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Reactions of Adamantanethione with Ketenes: Formation of a 1,3,5-Dioxathiane

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The reaction between adamantanethione **1** and diphenylketene **9** yields 2,4-bis(diphenylmethylidene)-1,3,5-dioxathiane **14** via ketene–thione zwitterions. This is the first example of the formation of a 1,3,5-dioxathiane in a ketene reaction.

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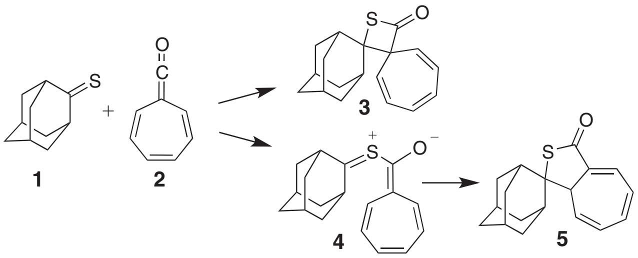
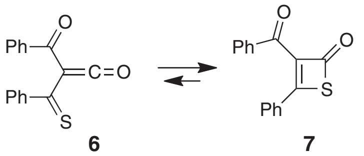
Recent interest in zwitterionic intermediates in reactions of thioketones with diazo compounds, ketenes, and related compounds[1] prompts us to report an unusual reaction of adamantanethione with diphenylketene. A few examples of [2+2] cycloaddition of ketenes to thioketones have been reported,[2] including the addition of the highly reactive and unstable 8-oxoheptafulvene **2** to adamantanethione **1** yielding the thietan-2-one **3** (Scheme 1).[3] A formal [2+8] cycloaddition product **5** is also formed in this reaction, possibly via a zwitterionic intermediate **4**. An analogous [2+8] cycloaddition product is formed from thiotropone and diphenylketene.[4] The intramolecular, electrocyclic, [2+2] addition of the ketene function to the C=S bond in benzoyl(thiobenzoyl)ketene **6** to form the corresponding thiet-2-one **7** and similar reactions of other α-thioxoketenes have also been described (Scheme 2).[5]

Some years ago we reported the first example of [2+4] cycloaddition of an α–oxoketene to a thione, viz. the reaction between dipivaloylketene **8** and adamantanethione **1** (Scheme 3).[6] More recently, competing cycloadditions of thiobenzophenone with benzoyl(phenyl)diazomethane (azibenzil), and with benzoyl(phenyl)ketene formed from it by Wolff rearrangement, have been reported.[7] Conversely, [2+4] cycloadditions of ketenes to α,β-unsaturated thioketones[8] and to *N*-thioacylimines[9] are also known. Further chemistry of adamantanethione has been summarised.[10]

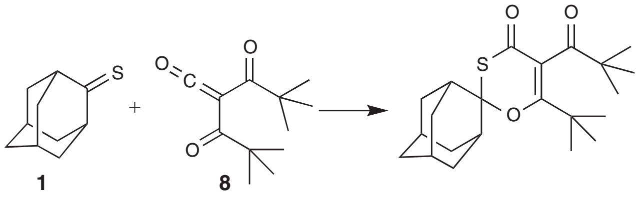
Here we report the reaction between adamantanethione **1** and diphenylketene **9**, which we had expected to result in a [2+2] cycloaddition to produce a spirocyclic thietanone **10** or oxathietane **11** (Scheme 4). However, neither of these compounds was isolable. Instead two molecules of the ketene reacted with one molecule of adamantanethione to produce a compound $C_{38}H_{34}SO_2$ (*m/z* 554) as the only discrete isolable product. This compound could have either of the structures **14**, **15**, or **16** (Scheme 4). However, structures **15** and **16** are ruled out because no carbonyl group is indicated in the ^{13}C NMR or in the infrared (IR) spectrum. The highest chemical shifts are 141 and 149 ppm, and the highest IR frequencies (other than C–H stretches) are at 1663 and 1597 cm^{-1}, which can be ascribed to aromatic C=C stretching. The compound was identified as **14** thanks to a full assignment of all carbon signals by means of a distortionless enhancement by polarisation transfer (DEPT)-135 experiment and an off-resonance decoupled ^{13}C NMR spectrum. There are 27 carbon resonances in all, including three methylene and three methine signals belonging to the adamantyl unit (demonstrating that the molecule has a plane of symmetry), 12 CH groups arising from the four phenyl groups, and four phenyl-*ipso*



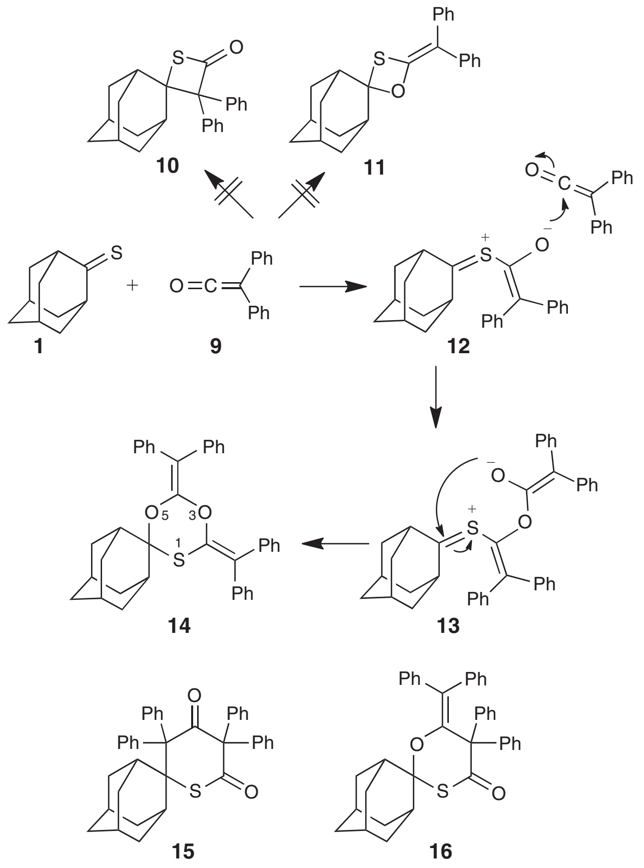
Scheme 1. [2+2] and [2+8] Cycloadditions of adamantanethione **1** with the transient 8-oxoheptafulvene **2**.



Scheme 2. Electrocyclic formation of 3-benzoyl-4-phenylthiet-2-one **7**.



Scheme 3. [2+4] Cycloaddition of adamantanethione **1** with dipivaloylketene **8**.



Scheme 4. Formation of 1,3,5-dioxathiane **14**.

carbons, the latter appearing as triplets in the proton-coupled spectrum (thus, all four phenyl groups are magnetically different). Other signals for carbons not carrying directly attached protons at 98, 106, and 124 ppm can be identified as the diphenylvinyl and spiro (C6 in the dioxathiane ring) carbons, because they become multiplets in the proton-coupled spectrum due to long-range C–H couplings. Two remaining vinyl-type carbons at 141 and 149 ppm, which remain singlets in the proton-coupled spectrum, are assigned to C2 and C4 in the dioxathiane ring in **14**.

The mass spectrum is also in good agreement with structure **14**. Important fragment peaks at *m/z* 166, 194, and 210 indicate cycloreversion reactions to form the molecular ions of adamantanethione, diphenylketene, and diphenylthioketene, respectively.

A logical mechanism for the formation of **14** involves the initial formation of a zwitterion **12** (Scheme 4) by nucleophilic attack of the thione on the ketene C=O group. Rather than cyclising to either **10** or **11**, the zwitterion is sufficiently long-lived to add to another molecule of diphenylketene, giving a new zwitterion **13**. Cyclisation of the latter affords the final product.

One may ask why a mono-addition product **10** or **11** is not formed in this case, when it is formed in the reaction shown in Scheme 1. A likely reason is that ketene **2** is very short-lived and has to be generated in situ. Hence the concentration of **2** will never build up sufficiently for a double addition. In contrast, diphenylketene is a relatively stable compound, which is available in excess from the beginning of the reaction. A concerted three-component [2+2+2] cycloaddition is of course also imaginable but entropically unlikely. The ubiquitous formation of sulfur-based zwitterions[1] makes the stepwise process shown in Scheme 4 more likely. We have shown previously that ketenes form zwitterions with tertiary amines including pyridines, with very low activation barriers (so-called ketene–pyridine zwitterions).[11] The present work indicates that ketene–thione zwitterions are also formed readily.

In conclusion, the reaction between adamantanethione **1** and diphenylketene **9** yields 2,4-bis(diphenylmethylidene)-1,3,5-dioxathiane **14** via ketene–thione zwitterions. To the best of our knowledge, this is the first example of the formation of a 1,3,5-dioxathiane in a ketene reaction.

Experimental

Adamantanethione **1**[12] and diphenylketene **9**[13] were prepared according to literature procedures.

2,4-Bis(diphenylmethylidene)-1,3,5-dioxathiane **14**

A mixture of adamantanethione **1** (0.34 g, 2.0 mmol) and diphenylketene **9** (0.37 g, 1.9 mmol), together with a crystal of hydroquinone to inhibit polymerisation, was placed in a flask under nitrogen for 72 h at room temperature. The contents of the flask first liquefied to form an orange oil, then after ~40 h started to solidify as white crystals. The reaction mixture was extracted several times with hexane, and the combined extracts were concentrated under vacuum to give a crude yield of 0.48 g of an off-white crystalline solid. IR spectroscopy demonstrated that this material was largely identical with the product purified by chromatography as described below. Column chromatography on silica gel 60, eluting with CH_2Cl_2/hexane 3/97 afforded **14** as white needles (0.23 g, 44 % based on diphenylketene), mp 176–178°C. (Found: C 81.97, H 6.15. Anal. Calc. for $C_{38}H_{34}SO_2$: C 82.28, H 6.18 %). δ_H ($CDCl_3$) 7.45–6.92 (m, 20H), 2.42–1.47 (m, 14H); δ_C ($CDCl_3$): assignment as C (not carrying any protons), CH or CH_2 on the basis of DEPT-135 spectrum; multiplicity in the H-coupled spectrum given, s = singlet, d = doublet (CH), t = triplet, m = multiplet: 148.9 (C, s), 140.9 (C, s), 139.6 (C, t), 138.6 (C, t), 138.3 (C, t), 137.6 (C, t), 130.7 (CH, d), 130.5 (CH, d), 130.4 (CH, d), 129.3 (CH, d), 128.2 (CH, d), 127.8 (CH, d), 127.7 (CH, d), 127.5 (CH, d), 127.2 (CH, d), 126.3 (CH, d), 126.1 (CH, d), 126.0 (CH, d), 124.4 (C, m), 106.3 (C, m), 97.7 (C, m), 38.5 (CH, d), 37.6 (CH_2, t), 34.5 (CH_2, t), 32.7 (CH_2, t), 26.6 (CH, d), 26.2 (CH, d); *m/z* (EI, 70 eV) 554 ($M^{+\cdot}$), 360 ($[M–Ph_2CCO]^{+\cdot}$), 332 ($[M–PH_2CCO–CO]^{+\cdot}$), 300 ($[M–Ph_2CCO–COS]^{+\cdot}$), 210 ($[Ph_2CCS]^{+\cdot}$), 194 ($[Ph_2CCO]^{+\cdot}$), 166 ($\mathbf{1}^{+\cdot}$), 165, 134 (adamantylidene$^{+\cdot}$), 77 ($Ph^{+\cdot}$); ν_{max} (KBr)/cm^{-1} 3054–2856, 1663, 1597, 1496, 1443, 1120, 1197, 1108.

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