SYNTHESIS OF ADAMANTANE DERIVATIVES. 36.[1] SYNTHESIS OF SOME BISADAMANTANE SPIRO THIAHETEROCYCLES *VIA* ADAMANTANETHIONE ADAMANTHYLIDE

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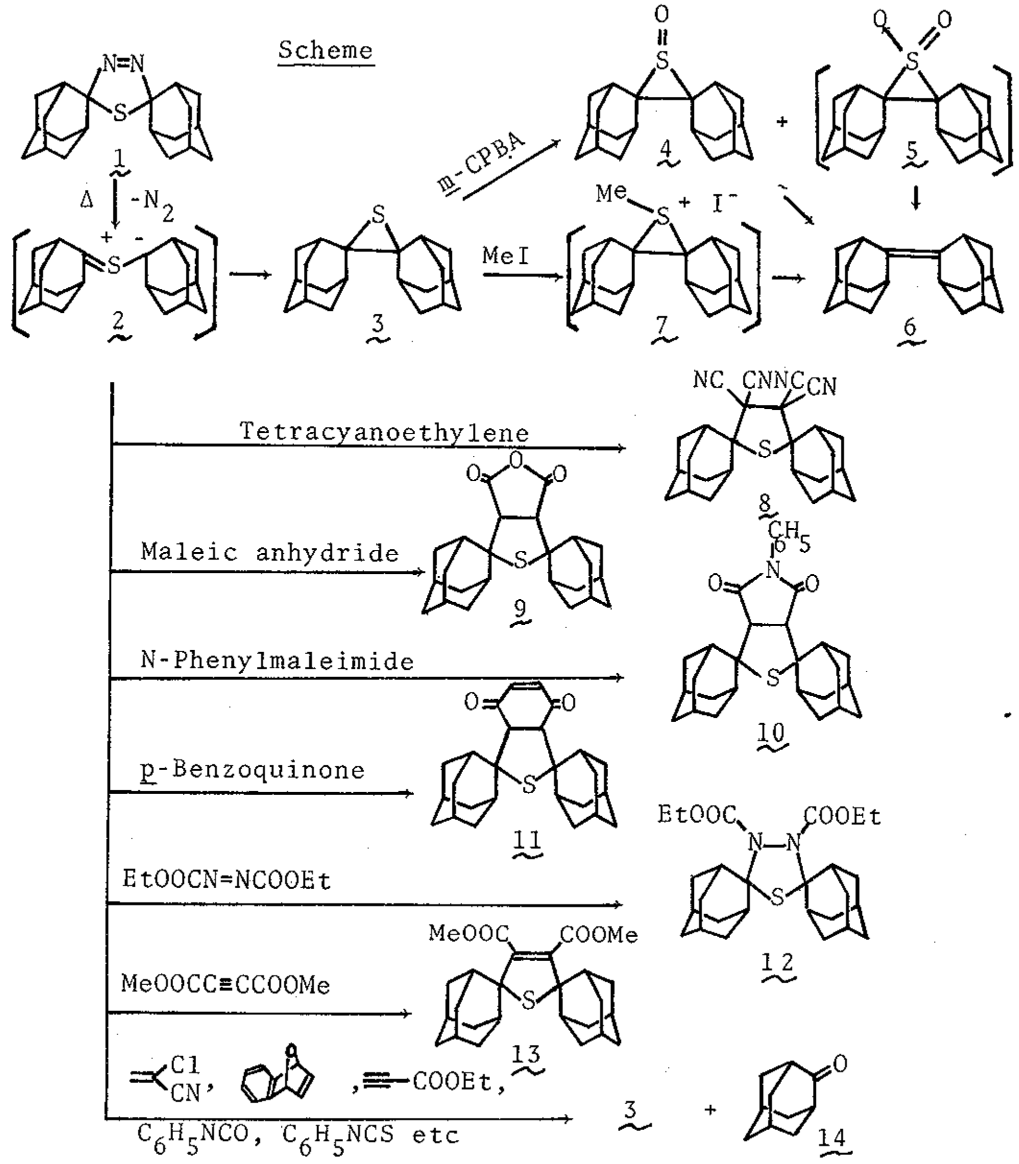
Adamantanethione adamanthylide (2) generated by thermal nitrogen extrusion reaction of thiadiazine 1 afforded thiirane 3 in good yield, and the same thermolysis of 1 in the presence of appropriate 1,3-dipolarophiles afforded bisadamantane spiro thiaheterocycles 8-13 in 25-77% yields.

Although thiadiazine is well known as a good precursor for generation of thiocarbonyl ylide or thione methylide,[2] 2',5'-dihydroadamantanespiro-2'-(1',3',4'-thiadiazine)-5'-spiroadamantane (1)[3] seems to be not used for such purpose heretofore. From our interest in adamantane spiro heterocycles,[4] we investigated thermal decomposition of 1 in order to generate the corresponding thiocarbonyl ylide 2 which is expected to be useful intermediate for synthesis of some bisadamantane spiro thiaheterocycles.

Thiadiazine 1 was converted smoothly to a nitrogen extruded product 3 on refluxing for 10 hr in *o*-xylene. 3 was obtained as colorless plates after recrystallization from aqueous ethanol in 78% yield and was assigned as adamantane-spiro-2'-thiirane-3'-spiroadamantane on the basis of analysis and spectral data (Table) as well as chemical conversions (Scheme). On treatment with *m*-chloroperbenzoic acid (4-fold excess to **3**) in $CHCl_3$ at 25° for 3 days and at 50° for 0.5 hr, **3** was converted to the corresponding sulfoxide **4** (32%) and adamantylideneadamantane (**6**)[5] (56%). **3** was converted also to **6** on refluxing with methyl iodide (5-fold excess to **3**) in $CHCl_3$ for 7.5 hr (47%). The formation of **6** and nonisolation of sulfone **5** and sulfonium salt **7** are similar results to the behavior of 2,3-di-*t*-butylthiirane, sterically crowded thiirane.[6] Furthermore, **3** was considerably stable in FSO_3H, thus, after standing for 1 day at 25°in FSO_3H, **3** was recovered in 85%. All of these results could be rationalyzed by assignment of **3** as a sterically crowded thiirane.

The thermal decomposition of **1** in the presence of 1,3-dipolarophiles was examined as a facile route to bisadamantane spiro thiaheterocycles. A mixture of **1** and tetracyanoethylene (1.3-fold excess to **1**) was refluxed in *o*-xylene for 14 hr and usual work-up followed by recrystallization (CH_2Cl_2-C_6H_6) gave the corresponding adduct **8** in 77% yield. The structure of **8** was evidenced by analytical and spectral data (Table). Similarly, maleic anhydride (1.3-fold excess to **1**, 12 hr), N-phenylmaleimide (1.1-fold excess, 18 hr), *p*-benzoquinone (1.5-fold excess, 18 hr), diethyl azodicarboxylate (5.9-fold excess, 13 hr) and dimethyl acetylenedicarboxylate (2-fold excess, 13 hr) on refluxing with **1** in *o*-xylene afforded the corresponding adducts, **9**-**13** in 50, 60, 59, 25 and 40% yields, respectively (Scheme and Table). However, α-chloroacrylonitrile, oxabenzonorbornadiene, ethyl propiolate, phenyl isocyanate and

Scheme



phenyl isothiocyanate on refluxing with 1 in *o*-xylene did not afford the corresponding adducts and only 3 (45-82%) and adamantanone (14)(40-1%) were produced. The formation of 14 may be due to the decomposition of 2, because thiirane 3 was stable under the reaction conditions and furthermore, thermal decomposition of 1 in the presence of 75% aqueous acetic acid yielded also 14 (50%).

Table   Physical and analytical data of 3, 4, and 8-13.

Compd (mp°C)	Ir(KBr) cm^{-1}	Nmr($CDCl_3$, 60MHz) δ	Formula	Analysis[a]			
					C	H	N
3 (157-158)	1100	2.90(s,4H), 2.2-1.5(m,24H)	$C_{20}H_{28}S$	F	80.14	9.40	
				C	79.95	9.39	
4 (160-162)	1030	2.6-1.5(m)	$C_{20}H_{28}OS$	F	75.98	8.85	
				C	75.90	8.92	
8 (119-122)	2230, 1100	2.9-1.7(m)	$C_{26}H_{28}N_4S$	F	73.07	6.65	12.81
				C	72.86	6.59	13.07
9 (257-258)	1855, 1755	3.9(s,2H), 2.8-1.4(m,28H)	$C_{24}H_{30}O_3S$	F	72.48	7.44	
				C	72.33	7.59	
10 (227-230)	1710, 1380	7.7-7.0(m,5H), 3.80(s,2H), 3.0-1.4(m,28H)	$C_{30}H_{35}O\,NS$	F	75.78	7.40	3.26
				C	76.07	7.45	2.96
11 (225-226)	1660, 1610	6.68(s,2H), 3.70(s,2H), 2.8-1.4(m,28H)	$C_{26}H_{32}O_2S$	F	76.58	7.73	
				C	76.43	7.89	
12 (160-163)	1720, 1310, 1110	4.08(q,4H)[b], 1.27(t,6H)[b], 3.1-1.4(m,28H)	$C_{26}H_{38}O_4N_2S$	F	65.96	8.09	5.70
				C	65.78	8.07	5.90
13 (258-260)	1720, 1580	3.80(s,6H), 2.7-1.6(m,28H)	$C_{26}H_{34}O_4S$	F	70.32	7.96	
				C	70.55	7.74	

[a] F= Found.   C= Calcd.   [b] *J*= 7.5Hz.

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Received, 2nd October, 1976