($COOC_2H_5$)), 258 (38), 185 (100), 169 (53); UV (methanol) λ_{max} 220, 272, 278, 288 nm; ^1H NMR δ 8.70 (br s, 1 H, N(13)H), 7.45–7.05 (m, 4 H, C(9)C(12)H), 4.95 (X part of MXAB spectrum, 1 H, C(13c)H)C(4a)*HC*(4)H_2); 4.70 (d, 1 H, C(13b)H, J = 7.5 Hz), 4.40 (q, 2 H, OCH_2CH_3), 3.80 (X part of ABX spectrum, 1 H, J_{XA} = 4.5 Hz, J_{XB} = 8.2 Hz, C(7)*HC*(8)H_2), 3.30–3.05 (AB part of ABX spectrum, 2 H, C(8)H_2C(7)H, and X part of AXM spectrum, 1 H, C(13b)HC(13c)*HC*(4a)H), 2.60–2.30 (m, 2 H, C(2)H_2), 2.20 (m, 4 H, C(3)H_2C(4)H_2), 1.30 (t, 3 H, OCH_2CH_3). Anal. Calcd for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.80; H, 6.25; N, 7.79.

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Thermal Cycloaddition Reactions of Thiocarbonyl Compounds. 4.[1] Synthesis of Novel Adamantane-2-spirothiaheterocycles via [4 + 2] Cycloaddition Reactions of Adamantanethione with Conjugated Dienes

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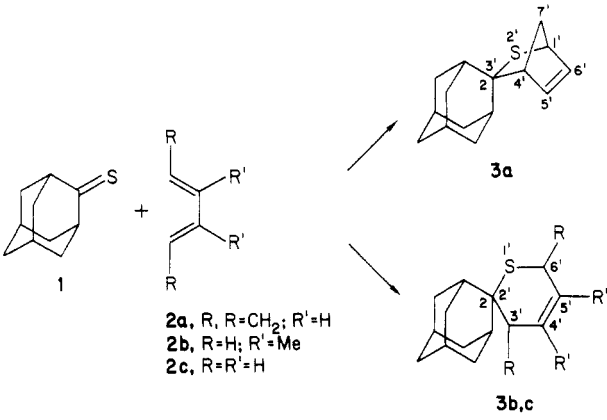
Thermal cycloaddition reactions of adamantanethione (1) with conjugated dienes such as cyclopentadiene, 2,3-dimethyl-1,3-butadiene, piperylene, isoindole, and isobenzofuran occurred smoothly at 20–110 °C to afford [4 + 2] cycloadducts (**3a**, **3b**, **3d**, **23a**, and **23b**) in good yields. On the other hand, similar treatment of 1 with isoprene gave a 45:55 mixture of regioisomers **3e** and **4e**. Furthermore, reaction of 1 with Danishefsky's diene (**2f**) occurred at 110 °C to afford regioselectively adamantane-2-spiro-(2′-thiacyclohex-5′-en)-4′-one (**9**) in a good yield after desilylative elimination of the initial adduct. On the other hand, reaction of thiobenzophenone (11) with **2f** gave 2,2-diphenyl-6-methoxythiacyclohexan-4-one (14) and 2,2-diphenylthiacyclohex-3-en-5-one (17) in 16% and 52% yields, respectively. The nature of these cycloadditions is discussed on the basis of FMO and steric effects.

The use of thiocarbonyl compounds as a cycloaddition component in organic synthesis has developed quite rapidly in recent years.[3-5] Numerous studies based on quantum theoretical calculations about [4 + 2] cycloaddition reactions have been reported,[6] and the methanistic aspect has been discussed at length.[7] Recently, the interest in cycloaddition reaction of thiocarbonyl compounds has grown significantly.[8] However, only a few reports are available on the cycloaddition reaction involving adamantanethione (1).[9] In this paper, we describe thermal [4 + 2] cycloaddition reactions of 1, a stable alicyclic thiocarbonyl compound, with conjugated dienes, which provided a facile route to some novel adamantane-2-spirothiaheterocycles.

Scheme I



Results and Discussion

Cycloaddition Reaction of 1 with Cyclic Polyenes. Reaction of 1 with an 8-fold excess of cyclopentadiene (**2a**) in dry benzene at 80 °C gave cycloadduct **3a** and thione dimer **5**[10] in 91% and 4% yields, respectively (Scheme I

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Table I. Reaction of Thiones 1 and 11 with Conjugated Dienes

entry	thione	diene	reactn conditns: solvent	temp (°C)	time (h)	product yield (%)[a]
1	1	**2a**	benzene	80	2	**3a** (91), 5[b] (4)
2	1	**2b**	toluene	110	72	**3b** (82), **5** (4)
3	1	**2c**	xylene	120	24	**3c** (56), **5** (12)
4	1	**2d**	toluene	110	48	**3d** (80), **5** (8)
5	1	**2e**	toluene	110	48	**3e** + **4e** (82), **5** (5) (ratio 45:55)
6	1	**2f**	toluene	110	24	**9** (64)
7	11	**2f**	benzene	40	24	**14** (16), **17** (52)
8	1	**21a**	chloroform	rt[d]	48	**23a** (96), **5** (3)
9	1	**21b**	chloroform[c]	rt	24	**23b** (79), **5** (4)

[a] Isolated yields after chromatography on a silica gel. [b] Thione dimer. [c] And then reaction mixture was heated in toluene at 100 °C for 24 h. [d] rt = room temperature.

Table II. Physical and Analytical Data of [4 + 2] Cycloadducts

compd[a] (mp, °C)	IR,[b] cm^{-1}	^1H NMR,[c] δ	mass spectrum, m/e (rel intensity)	mol form, anal. calcd/found: C	H	N
3a (43.5–44.5)	3050, 3000, 2910, 2800, 1460, 1338, 1268, 1050, 762, 738	6.45–6.25 (m, 1), 6.05–5.80 (m, 1), 3.98 (br s, 1), 3.50 (br s, 1), 2.40–1.30 (m, 16)	232 (11),[d] 199 (3.9), 167 (68), 166 (100), 133 (50), 111 (15), 91 (16), 66 (18)	$C_{15}H_{20}S$ 77.53 / 77.39	8.67 / 8.81	
3b (57.0–58.0)	2900, 2840, 1445, 1410, 1345, 1165, 1090, 960	3.00 (br s, 2), 2.72–2.30 (m, 4), 2.30–1.35 (m, 18)	248 (75),[d] 233 (10), 215 (80), 166 (100), 133 (35), 105 (40), 93 (50)[e]	$C_{16}H_{24}S$ 77.36 / 77.40	9.74 / 9.70	
3c (43.0–44.0) [lit.[11] 44–48]	3050, 2920, 2860, 1665, 1460, 1420, 1350, 1182, 1005, 980, 810	5.74 (s, 2), 3.30–3.20 (m, 2), 2.80–2.30 (m, 4), 2.30–1.38 (m, 12)	220 (40),[d] 187 (72), 166 (100), 133 (52)	$C_{14}H_{20}S$ 76.30 / 76.31	9.15 / 9.14	
3d (oil)	3000, 2910, 2850, 1660, 1450, 1240, 1098, 962, 802, 710	5.66 (s, 2), 3.70–2.90 (m, 1), 2.88–2.50 (m, 2), 2.50–2.30 (m, 2), 2.30–1.35 (m, 12), 1.28 (d, J = 7.2 Hz, 3)	234 (75),[d] 202 (65), 201 (100), 166 (90), 145 (30), 135 (60), 133 (42), 107 (35)[e]	$C_{15}H_{22}S$ 76.86 / 76.93	9.46 / 9.39	
3e + **4e** (oil)	3025, 2910, 2810, 1670, 1445, 1420, 1102, 770	5.65–5.30 (m, 1), 3.20–2.85 (m, 2), 2.80–2.30 (m, 4), 2.28–1.35 (m, 15)	234 (34),[d] 201 (100), 191 (35), 166 (85), 135 (60), 133 (42), 107 (43), 105 (84)[e]	$C_{15}H_{22}S$ 76.86 / 76.81	9.46 / 9.51	
9 (143–145)	3010, 2900, 2850, 1640, 1550, 1455, 1365, 1220, 1070, 728	7.26 (d, J = 10.0 Hz, 1), 6.00 (d, J = 10.0 Hz, 1), 2.98 (s, 2), 2.50–1.30 (m, 14)[f]	234 (100),[d] 217 (11), 201 (16), 148 (53), 113 (25), 105 (23), 91 (45), 79 (31)[e]	$C_{14}H_{18}OS$ 71.75 / 71.63	7.74 / 7.86	
14 (oil)	3050, 2925, 1710, 1598, 1488, 1400, 1100, 1080, 740, 695	8.15–7.85 (m, 2), 7.50–7.10 (m, 8), 4.38 (dd, J = 6.0, 9.0 Hz, 1), 3.08 (s, 3), 3.20–2.65 (m, 4)[f]	298 (18),[d] 266 (2.11), 210 (10), 198 (100), 165 (85), 151 (13), 121 (54), 100 (50), 115 (29)	$C_{18}H_{18}O_2S$ 72.47 / 72.32	6.08 / 6.23	
17 (124 dec)	3050, 1670, 1490, 1440, 1380, 1260, 1132, 895, 760, 752, 740, 700	8.10–7.00 (m, 11), 5.98 (d, J = 10.5 Hz, 1), 3.17 (s, 2)[f]	266 (6.6),[d] 223 (13), 214 (60), 213 (38), 182 (100), 165 (87), 121 (27), 105 (80)	$C_{17}H_{14}OS$ 76.66 / 76.80	5.30 / 5.35	
23a (180–182)	3045, 2975, 2850, 1750, 1385, 1250, 1160, 1092, 940, 755, 680	7.48–7.05 (m, 4), 6.10 (br s, 1), 5.72 (br s, 1), 2.60–1.45 (m, 13), 1.45 (s, 9), 1.05 (br s, 1)	383 (0.6),[d] 218 (5.1), 217 (30), 166 (43), 161 (90), 133 (13), 117 (100), 91 (30)	$C_{23}H_{29}NO_2S$ 72.03 / 72.03	7.62 / 7.62	3.65 / 3.64
23b (170–171)	3045, 2920, 2850, 1470, 1345, 1218, 975, 860, 760, 742, 680, 665	7.55–7.00 (m, 4), 6.32 (s, 1), 5.78 (s, 1), 2.50–1.50 (m, 13), 1.10 (br s, 1)	284 (30),[d] 252 (6.3), 251 (17), 166 (8.5), 119 (32), 118 (100), 91 (21)	$C_{18}H_{20}OS$ 76.01 / 75.98	7.09 / 7.12	

[a] Purified by chromatography on silica gel. [b] Scanned in KBr disks. [c] ^1H NMR spectra were measured in $CDCl_3$ at 60 MHz, see Table III for ^1H NMR data at 500 MHz. [d] M^+ ion peaks. [e] At 70 eV. [f] In CCl_4.

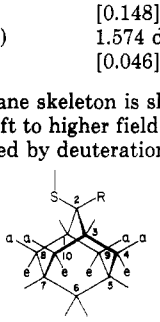
and Table I). The cycloadduct **3a** was characterized as adamantane-2-spiro-(3′-2′-thia-5′-norbornene) on the basis of elemental analysis and spectral data (Table II). In the mass spectrum, appearance of a molecular ion at m/e 232 (11%) and fragment ions due to a retrocycloaddition at m/e 166 (100%, **1**) and 66 (18%, **2a**) supported the **3a** structure. Furthermore, characteristic ^1H NMR signals at δ 6.45–6.25 (m, $H_{6'}$), 6.05–5.80 (m, $H_{5'}$), 3.90 (br s $H_{1'}$), 3.50 (br s, H_4), and 2.40–1.30 (m, adamantane proton and H_7) in a 1:1:1:1:16 ratio and ^{13}C NMR signals at δ 137.4 (d, $C_{6'}$), 131.6 (d, $C_{5'}$), 71.6 (s, C_2), 51.2 (d, $C_{1'}$ or $C_{4'}$), and 49.8 (d, $C_{4'}$ or $C_{1'}$) were compatible with **3a**.

Tetraphenylcyclopentadiene, 9,10-dimethylanthracene, and 6,6-diphenylfulvene were found to be inert in the reaction with **1** even after heating at 100–130 °C for 1 week and **1** was recovered unchanged, whereas the reactions with

Table III. ^{1}H NMR Data for Cycloadducts 3b, 3c, 3e, and 4e[a,b]

proton	chemical shift, δ (J, Hz)/[Δ, ppm][c]				
	3b	3c	3e	4e	2-Me-2-OH-adamantane[f]
H-vinyl		5.776 m	5.545 m, 5′H	5.454 m, 4′H	
		[0.196]	[0.195]	[0.104]	
H-6′,6′	2.990 s	3.103 s	3.097 m	2.979 s	
	[0.132]	[0.221]	[0.145]	[0.175]	
H-3′,3′	2.491 s	2.584 s	2.477 s	2.547 m	
	[0.025]	[0.135]	[0.077]	[0.059]	
H-methyl	1.700 s		1.722 s	1.722 s	1.337 s
	[0.207, 0.125]		[0.128]	[0.208]	[0.187]
H-4,9a	2.480 d (12.5)	2.551 d (12.5)	2.532 d (13.1)	*d*	2.184 d (12.5)
	[−0.274]	[−0.210]	[−0.23]		[−0.156]
H-8,10a	2.047 d (12.2)	2.026 d (12.5)	2.043 d (12.5)[e]	2.017 d (12.8)[e]	1.868 d (12.8)
	[0.125]	[0.194]	[0.159]	[0.133]	[0.161]
H-1,3	1.862 s	1.866 s	1.868 s or t	*d*	1.805 s
	[0.047]	[0.064]	[0.065]		[0.198]
H-5,7	1.777 s	1.827 s	1.800 s or t	*d*	1.680 s
	[0.053, −0.086]	[0.136, −0.017]	[0.087, −0.070]		[0.023, −0.060]
H-6,6	1.699 s	1.719 s	1.722 s	*d*	1.680 s
	[0.047]	[0.093]	[0.075]		[0.144]
H-8,10e	1.660 d (12.8)	1.670 d (12.5)	1.676 d (11.9)	1.652 d (12.2)	1.739 d (13.1)
	[0.128]	[0.165]	[0.148]	[0.124]	[0.139]
H-4,9e	1.553 d (12.8)	1.574 d (12.5)	1.574 d (12.8)	*d*	1.557 d (12.5)
	[0.021]	[0.067]	[0.046]		[0.110]

[a] 500 MHz, 25 °C in $CDCl_3$. [b] The numbering of adamantane skeleton is shown below. [c] Aromatic solvent-induced shift; Δ = δ(C_6D_6) − δ($CDCl_3$). A positive value of the solvent shift indicates a shift to higher field, i.e., more shielding in aromatic solvent. [d] Same as **3e**. [e] The assignment may be interchangeable. [f] OH proton was removed by deuteration.



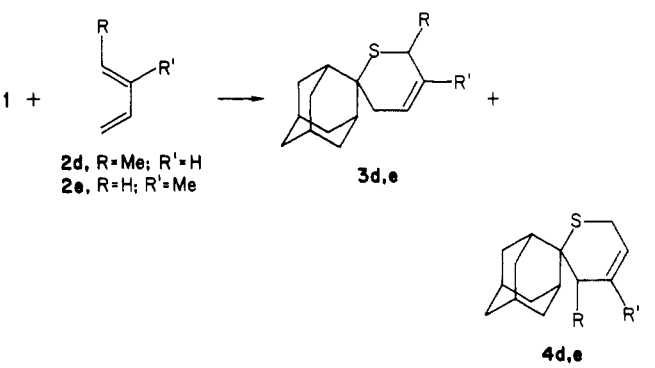
norbornadiene, 1,3-cyclohexadiene, hexachloropentadiene, and 6,6-dimethylfulvene resulted in the formation of an intractable complex mixture, from which no products could be characterized.

Cycloaddition Reaction of 1 with Substituted Butadienes. When a mixture of **1** and 2,3-dimethyl-1,3-butadiene (**2b**) in toluene was heated at 110 °C, the characteristic reddish orange color of **1** had completely disappeared in about 72 h. A single crystalline cycloadduct (**3b**, 82%) was isolated accompanied by a small amount of the thione dimer **5** (4%) (Scheme I). The adduct **3b** was characterized as adamantane-2-spiro-2′-4′,5′-dimethylthiacyclohex-4′-ene on the basis of elemental analysis and spectral data (Table II). In the mass spectrum, the molecular ion at *m/e* 248 (75%) as well as fragment ions at *m/e* 215 (80%, M^+ − SH) and 166 (100%, **1**) supported the **3b** structure. The appearance of characteristic signals in the ^{1}H NMR spectrum at δ 3.00 (br s, $H_{6'}$), 2.72–2.30 (m, $H_{3'}$ and adamantane 4,9-axial protons, cf. Table III), and 2.30–1.35 (m, Me and other adamantane protons) in a 2:4:18 ratio was also compatible with **3b**.

Similarly, the reaction of **1** with 1,3-butadiene (**2c**) generated from thermal decomposition of 3-sulfolene in xylene at 120 °C gave adamantane-2-spiro-(2′-thiacyclohex-4′-ene) (**3c**) (56%). The same adduct of **3c** was obtained by the reaction of **1** with **2c** at 100 °C in a 64% yield.[11]

The reaction of **1** with unsymmetrical dienes such as piperylene (**2d**) and isoprene (**2e**) raises the regioselectivity problem. In fact, the formation of two regioisomers from the reaction of thiobenzophenone with **2e** or chloroprene was reported.[12] However, when a mixture of **1** and a

Scheme II



10-fold excess of **2d** in toluene was heated at 110 °C for 48 h, only a single cycloadduct (**3d**,[13] 80%) was isolated (Scheme II, Table I). No trace of regioisomer **4d** could be detected. The mass spectral molecular ion at *m/e* 234 (75%) as well as fragment ions at *m/e* 201 (100%, M^+ − SH) and 166 (90%, **1**) was compatible with the given structure **3d**.

Characteristic signals in the ^{1}H NMR spectrum at δ 5.66 (s, $H_{4'}$ and $H_{5'}$), 3.70–2.90 (m), 2.88–2.50 (m), 2.50–2.30 (m), 2.30–1.35 (m), and 1.28 (d, Me) in a 2:1:2:2:12:3 ratio and in the ^{13}C NMR spectrum at δ 129.9 (d), 125.7 (d), and 51.4 (s, C_2) supported **3d** but not **4d**. The compound **3d** was reported as a methylation product of **3c**.[11] The reported ^{1}H NMR spectrum was superimposable, supporting the given cycloadduct structure. On the other hand, the similar reaction of **1** with 10-fold excess of isoprene (**2e**) oc-

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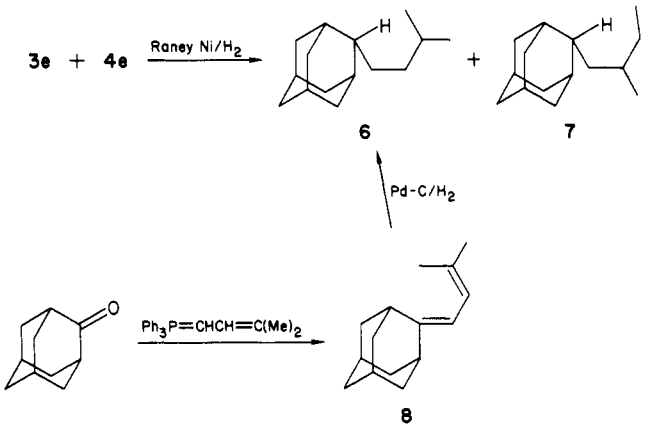
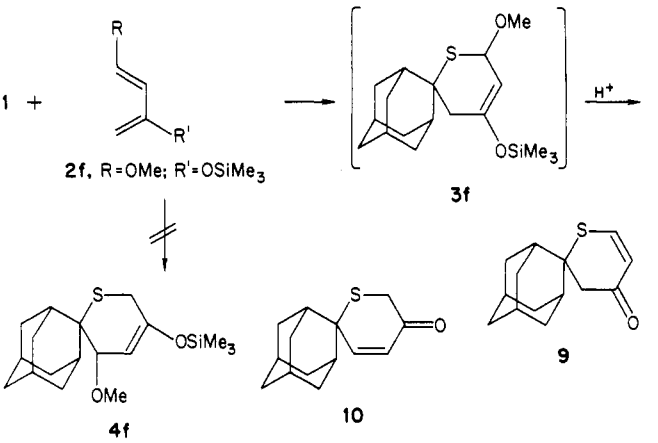
(13) Compound **3d** should be a mixture of configurational isomers at the 6′-methyl group.

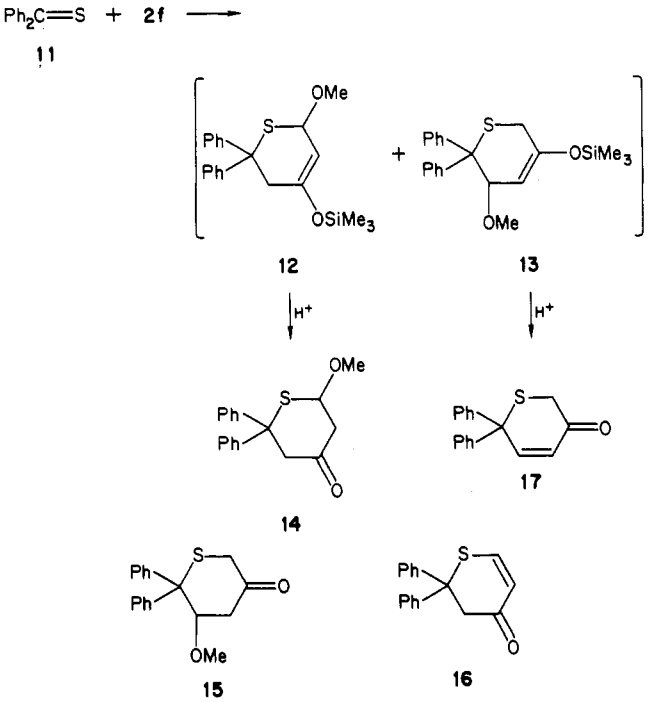
Scheme III



Scheme IV



Scheme V



curred to afford an inseparable mixture of regioisomers (**3e** and **4e**) (82%) after the usual workup and chromatography.[14] The cycloadducts **3e** and **4e** were characterized as adamantane-2-spiro-(5′-methyl- and -4′-methylthiacyclohex-4′-ene), respectively, by elemental analysis and spectral data (Scheme II, Table II). The mass spectral molecular ion at *m/e* 234 (34%) as well as fragment ions at *m/e* 201 (100%, $M^+ - SH$) and 166 (85%, **1**) supported the given structure **3e** and/or it's regioisomer **4e**. Characteristic ^1H NMR signals (60 MHz) at δ 5.65 (m, $H_{4'}$ and/or $H_{5'}$), 3.20–2.85 (m, $H_{6'}$), 2.80–2.30 (m, $H_{3'}$ and adamantane 4,9-axial protons), and 2.28–1.35 (m, other adamantane protons and Me) in a 1:2:4:15 ratio were also compatible with **3e** and/or **4e**. The 60-MHz ^1H NMR data of the mixture do not allow us to assign the regioisomers, but the 500-MHz ^1H NMR data permitted us to assign the regioisomers (Table III). Both vinyl proton and 6′,6′-methylene protons chemical shifts are completely resolved for each of regioisomers. The vinyl proton of **3e** and **4e** appears at δ 5.454 and 5.545, respectively, and 6′,6′-methylene protons of **3e** and **4e** resonate at δ 2.979 and 3.097, respectively. The ratio of **3e** and **4e** was determined as 45:55 by integration of the above four characteristic ^1H NMR signals. Assignments of other peaks due to regioisomers **3e** and **4e** as summarized in Table III were based on the characteristic aromatic solvent-induced shifts (A.S.I.S.) as well as data of **3b**, **3c**, and 2-methyl-2-hydroxyadamantane as model compounds and literature data.[10b,15] The lanthanide shift reagent Eu(fod)$_3$ had no effect on these thiaheterocycles. Additional support for the structural assignments can be drawn from ^{13}C NMR spectrum. In the ^{13}C NMR spectrum, the appearance of characteristic four signals due to double-bond carbons at $C_{4'}$ and $C_{5'}$ in **3e** [δ 121.2 (d) and 129.9 (s)] and in **4e** [δ 134.0 (s) and 116.8 (d)] were also compatible with an approximately 45:55 mixture of regioisomers **3e** and **4e**. Catalytic hydrogenation of the cycloadducts **3e** and **4e** with Raney Ni (W-4 type) in ethyl acetate afforded also an inseparable mixture of 2-(3-methylbutyl)- (**6**) and 2-(2-methylbutyl)adamantane (**7**)[16] (Scheme III), but compound **6** could be identified by comparison of it's spectral data (500-MHz ^1H NMR and ^{13}C NMR analyses) with an authentic sample as below. The Wittig reaction of adamantanone with 3-methyl-2-butenylidenetriphenylphosphorane gave diene **8**, which was hydrogenated to give **6** as a colorless oil (see Experimental Section).

The reaction of **1** with Danishefsky's diene [1-methoxy-3-(trimethylsiloxy)-1,3-butadiene] (**2f**)[17] in toluene at 110 °C for 24 h afforded single cycloadduct **9** (64%) after chromatography (silica gel) (Scheme IV). No traces of regioisomer **10** could be detected. The adduct **9** was characterized as adamantane-2-spiro-(2′-thiacyclohex-5′-en)-4′-one on the basis of elemental analysis and spectral data (Table II). In the mass spectrum, the molecular ion at *m/e* 234 (100%) as well as fragment ions at *m/e* 217 (11%, $M^+ - OH$) and 201 (16%, $M^+ - SH$) supported the **9** structure. Characteristic ^1H NMR signals at δ 7.26 (d, J = 10.0 Hz, $H_{6'}$), 6.00 (d, J = 10.0 Hz, $H_{5'}$), 2.98 (s, $H_{3'}$), and 2.15–1.30 (m, adamantane protons) in a 1:1:2:14 ratio and ^{13}C NMR signals at δ 195.2 (s, $C_{4'}$), 144.8 (d, $C_{6'}$), 122.0

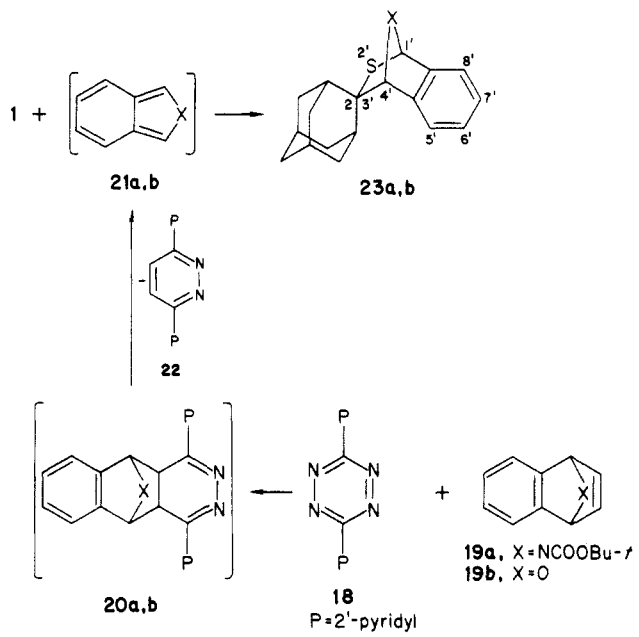
(14) Attempted separation of the regioisomers **3e** and **4e** by TLC (Merck silica gel 60F-254 precoated glass-backed plate, *n*-hexane), GLC (Silicone SE-30 stainless steel capillary column, 0.5 mm × 45 m or Silicone SE-30 column, 5.0 mm × 4 m), and HPLC (Merck LiChrosorb RP-18, 250 mm × 4 mm or LiChrosorb NH_2, 250 mm × 4 mm) proved to be all unsuccessful.

(15) Deursen, F. W.; Korver, P. K. *Tetrahedron Lett.* **1967**, 3923.

(16) Attempted separation of the regioisomers **6** and **7** by TLC (Merck silica gel 60F-254 precoated glass-backed plate, *n*-hexane), GLC (Silicone SE-30 stainless steel capillary column, 0.5 mm × 45 m or Silicone SE-30 column, 5.0 mm × 4 m), and HPLC (Merck LiChrosorb RP-18, 250 mm × 4 mm or LiChrosorb NH_2, 250 mm × mm) proved to be all unsuccessful.

(17) (a) Danishefsky, S.; Kitahara, T. *J. Am. Chem. Soc.* **1974**, *96*, 7807. (b) Danishefsky, S.; Kitahara, T.; Yan, C. F.; Morris, J. *Ibid.* **1979**, *101*, 6996. (c) Danishefsky, S.; Larson, E. R.; Askin, D. *Ibid.* **1982**, *104*, 6457. (d) Danishefsky, S. *Acc. Chem. Res.* **1981**, *14*, 400.

Scheme VI



(d, $C_{5'}$), 58.7 (s, C_2), and 48.4 (t, $C_{3'}$) were compatible with **9** but not **10**. The UV maximum of **9** at 303 nm (log ϵ 3.96) in *n*-hexane indicated the *β-s*-substituted enone structure.[18,19] The formation of **9** was explained by desilylation, followed by concerted or stepwise elimination of methanol from the initial cycloadduct **3f** during workup (acidic conditions: silica gel chromatography or HCl catalytic hydrolysis).[17b] The reactions of thiobenzophenone (**11**)[20] with diene **2f** was examined also. The cycloaddition of **11** and **2f** took place at 40 °C for 24 h and then crude adducts were subjected to acidic (1 N HCl) workup. The cycloadducts 2,2-diphenyl-6-methoxythiacyclohexan-4-one (**14**) and 2,2-diphenylthiacyclohex-3-en-5-one (**17**) were obtained in 16% and 52% yields, respectively, accompanied with benzophenone (18%) (Scheme V). The formation of **14** was explained by a simple elimination of only a trimethylsilyl group from initial cycloadduct **12**. In contrast, the formation of **17** was explained by desililation, followed by elimination of methanol form cycloadduct **13**. In this case, no trace of regioisomers **15** and **16** could be detected. Because thiacyclohexenones seem to be not recorded in the literature, the above [4 + 2] cycloaddition of thiones **1** and **11** with Danishefsky's diene provides a novel route to one of hitherto unknown thiacyclohexenone ring systems.

Cycloaddition Reactions of 1 with Isoindole and Isobenzofuran. In connection with the above-mentioned study on the cycloaddition reactivity of **1**, we also investigated the cycloaddition reactions of isoindole (**21a**) and isobenzofuran (**21b**). The reaction of **1** with **21a** generated in situ from 3,6-di-2'-pyridyl-*s*-tetrazine (**18**)[21] and 1,4-[(*tert*-butyloxycarbonyl)imino]-1,4-dihydronaphthalene (**19a**)[22] in chloroform at 0–25 °C as usual occurred smoothly at room temperature to afford the cycloadduct **23a** (96%) after chromatography (Scheme VI). The cycloadduct **23a** was characterized as adamantane-2-spiro-[3'-(1',4'-(*tert*-butyloxycarbonyl)imino]-1',4'-dihydro-2'-thianaphthalene] on the basis of elemental analysis and spectral data (Table II). The similar reaction of **1** with isobenzofuran (**21b**) generated in situ from tetrazine **18** and 1,4-epoxy-1,4-dihydronaphthalene (**19b**)[23] in chloroform as usual afforded a single cycloadduct (**23b**, 79%) (Scheme VI). The adduct **23b** was characterized as adamantane-2-spiro-(3'-1',4'-epoxy-1',4'-dihydro-2'-thianaphthalene) by elemental analysis and spectral data (Table II).

Attempted reactions of **1** with furan and 1,3-diphenylisobenzofuran were unsuccessful even after heating in toluene at 100–130 °C for 1 week. No cycloadducts were obtained and **1** was recovered unchanged.

Regiochemistry. The observed regiochemistry in the above [4 + 2] cycloadditions should be explained in terms of frontier molecular orbital (FMO) interactions[24] if the steric factor was negligibly small. The orbitals of thione **1**,[9] piperylene (**2d**),[24,25] and isoprene (**2e**)[7b,24,25] based on CNDO/2 calculation have been reported in the literature. The interaction of HOMO-diene with LUMO-dienophile is larger (HOMO-controlled or normal Diels–Alder-type reaction).[7a,b] This predicts a regioselective formation of **4d** for piperylene (**2d**) and **3e** for isoprene (**2e**). But **2e** in the reaction with **1** showed no regioselectivity, affording a 45:55 mixture of regioisomers **3e** and **4e**. On the other hand, **2d** in the reaction with **1** showed the regioselectivity to be different from the FMO prediction, affording **3d** but not **4d**. This observed regiochemistry was, however, the sterically favored one on the basis of the steric approach control. The substituent on the terminal carbon atom of butadiene plays an important role in the regioselection. The methyl group of **2d** interferes severely with the bulky adamantyl group of **1** at the transition state to **4d**: hence, opposite regioisomer **3d** can be produced exclusively. Similarly, the methoxy group on the terminal of **2f** prohibited sterically the formation of a regioisomer **4f** (or **10**) and only regioisomer **3f** (i.e., **9**) was produced. On the contrary, in the case of thiobenzophenone (**11**), steric hindrance may not to be the major regiocontrolling factor.

In summary, [4 + 2] cycloaddition reaction of adamantanethione (**1**) as well as thiobenzophenone (**11**) provides convenient route to some novel thiacyclohexanes and thiacyclohexenones, which are difficult to prepare by other routes.

Experimental Section

Melting points were taken in a sealed tube on a Yanagimoto micromelting point aparatus and are uncorrected. IR spectra were obtained on a JASCO IRA-1 infrared spectrophotometer. UV spectra were performed on a Hitachi 124 spectrophotometer. ^{1}H NMR spectra were taken with a JEOL JNM-C-60HL instument at 60 MHz and a JEOL GX 500 spectrometer at 500 MHz. ^{13}C NMR spectra were recorded on a JEOL JNM-FX-60 FT NMR instrument at 15.04 MHz. Chemical shifts are reported in parts per million (δ) relative to Me_4Si as an internal standard in $CDCl_3$ or CCl_4. Mass spectra were obtained with a JEOL JMS-D10 instrument at 75 eV or a Hitachi RMU-6M mass spectrometer at 70 eV. Microanalyses were performed with a Perkin-Elmer 240B elemental analyzer. GLC analyses were carried out on a Hitachi 163 or a Hitachi 663-30 gas chromatograph on a 1- or 4-m

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(19) We are very grateful to a referee for suggesting the UV measurement.
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(21) Geldard, J. F.; Lions, F. *J. Org. Chem.* **1965**, *30*, 318.
(22) (a) Carpino, L. A.; Barr, D. E. *J. Org. Chem.* **1966**, *31*, 764. (b) Sasaki, T.; Manabe, T.; Nishida, S. *Ibid.* **1980**, *45*, 476. (c) Priestley, G. M.; Warrener, R. N. *Tetrahedron Lett.* **1972**, 4295.
(23) (a) Warrener, R. N. *J. Am. Chem. Soc.* **1971**, *93*, 2346. (b) Ziegler, G. R. *Ibid.* **1969**, *91*, 446. (c) Sasaki, T.; Kanematsu, K.; Hayakawa, K.; Uchida, M. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2750.
(24) (a) Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 7310. (b) Houk, K. N.; Sims, J.; Duke, R. E.; Strozier, R. M.; George, J. K. *Ibid.* **1973**, *95*, 7287. (c) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: New York, 1976.
(25) Eisenstein, O.; Lefour, J. M.; Anh, N. T. *Tetrahedron* **1977**, *33*, 523.

Silicone SE-30 column or a 45-m Silicone SE-30 stainless steel capillary column at 80–200 °C. HPLC analyses were obtained on a JASCO TRI ROTAR-V instrument equipped with a JASCO UVIDEC-100 detecter and using 250 mm × 4 mm LiChrosorb RP-18 and LiChrosorb NH_2 packed columns (Merck).

Materials. Adamantanethione (**1**) was prepared by the reported method[10] and purified by silica gel (Kiesel gas 60, 70–230 mesh, Merck) column chromatography eluting with *n*-hexane. 3,6-Di-2′-pyridyl-*s*-tetrazine (**18**),[21] 1,4-[(*tert*-butyloxycarbonyl)imino]-1,4-dihydronaphthalene (**19a**),[22] and 1,4-epoxy-1,4-dihydronaphthalene (**19b**)[23] were prepared according to the procedures in the literatures. The other reagents were commercial materials. All the solvents were carefully dried and distilled before use.

Adamantane-2-spiro-(3′-2′-thia-5′-norbornene) (3a). A mixture of **1** (120 mg, 0.72 mmol), cyclopentadiene (**2a**) (400 mg, 6.06 mmol), and hydroquinone (5 mg, 0.045 mmol) in dry benzene (4 mL) was heated in a sealed tube (12 mm diameter × 260 mm length) at 80 °C for 2 h under argon until the characteristic orange color of the mixture disappeared completely. Removal of the solvent and excess **2a** under reduced pressure gave an oily residue which was chromatographed on a silica gel column by elution with *n*-hexane–chloroform (4:1 v/v). The early fractions gave the dimer of **1**, **5** (5 mg, 4%), mp >300 °C.[10] Later fractions gave the adduct **3a** (144 mg, 91%) as a white precipitate. Analytical sample **3a** was obtained by recrystallization from *n*-hexane. Adduct **3a**: ^{13}C NMR ($CDCl_3$) δ 137.4 (d, 1 C), 131.6 (d, 1 C), 71.6 (s, 1 C), 51.2 (d, 1 C), 49.8 (d, 1 C), 49.6 (t, 1 C), 38.8 (d, 1 C), 38.6 (t, 1 C), 38.5 (t, 1 C), 37.5 (t, 1 C), 36.9 (d, 1 C), 35.6 (t, 1 C), 35.5 (t, 1 C), 26.7 (d, 1 C), 26.2 (d, 1 C); for other physical data, see Table II.

Adamantane-2-spiro-(2′-4′,5′-dimethylthiacyclohex-4′-ene) (3b). A solution of **1** (166 mg, 1.00 mmol), 2,3-dimethyl-1,3-butadiene (**2b**) (82 mg, 10.0 mmol), and hydroquinone (5 mg, 0.05 mmol) in toluene (4 mL) was heated at 110 °C for 72 h. Workup as described above and followed by chromatography on a silica gel (*n*-hexane–benzene, 9:1 v/v) gave **5** (4 mg, 4%) and adduct **3b** (204 mg, 82%) as a white precipitable in order of elution. Analytical sample **3b** was obtained after recrystallization from methanol: ^{13}C NMR ($CDCl_3$) δ 126.2 (s, 1 C), 122.5 (s, 1 C), 50.6 (s, 1 C), 42.5 (t, 1 C), 39.2 (t, 1 C), 35.1 (d, 2 C), 33.8 (t, 2 C), 33.1 (t, 2 C), 29.4 (t, 1 C), 28.0 (d, 1 C), 27.7 (d, 1 C), 20.9 (q, 1 C), 18.9 (q, 1 C); for other physical data, see Tables II and III.

Adamantane-2-spiro-(2′-thiacyclohex-4′-ene) (3c). A mixture of **1** (100 mg, 0.60 mmol) and 3-sulfolene (500 mg, 4.24 mmol) in xylene (4 mL) was heated in a sealed tube at 120 °C for 24 h. Similar workup gave **5** (12 mg, 12%) and adduct **3c**[11] (72 mg, 56%) in order of elution. Adduct **3c**: for physical data, see Table II and III.

Adamantane-2-spiro-(2′-6′-methylthiacyclohex-4′-ene) (3d). A mixture of **1** (166 mg, 1.00 mmol) and piperylene (**2d**) (680 mg, 10.0 mmol) in toluene (5 mL) was heated in a sealed tube at 110 °C for 48 h. Workup as described above followed by preparative TLC on a silica gel (*n*-hexane) gave **5** (8 mg, 8%) and adduct **3d** (188 mg, 80%) as a colorless oil. Adduct **3d**: ^{13}C NMR ($CDCl_3$) δ 129.9 (d, 1 C), 125.7 (d, 1 C), 51.4 (s, 1 C), 39.3 (t, 1 C), 38.0 (d, 1 C), 35.6 (t, 1 C), 33.5 (t, 2 C), 33.3 (t, 1 C), 32.7 (t, 1 C), 32.6 (d, 1 C), 31.9 (d, 1 C), 28.1 (d, 1 C), 27.7 (d, 1 C), 20.9 (q, 1 C); for other physical data, see Table II.

Reaction of 1 with Isoprene (2e). A mixture of **1** (166 mg, 1.00 mmol) and **2e** (680 mg, 10.0 mmol) in toluene (5 mL) was heated in a sealed tube at 110 °C for 48 h. Similar workup gave **5** (5 mg, 5%) and a mixture of regioisomers **3e** and **4e** (192 mg, 82%) (ratio 45:55 on the basis of 500-MHz ^1H NMR and ^{13}C NMR analyses) as a colorless oil. Adducts **3e** and **4e**: ^{13}C NMR ($CDCl_3$) δ 134.0 (s, 0.55 C), 129.9 (s, 0.45 C), 121.2 (d, 0.45 C), 116.8 (d, 0.55 C), 49.9 (s), 49.0 (s), 40.9 (t), 39.3 (t), 36.4 (t), 34.8 (t), 34.7 (d), 33.7 (t), 33.0 (t), 28.2 (d), 27.8 (d), 25.3 (q), 24.1 (d), 23.7 (q); for other physical data, see Tables II and III.

2-Adamantylidene-3-methyl-2-butene (8). To stirred and water-cooled solution of sodium (methylsulfinyl)carbanion, prepared from sodium hydride (2.5 mmol) and dimethyl sulfoxide (10 mL), was added dropwise a solution of (3-methyl-2-butenyl)triphenylphosphonium bromide (1.03 g, 2.5 mmol) in dimethyl sulfoxide (10 mL). After stirring at room temperature for 15 min, adamantanone (300 mg, 2.0 mmol) was added and stirring was continued at room temperature for 15 h and then at 40 °C for 2 h. The cooled mixture was poured into water and extracted with *n*-pentane (20 mL × 3). The combined extracts were dried (Na_2SO_4). After removal of the solvent, the resulting residue was purified by preparative TLC (Kiesel gel 60F-254, *n*-hexane) to give 102 mg of **8** (25%) as a colorless oil: IR (neat) 3020, 2910, 2845, 1618, 1445, 1375, 1095, 950, 850, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.05–5.90 (m, 2 H), 3.02 (br s, 1 H), 2.40 (br s, 1 H), 2.10–1.70 (m, 18 H).

Anal. Calcd for $C_{15}H_{20}$: C, 89.04; H, 10.96. Found: C, 88.96; H, 11.04.

2-(3-Methylbutyl)adamantane (6). A mixture of **8** (60 mg, 0.3 mmol) and Pd–C (10%, 100 mg) in ethyl acetate (5 mL) was stirred at room temperature for 48 h and then at 60 °C for 1 h under atmosphere of hydrogen. After filtration of the catalyst through Celite 545 and washing with ethyl acetate, the combined filtrate and washings were evaporated under reduced pressure followed by preparative TLC (*n*-hexane) to afford **6** (38 mg, 62%) as a colorless oil: IR (neat) 2920, 2850, 1468, 1455, 1380, 1362, 1260, 1105, 800 cm^{-1}; 60-MHz ^1H NMR ($CDCl_3$) δ 2.15–0.75; 500-MHz ^1H NMR ($CDCl_3$) δ 1.90–1.42 (m, 16 H, adamantane protons and one methine proton of side chain), 1.395 (q of m, J = 7.9 Hz, 2 H, 2-methylene protons), 1.141 (q of m, J = 8.0 Hz, 2 H, 1-methylene protons), 0.882 (d, J = 6.7 Hz, 6 H, Me × 2); ^{13}C NMR ($CDCl_3$) δ 44.8 (d, 1 C), 39.4 (t, 2 C), 38.6 (t, 1 C), 37.1 (t, 1 C), 32.0 (d, 2 C), 31.7 (t, 2 C), 30.4 (t, 1 C), 28.5 (d, 1 C), 28.3 (d, 1 C), 28.2 (d, 1 C), 22.8 (q, 2 C).

Anal. Calcd for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 87.27; H, 12.73.

Reduction of Regioisomers 3e and 4e with Raney Ni. A 45:55 mixture of regioisomers **3e** and **4e** (93 mg, 0.40 mmol) and Raney Ni (W-4 type, ca 1 mL) in ethyl acetate (5 mL) was stirred at 40 °C for 24 h under atmosphere of hydrogen. Workup as above gave a 1:1 mixture of 2-(3-methylbutyl)- (**6**) and 2-(2-methylbutyl)adamantane (**7**) as a colorless oil (66 mg, 80%): IR (neat) 2920, 2855, 1455, 1105 cm^{-1}; mass spectrum, m/e (relative intensity) 206 (M^+, 81), 149 (100), 147 (45), 135 (77), 107 (64), 97 (89); 60-MHz ^1H NMR ($CDCl_3$) δ 2.1–0.6 (m); 500-MHz ^1H NMR ($CDCl_3$) δ 1.90–1.41 (m, 32 H, adamantane protons and one methine proton of side chain), 1.393 (q of m, J = 8.0 Hz, ca. 2 H, 2-methylene protons of **6**), 1.29–1.35 (m, ca. 2 H, 3-methylene protons of **7**), 1.17–1.06 (m, 4 H, 1-methylene protons of **6** and **7**), 0.880 (d, J = 6.4 Hz, ca. 3 H, Me × 2 of **6**), 0.867 (t, J = 7.3 Hz, ca. 1.5 H, 4-methyl protons of **7**), 0.845 (d, J = 6.4 Hz, ca. 1.5 H, 2-methyl protons of **7**). (The methyl proton signals supported the structures given); ^{13}C NMR ($CDCl_3$) δ 44.7, 41.5, 39.7, 39.4, 38.6, 37.1, 32.8, 32.0, 31.8, 31.7, 31.6, 31.5, 30.4, 29.9, 28.5, 28.3, 28.2, 22.7, 19.5, 11.4 [underlined signals were due to **6**, some signals due to **7** were superimposed on them].

Adamantane-2-spiro-(2′-thiacyclohex-5′-en)-4′-one (9). A mixture of **1** (120 mg, 0.72 mmol) and 1-methoxy-3-(trimethylsiloxy)-1,3-butadiene (**2f**) (350 mg, 2.0 mmol) in toluene (5 mL) was heated in a sealed tube at 110 °C for 24 h. After removal of the solvent and excess diene under reduced pressure, the resulting residue was treated with 1 N hydrochloric acid (1 mL) in ether (10 mL) at room temperature for 1 h. The organic layer was separated and aqueous layer was extracted with *n*-hexane (30 mL × 3). The combined organic layers were washed with water and dried over $MgSO_4$ and then evaporated. Preparative TLC on a silica gel (dichloromethane–ethyl acetate, 4:1 v/v) followed by recrystallization from *n*-hexane–ether gave adduct **9** (108 mg, 64%) as a white precipitate: ^{13}C NMR ($CDCl_3$) δ 195.2 (s, 1 C), 144.8 (d, 1 C), 122.0 (d, 1 C), 58.7 (s, 1 C), 48.4 (t, 1 C), 38.5 (t, 1 C), 34.3 (d, 2 C), 34.0 (t, 2 C), 32.1 (t, 2 C), 27.1 (d, 2 C); UV (*n*-hexane) λ_{max} 303 nm (log ε 3.96); for other physical data, see Table II.

2,2-Diphenyl-6-methoxythiacyclohexan-4-one (14) and 2,2-Diphenylthiacyclohex-3-en-5-one (17). A mixture of thiobenzophenone (**11**)[20] (100 mg, 0.50 mmol) and **2f** (350 mg, 2.0 mmol) in benzene (5 mL) was heated in a sealed tube at 40 °C for 24 h. The cooled mixture was treated with 1 N hydrochloric acid (1 mL) in benzene (100 mL) at room temperature for 1 h. Workup as above and followed by preparative TLC on a silica gel (dichloromethane–*n*-hexane, 1:1 v/v) gave benzophenone (17 mg, 18%) [R_f 0.6], thiacyclohexanone **14** (24 mg, 16%) [R_f 0.3], and thiacyclohexenone **17** (70 mg, 52%) [R_f 0.45]. Adduct **17**:

UV (*n*-hexane) 228 nm (shoulder, log ε 4.03); for other physical data of **14** and **17**, see Table II.

Adamantane-2-spiro-[3′-[1′,4′-(*tert*-butyloxycarbonyl)imino]-1′,4′-dihydro-2′-thianaphthalene] (23a). A mixture of [1,4-(*tert*-butyloxycarbonyl)imino]-1,4-dihydronaphthalene (**19a**)[22] (234 mg, 1.00 mmol) and 3,6-di-2′-pyridyl-*s*-tetrazine (**18**)[21] (236 mg, 100 mmol) in chloroform (5 mL) was stirred at 0 °C until the red color of the tetrazine **18** had disappeared (4 h), and then the thione **1** (150 mg, 0.90 mmol) was added. After stirring for 2 days at room temperature, evaporation to dryness at reduced pressure followed by chromatography on silica gel eluting with *n*-hexane–dichloromethane (1:1 v/v) gave the dimer of **1**, **5** (4 mg, 3%), and adduct **23a** (330 mg, 96%) as a white precipitate in order of elution. An analytical sample was obtained after recrystallization from *n*-hexane–chloroform (1:1 v/v). Adduct **23a**: ^{13}C NMR ($CDCl_3$) δ 150.8 (s, 1 C), 146.5 (s, 1 C), 140.0 (s, 1 C), 127.3 (d, 1 C), 125.3 (d, 1 C), 122.1 (d, 1 C), 116.9 (d, 1 C), 80.6 (s, 1 C), 73.8 (s, 1 C), 65.6 (d, 1 C), 64.9 (d, 1 C), 38.4 (t, 1 C), 38.1 (d, 1 C), 37.5 (d, 1 C), 37.1 (t, 1 C), 36.8 (d, 1 C), 35.6 (t, 1 C), 35.1 (t, 1 C), 28.2 (q, 3 C), 26.7 (t, 1 C), 26.2 (d, 1 C); for other physical data, see Table II.

Adamantane-2-spiro-(3′-1′,4′-epoxy-1′,4′-dihydro-2′-thianaphthalene) (23b). A solution of 1,4-epoxy-1,4-dihydronaphthalene (**19b**)[23] (144 mg, 1.00 mmol) and tetrazine **18** (236 mg, 1.00 mmol) in chloroform (5 mL) was stirred at 0 °C for 4 h. The reaction mixture was turned to pale red color, and then thione **1** (155 mg, 0.93 mmol) was added. After being stirred for 1 day at room temperature, the reaction mixture was heated in toluene (10 mL) at 100 °C for 1 day. After removal of the solvent under reduced pressure, the resulting residue was chromatographed on a silica gel column by elution with *n*-hexane–benzene (5:1 v/v) to give **5** (4 mg, 4%) and unreacted **1** (45 mg) and then by elution with *n*-hexane–benzene (1:1 v/v) followed by recrystallization from *n*-hexane–chloroform to give adduct **23b** (148 mg, 79%) as a colorless crystal. Adduct **23b**: ^{13}C NMR ($CDCl_3$) δ 147.3 (s, 1 C), 139.7 (s, 1 C), 127.5 (d, 1 C), 125.8 (d, 1 C), 121.6 (d, 1 C), 116.4 (d, 1 C), 85.6 (d, 1 C), 84.9 (d, 1 C), 72.1 (s, 1 C), 39.0 (t, 1 C), 38.1 (t, 1 C), 37.6 (d, 1 C), 37.0 (t, 1 C), 36.4 (d, 1 C), 35.6 (t, 1 C), 35.4 (t, 1 C), 26.7 (d, 1 C), 26.4 (d, 1 C); for other physical data, see Table II.

Registry No. **1**, 23695-65-0; **2a**, 542-92-7; **2b**, 513-81-5; **2c**, 106-99-0; **2d**, 504-60-9; **2e**, 78-79-5; **2f**, 59414-23-2; **3a**, 99727-21-6; **3b**, 99727-22-7; **3c**, 61714-02-1; **3d**, 61713-96-0; **3e**, 99727-23-8; **4e**, 99727-24-9; **5**, 31023-85-5; **6**, 99727-25-0; **7**, 99727-26-1; **8**, 99727-27-2; **9**, 99727-28-3; **11**, 1450-31-3; **14**, 99727-29-4; **17**, 99727-30-7; **18**, 1671-87-0; **19a**, 5176-28-3; **19b**, 573-57-9; **23a**, 99727-31-8; **23b**, 99727-32-9; (3-methyl-2-butenyl)triphenylphosphonium bromide, 1530-34-3; adamantanone, 700-58-3; benzophenone, 119-61-9.

Fluorocarbanion Chemistry. A Versatile Synthesis of Functionalized Fluoro Ketones†

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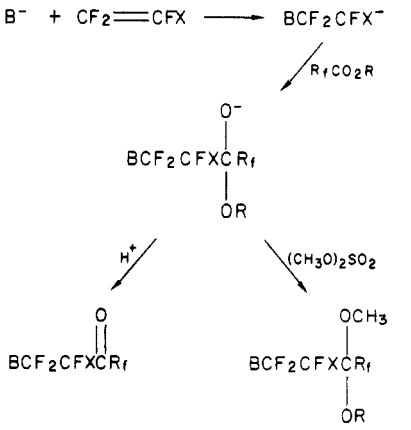
Fluorocarbanions generated by the addition of an anion to a fluoro olefin can be trapped by fluoro esters, thereby providing a versatile, one-step synthesis of functionalized fluoro ketones. The most efficient anions include CN^-, N_3^-, $C_6H_5O^-$, RO^-, and RS^-. The reaction has been extended in one case to prepare a sulfinate ester.

We recently showed that a fluorocarbanion generated by the addition of any one of several anions to a polyfluoroethylene can be captured by carbon dioxide, sometimes very efficiently.[1] The reaction thus directly provides β-substituted polyfluoropropionates whose functionality is derived from the anion. We also adduced evidence that a successful fluoropropionate synthesis depends upon formation of a relatively stable carbanionic intermediate in which the incoming anion (B^-) remains anti to the unshared pair of electrons. Since the carbanions BCF_2CFX^- appeared to be long-lived as well as readily formed, we became interested in trapping them with agents other than carbon dioxide to give new polyfunctional fluorochemicals. We report here on the use of fluorinated esters, a fluoro amide, and bis(2,2,2-trifluoroethyl) sulfite to trap fluorocarbanions.

Results and Discussion

Fluoro esters have been found to be a class of effective trapping agents that form stable adducts with fluorocarbanions generated in situ. The general reactions that provide functionalized fluoro ketones and fluoro ketals in 30–90% yields for various anions B^- and fluoro esters R_fCO_2R are outlined in Scheme I.

Scheme I



The reactions were carried out by contacting a mixture of the anion salt and fluoro ester in a polar solvent with the fluoro olefin at 10–50 °C under autogenous pressure. Care must be taken that the fluoro ester does not alkylate the nucleophile prior to introduction of the fluoro olefin. For instance, methyl polyfluorocarboxylates methylated

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(1) (a) Krespan, C. G.; Van-Catledge, F. A.; Smart, B. E. *J. Am. Chem. Soc.* **1984**, *106*, 5544. (b) Krespan, C. G. U.S. Patent 4474700, 1984.

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