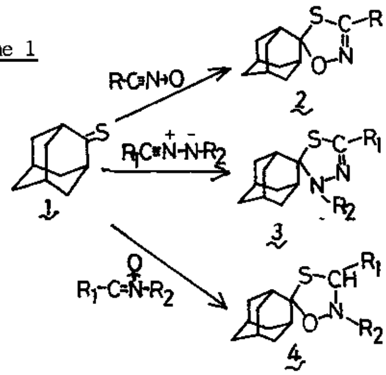
THERMAL CYCLOADDITION REACTIVITY AND REGIOSELECTIVITY OF ADAMANTANETHIONE

Tadashi Sasaki, Shoji Eguchi, and Tomonori Katada
Institute of Applied Organic Chemistry, Faculty of Engineering,
Nagoya University, Nagoya 464, Japan

The cycloaddition reaction of thiocarbonyl compounds has interesting features from both synthetic and theoretical points of view. P.de Mayo et al.(JACS,1976,98,2219) reported systematic studies of photochemical cycloaddition of adamantanethione. However, only few reports of it's thermal cycloadditions have been known. We wish to report thermal cycloadditions of adamantanethione toward some 1,3-dipoles, dienes, and heterodienes. These reactions provided a facile route to novel adamantane-2-spiro thiaheterocycles.

Scheme 1



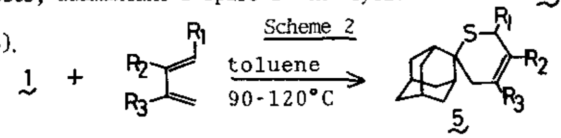
1,3-Dipolar Cycloaddition Reactions

Adamantanethione 1 underwent 1,3-dipolar cycloaddition reaction with nitrile oxides, nitrile imines, and nitrones to yield adamantane-2-spiro-2'-1',4',2'-oxathiazolines 2, -1',3',4'-thiadiazolines 3, and -1',2',4'-oxathiazolidines 4, respectively in good yields (Scheme 1).

Diels-Alder Reactions

When 1 was heated with sulfolene, 2,3-dimethyl butadiene, piperylene, and isoprene, the cycloadducts, adamantane-2-spiro-2'-thiacyclohex-4'-enes 5 were obtained in the yields shown below (Scheme 2).

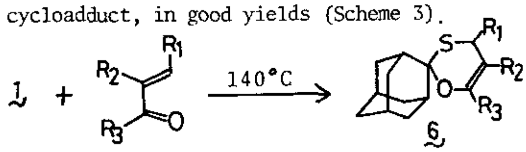
Scheme 2



	R^1	R^2	R^3	Yield,%
5a	H	H	H	43
b	H	Me	Me	82
c	Me	H	H	81
d	H	Me	H	79

Furthermore, treatment of 1 with α,β-unsaturated carbonyl compounds such as acrolein, methacrolein, and methyl vinyl ketone, in toluene afforded adamantane-2-spiro-2'-1',3'-oxathia-4'-enes 6 as a cycloadduct, in good yields (Scheme 3).

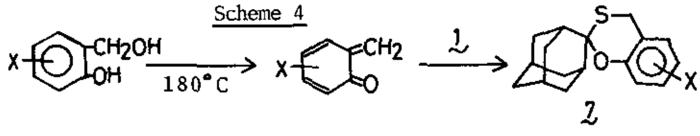
Scheme 3



	R^1	R^2	R^3	Yield,%
6a	H	H	H	94
b	H	Me	H	71
c	H	H	Me	82

A similar reaction of 1 with o-methide quinones, generated by thermal decomposition of salicyl alcohols, in xylene gave 1:1 Diels-Alder adducts 7 in good yields (Scheme 4).

Scheme 4



	X	Yield,%
7a	H	72
b	3-Me	69
c	5-NO_2	89

These results will be discussed on the basis of FMO and steric effects.