Tetrahedron Letters 53 (2012) 3095–3099

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

The first examples of cycloadditions of 2-diazo-1,3-dicarbonyl compounds to aromatic thioketones

Valerij A. Nikolaev [a,*], Alexey V. Ivanov [a], Anton A. Shakhmin [a], Joachim Sieler [b], Ludmila L. Rodina [a]

[a] Saint-Petersburg State University, University prosp. 26, St.-Petersburg 198504, Russia
[b] Universität Leipzig, Institut für Anorganische Chemie, Johannisallee 29, D-04103 Leipzig, Germany

ARTICLE INFO

Article history:
Received 14 February 2012
Revised 24 March 2012
Accepted 5 April 2012
Available online 16 April 2012

Keywords:
2-Diazo-1,3-diazocarbonyl compounds
Thioketones
Oxathioles
Thiadiazoline
Thiocarbonyl ylides
2-Oxoketenes
Pyrandiones
Cycloaddition
1,5-Electrocyclization

ABSTRACT

Acyclic 2-diazo-1,3-dicarbonyl compounds react at 20–50 °C with aromatic thioketones and through a cascade process, involving the cycloaddition of a diazo group dipole with the C=S bond, elimination of nitrogen from the arising thiadiazoline, and subsequent [1,5]-electrocyclization of the intermediate C=S-ylide, the relevant oxathioles being formed in yields of up to 70%. Carbocyclic 2-diazo-1,3-diketones at room temperature react with thiones much more slowly, but with increasing temperature they partly decompose to produce, via Wolff rearrangement, 2-oxoketenes, which yield [4+2]-cycloaddition products, that is oxathiinones and/or oxoketene dimers.

Cycloaddition of aliphatic diazo compounds with unsaturated compounds is well-known and is widely used for the preparation of a variety of nitrogenous and other heterocycles.[1–5] The most reactive dipoles in these processes are diazoalkanes and 2-diazoketones, while the cycloaddition of 2-diazo-1,3-dicarbonyl compounds with ordinary dipolarophiles is considered to be far less common.[6,7] To the best of our knowledge, detailed studies of cycloaddition reactions of diazodicarbonyl compounds have not been conducted, and the literature data on this matter is somewhat contradictory.

In pioneering work by Huisgen and Reissig, it was established that diazomalonic ester and dibenzoyldiazomethane react easily with the carbon–carbon triple and double bonds of dialkylpropyne and an enamine to produce the standard [3+2]-cycloaddition products, pyrazoles, and pyrazolines, respectively.[8,9] At the same time, attempts to carry out the analogous reaction of dibenzoyldiazomethane and diazodimedone with DMAD failed.[7]

Similar inconsistency was observed upon investigation of the reactions of 2-diazo-1,3-dicarbonyl compounds with aromatic thioketones ('superdipolarophiles'[10]). According to recent results,[11,12] diazomalonic ester and diazodimedone under standard reaction conditions, do not interact with the C=S-bond of one of the most active superdipolarophiles in these reactions, that is thiobenzophenone, and only after the addition of Rh(II)-catalyst to the reaction mixture, were the adducts of $Ph_2C{=}S$ with Rh(II)-carbenoids formed. At the same time, we established[13] that diazoacetylacetone, the first member of the acyclic diazodiketone series, reacts with thiobenzophenone even at room temperature giving rise to an oxathiole. The latter is the typical product of the reaction of diazoketones with the C=S-bond of thiocarbonyl compounds.[14,15]

The main goal of our research was to perform a comprehensive study of a variety of reactions of 2-diazo-1,3-dicarbonyl compounds with aromatic thioketones, to elucidate the key features of these processes, and to establish their feasibility for the preparation of oxathioles and other heterocyclic compounds.

Typical representatives of 2-diazo-1,3-dicarbonyl compounds of different types were used in this study. These included acyclic diazodiketones **1a–c**, diazoketoester **1d,** and carbocyclic diazodiketones **1e–h**. As dipolarophiles, three aromatic thioketones were used, thiobenzophenone **2a**, 4,4'-dimethoxythiobenzophenone **2b,** and thiofluorenone **2c**, which are known to possess considerably different reactivity in cycloaddition processes (Fig. 1).[10]

The reactions were carried out in benzene or toluene solutions at various temperatures (18–23, 50 or 80 °C) depending on the reactivity of the diazodicarbonyl compound.

It was found that acyclic diazo compounds **1a–d**, even at standard temperatures (18–23 °C), reacted with thiobenzophenone **2a** to produce oxathioles as the sole reaction products (Scheme 1).[16]

---

* Corresponding author at present address: 8 Linija 35, Apt. 5, St.-Petersburg 199004, Russia. Tel.: +7 812 323 10 68; fax: +7 812 428 69 39.

E-mail address: vnikola@VN6646.spb.edu (V.A. Nikolaev).

0040-4039/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2012.04.036

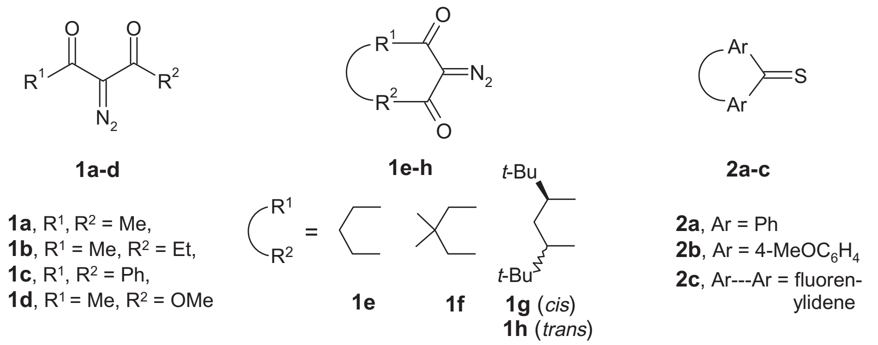


Figure 1. Structures of the diazodicarbonyl compounds **1a–h** and thioketones **2a–c** used in this study.

In the case of unsymmetrically substituted diazodicarbonyl compound **1b** (R^1 = Me, R^2 = Et), two regioisomeric oxathioles **3** and **3′** were formed (15% and 25% yields, respectively), while with methyl diazoacetate **1d**, possessing acetyl and methoxycarbonyl substituents on the diazo group, the reaction occurred regioselectively giving rise to only one isomer of oxathiole **3d** (R^2 = OMe, 70%).

At 50 °C the rate of the reaction of the acyclic diazodiketones **1a**,**b** with thiobenzophenone **2a** increased by approximately seven times, but the only reaction products (from ^{1}H NMR spectroscopy) under these conditions were still oxathioles **3** and **3′**, and their yields remained essentially the same (54–56%) (Scheme 1).

Di(4-methoxy)thiobenzophenone **2b** reacted with acyclic diazodiketones **1a**,**b** similarly to thiobenzophenone **2a** to produce oxathioles **4a**,**b** and **4b′**, however the reactions proceeded very slowly.[17] By contrast, the reactions of diazodiketones **1a**,**b** with thiofluorenone **2c** were completed in 20–24 h, but the yields of the corresponding oxathioles **5a**,**b** and **5′b** were low (22–44%),[18] apparently due to participation of this highly reactive thioketone in side processes.[19]

Carbocyclic diazodiketones **1e–h** were found to be far less reactive than their acyclic analogues **1a–d** at 18–23 °C.[20] Increasing the temperature to 80 °C notably speeded up the process, but partial decomposition of diazodiketones **1e–h** was observed, along with side processes that gave rise to the formation (along with oxathioles **3e–h**) of oxathiinones **6f–h** and pyrandiones **7e–h** (Scheme 2).

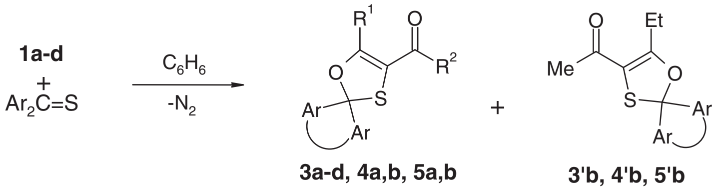
In the case of sterically overcrowded, and thermally the least stable carbocyclic diazodiketones **1g**,**h** (see below), the main reaction products proved to be oxathiinones **6g**,**h** and pyrandiones **7g**,**h**.

The structures of isolated compounds **3a–h**, **3′b**, **6f–h**, **7e–g** were verified by ^{1}H, ^{13}C NMR and IR spectroscopy, and mass spectrometry.[22] The most reliable indicators of the 1,3-oxathiolic structure were the signals of the **C**=C–O carbon atoms of the heterocycle in the ^{13}C NMR spectra, which for most of the isolated oxathioles **3**, **3′** (except for **3d**) were in a relatively narrow region of the spectra at 111–114 ppm. The oxathiole **3d** prepared from diazoketoester **1d** had this signal at 102.0 ppm. The signals of the corresponding carbon atoms of the oxathiinone system in compounds **6f–h** were observed at lower field (at 117–120 ppm).[22] This allows reliable discrimination of the oxathiole **3** and oxathiinone **6** structures from ^{13}C NMR spectroscopic data.

The regioisomeric structures **3b** and **3′b** were easily identified by the locations of the signals of the CH$_3$CO and CH$_3$ groups in the ^{1}H and ^{13}C NMR spectra. Thus, the acetyl group of isomer **3b** appeared at 2.38 and 31.0 ppm in the ^{1}H and ^{13}C NMR spectra which were very close in value to the signals of the similar group in oxathiole **3a** (2.38, 30.5 ppm) obtained from diazoacetylacetone **1a**. In contrast, the proton and carbon signals of the CH$_3$ group on the C=C double bond of isomer **3′b** (2.25, 16.0 ppm) were rather close to those positions of the signals of the similar group in the structure of **3a** (2.26, 15.7 ppm).

The structures of a few key reaction products, oxathiole **3d** and oxathiinone **6f**, were established unambiguously by X-ray crystal structure analysis (Figs. 2 and 3).[23]

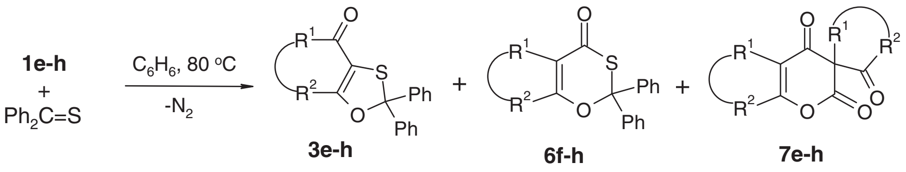
Thus, the main products from the reactions of acyclic diazodicarbonyl compounds **1a–d** with aromatic thiones **2a–c** were oxathioles. According to the commonly accepted mechanism,[14,15] as applied to 2-diazo-1,3-dicarbonyl compounds **A**, the formation of oxathioles **B** under standard conditions (rt, absence of a catalyst)



Diazo compound	R^1, R^2	Temp (°C)	Time	Yields of reaction products (%) [a]
1a	Me, Me	18-23	7 d	53 (**3a**)
1b	Me, Et	18-23	7 d	40 (**3b**+**3'b**; 1/1.7)
1c	Ph, Ph	18-23	62 d	61 (**3c**)
1d	Me, OMe	18-23	62 d	70 (**3d** only)
1a	Me, Me	50	24 h	54 (**3a**)
1b	Me, Et	50	30 h	56 (**3b**+**3'b**; 1/1.7)

[a] Yield of isolated compounds.

Scheme 1. Reactions of acyclic diazodicarbonyl compounds **1a–d** with thioketones **2a–c**.



Diazo compound	R^1, R^2	Time (h)	Yields of reaction products (%) [a]		
			3e-h	**6f-h**	**7e-h**
1e	-$(CH_2)_3$-	60	15 (28)	–[b]	22 (42)
1f	-$CH_2C(Me_2)CH_2$-	100	27 (53)	8 (19)	11 (26)
1g	*cis*-CH(*t*-Bu)CH_2CH(*t*-Bu)-	1	8	24	50 [c]
1h	*trans*-CH(*t*-Bu)CH_2CH(*t*-Bu)-	3	11	19(71)	(14) [d]

[a] Yields determined by ^{1}H NMR spectroscopy are given in brackets.

[b] Not isolated from the reaction mixture.

[c] Unseparable (by chromatography) mixture of two diastereoisomers.[21]

[d] One diastereoisomer according to ^{1}H NMR spectroscopy. [21]

Scheme 2. Reactions of carbocyclic diazodiketones **1e**–**h** with thiobenzophenone **2a**. (See above-mentioned references for further information.)

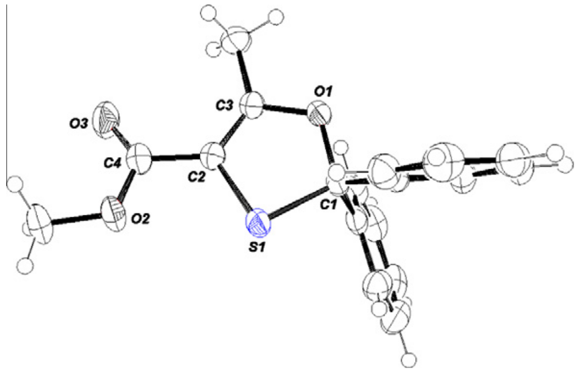


Figure 2. ORTEP-generated[24] structure of oxathiole **3d**.[23] The ellipsoids denote 50% probability.

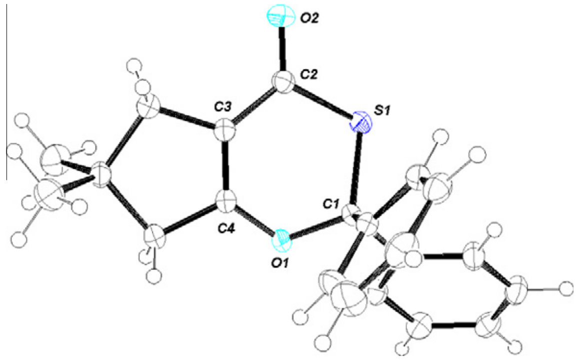


Figure 3. ORTEP-generated[24] structure of oxathiole **6f**.[23] The ellipsoids denote 50% probability.

can be rationalized via the initial cycloaddition of the diazo group dipole with the C═S bond of the thioketone giving rise to thiadiazoline **C**, which is usually extremely unstable. This eliminates a molecule of N_2, and following 1,5-electrocyclization ([1,5]-EC) of the resulting thiocarbonyl ylide **D**, the oxathiole **B** is formed (Scheme 3).

At elevated temperatures or on Rh-catalyzed decomposition of diazodicarbonyl compound **A** in the presence of the thioketone, the generation of the C═S-ylide **D** is also possible via an alternative pathway—owing to interaction of the assumed diacylcarbene (or Rh-carbenoid) **E** with the sulfur atom of the thiocarbonyl group.[14,15] Subsequent intramolecular 1,5-electrocyclization of the thiocarbonyl ylide **D** formed will afford the same oxathioles **B** (Scheme 3).

To clarify the possibility of thermal decomposition of the diazodicarbonyl compounds and the probability of the 'carbenic' pathway under the reaction conditions studied, the thermal stability of a series of 2-diazo-1,3-dicarbonyl compounds **1** was estimated.[25]

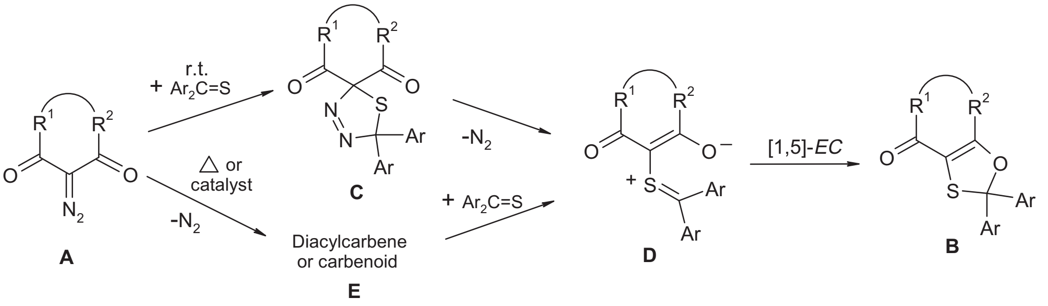
It turned out that all the diazodicarbonyl compounds **1a, c–e, g, h** studied were relatively stable in benzene at 18–20 °C, and according to ^{1}H NMR data, did not undergo notable decomposition or other changes over a few months under these conditions [$\tau_{1/2}$ (18–23 °C) >> 3 months]. On raising the temperature to 50 °C, diazoacetoacetic ester **1d**, diazocyclohexanedione **1e** and diazodimedone **1f** also remain unchanged for months. The least stable at elevated temperatures, as was to be expected from literature data,[26,27] were acyclic **1a**–**c** and sterically crowded diazodiketones **1g,h**, with lifetimes of 32–96 h and 0.7–2.3 h at 50 and 77 °C, correspondingly.

The data obtained enabled us to conclude that at standard temperatures (18–23 °C) the formation of oxathioles **D** from diazodicarbonyl compounds **A** and thioketones $Ar_2C{=}S$ occured via cycloaddition of the diazo compounds with the C═S bond of the thiones (Scheme 3), and not via the initial decomposition of diazo compound **A** and the generation of the intermediate thiocarbonyl ylides **D** via diacylcarbene **E**. At the same time, on the basis of the experimental data in hand we cannot rule out completely the possibility of the 'carbenic' pathway (Scheme 3) at elevated temperatures (>50 °C).

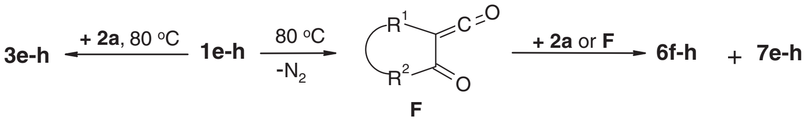
The formation of oxathiinones **6f–h** and pyrandiones **7e–h** (in addition to oxathioles **3e–h**) in the reactions of carbocyclic diazodiketones **1e–h** at 80 °C is evidently caused by partial decomposition and Wolff rearrangement of the diazodiketones **1e–h** at elevated temperature, which gives rise to the appearance of 2-oxoketenes **F** in the reaction medium (Scheme 4).[28,29]

Ketene **F** reacts either with thioketone **2a** or with the other molecule of acylketene, and through Diels–Alder [4+2]-cycloaddition with the C═S bond of the thioketone or C═C bond of the ketene molecule, oxathiinones **6f–h,** and pyrandiones **7e–h** are formed.

In summary, we have established for the first time that acyclic and carbocyclic 2-diazo-1,3-dicarbonyl compounds **1a–h** react at 18–23 °C with aromatic thioketones **2a–c** via a cascade process,



Scheme 3. Two pathways for the formation of oxathioles **B** from diazodicarbonyl compounds **A**.



Scheme 4. Two directions for the transformations of carbocyclic diazodiketones **1e**–**h** at 80 °C.

involving the cycloaddition of the diazo group dipole with the C=S bond, elimination of nitrogen from the intermediate thiadiazoline, and ensuing [1,5]-electrocyclization of the resultant C=S-ylide, to give oxathioles in yields of up to 70%.

The carbocyclic 2-diazo-1,3-diketones react more slowly than their acyclic counterparts. Also, incorporation of an electron-donating group at the *para* position of the aryl ring of the thioketone diminishes considerably the efficiency of the addition of the diazodicarbonyl compounds to the C=S bond of the thione.

On increasing the temperature, the rate of cycloaddition of the diazodicarbonyl compound increases considerably, but with carbocyclic 2-diazo-1,3-diketones, partial thermolysis, and Wolff rearrangement occurs resulting in the generation of 2-oxoketenes, that leads via [4+2]-cycloaddition to the formation of oxathiinones and/or oxoketene dimers.

References and notes

1. (a) Huisgen, R. *Angew. Chem.* **1955**, *67*, 439–463; (b) Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1, pp 1–176.
2. Korobizina, I.; Rodina, L. L. In *Methodicum Chimicum*; Georg Thieme: Stuttgart, 1974; Vol. 6, pp 260–307.
3. Regitz, M.; Heydt, H. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1, pp 393–558.
4. Zollinger, H. *Diazo Chemistry II*; VCH: Weinheim, 1995. pp 191–240.
5. Maas, G. In Padwa, A., Ed.; The Chemistry of Heterocyclic Compounds; Wiley: New York, 2002; Vol. 59, pp 539–622.
6. Huisgen, R.; Grashey, R.; Sauer, J. In *Alkene Chemistry*; Patai, S., Ed.; Wiley: New York, 1964; pp 806–977.
7. (a) Korobitsyna, I. K.; Bulusheva, V. V.; Rodina, L. L. *Chem. Heterocycl. Compd.* **1978**, 471; (b) Bulusheva, V. V. *Ph.D. Dissertation*; Leningrad University, 1975.
8. Huisgen, R.; Reissig, H.-U. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 330.
9. Huisgen, R.; Reissig, H.-U. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 694.
10. Huisgen, R.; Langhals, E. *Tetrahedron Lett.* **1989**, *30*, 5369.
11. Mlostoń, G.; Heimgartner, H. *Helv. Chim. Acta* **1996**, *79*, 1785.
12. Kelmendi, B.; Mlostoń, G.; Heimgartner, H. *Heterocycles* **2000**, *52*, 475.
13. Ivanov, A. V.; Rodina, L. L.; Nikolaev, V. A. *Abstracts of Papers*, Vth International Symposium 'Chemistry of Aliphatic Diazo Compounds' (Diazo-2011), Saint-Petersburg, Russia, Jun 6–8, 2011; p 64.
14. (a) Ibata, T.; Nakano, H. *Chem. Express* **1989**, *4*, 93; (b) Ibata, T.; Nakano, H. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3096; (c) Nakano, H.; Ibata, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 238; (d) Nakano, H.; Ibata, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1393.
15. (a) Mlostoń, G.; Heimgartner, H. In Padwa, A., Ed.; The Chemistry of Heterocyclic Compounds; Wiley: New York, 2002; Vol. 59, pp 315–360; (b) Mlostoń, G.; Heimgartner, H. *Curr. Org. Chem.* **2011**, *15*, 675.
16. *General procedure for the reaction of diazo compounds **1** with thioketones **2***: To a stirred solution of freshly prepared thioketone **2** (2–4 mmol) in 2–5 ml of benzene (or toluene), diazo compound **1** (5–10% excess) was added in one portion. Argon was bubbled through the reaction mixture and it was allowed to react at a distinct temperature until complete conversion of the thione **2** as indicated by the disappearance of thioketone colour and TLC. The solvent was removed and the residue was recrystallized from an appropriate solvent or separated by column chromatography.
17. The yields of oxathioles **4a**,**b** and **4′b** from thioketone **2b** and diazodiketones **1a**,**b** over 28 days were only 4–5% (according to ^{1}H NMR spectroscopy).
18. The yields of oxathioles **5a**,**b** and **5′b** in the reaction of thiofluorenone **2c** with diazoacetylacetone **1a** and diazopropionylacetone **1b** were 22–44%, presumably due to side reactions of thiofluorenone, i.e. dimerization, oxidation, and hydrolysis.
19. Scheibye, S.; Shabana, R.; Lawesson, S.-O.; Romming, C. *Tetrahedron* **1982**, *38*, 993.
20. After 3 months at 18–23 °C the reaction mixture of diazocyclohexanedione **1e** and thiobenzophenone **2a**, according to ^{1}H NMR data contained only 8–10% of oxathiole **3e**. In the reaction of diazodimedone **1f** and sterically crowded diazodiketones **1g**,**h** with thioketone **2a** over the same period of time, no evidence of any reaction was observed.
21. Nikolaev, V. A.; Korneev, S. M.; Terent'eva, I. V.; Korobitsyna, I. K. *J. Org. Chem. USSR* **1991**, *27*, 1845.
22. Characterisation data for representative examples of compounds **3** and **6**. *4-Acetyl-5-methyl-2,2-diphenyl-1,3-oxathiole (**3a**)*. Colourless crystals, mp 54–56 °C (from MTBE). R_f 0.45 (PE/MTBE, 2:1). UV (in MeOH), $\lambda_{max.}$ (lgε): 283 (3.14), 332 (3.26). IR (THF, 0.03 M), cm^{-1} ($I_{rel.}$, %): 1679 (53), 1649 (30), 1592 (100), 1449 (42), 1362 (30), 1271 (35), 981 (24), 701 (57). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.54–7.46 (m, 4H, Ph), 7.39–7.28 (m, 6H, Ph), 2.38 (s, 3H, C$\mathbf{H_3}$CO), 2.26 (s, 3H, C$\mathbf{H_3}$C=C) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ 191.3 (**C**=O), 157.1 (O–**C**=C), 142.9, 128.5, 128.2, 126.4 (all C$_{Ar}$), 112.6 (**C**=C–O), 101.1 (**C**Ph$_2$), 30.5 (**C**H$_3$C=O), 15.7 (**C**H$_3$C=C) ppm. MS (ESI), *m*/*z*: 297 [M+H]$^+$, 319 [M+Na]$^+$, 335 [M+K]$^+$. Anal. Calcd for $C_{18}H_{16}O_2S$: C, 72.94; H, 5.44. Found: C, 72.81; H 5.41. *Methyl 5-methyl-2,2-diphenyl-1,3-oxathiole-4-carboxylate (**3d**)*. Colourless crystals, mp 72–73 °C (from PE). R_f 0.42 (PE/MTBE, 3:1). UV (in MeOH), λ_{max} nm (lgε): 246 (3.44), 272 (3.42), 278 (3.43), 311 (3.44). IR (THF, 0.03 M), cm^{-1} ($I_{rel.}$, %): 1713 (100), 1629 (68), 1284 (57), 787 (13), 759 (35), 724 (49), 700 (44). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.52–7.44 (m, 4H, Ph), 7.38–7.29 (m, 6H, Ph), 3.72 (s, 3H, OC$\mathbf{H_3}$), 2.38 (s, 3H, C$\mathbf{H_3}$C=C) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ 163.5 (**C**O), 158.4 (O–**C**=C), 142.9, 128.4, 128.1, 126.3 (all C$_{Ar}$), 101.8, 101.1 (**C**=C–O, **C**Ph$_2$), 51.7 (O**C**H$_3$), 14.7 (**C**H$_3$C=C) ppm. MS (ESI), *m*/*z* ($I_{rel.}$, %): 281.06 (38) [M–OCH$_3$]$^+$, 313.09 (100) [M+H]$^+$, 330.11 (13) [M+18]$^+$, 335.07 (19) [M+Na]$^+$, 351.04 (15) [M+K]$^+$. Anal. Calcd for $C_{18}H_{16}O_3S$: C, 69.21; H, 5.16. Found: C, 69.39; H 5.34. *cis-5,7-Di-tert-butyl-2,2-diphenyl-6,7-dihydrocyclopenta[e][1,3]oxathiin-4(5H)-one (**6g**)*. Yellowish crystals, mp 152–153 °C (from PE). R_f 0.34 (PE/acetone, 1.5:1). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.68–7.65 (m, 4H, Ph), 7.38–7.33 (m, 6H, Ph), 2.79–2.77 (m, 2H, C$\mathbf{H_2}$), 1.88 (m, 1H, C**H**), 1.27 (m, 1H, C**H**), 0.99 (s, 9H, *t*-Bu), 0.67 (s, 9H, *t*-Bu) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ 182.8 (**C**=O), 174.4 (C=**C**–O), 142.2, 140.5, 129.7, 129.6, 128.9, 128.8, 128.3, 126.6 (C Ar); 119.5 (**C**=C–O), 96.8 (CPh$_2$), 54.8, 48.9 (2 **C** *t*-Bu), 35.5, 33.9 (2 **C**Me$_3$), 28.2, 28.8 (**C**H$_3$), 24.3 (**C**H$_2$) ppm. MS, *m*/*z*, ($I_{rel.}$, %): 420 (6) [M]$^+$, 341 (11), 222 (43), 221 (23), 198 (51), 182 (98), 151 (31), 137 (51), 109 (49), 105 (100), 69 (77), 41 (>100), 39 (49).
23. Single crystals of compounds **3d** and **6f** suitable for X-ray diffraction were selected from analytical samples. Crystallographic measurements were made using an IPDS1 diffractometer [Fa. STOE, Darmstadt, graphite monochromated MoKα radiation (λ 0.71073 Å)]. The structures were solved by direct methods using the program *SIR*2002[30] and were refined using anisotropic approximation for the non-hydrogen atoms using *SHELX-90*.[31] All hydrogen atoms were calculated and refined in riding modus. CCDC 865469 for **3d** and CCDC 865470 for **6f** contain the supplementary crystallographic data. These

data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif from the Cambridge Crystallographic Data Centre.

24. Johnson, C. K. *ORTEP II, Report ORNL-5138*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.
25. A solution of diazo compound **1** in CCl_4 was placed in tightly-closed thick-walled glass flask or in a sealed glass ampoule and kept at a certain temperature over the required time. The kinetic measurements of the thermal decomposition of diazo compounds were carried out using IR spectroscopy.
26. (a) Regitz, M.; Bartz, W. *Chem. Ber.* **1970**, *103*, 1477; (b) Regitz, M.; Maas, G. *Diazo Compounds. Properties and Synthesis*; Academic Press: Orlando-Toronto, 1986.
27. Popik, V. V.; Nikolaev, V. A. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1971.
28. (a) Tidwell, T. T. *Ketenes II*; Wiley: Hoboken, 2006; (b) Wentrup, C.; Heilmayer, W.; Collenz, G. *Synthesis* **1994**, 1219.
29. (a) Stetter, H.; Kiehs, K. *Chem. Ber.* **1965**, *98*, 1181; (b) Verschambre, H.; Vocelle, D. *Can. J. Chem.* **1969**, *47*, 1981; (c) Nikolaev, V. A.; Frenkh, Yu.; Korobitsyna, I. K. *J. Org. Chem. USSR* **1978**, *14*, 1069.
30. Burla, M. C.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **2003**, *36*, 1103.
31. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.