**1**) [*e.g.* compound (I) had a spiro-carbon signal at δ 71.6 (s)[14]]. When



(**1**)

the cycloaddition was carried out in a more polar solvent (*e.g.* acetonitrile), the same adduct (**4a**) was obtained in 96% yield; none of the regioisomer (**5a**) could be detected, although



Scheme 1.

interesting changes in regioselectvity as a function of solvent have been observed for the cycloaddition of (**1**) with diazomethane.[7a,15]

The cycloaddition of (**1**) with the substituted benzonitrile oxides (**3b—d**), adamantane-1-carbonitrile oxide (**3e**) and benzoylnitrile oxide (**3f**) occurred similarly at room temperature

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Table 1. Reaction of adamantanethione (**1**) with nitrile oxides (**3a—f**) at room temperature

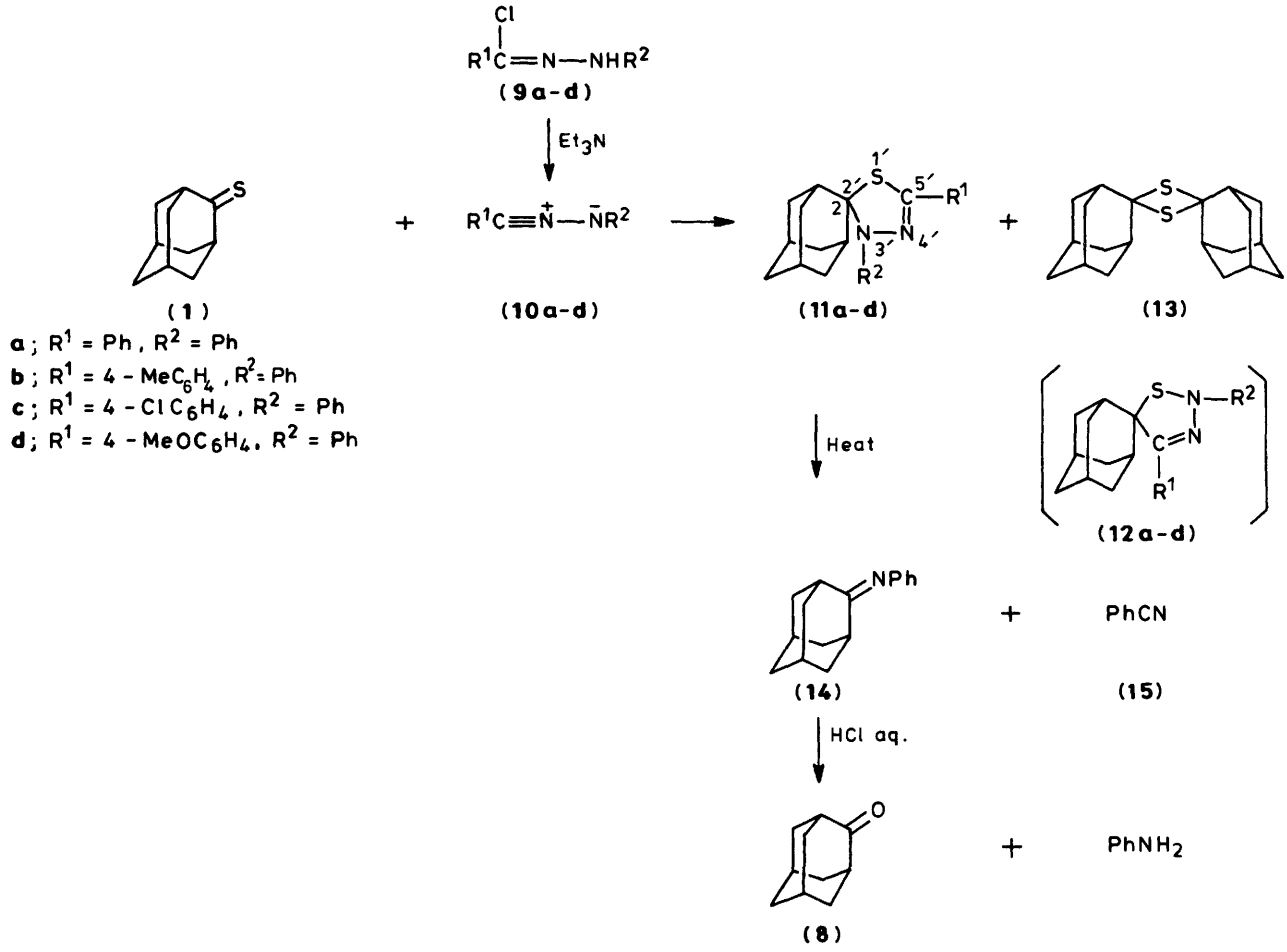
RC≡N→O	Mol ratio to (**1**)	Solvent	Time (h)	Product (yield, %)[a]
(**3a**)	1.2	Et_2O	3	(**4a**) (85)
(**3a**)	1.2	MeCN	3	(**4a**) (96)
(**3b**)	1.4	Et_2O	12	(**4b**) (84)
(**3c**)	1.2	Et_2O	3	(**4c**) (85)
(**3d**)	1.2	Et_2O	12	(**4d**) (78)
(**3e**)	1.4	Et_2O	2	(**4e**) (97)
(**3f**)	1.2	Et_2O	2	(**4f**) (95)

[a] Isolated yields after silica gel chromatography (see Table 4).

adamantyl isothiocyanate (**7e**)[16] and (**8**) in 71 and 84% yields, respectively. These results were also compatible with the regiochemistry of (**4**).[17]

Since in all these reactions, none of the regioisomer (**5**) could be detected, the cycloaddition of (**1**) with nitrile oxides was clearly regiospecific.

1,3-*Dipolar Cycloadditions of* (**1**) *with Nitrilimines.*—The reaction of (**1**) with diphenylnitrilimine (**10a**), generated *in situ* from α-chlorobenzylidenephenylhydrazine (**9a**)[10a] and triethylamine in benzene, afforded a single crystalline cycloadduct (**11a**) (94%) and the thione dimer (**13**) (3%) after chromatography (Scheme 2). The cycloadduct (**11a**) was characterized as 3′,5′-diphenyladamantane-2-spiro-2′-(1′,3′,4′-thiadiazoline)



Scheme 2.

to afford the corresponding adamantane-2-spiro-5′-(1′,4′,2′-oxathiazolines) (**4b—f**) in 78—97% yields (Table 1). The given structures were supported by analytical and spectral results (Table 4). Furthermore, the cycloadducts (**4a**), (**4b**), and (**4e**) were readily oxidized by *m*-chloroperbenzoic acid (*m*-CPBA) to afford the corresponding *S*-oxides (**6a**), (**6b**), and (**6e**) in 81—89% yields. These *S*-oxides exhibited characteristic i.r. absorptions at 1 055—1 035 cm^{-1} (ν_{SO}). On the other hand, the cycloadduct (**4**) decomposed thermally to afford the corresponding isothiocyanate (**7**) and adamantanone (**8**). For example, thermolysis of (**4a**) at 185 °C for 0.5 h afforded phenyl isothiocyanate (**7a**) and (**8**) in 93 and 73% yields, respectively (g.l.c. analysis) and that of (**4e**) at 250 °C for 0.5 h gave 1-

based on elemental analysis and spectral results (Table 4). In the mass spectrum, appearance of the molecular ion at *m/z* 360 (5%) and fragment ions at *m/z* 225 (100%, adamantylideneaniline) and 103 (63%, PhCN) supported structure (**11a**) but not (**12a**). Furthermore, ^{13}C n.m.r. signals at δ 157.5 (s, C-5′) and 94.6 (s, C-2) were compatible with (**11a**). When the cycloaddition was carried out in acetonitrile the same products (**11a**) and (**13**) were obtained in 93 and 4% yields, respectively: no regioisomer (**12a**) could be detected.

As expected from the mass spectral fragmentation, thermolysis of the adduct (**11a**) at 200 °C for 1 h afforded *N*-adamantylideneaniline (**14**)[18] and benzonitrile (**15**) (70%) (Scheme 2). The Schiff base (**14**) is known to be very unstable in

Table 2. Reaction of adamantanethione (**1**) with nitrilimines (**10a—d**) at 80 °C

Compd.	Mol ratio to (**1**)	Solvent	Time (h)	Product (yield, %)[a]
(**10a**)	1.0	PhH	0.5	(**11a**) (94) (**13**) (3)
(**10a**)	1.0	MeCN	0.5	(**11a**) (93) (**13**) (4)
(**10b**)	1.1	PhH	1.0	(**11b**) (94) (**13**) (2)
(**10c**)	1.1	PhH	1.0	(**11c**) (93) (**13**) (4)
(**10d**)	1.1	PhH	1.5	(**11d**) (92) (**13**) (2)

[a] Isolated yields after silica gel column chromatography (see Table 4).

Table 3. Reaction of adamantanethione (**1**) with diazomethane (**20a**) at 0 °C

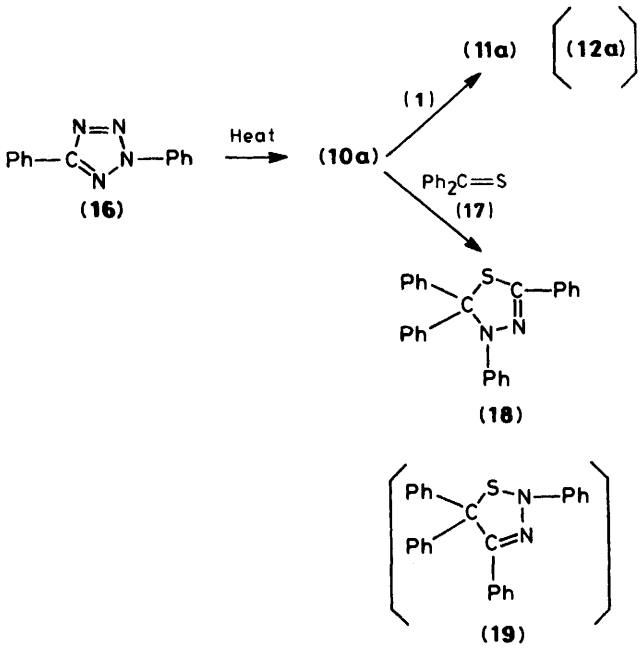
Solvent	Amine	Mol ratio (**1**)/amine	Product (%)[a] (**21a**)	(**22a**)
Et_2O			80[b]	20[b]
Et_2O	Et_3N	1.0	81	19
Et_2O	C_6H_5N	1.0[c]	78	22
MeOH			30[b]	70[b]
MeOH	Et_3N	1.0	22	78
MeOH	C_6H_5N	1.0	25	75

[a] Thiadiazolines (**21a**) and (**22a**) exhibit singlets at δ 5.72 and 4.93, respectively. The percentage ratios are based on each area integration of these singlets. [b] Ref. 7*a*. [c] Same result was obtained also with a 3.0 mol ratio.

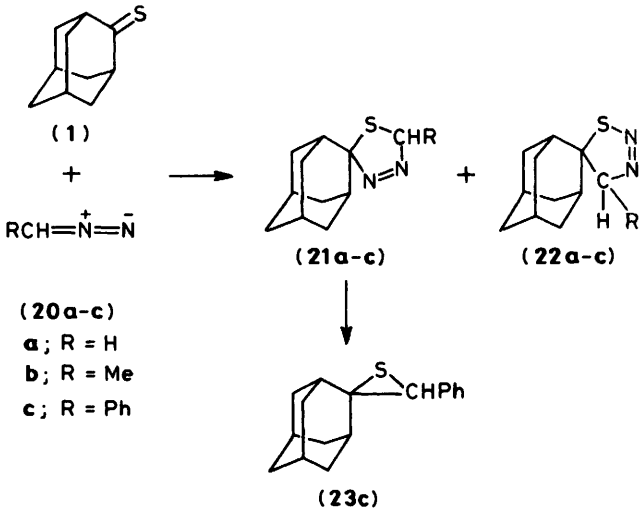
the atmosphere[18] and, therefore, the crude pyrolyzate was treated with 2M-hydrochloric acid to afford adamantanone (**8**) (50%), benzonitrile (**15**) (70%), and aniline (61%). These results supported unequivocally the given regiochemistry of (**11a**).

The reaction of (**1**) with other substituted diarylnitrilimines (**10b—d**) gave the corresponding thiadiazolines (**11b—d**) in high yields (Table 2). Again none of the regioisomer could be detected.

The thermal generation of the nitrilimine (**10**) from 2,5-disubstituted tetrazoles (**16**) has also been applied.[6a,19] The reaction of (**1**) with an equimolar amount of 2,5-diphenyltetrazole (**16**) in xylene at 150 °C for 12 h gave the same cycloadduct (**11a**) in 58% yield. A parallel reaction of thiobenzophenone (**17**) gave only the known cycloadduct,[6b] 2,2,3,5-tetraphenyl-1,3,4-thiadiazoline (**18**), in 60% yield. In these cases, no regioisomer (**12a**) or (**19**) was obtained thus indicating the regiospecifity of the cycloaddition (Scheme 3).



Scheme 3.



Scheme 4.

1,3-Dipolar Cycloadditions of (**1**) *with Diazoalkanes.*—Krapcho and co-workers[7a] have shown that the cycloaddition of (**1**) with diazomethane (**20a**) affords a mixture of the regioisomers, Δ^3-1,3,4-thiadiazoline (**21a**) and Δ^2-1,2,3-thiadiazoline (**22a**). Change of solvent changed the ratio of regioisomers obtained: (**21a**) was the major product in ether or benzene, while (**22a**) was the major product in methanol or acetonitrile. Fukui and co-workers[15] attributed this regiochemical change to interaction of the sulphur atom d-orbital with lone-pairs on methanol or acetonitrile prior to attack by diazomethane (**20a**). We examined the effect of tertiary amines on the regioselectivity of the reaction.

When the reaction of (**1**) with (**20a**) in ether was carried out in the presence of an equimolar amount of triethylamine and/or pyridine at 0 °C, no appreciable change was observed and the cycloadducts (**21a**) and (**22a**) were produced in 81 and 19% yields, respectively (^{1}H n.m.r. analysis). On the other hand, similar treatment of (**1**) in methanol gave (**21a**) and (**22a**) in 22 and 78% yields, respectively. These results are summarized in Table 3. It is possible that the change in regioselectivity is only due to solvent polarity or some other causes.[20]

The reaction of (**1**) with diazoethane (**20b**) in ether at 0 °C affords a cycloadduct (**21b**) in 93% yield after chromatography (Scheme 4). The cycloadduct (**21b**) was isolated and characterized as adamantane-2-spiro-2′-($\Delta^{3'}$-1′,3′,4′-thiadiazoline) based on analysis and spectral results (Table 4). Appearance of characteristic signals in the ^{1}H n.m.r. spectrum at δ 5.95 (q, 5′-H) and of characteristic absorption in the i.r. spectrum at 1 585 cm^{-1} was compatible with structure (**21b**). When the cycloaddition was carried out in methanol, (**21b**) was again obtained. The exclusive formation of (**21b**) is rationalized by FMO theory and steric effects as discussed below.

When a mixture of (**1**) and a three-fold excess of phenyldiazomethane (**20c**) in ether[21] was stirred at room temperature for 12 h, a single cycloadduct (**23c**) (94%) was isolated after work-up and chromatography (silica gel) (Scheme 4). Structure

Table 4. Physical and analytical data for adamantane-2-spiro derivatives (**4a**—**f**), (**11a**—**d**), (**21b**), and (**23c**)

Compound.[a] (m.p., °C)	λ/cm^{-1} [b]	δ_H [c]	*m/z* (%)	Mol formula	Elemental analysis (%) Found (required) C	H	N
(**4a**) (86.0—87.0)	3 050, 2 910, 2 850, 1 540, 1 450, 1 270, 1 110, 1 055, 985, 920, 780, 690	7.80—7.15 (m, 5), 2.60—1.50 (m, 14)	285 (50),[d] 166 (38), 150 (56), 135 (100), 104 (56), 103 (44), 80 (93), 79 (93)	$C_{17}H_{19}NOS$	71.50 (71.54)	6.64 (6.71)	5.03 (4.91)
(**4b**) (129—130)	3 050, 2 910, 2 845, 1 610, 1 450, 1 270, 1 110, 1 045, 980, 820	7.75—7.10 (m, 4), 2.60—1.50 (m, 17)	299 (25),[d] 166 (29), 150 (50), 117 (100), 116 (58), 91 (50), 79 (50)	$C_{18}H_{21}NOS$	72.19 (72.20)	7.02 (7.07)	4.75 (4.68)
(**4c**) (142—143)	3 040, 2 900, 2 860, 1 590, 1 570, 1 450, 1 395, 1 275, 1 095, 970, 910, 825	7.75—7.10 (m, 4), 2.60—1.50 (m, 14)	319 (13),[d] 169 (45), 166 (29), 150 (63), 139 (34), 137 (100), 80 (36), 79 (47)	$C_{17}H_{18}NOSCl$	64.01 (63.84)	5.61 (5.67)	4.24 (4.38)
(**4d**) (125—126)	3 025, 2 910, 2 850, 1 600, 1 500, 1 450, 1 270, 1 055, 1 005, 975, 820, 700	7.80—6.80 (m, 4), 3.92 (s, 3), 2.60—1.50 (m, 14)	315 (1.8),[d] 169 (41), 167 (100), 166 (8.8), 150 (94), 134 (41), 79 (56)	$C_{18}H_{21}NOS$	68.67 (68.54)	6.69 (6.71)	4.33 (4.44)
(**4e**) (245—247)	2 900, 2 840, 1 560, 1 445, 1 210, 1 100, 1 045, 1 010, 980, 885, 835	2.50—1.40 (m)	343 (13),[d] 166 (17), 161 (50), 150 (100), 135 (80), 134 (90), 93 (70)	$C_{21}H_{29}NOS$	73.49 (73.42)	8.46 (8.50)	4.05 (4.08)
(**4f**) (60.0—61.5)	3 050, 2 920, 2 850, 1 645, 1 520, 1 445, 1 310, 1 135, 972, 938, 870, 710	8.35—8.08 (m, 2), 7.70—7.30 (m, 3)	313 (6.8),[d] 166 (16), 150 (50), 131 (25), 105 (100), 80 (25), 79 (32)	$C_{18}H_{19}NO_2S$	68.87 (68.98)	6.20 (6.11)	4.48 (4.47)
(**11a**) (155—157)	3 050, 2 900, 1 590, 1 535, 1 490, 1 450, 1 270, 965, 775, 760, 700, 690	8.00—7.20 (m, 10), 2.50—1.25 (m, 14)	360 (5.0),[d] 225 (100), 148 (35), 106 (25), 104 (26), 103 (63), 77 (30)[f]	$C_{23}H_{24}N_2S$	76.69 (76.63)	6.73 (6.71)	6.79 (7.77)
(**11b**) (179—180)	3 040, 2 910, 2 850, 1 592, 1 490, 1 450, 1 272, 965, 825, 770, 700	7.82—7.05 (m, 9), 2.35 (s, 3), 2.50—1.25 (m, 14)	374 (4.0),[d] 225 (100), 148 (20), 117 (60) 106 (26), 91 (20), 77 (29)[f]	$C_{24}H_{26}N_2S$	77.10 (76.96)	7.04 (7.00)	7.29 (7.48)
(**11c**) (185—186)	3 060, 2 905, 2 845, 1 590, 1 480, 1 440, 1 260, 1 085, 960, 832, 768, 698	7.90—7.15 (m, 9), 2.50—1.30 (m, 14)	394 (3.2),[d] 225 (100), 148 (38), 137 (64), 106 (30), 102 (30), 77 (26)[f]	$C_{23}H_{23}N_2SCl$	69.99 (69.94)	5.95 (5.87)	6.97 (7.09)
(**11d**) (171—172)	3 050, 2 900, 1 604, 1 500, 1 460, 1 300, 1 255, 1 165, 1 032, 962, 830, 700	7.90—6.85 (m, 9), 3.80 (s, 3)	390 (4.8),[d] 225 (100), 148 (6.5), 134 (52), 106 (23), 77 (26)[f]	$C_{24}H_{26}N_2OS$	73.88 (73.81)	6.72 (6.71)	7.09 (7.17)
(**21b**) (Oil)	2 920, 2 860, 1 585, 1 455, 1 220, 1 102, 1 055, 1 010, 985, 898	5.95 (q, *J* 7.0 Hz, 1), 1.75 (d, *J* 7.0 Hz, 3), 3.0—1.2 (m, 14)	(222),[e] 195 (24), 166 (63), 135 (49), 133 (34), 105 (34), 91 (100), 80 (59)	$C_{12}H_{18}N_2S$	64.90 (64.82)	8.24 (8.15)	12.31 (12.60)
(**23c**) (Oil)	3 060, 3 030, 2 920, 2 855, 1 600, 1 505, 1 455, 1 360, 1 108, 1 085, 760, 705	7.60—7.10 (m, 5) 3.69 (s, 1), 2.40—1.25 (m, 14)	256 (54),[d] 224 (100), 223 (36), 167 (31), 166 (29), 141(27), 135 (47), 90 (39)	$C_{17}H_{20}S$	79.54 (79.63)	7.95 (7.86)	

[a] Purified by chromatography on silica gel or alumina. [b] Scanned in KBr disks. [c] All ^{1}H n.m.r. spectra were measured in $CDCl_3$. [d] M^+ Ion peaks. [e] M^+ Ion peak was not observed. [f] At 20 eV.

(**23c**) was assigned on the basis of elemental analysis and spectral results. The reaction when performed at −25 °C for 3 days also gave (**23c**) as the product. In these cases, the cycloadducts (**21c**) and/or (**22c**) were not isolable presumably because of their instability. The formation of the thiirane (**23c**) is best explained by extrusion of N_2 from (**21c**) although a similar extrusion from (**22c**) cannot be excluded.

Regiochemistry.—The frontier orbitals of adamantanethione (**1**),[1] benzonitrile oxide (**3a**), diphenylnitrilimine (**10a**), and diazomethane (**20a**) based on CNDO/2 calculations[22] are schematically shown in Figure 1.* The solid arrows indicate the dominant interaction, *i.e.* the overlap of the dipolarophile-LUMO with the dipole-HOMO is larger for (**10a**) and (**20a**) (dipole HOMO-controlled), while that of the dipolarophile-HOMO with dipole-LUMO is larger for (**3a**) (dipole LUMO-controlled).[23] This rationalized the experimentally observed regioselectivity in forming (**4a**) and (**21b**). The structures of these products were also the sterically favoured ones based on steric approach control. The nitrilimine (**10a**) in the reaction with (**1**) gave the opposite regioisomer [(**11a**) rather than (**12a**)] from that expected by FMO prediction.[24]† This observed regiochemistry was, however, favoured sterically. Recently, Toubro and Holm[10b] reported that the ground-state structure of nitrilimine (**10a**) was best described as a localized triple bond with a linear array of the CNN atoms (Figure 2). It is likely that the phenyl group on the carbon atom of diphenylnitrilimine (**10a**) plays an important role in the regioselectivity. The phenyl group on the carbon atom of (**10a**) (Ph–CNN: straight geometry) interfers severely with the approach of (**10a**) to the bulky adamantyl group of (**1**) (B): therefore no cycloadduct (**12a**) can be produced. On the other hand, the phenyl group on the nitrogen atom of (**10a**) (CN–N–Ph: bent geometry) seems to allow a reasonable approach of (**10a**) to (**1**) (A) (molecular model study), and hence, the cycloadduct (**11a**) is produced as the exclusive product.

Experimental

M.p.s. were taken in a sealed tube on a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were performed with a Perkin-Elmer 240B elemental analyzer. I.r. spectra were recorded on a JASCO A-100 i.r.

* NLUMO's are actually depicted as in several cases (see ref. 22e).
† More detailed MO calculation on thioaldehydes has appeared recently (see ref. 24).

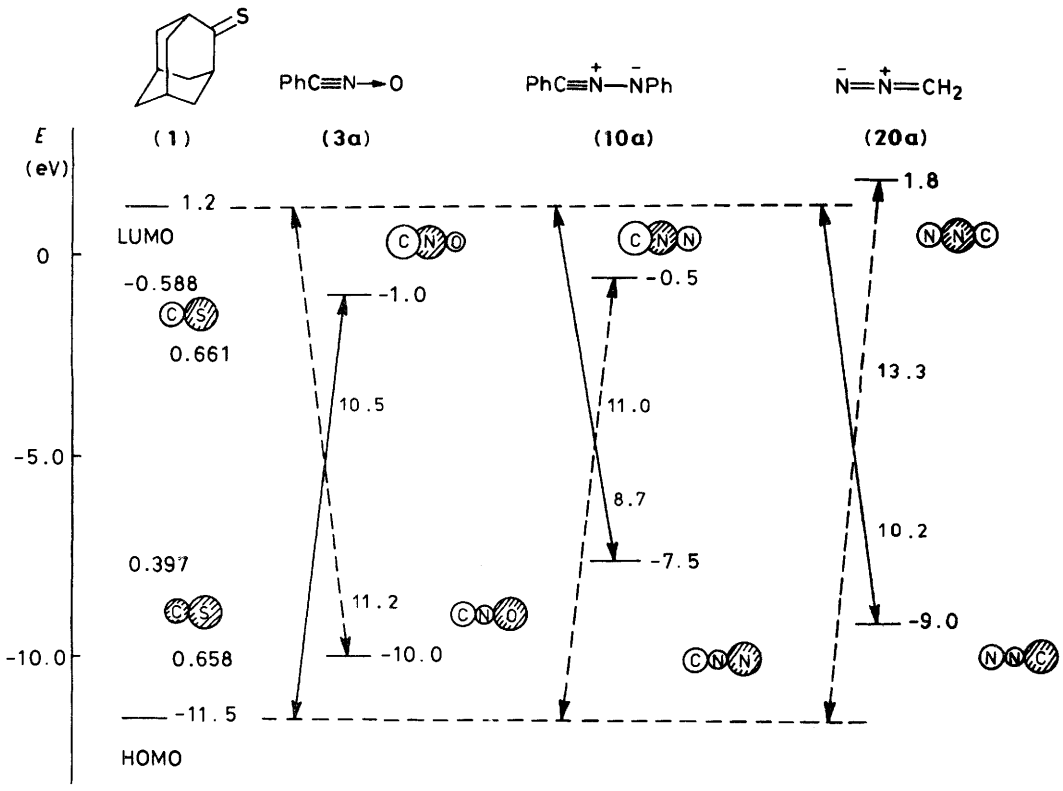
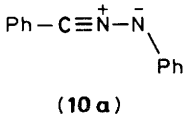
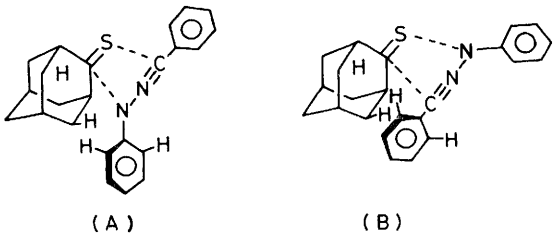


Figure 1. Frontier orbital coefficients and energies (CNDO/2)



(10a)



(A) (B)

Figure 2.

spectrometer. ^1H and ^{13}C N.m.r. spectra were taken at 25 °C with a JEOL JMN-C-60HL instrument at 60 MHz and a JEOL-FX-60FT spectrometer at 15.04 MHz using $SiMe_4$ as an internal standard in $CDCl_3$. Mass spectra were obtained with a JEOL JMS-D-10 mass spectrometer at 75 eV. G.l.c. analyses were carried out by using a JEOL JGC-20K gas chromatograph on 1 or 2 m-Silicone SE-30 column at 100—200 °C.

Materials.—Adamantanethione (**1**) was prepared by the reported method[12] and purified on a silica gel (Kieselgel 60, 70—230 mesh) column with n-hexane as eluant. The nitrile oxides (**3a**—**f**) were prepared from the corresponding hydroximidoyl chlorides (**2a**—**f**) and triethylamine according to the literature.[8b] The nitrilimines (**10a**—**d**) were generated by dehydrochlorination of the corresponding substituted α-chlorobenzylidenephenylhydrazines (**9a**—**d**) and triethylamine,[10a] and (**10a**), by the thermal decomposition of 2,5-diphenyltetrazole (**16**)[19,25]: (**9b**), m.p. 131—133 °C, ν_{NH} 3 315 cm^{-1}; (**9c**), m.p. 150—151 °C, ν_{NH} 3 320 cm^{-1}; (**9d**), m.p. 126—128 °C, ν_{NH} 3 310 cm^{-1}. A 90% grade *m*-chloroperbenzoic acid (*m*-CPBA) was employed. All the solvents were dried over 4A molecular sieves and distilled before use.

4'-Phenyladamantane-2-spiro-5'-(1',4',2'-oxathiazoline) (**4a**).—Triethylamine (142 mg, 1.4 mmol) was added to a stirred ice-cold solution of benzohydroximidoyl chloride (**2a**)[26] (215 mg, 1.4 mmol) in ether (10 ml). Stirring was continued for 5 min, and then the mixture was washed with ice–water and dried (Na_2SO_4). Adamantanethione (**1**) (166 mg, 1.0 mmol) was added to this solution and the mixture was stirred for 3 h at room temperature (20—25 °C), and then refluxed for 0.5 h. After removal of the solvent, the solid residue was purified on a silica gel column by elution with n-hexane–benzene (2:1 v/v) to give (**4a**) (241 mg, 85%), $\delta_C(CDCl_3)$ 156.3 (1 C, s), 130.6 (1 C, d), 128.9 (1 C, s), 128.5 (2 C, d), 127.6 (2 C, d), 112.3 (1 C, s), 39.4 (2 C, d), 37.3 (2 C, t), 37.1 (1 C, t), 33.6 (2 C, t), 26.9 (1 C, d), and 26.2 (1 C, d); for other physical data, see Table 4.

The cycloaddition of (**1**) with other nitrile oxides (**3b**—**f**) was carried out similarly and the results are summarized in Tables 1 and 4.

Oxidation of the Cycloadduct (**4a**) *with* m-*CPBA.*—*m*-CPBA (33 mg, 0.19 mmol) in dichloromethane (2 ml) was added gradually to a stirred ice-cold solution of the cycloadduct (**4a**) (50 mg, 0.18 mmol) in dichloromethane (5 ml). The mixture was stirred overnight at room temperature. After removal of the solvent, the resulting residue was purified by preparative t.l.c. (Kieselgel 60 F-254, dichloromethane) to give 4'-phenyl-

adamantane-2-spiro-5'-(1',4',2'-oxathiazoline) *S*-oxide (**6a**) (85% yield), m.p. 160—162 °C (lit.,[27] m.p. 166—168 °C).

3'-p-*Tolyladamantane*-2-*spiro*-5'-(1',4',2'-*oxathiazoline*) *S*-*Oxide* (**6b**).—Treatment of (**4b**) (60 mg, 0.20 mmol) with *m*-CPBA (42 mg, 0.22 mmol) in dichloromethane (10 ml) as above, followed by evaporation of the solvent and chromatography on silica gel (dichloromethane) gave (**6b**) (53 mg, 87%), m.p. 123—125 °C (Found: C, 68.45; H, 6.75; N, 4.5. $C_{18}H_{21}NO_2S$ requires C, 68.54; H, 6.71; N, 4.44%); $\nu_{max.}$(KBr) 3 020, 2 880, 1 605, 1 450, 1 270, 1 178, 1 100, 1 082, 1 055, 1 032, 970, 935, 890, and 820 cm^{-1}; $\delta_H(CDCl_3)$ 7.82 (d, *J* 8.5 Hz, 2), 7.26 (d, *J* 8.5 Hz, 2), 2.38 (s, 3), and 2.8—1.5 (m, 14); *m/z* 165 (23), 150 (90, adamantanone), 117 (100, 4-MeC_6H_4CN), and 116 (52).*

4'-*Adamantyladamantane*-2-*spiro*-5'-(1',4',2'-*oxathiazoline*) S-*Oxide* (**6e**).—The cycloadduct (**4e**) (65 mg, 0.19 mmol) was oxidized with *m*-CPBA (40 mg, 0.21 mmol) in dichloromethane (10 ml) as above and then worked up and subjected to column chromatography on silica gel (dichloromethane) to afford (**6e**) (55 mg, 81%), m.p. 182—183 °C (Found: C, 70.05; H, 8.15; N, 4.0. $C_{21}H_{29}NO_2S$ requires C, 70.16; H, 8.13; N, 3.90%); $\delta_H(CDCl_3)$ 2.7—1.4 (m); *m/z* 161 (50%, Ad–CN), 150 (100, adamantanone), 135 (50), and 134 (75).*

Thermal Decomposition of the Cycloadduct (**4a**).—The oxathiazoline (**4a**) (60 mg, 0.21 mmol) was heated at 185 °C for 0.5 h using a Kuegelrohr distillation apparatus under reduced pressure (*ca.* 30 mmHg).[17a] Distilled and/or sublimed product was subjected to column chromatography on silica gel (benzene) to afford (**7a**) (26 mg, 93%) and adamantanone (**8**) (23 mg, 73%). These products were identified by comparison with authentic samples (g.l.c. analysis).

Thermal Decomposition of (**4e**).—The cycloadduct (**4e**) (60 mg, 0.17 mmol) was heated at 250 °C for 0.5 h as above. Chromatography of the sublimed mixture on silica gel (benzene) gave (**7e**)[16] (23 mg, 71%) and (**8**) (22 mg, 84%). These compounds were identified with authentic samples (i.r. and g.l.c. analyses).

3',5'-*Diphenyladamantane*-2-*spiro*-2'-(1',3',4'-*thiadiazoline*) (**11a**).—A solution of triethylamine (202 mg, 2.0 mmol) in dry benzene (5 ml) was added slowly to a stirred solution of (**1**) (166 mg, 1.0 mmol) and α-chlorobenzylidenephenylhydrazine (**9a**) (230 mg, 1.0 mmol) in benzene (5 ml) at room temperature. After being heated at reflux for 0.5 h, the mixture was allowed to react at room temperature overnight. The precipitate (Et_3N·HCl, 135 mg) was filtered off and the filtrate concentrated under reduced pressure. The solid residue was chromatographed on a silica gel column. Elution with n-hexane–benzene (3:1 v/v) gave a dimer of (**1**), (**13**)[12] (5 mg, 3%), m.p. >300 °C from the early fractions. Later fractions gave (**11a**) (333 mg, 94%). The analytical sample was obtained by recrystallization from $CHCl_3$–n-hexane (1:5 v/v). Adduct (**11a**): $\delta_C(CDCl_3)$ 157.5 (1 C, s), 144.1 (1 C, s), 131.8 (1 C, s), 130.2 (2 C, d), 128.5 (2 C, d), 128.3 (3 C, d), 128.0 (3 C, d), 94.6 (1 C, s), 38.0 (1 C, t), 37.7 (2 C, t), 37.6 (2 C, d), 33.4 (2 C, t), 26.9 (1 C, d), and 26.5 (1 C, d); for other physical data, see Table 4.

The 1,3-dipolar cycloadditions of (**1**) with other nitrilimines (**10b—d**) were carried out similarly and the results are summarized in Tables 2 and 4.

* M^+ Ion peak could not be observed.

Thermal Decomposition of the Thiadiazoline (**11a**).—The cycloadduct (**11a**) (60 mg, 0.16 mmol) was heated at 200 °C for 1 h in a Kuegelrohr (*ca.* 30 mm). The distilled and sublimed mixture had strong characteristic absorption in its i.r. spectrum at 2 240 ($\nu_{C\equiv N}$) and 1 655 cm^{-1} ($\nu_{C=N}$) which were indicative of the benzonitrile (**15**) and *N*-adamantylideneaniline (**14**) respectively. A solution of this mixture in ether (20 ml) and 2M-hydrochloric acid (10 ml) was stirred for 2 h at room temperature. The mixture was poured into cold water (20 ml) and extracted with ether (20 ml × 2). The combined extracts were washed with saturated aqueous sodium carbonate, dried (Na_2SO_4), and evaporated to afford a solid residue which was chromatographed on silica gel (benzene) to give (**8**) (12 mg, 50%) and (**15**) (12 mg, 70%) as a colourless oil. The combined aqueous layers were basified with 10% aqueous sodium hydroxide and extracted with ether (10 ml × 3). The combined extracts were dried (Na_2SO_4) and evaporated to afford aniline (9 mg, 61%). These products were identified by comparison of their spectral data and g.l.c. analyses using authentic samples.

Reaction of (**1**) *with Tetrazole* (**16**).—A mixture of (**1**) (166 mg, 1.0 mmol) and 2,5-diphenyltetrazole (**16**)[25] (222 mg, 1.0 mmol) in xylene (5 ml) was heated at 150 °C for 12 h. Evaporation of the solvent and chromatography on silica gel (dichloromethane–n-hexane, 2:1) gave (**11a**) (208 mg, 58%).

Reaction of Thiobenzophenone (**17**) *with Tetrazole* (**16**).—A solution of the thione (**17**) (100 mg, 0.51 mmol) and (**16**) (112 mg, 0.51 mmol) in xylene (5 ml) was heated at 150 °C for 12 h. Chromatography on silica gel (dichloromethane–n-hexane, 4:1), followed by recrystallization from ether–n-hexane gave 2,2,3,5-tetraphenyl-1,3,4-thiadiazoline (**18**) (120 mg, 60%), m.p. 161—163 °C (lit.,[6b] 158—160 °C).

5'-*Methyladamantane*-2-*spiro*-2'-(1',3',4'-*thiadiazoline*) (**21b**).—A slight excess of ethereal diazoethane (**20b**) generated from *N*-nitrosoethylurea (200 mg, 1.7 mmol) and 40% aqueous potassium hydroxide at 0 °C was added to a solution of the thione (**1**) (166 mg, 1.0 mmol) in ether (20 ml) at 0 °C. The addition was continued until the orange colour of (**1**) disappeared and the yellow colour of (**20b**) persisted. The solvent and excess (**20b**) were removed under reduced pressure at 0 °C to afford the cycloadduct (**21b**) (205 mg, 93%) as a colourless oil. This product was stable at 0 °C; an analytical sample was obtained by preparative t.l.c. on silica gel (n-hexane).

3'-*Phenyladamantane*-2-*spiro*-2'-*thiirane* (**23c**).—An excess of ethereal phenyldiazomethane (**20c**) generated from *N*-nitroso-*N*-benzyl-toluene-*p*-sulphonamide (870 mg, 3.0 mmol) and sodium methoxide (162 mg, 3.0 mmol) was added to (**1**) (166 mg, 1.0 mmol) in ether (20 ml) at 0 °C during 1 h and the mixture was stirred at room temperature for 12 h. Removal of the solvent and excess of (**20c**) under reduced pressure followed by chromatography on silica gel (chloroform) gave (**23c**) as a colourless oil (208 mg, 94%).

Although the reaction was also carried out at −25 °C for 3 days, the same cycloadduct (**23c**) was obtained (91% yield). For physical data, see Table 4.

References

1 This is also considered as Part 71 of the series Synthesis of Adamantane Derivatives. For Part 70 (Part 1 of the series Thermal Cycloaddition Reactions of Thiocarbonyl Compounds); see T. Katada, S. Eguchi, T. Esaki, and T. Sasaki, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1869.

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