HETEROCYCLES, Vol. 4, No. 12, 1976

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

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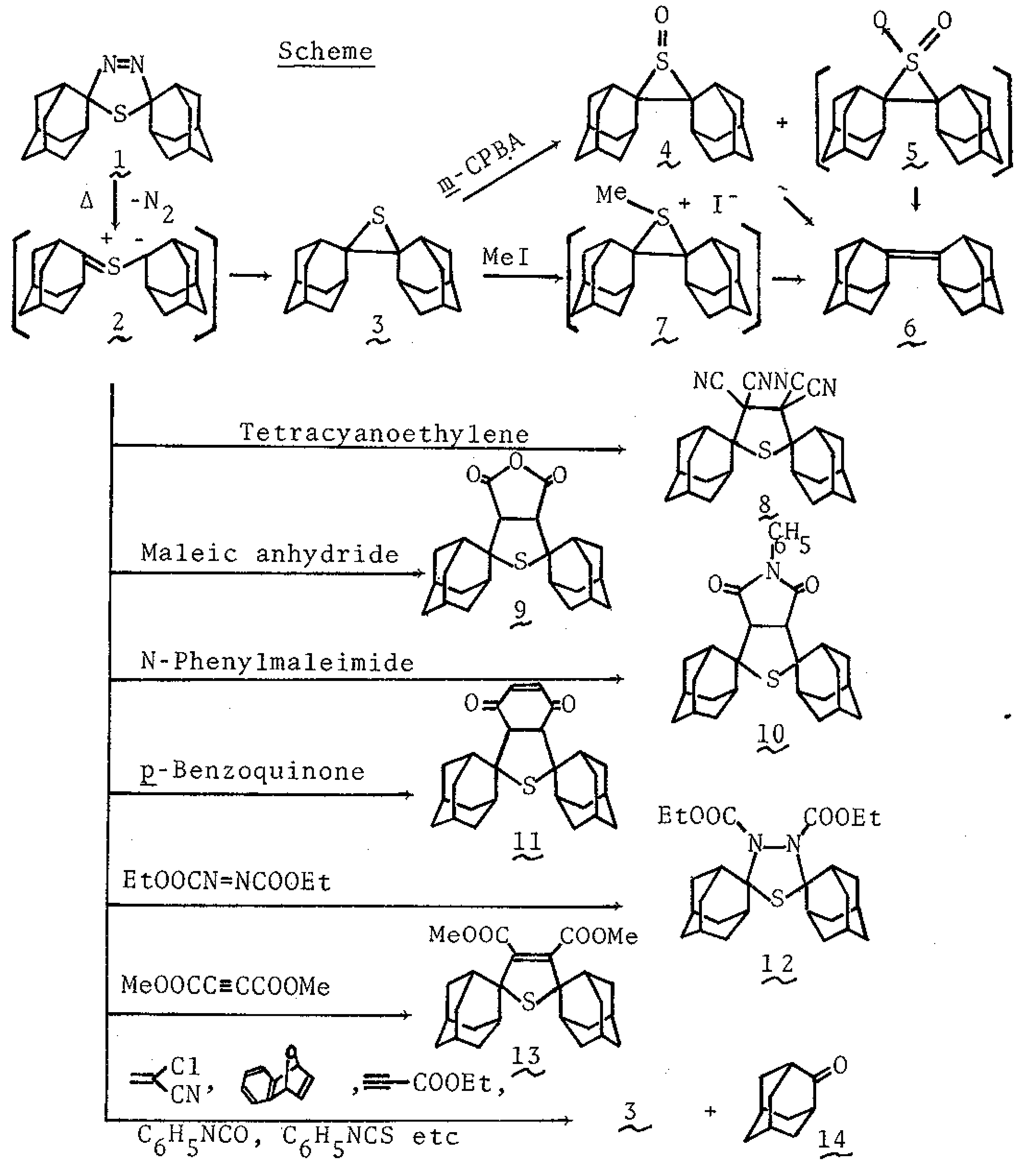
Adamantanethione adamanthylide (**2**) generated by thermal nitrogen extrusion reaction of thiadiazine **1** afforded thiirane **3** in good yield, and the same thermolysis of **1** in the presence of appropriate 1,3-dipolarophiles afforded bisadamantane spiro thiaheterocycles **8**-**13** in 25-77% 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 C	80.14 79.95	9.40 9.39	
4 (160-162)	1030	2.6-1.5(m)	$C_{20}H_{28}OS$	F C	75.98 75.90	8.85 8.92	
8 (119-122)	2230, 1100	2.9-1.7(m)	$C_{26}H_{28}N_4S$	F C	73.07 72.86	6.65 6.59	12.81 13.07
9 (257-258)	1855, 1755	3.9(s,2H), 2.8-1.4(m,28H)	$C_{24}H_{30}O_3S$	F C	72.48 72.33	7.44 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 C	75.78 76.07	7.40 7.45	3.26 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 C	76.58 76.43	7.73 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 C	65.96 65.78	8.09 8.07	5.70 5.90
13 (258-260)	1720, 1580	3.80(s,6H), 2.7-1.6(m,28H)	$C_{26}H_{34}O_4S$	F C	70.32 70.55	7.96 7.74	

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

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Received, 2nd October, 1976