

Thermal Cycloaddition Reactions of Thiocarbonyl Compounds. Part 1. A Novel [4 + 2] Cycloaddition Reaction of Adamantanethione with α,β -Unsaturated Carbonyl Compounds¹

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The thermal cycloaddition reaction of adamantanethione (**1**) with α,β -unsaturated carbonyl compounds such as acrolein, methacrolein, and methyl vinyl ketone occurred smoothly at 80–140 °C to afford, regioselectively, adamantane-2-spiro-2'-(1'-oxa-3'-thiacyclohex-5'-enes) (**3a–e**) as novel [4 + 2] cycloadducts in good yield. The nature of this cycloaddition is discussed on the basis of kinetics, solvent effects, and FMO theory.

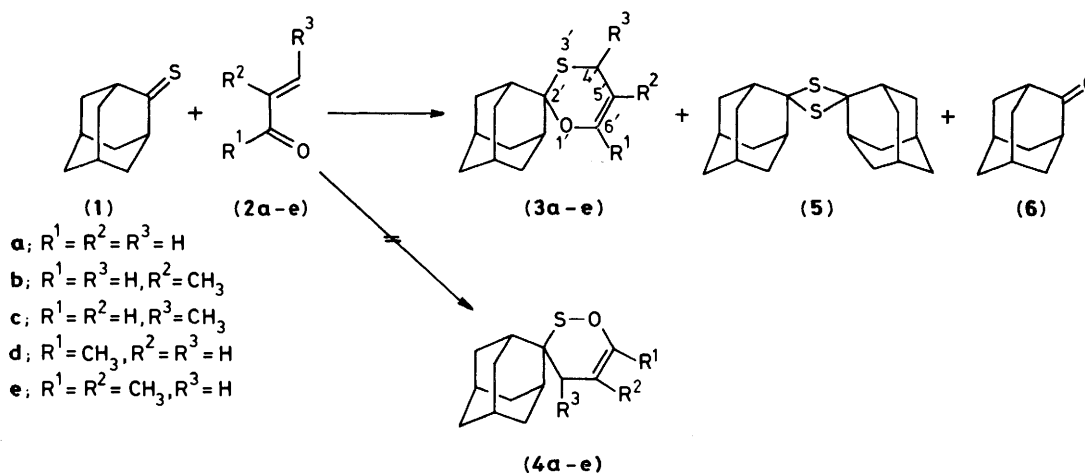
The use of thiocarbonyl compounds as cycloaddition components in organic synthesis has developed quite rapidly in recent years.^{2–5} However, thiocarbonyl compounds have not yet been utilized as heterodienophiles with heterodienes, even though these combinations appear to offer an increased synthetic potential. We describe here thermal cycloaddition reactions of adamantanethione as a stable alicyclic thiocarbonyl compound with α,β -unsaturated carbonyl compounds as heterodienes,⁶ which provided a convenient route to some novel adamantane-2-spiro-oxathiaheterocycles.

Results and Discussion

Product Analysis.—When a mixture of adamantanethione (**1**),⁷ a 15-fold excess of acrolein (**2a**), and a small amount of hydroquinone in dry benzene was heated at 80 °C, the characteristic reddish orange colour of (**1**) disappeared

in a 1:1:2 intensity ratio was compatible with structure (**3a**), and furthermore, ¹³C n.m.r. signals at δ_c 142.6 (d, C-6'), 98.9 (d, C-5'), 88.0 (s, C-2),† and 38.1 (t, C-4') support structure (**3a**).

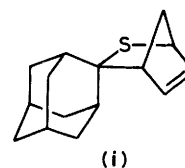
The cycloaddition reaction of compound (**1**) with other α,β -unsaturated carbonyl compounds such as methacrolein (**2b**), crotonaldehyde (**2c**), methyl vinyl ketone (**2d**), and 3-methylbut-3-en-2-one (**2e**) occurred similarly on heating at 95–140 °C to afford the corresponding adamantane-2-spiro-2'-(1'-oxa-3'-thiacyclohex-5'-enes) (**3b–e**) in 94–23% yield (Table 1). The structures given are supported by analytical and spectral data (Table 2). Variable amounts of the thione dimer (**5**) and adamantanone (**6**) were also isolated after chromatography. The formation of (**6**) is ascribed to decomposition of adducts (**3b–e**) during chromatography based on a control experiment (see below), and hence the cycloaddition could be considered to afford the adducts in good yield (56.5–94.4%) in general. The amount of the thione dimer (**5**) may be an indication of



Scheme 1.

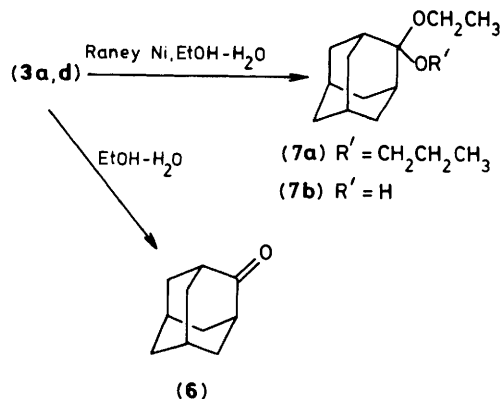
completely after 4 h. A single crystalline cycloadduct (**3a**) (94%) was isolated, accompanied by a small amount of the thione dimer (**5**)⁷ (1.2%) after chromatography (silica gel) (Scheme 1). The structure of (**3a**) was determined as adamantane-2-spiro-2'-(1'-oxa-3'-thiacyclohex-5'-ene) based on analysis and spectral data. In the mass spectrum, the molecular ion peak at m/z 222 (5%) as well as ion peaks at m/z 166 (100%, adamantanethione) and 150 (9%, adamantanone) supported structure (**3a**) rather than the isomer (**4a**). The appearance of characteristic signals in the ¹H n.m.r. spectrum at δ 6.47 (dt, J 6.5 and 1.8 Hz, 6'-H), 4.88 (dt, J 6.5 and 3.8 Hz, 5'-H), and 3.06 (dd, J 1.8 and 3.8 Hz, 4'-H₂)

† The spiro-carbon in (**4a**) should appear at higher field around δ_c 70–75 p.p.m., based on the spiro-carbon of the Diels–Alder adduct of (**1**), e.g. compound (**i**) had the spiro-carbon signal at δ_c 71.6 p.p.m. (s) (our unpublished data).



heterodiene reactivity. The formation of (5) in $\geq 10\%$ yield from the reactions with (2c) and (2e) indicates the somewhat lower reactivity of these heterodienes.⁸ The stability of the cyclo-adducts (3a–e) depended considerably on the substituents. Thus, (3a) was fairly stable: crystals of (3a) withstood exposure to the atmosphere at room temperature for more than a week without change, while (3d) was an extremely unstable oil, decomposing to adamantanone (6) and unidentified products even at 5 °C, and/or by chromatography on a silica gel column.

Catalytic hydrogenation of (3a) with Raney Ni (W-4 type) in ethanol containing a trace of water afforded 2-ethoxy-2-propoxyadamantane (7a) (79%) (Scheme 2), while similar treatment of (3d) gave 2-ethoxyadamantan-2-ol (7b) (68%). The formation of (7a) is explained by initial ethanolysis followed by hydrogenation, while the formation of (7b) is apparently caused by initial ethanolysis followed only by hydrolysis. These results indicate ready ethanolysis and/or hydrolysis of the oxathia-cyclohexene ring of compounds (3a–e).



Scheme 2.

Table 1. Reaction of (1) with (2a–e)

Substrate	ratio (2) to (1) ^a	Solvent	Temp. (°C)	Time (h)	Products (% yield) ^b
(2a)	15.0	benzene	80	4	(3a) (94.0), (5) (1.2)
(2a)	15.0	toluene	140	2	(3a) (94.4), (5) (2.0)
(2b)	15.0	toluene	95	168	(3b) (42.6), (5) (5.2), (6) (13.9)
(2b)	20.0	toluene	140	12	(3b) (71.3), (5) (5.7), (6) (12.6)
(2c)	20.0	toluene	140	14	(3c) (29.1), (5) (15.7), (6) (38.7)
(2d)	15.0	toluene	95	120	(3d) (42.6), (5) (5.2), (6) (13.9)
(2d)	20.0	toluene	140	14	(3d) (82.0), (5) (3.3), (6) (8.3)
(2e)	15.0	toluene	95	120	(3e) (22.5), (5) (10.0), (6) (38.4)

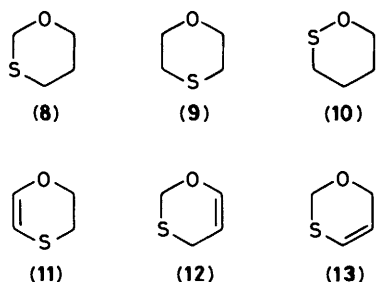
^a All reactions were carried out in the presence of hydroquinone [4.5 mol % of (1)] as a polymerization inhibitor under argon (see Experimental section). ^b Isolated yields after chromatography (see Table 2). The adducts (3b–e) decomposed during chromatography, e.g. (3d) decomposed to (6) (>90%) after being kept overnight on a silica gel column.

Table 2. Physical and analytical data of adamantane-2-spiro-2'-(1'-oxa-3'-thiacyclohex-5'-enes) (3a–e)

Compound (M.p., °C) ^a	I.r. ^b (cm ⁻¹) ^b	¹ H n.m.r. (δ) ^c	Mass spectrum m/z (%)	Molecular formula	Analysis required (Found)	
					C	H
(3a) (38.5–39.0)	3 050, 2 900, 2 850, 1 650, 1 445, 1 250, 1 100, 1 080, 1 060, 980, 962, 900, 885, 715	6.47 (dt, <i>J</i> 6.5 and 1.8, 1 H), 4.88 (dt, <i>J</i> 6.5 and 3.8, 1 H), 3.06 (dd, <i>J</i> 1.8 and 3.8, 2 H), 2.5–1.4 (m, 14 H)	222 (6.0) ^d , 167 (15), 166 (100), 150 (9.0), 133 (12), 124 (12), 91 (27), 79 (18)	C ₁₃ H ₁₈ OS	70.23 (70.20)	8.16 (8.18)
(3b) (47.5–48.0)	3 060, 2 900, 2 845, 1 675, 1 450, 1 265, 1 180, 1 165, 1 135, 1 100, 1 000, 970, 960	6.28 (q, <i>J</i> 1.5, 1 H), 2.98 (m, 2 H), 2.50–1.35 (m, 14 H), 1.62 (s)	236 (6.0) ^d , 167 (14), 166 (100), 151 (7.0), 150 (8.0), 133 (14), 124 (16), 91 (27), 79 (19)	C ₁₄ H ₂₀ OS	71.14 (71.16)	8.53 (8.51)
(3c) (oil)	3 050, 2 900, 2 850, 1 650, 1 450, 1 260, 1 225, 1 125, 1 105, 1 060, 980, 900, 740	6.42 (dd, <i>J</i> 7.0 and 2.5, 1 H), 4.72 (dd, <i>J</i> 7.0 and 2.5, 1 H), 3.51 (qt, <i>J</i> 7.0 and 2.5, 1 H), 2.7–1.4 (m, 14 H), 1.30 (d, <i>J</i> 7.0, 3 H)	236 (5.0) ^d , 167 (15), 166 (100), 151 (4.0), 150 (5.0), 133 (12), 124 (12), 91 (21), 84 (25)	C ₁₄ H ₂₀ OS	71.14 (71.19)	8.53 (8.49)
(3d) (oil)	3 030, 2 900, 2 840, 1 675, 1 450, 1 375, 1 325, 1 260, 1 170, 1 100, 1 080, 1 065, 1 020, 965, 900, 880, 750	4.72 (tq, <i>J</i> 4.0 and 1.0, 1 H), 3.08 (dq, <i>J</i> 4.0 and 1.8, 2 H), 2.5–1.4 (m, 17 H)	236 (7.0) ^d , 167 (14), 166 (100), 151 (5.0), 150 (7.0), 133 (14), 124 (14), 91 (24), 79 (14), 77 (10)	C ₁₄ H ₂₀ OS	71.14 (71.38)	8.53 (8.56)
(3e) (oil)	2 920, 2 880, 2 840, 1 645, 1 445, 1 350, 1 270, 1 200, 1 095, 960, 830	3.18 (br s, 2 H) 2.7–1.4 (m, 20 H)	250 (4.6) ^d , 236 (33), 166 (22), 151 (26), 150 (94), 117 (100), 104 (77), 91 (94)	C ₁₅ H ₂₂ OS	71.95 (72.10)	8.86 (8.89)

^a Purified on a silica gel or alumina column. ^b Solid compounds were scanned in KBr disks and oils were scanned as neat films. ^c All ¹H n.m.r. spectra were measured in CDCl₃. Multiplicities and *T* values (Hz) are given in parentheses. ^d M⁺ ion peaks.

Among six-membered oxathiaheterocycles, 1,3-oxathiane (1-oxa-3-thiacyclohexane) (**8**),⁹ 1,4-oxathiane (1-oxa-4-thiacyclohexane) (**9**),¹⁰ and '1,4-oxathiene' (1-oxa-4-thiacyclohex-2-ene) (**11**),¹¹ are known rings, while 1,2-oxathiane (1-oxa-2-thiacyclohexane) (**10**) and (4*H*- and 6*H*-1,3-oxathiine (1-oxa-3-thiacyclohex-5-ene and -4-ene) (**12**) and (**13**) seem not to be recorded in the literature. In view of this, the above [4 + 2] cycloaddition of (**1**) with α,β -unsaturated carbonyl compounds provides a convenient route to the hitherto unknown 4*H*-1,3-oxathiine ring system.



The cycloadditions of thiobenzophenone and thioxanthone with acrolein also took place at 140 °C but the cycloadducts were not isolable because of ready decomposition in the atmosphere and/or during chromatography.

Theoretical Treatment. A Frontier Molecular Orbital Approach.—The product formation and regioselectivity observed in the above cycloadditions are discussed in terms of frontier molecular orbital (FMO) interactions.¹² The frontier orbital coefficients and energies as well as the dipole moment and electron densities of (**1**) from CNDO/2 calculation are summarized in Figure 1. The frontier orbitals of (**1**), acrolein (**2a**),¹³ and methyl vinyl ketone (**2d**)¹⁴ (CNDO/2) are schematically shown in Figure 2. The solid arrows indicate

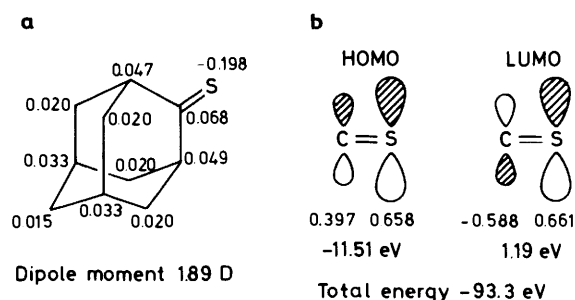


Figure 1. (a) Electron densities and dipole moment of adamantanethione (**1**). (b) Frontier orbital energies and coefficients of (**1**) (CNDO/2).

dominant overlap, *i.e.* the interaction of LUMO-diene with HOMO-dienophile is larger (LUMO-controlled or inverse Diels–Alder-type reaction)¹⁵ in each pair. This predicts the experimentally observed regioselectivity to afford (**3a**) or (**3d**). A similar rationalization of the regioselectivity in the cycloaddition of vinyl ether and enamines with α,β -unsaturated carbonyl compounds has been advanced (see ref. 6 and references cited therein).

Kinetic Studies.—The above cycloaddition of adamantanethione (**1**) with acrolein (**2a**) was monitored by the disappearance of the thione absorption in the 400–600 nm region, because compound (**1**) has λ_{max} at 498 nm (ϵ 15.0) and a shoulder at 536 nm (ϵ 2.8) in benzene from the $n \rightarrow \pi^*$ transition, while (**2a**), the cycloadduct (**3a**), hydroquinone, and employed solvents had no strong absorptions in the visible region. The 498 nm band for (**1**) obeyed the Lambert–Beer law within the concentration range 0.1–0.001M. The reaction rate constants were calculated from the integrated second-order rate expression using a 10-fold excess of (**2a**). A plot of time *vs.* $\ln b(a-x)/a(b-x)$ [a = molar concentration of (**2a**), b =

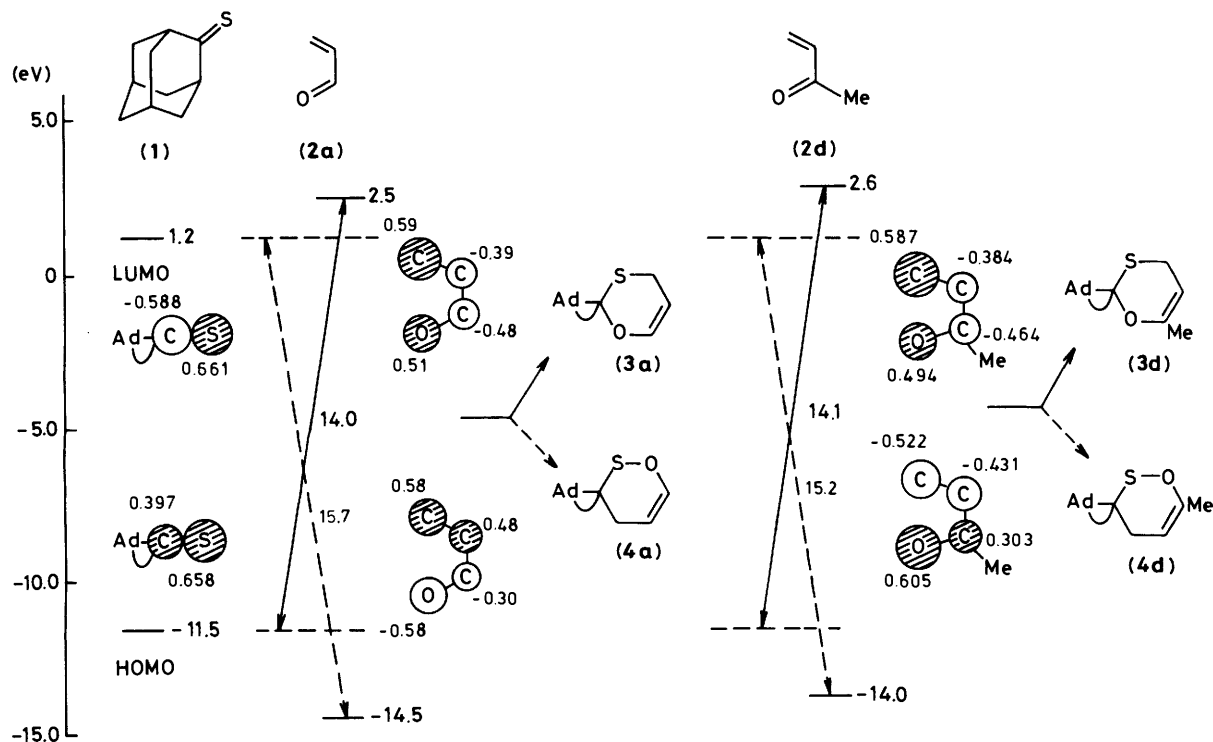
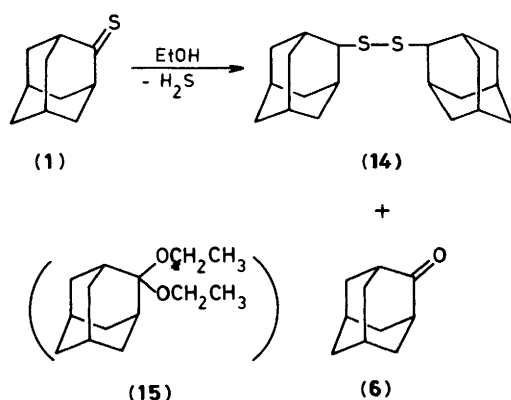


Figure 2. Frontier orbital coefficients and energies (CNDO/2)

molar concentration of (1)] gave a straight line, from the slope of which the second-order rate constant k_2 was calculated (see Experimental section). Average values of two or four measurements in various solvents at 80 °C are summarized in Table 3.

With different initial concentrations of (2a), the obtained k_2 values in benzene are essentially constant (k_2 1.45–1.49 $\times 10^{-5}$ l mol⁻¹ s⁻¹, Table 4), supporting second-order kinetics for the cycloaddition. To obtain the thermodynamic parameters, the rate constants were also measured over the range 60–90 °C in benzene (Table 5). From the slope of the plot of $\log k_2$ vs. $1/T$, the activation energy, E_a , was found to be 15.8 kcal mol⁻¹, the frequency factor 8.89×10^5 l mol⁻¹ s⁻¹ ($\log A$ 5.949), the activation enthalpy H^\ddagger 15.1 kcal mol⁻¹, and the activation entropy ΔS^\ddagger -33.9 cal K⁻¹ mol⁻¹ at 80 °C were obtained.

As the data in Table 3 indicate, the rate constants are not much affected by the solvent polarity, except in ethanol. In ethanol, adamantanethione (1) decomposed rapidly to afford di-(2-adamantyl) disulphide (14) and adamantanone (6) with evolution of hydrogen sulphide (Scheme 3)* (cf. ref. 2b), in addition, the cycloadduct (3a) was not stable under these conditions as noted above (Scheme 2). It should be emphasized that the activation parameters for the present cycloaddition are similar to those reported for 'conventional' Diels–Alder reactions.¹⁶



Scheme 3.

Reaction Mechanism.—For conventional [4 + 2] cycloadditions, Sauer and Sustmann summarized the solvent effect on kinetics characteristics as follows:¹⁶ (1) The influence of the solvent on the reaction rate is relatively small. (2) The nature of the dienophiles (C=C, N=N, N=O) has just as little influence on the solvent dependence as has that of the diene. (3) The same small solvent dependence is also observed in both normal and inverse Diels–Alder reactions. On the other hand, huge solvent dependence is well recognized in cycloadditions *via* zwitterionic intermediates, e.g. thermal [2 + 2] cycloadditions.¹⁷ Both the stepwise mechanism *via* a dipolar or a zwitterionic intermediate and a synchronous one have been postulated for some formal [4 + 2] cycloadditions of α,β -unsaturated carbonyl compounds with vinyl ethers.^{6,18} However, for the present cycloadditions of (1) and (2a), the observed small influence of the solvent polarity as well as the activation parameters support a similar transition state to the 'conventional' Diels–Alder-type reactions. An alternative stepwise mechanism proceeding through a biradical or a zwitterion intermediate seems incompatible with the present kinetic data. Because the present cycloaddition was not affected by the presence of hydroquinone

* Compound (15) was not isolated, presumably because of its decomposition to (6).

Table 3. Second-order rate constants for the cycloaddition of adamantanethione (1) with acrolein (2a) in various solvents at 80 °C^a

Solvent	$10^5 k_2$ [l mol ⁻¹ s ⁻¹]	k_{rel}	ϵ^b	μ^c	E_T^d
Acetonitrile	6.77	1.0	37.5	3.5	46.0
Tetrahydrofuran	8.38	1.24	7.4	1.7	37.4
Chloroform	13.0	1.92	4.7	1.1	39.1
Benzene	14.7	2.17	2.3	0	34.5
n-Hexane	20.6	3.04	1.9	0	30.9
Tetrachloromethane	24.2	3.57	2.2	0	32.5
1,4-Dioxane	25.7	3.80	2.2	0.4	36.0
Ethanol	136 ^e	20.0	32.6	1.7	51.9

^a An average value of two to four determinations (see Experimental section). ^b Dielectric constant. ^c Dipole moment (D). ^d Solvent polarity parameter (kcal mol⁻¹) (see C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, 1965, 4, 29). ^e In this solvent, both thione (1) and cycloadduct (3a) decomposed (see text).

Table 4. Effect of [(2a)] on the rate constants for cycloaddition of (1) with (2a)^a

(2a)/(1) ^b	$10^5 k_2$ [l mol ⁻¹ s ⁻¹]
6.0	14.9
10.0	14.7
15.0	14.5
20.0	14.8
25.0	14.8
av. 14.7 \pm 0.2	

^a In benzene at 80 °C. ^b Mol. ratio of (2a) to (1). [(1)] = 0.05M.

Table 5. Rate constants for cycloaddition of (1) with (2a) at 60–90 °C^a and kinetic parameters^b

Temp. (°C)	$10^5 k_2$ (l mol ⁻¹ s ⁻¹)	E_a (kcal mol ⁻¹)	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (cal K ⁻¹ mol ⁻¹)
60	3.68			
70	7.70			
80	14.7	15.8	15.1	-33.9
90	26.2			

^a In benzene. ^b At 80 °C.

as a radical scavenger or inhibitor of dimerization, the out-of-cage free radical mechanism¹⁹ is not operating. A zwitterionic mechanism of [4 + 2] type or [2 + 2] type followed by a 1,3-sigmatropic shift can also be excluded because of the small solvent effects.†

Experimental

M.p.s were taken in a sealed tube on a Yanagimoto micro-melting point apparatus and are uncorrected. Microanalyses were performed with a Perkin-Elmer 240 B elemental analyser. U.v. and visible spectra were determined with a Hitachi spectrophotometer, Model 200–10. ¹H and ¹³C n.m.r. spectra were taken at 25 °C with a JEOL JMN-C-60HL instrument at 60 MHz and a JEOL-FX-60 FT spectrometer at 15.04 MHz, respectively, using Me₄Si as internal standard in CDCl₃. I.r. spectra were recorded on a JASCO A-100 spectrophotometer. Mass spectra were obtained with a JEOL JMS-D10 mass spectrometer at 75 eV.

Materials.—Adamantanethione (1) was prepared by the reported method⁷ and purified on a silica gel (Kiesel gel 60, 70—

† For photochemical [2 + 2] cycloadditions, see ref. 5.

230 mesh) column by elution with n-hexane. Commercial acrolein (**2a**) was distilled before use. The other reagents were commercial materials. All the solvents were carefully dried and distilled before use.

Calculations.—The calculations were carried out on a FACOM M-200 computer at the Nagoya University Computation Center. The geometry of adamantanethione (**1**) required for the CNDO/2 calculation²⁰ was estimated from an assumed structure made up with the standard bond length and angles.

Adamantane-2-spiro-2'-(1'-oxa-3'-thiacyclohex-5'-ene) (3a).—A mixture of compound (**1**) (166 mg, 1.00 mmol), acrolein (**2a**) (850 mg, 15.0 mmol), and hydroquinone (5 mg, 0.045 mmol) in dry benzene (4.0 ml) was heated at 80 °C in a sealed tube (12 mm diameter × 260 mm length) for 4 h under argon until the characteristic orange colour of the mixture disappeared completely. Removal of the solvent and excess of acrolein under reduced pressure gave a solid residue which was chromatographed on a silica gel column by elution with n-hexane–benzene (10:1 v/v). The first fractions gave the dimer of (**1**), compound (**5**) (2 mg, 1.2%),⁷ m.p. >300 °C. The second fractions gave the adduct (**3a**) as crystals (208 mg, 94.0%), $\delta_c(\text{CDCl}_3)$ 142.6 (d, 1 C), 98.9 (d, 1 C), 88.0 (s, 1 C), 38.1 (t, 1 C), 35.5 (d, 2 C) 34.3 (t, 2 C), 32.7 (t, 2 C), 27.6 (d, 1 C), 27.1 (d, 1 C), and 20.2 p.p.m. (t, 1 C); for other physical data, see Table 2.

The cycloadditions of (**1**) with other α,β -unsaturated carbonyl compounds (**2b–e**) were carried out similarly and the results are summarized in Tables 1 and 2.

Reduction of (3a) with Raney Ni.—A mixture of (**3a**) (80 mg, 0.36 mmol) and Raney Ni (W-4 type, ca. 1 ml) in ethanol (3 ml) was stirred at room temperature under hydrogen. The mixture was filtered through Celite 545 and the latter washed with ethanol; the combined filtrate and washings were evaporated under reduced pressure to afford practically pure 2-ethoxy-2-propoxyadamantane (**7a**) as an oil (68 mg, 79.0%) (Found: C, 75.9; H, 11.0. $\text{C}_{15}\text{H}_{26}\text{O}_2$ requires C, 75.58; H, 10.99%); $\nu_{\text{max.}}$ (film) 2 950, 2 910, 2 850, 1 450, 1 380, 1 315, 1 285, 1 215, 1 160, 1 125, 1 090, 1 060, 1 025, and 935 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.43 (2 H q, J 7.5 Hz), 3.32 (2 H t, J 7.5 Hz), and 2.35–1.30 (16 H, m); m/z 238 (M^+ , 2.0%), 193 ($M^+ - \text{OEt}$, 23), 180 (18), 179 ($M^+ - \text{OPr}$, 100), 152 (9.1), 151 (59), 150 (9.1), 134 (18), 121 (11), 93 (14), 92 (14), 91 (14), and 79 (18).

Compound (**7a**) was easily decomposed to adamantanone (**6**) by chromatography on a silica gel or an alumina column.

Reduction of (3d) with Raney Ni.—Similar treatment of (**3d**) (50 mg, 0.21 mmol) with Raney Ni (W-4 type, ca. 1 ml) in ethanol (3 ml) and work-up as above gave 2-ethoxyadamantan-2-ol (**7b**) as an oil (28 mg, 67.5%) (Found: C, 73.7; H, 10.25. $\text{C}_{10}\text{H}_{20}\text{O}_2$ requires C, 73.43; H, 10.27%); $\nu_{\text{max.}}$ (film) 3 200, 2 950, 2 920, 2 850, 1 450, 1 380, 1 125, 1 090, 1 060, 1 020, and 940 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.85 (1 H, br s, D_2O -exchangeable, OH), 3.42 (2 H, q, J 7.5 Hz), 3.35–1.25 (14 H, m), and 1.17 (3 H, t, J 7.5 Hz); m/z 196 (M^+ , 1.0%), 180 (19), 179 ($M^+ - \text{OH}$, 100), 151 (11), 150 ($M^+ - \text{OEt}$, 46), 134 (11), 121 (11), 121 (11), 91 (11), and 79 (11).

Ethanolysis of Adamantanethione (1).—A solution of (**1**) (100 mg, 0.60 mmol) in ethanol (4.0 ml) was heated at 80 °C for 14 h in a sealed tube under argon. The evolution of hydrogen sulphide was confirmed by its odour and a positive lead acetate paper test. After removal of the solvent, the oily residue was chromatographed on a silica gel column and eluted with n-hexane–benzene (10:1 v/v) to afford di-(2-adamantyl) disulphide²¹ (**14**) (20 mg, 20%), m.p. 198–200 °C (lit.,²¹ 275 °C)

as the first fraction. Elution with dichloromethane gave adamantanone (**6**) (57 mg, 67%) after sublimation (80 °C/20 mmHg).

Kinetic Measurements.—The concentration of (**1**) was followed spectrophotometrically using spectral grade solvents such as benzene, acetonitrile, 1,4-dioxane, n-hexane, methanol, ethanol, tetrachloromethane, and chloroform (alcohol-free). A mixture of (**1**) (41.5 mg, 0.25 mmol), acrolein (**2a**) (140 mg, 2.5 mmol), and hydroquinone (2.0 mg, 0.018 mmol) in an appropriate solvent (5.0 ml) was heated in a sealed tube under argon at 60, 70, 80, and 90 ± 0.3 °C. Periodically, portions (3.0 ml) of the sample were quenched by being cooled at 10–20 °C and their visible spectra were measured. The reactions were followed during 30–70% conversion. For the calculation of the rate constants, the absorption values of λ_{max} at 480 nm^{26*} were employed. The rate constants were calculated from the integrated second-order rate expression (A) where a = molar concentration of acrolein, b = molar concentration of (**1**), and t = time (s). Because a 10-fold molar excess of acrolein was employed, equation (A) becomes (B) where b = absorbance at $t = 0$ (the intensity of maximum absorption in the visible region, i.e. absorbance at 498 nm in benzene), $b - x$ = absorbance at time t , and $x = b - (b - x)$. These results are summarized in Tables 3–5.

$$k_2 t = 1/(a - b) \cdot \ln b(a - x)/a(b - x) \quad (\text{A})$$

$$k_2 = 1/9b \cdot \ln(10b - x)/10(b - x) = 1/9b \cdot \ln[1 + 9x/10(b - x)] \quad (\text{B})$$

References

- This paper is taken to be Part 70 of the series Synthesis of Adamantane Derivatives. Part 69: T. Sasaki, S. Eguchi, T. Okano, and N. Nakamura, preceding paper.
- For reactions as heterodienophiles, see (a) S. Weinreb and R. R. Staib, *Tetrahedron*, 1982, **38**, 3087; (b) F. Duns, 'Comprehensive Organic Chemistry,' eds. D. H. Barton and W. D. Ollis, Pergamon, Oxford, 1978, vol. 3, p. 388; (c) E. Block, 'Reactions of Organosulfur Compounds,' Academic Press, New York, 1973, p. 268; (d) J. Hamer and J. A. Turner, '1,4-Cycloaddition Reactions,' ed. J. Hamer, Academic Press, New York, 1967, p. 211; (e) E. Vedejs, T. H. Eberlein, and D. L. Varie, *J. Am. Chem. Soc.*, 1982, **104**, 1445; (f) E. Vedejs and D. A. Perry, *ibid.*, 1983, **105**, 1683 and references cited therein.
- For use as heterodienes, see T. Karakasa and S. Motoki, *J. Org. Chem.*, 1978, **43**, 4147; J. B. Rasmussen, R. Shabana, and S.-O. Lawesson, *Tetrahedron*, 1982, **38**, 1705; H. Bock, S. Mohmand, T. Hirabayashi, and A. Semkow, *J. Am. Chem. Soc.*, 1982, **104**, 312 and references cited therein.
- For use as 1,3-dipolarophiles, see R. Huisgen, *Angew. Chem.*, 1963, **75**, 605, 742; *Angew. Chem., Int. Ed. Engl.*, 1963, **2**, 263, 633; A. P. Krapcho, M. P. Silvon, I. Goldberg, and E. G. E. Jahngen, Jr., *J. Org. Chem.*, 1974, **39**, 860; D. St. C. Black and K. G. Watson, *Aust. J. Chem.*, 1973, **26**, 2491.
- For photocycloadditions, see P. de Mayo, *Acc. Chem. Res.*, 1971, **4**, 41; J. D. Coyle, *Chem. Soc. Rev.*, 1975, **4**, 523; H. Durr, 'Methoden der Organischen Chemie,' ed. E. Muller, Houben-Weyl, Stuttgart, 1975, Band IV/15b, Part II, p. 1959.
- For a review on heterodiene synthesis with α,β -unsaturated carbonyl compounds, see G. Desimoni and G. Tacconi, *Chem. Rev.*, 1975, **75**, 651.
- J. W. Greidanus and W. Schwalm, *Can. J. Chem.*, 1969, **47**, 3715; J. W. Greidanus, *ibid.*, 1970, **48**, 3530, 3593.
- For Diels–Alder reactivity differences in substituted buta-1,3-dienes,

* λ_{max} . In various solvents: n-hexane, 498 nm; acetonitrile, 478 nm; 1,4-dioxane 484 nm; chloroform, 484 nm; tetrachloromethane 497 nm; and ethanol, 482 nm, respectively.

- see L. A. Paquette, A. G. Schaefer, and J. F. Blount, *J. Am. Chem. Soc.*, 1983, **105**, 3642 and references cited therein.
- 9 C. Djerassi and M. Gorman, *J. Am. Chem. Soc.*, 1953, **75**, 3704.
- 10 E. Fromm and B. Ungar, *Ber.*, 1923, **56**, 2286; H. T. Clarke, *J. Chem. Soc.*, 1912, **101**, 1788.
- 11 W. E. Parham, J. Gordon, and J. D. Swalen, *J. Am. Chem. Soc.*, 1952, **74**, 1824.
- 12 K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *J. Am. Chem. Soc.*, 1973, **95**, 7310; K. N. Houk, J. Sims, R. E. Duke, R. M. Strozier, and J. K. George, *ibid.*, p. 7287; K. N. Houk, *Acc. Chem. Res.*, 1975, **8**, 361; I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' Wiley, New York, 1976.
- 13 K. N. Houk and R. W. Strozier, *J. Am. Chem. Soc.*, 1973, **95**, 4093; P. V. Alston and D. D. Shillady, *J. Org. Chem.*, 1974, **39**, 3402.
- 14 K. B. Lipkowitz and B. P. Mundy, *Tetrahedron Lett.*, 1977, 3417.
- 15 R. Sustmann, *Tetrahedron Lett.*, 1971, 2717; R. Sustmann, *Pure Appl. Chem.*, 1974, **40**, 569.
- 16 For reviews, see A. Wassermann, 'Diels-Alder Reaction,' Elsevier, New York, 1965; J. Sauer and R. Sustmann, *Angew. Chem.*, 1980, **92**, 773; *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 779.
- 17 R. Huisgen, *Acc. Chem. Res.*, 1977, **10**, 117 and references cited therein.
- 18 G. Desimoni, G. Cellerino, and G. Minoli, *Tetrahedron*, 1972, **28**, 4003; M. Mizuta, A. Suzuki, and Y. Ishii, *Kogyo Kagaku Zasshi*, 1966, **69**, 77 (*Chem. Abstr.*, 1966, **65**, 5320); for the diradical mechanism, see C. W. Smith, D. G. Norton, and S. A. Ballard, *J. Am. Chem. Soc.*, 1951, **73**, 5273; for a pseudoaromatic cyclic transition state mechanism, see R. B. Woodward and T. J. Katz, *Tetrahedron*, 1959, **5**, 70.
- 19 A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *Tetrahedron*, 1969, **25**, 871.
- 20 J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970, p. 163.
- 21 J. R. Bolton, K. S. Chen, A. H. Lawrence, and P. de Mayo, *J. Am. Chem. Soc.*, 1975, **97**, 1832.

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