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The first example of a domino Diels-Alder/retro-Diels-Alder reaction of 1,3-dienic δ-sultones with alkynes: a simple synthesis of *m*-terphenyl dicarboxy derivatives from 4,6-diphenyl-[1,2]oxathiine 2,2-dioxide

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[1,1′;3′,1″]Terphenyl-4′,5′-dicarboxylic acid derivatives were prepared from 1,3-dienic δ-sultone 4,6-diphenyl-[1,2]oxathiine 2,2-dioxide via Diels-Alder/retro-Diels-Alder reaction with dimethyl acetylenedicarboxylate under thermal, microwave or high-pressure activation.

Keywords: alkynes; sultones; Diels-Alder reaction; *m*-terphenyl derivatives; high pressure

1. Introduction

Benzene derivatives are important intermediates in the synthesis of bioactive natural products and functional materials. Since it is often complicated or impossible to achieve a desired product with required arrangement by the benzene core's substitution, it is essential to develop novel reactions leading to substituted benzenes. An attractive process in this respect is the domino Diels-Alder/retro-Diels-Alder reaction of α-2H-pyranones (*1–5*) or 1,2-diazines (*6*) with acetylene derivatives to provide substituted benzenes by elimination of either CO_2 or N_2, respectively. However, the corresponding transformation of δ-sultones embedding a 1,3-diene moiety, the sulfonic acid analog to α-2H-pyranones, has not been described yet. To the best of our knowledge, only one example of a Diels-Alder reaction of a 1,3-dienic δ-sultone has been reported. In this case, a highly substituted δ-sultone was converted into a complex macrocyclic benzene derivative in low yield, probably by a cycloaddition reaction with an intermediate enedione derived from another equivalent of this sultone (*7*).

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†X-ray diffraction analysis.

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2. Results

We have previously investigated a simple synthesis of the 1,3-dienic δ-sultone 4,6-diphenyl-[1,2]oxathiine 2,2-dioxide **1** using the new reaction of phenylacetylene with sulfuric acid or sulfur trioxide (*8*, *9*). As a consequence, sultone **1** became a rather available compound. In this work, we first demonstrate the possibility of converting sultone **1** as a 1,3-diene component into benzene derivatives via a domino Diels-Alder/retro-Diels-Alder reaction with acetylenes. To this end, sultone **1** was mixed with an excess of dimethyl acetylenedicarboxylate **2** (Figure 1, Table 1).

It is well known that microwave irradiation leads to reduced reaction times and increased product yields compared to classical heating methods in a number of published examples, especially for Diels-Alder reactions (*10–14*). High-pressure activation is also an effective method for the promotion of Diels-Alder reactions (*15*, *16*). Thus, the 1300 MPa intramolecular Diels-Alder cycloadditions in our recently published work were associated with higher product yields than the reflux/ambient pressure processes (*17–20*). Therefore, along with a purely thermal activation at atmospheric pressure, activation by microwave irradiation and also high pressure at room temperature were tested in this work.

Moreover, the structure of sultone **1** prepared earlier (*8*, *9*) was confirmed by X-ray-crystal structure analysis[1] (Figure 2).

We noticed that the pericyclic reaction does not run easily: a high amount of activation energy is needed to start the desired transformation. We did not observe any conversion in toluene under microwave irradiation at 110–120 °C after 30 min, but in the absence of solvent at 150°C the reaction gave the desired cycloaddition products [1,1′;3′,1″]terphenyl-4′,5′-dicarboxylic acid dimethyl ester **3** and [1,1′;3′,1″]terphenyl-4′,5′-dicarboxylic acid anhydride **4** in a total yield of 44% (Table 1) with complete conversion of sultone **1**. A decrease of the reaction time to 20 min combined with a larger excess of acetylene **2** in the mixture led to a total yield of 54%, also with 100% conversion of **1** and an equal ratio of **3** and **4**. A purely thermal activation without

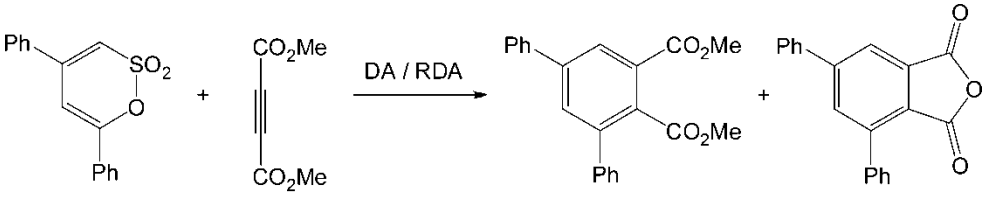

Figure 1. Diels-Alder/retro-Diels-Alder reaction of 4,6-diphenyl-[1,2]oxathiine 2,2-dioxide **1** with dimethyl acetylenedicarboxylate **2**.

Table 1. Diels-Alder/retro-Diels-Alder reaction of 4,6-diphenyl-[1,2]oxathiine 2,2-dioxide **1** with dimethyl acetylenedicarboxylate **2**.

	Ratio **1**:**2** (mol/mol)	Temperature (°C)	Reaction time	Solvent	Yield **3** + **4** (%)	Ratio **3**:**4** (mol/mol)
1	1:5	120[a]	30 min	toluene	0	–
2	1:5	150[a]	30 min	–	44	73:27
3	1:8	150[a]	20 min	–	54	74:26
4	1:8	150	18 h	–	55	60:40
5	1:8	25[b]	72 h	dichloromethane	67	100:0

Notes: [a]Microwave 100 W.
[b]Pressure 1300 MPa.

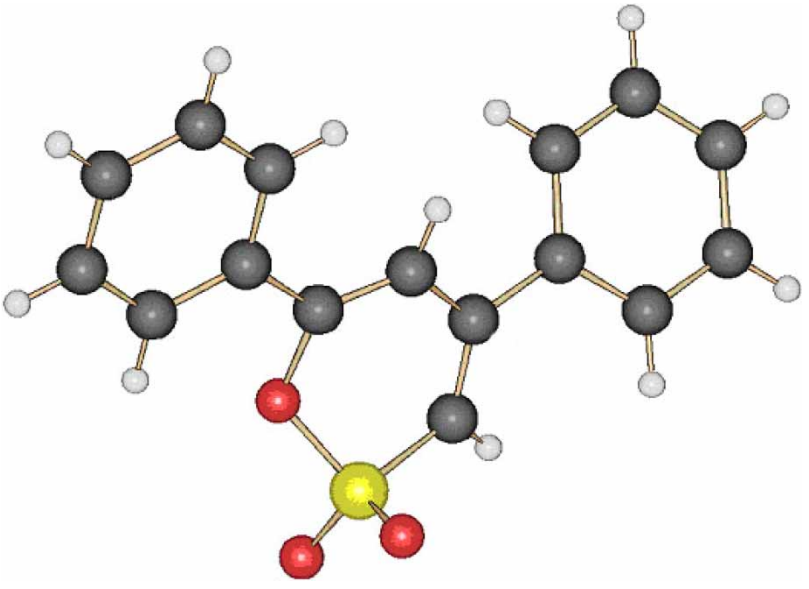

Figure 2. X-ray crystal structure of sultone **1**.

microwave irradiation, also without any solvent, provided **3** and **4** in a total yield of 55% after 18 h with an increase of the relative amount of anhydride **4**. The best yield of product **3** (67%) was achieved under high-pressure activation for three days. The reaction occurred in dichloromethane at room temperature with complete conversion of sultone **1**. Under these conditions, side reactions were largely suppressed, leading to a significantly higher yield of **3**, while anhydride **4** was not observed at all.

In conclusion, the first example of a domino Diels-Alder/retro-Diels-Alder reaction of a 1,3-dienic δ-sultone is reported. [1,1′;3′,1″]Terphenyl-4′,5′-dicarboxylic acid derivatives are prepared from 4,6-diphenyl-[1,2]oxathiine 2,2-dioxide and dimethyl acetylenedicarboxylate under thermal, microwave or high-pressure conditions. Further preparations of new 1,3-dienic sultones and highly substituted *m*-terphenyl derivatives will be reported in due course.

3. Experimental section

3.1. *General procedures*

Starting sultone **1** has been synthesized according to our method (*8*, *9*). All commercially available compounds were used as received unless stated otherwise. Flash chromatography: Merck silica gel 60 (40–63 μm). Thin-layer chromatography: Merck silica gel 60 F254 plates with UV detection of the spots. Solvent mixtures for chromatography are reported as vol/vol ratios. Melting points: Kleinfeld Labortechnik Electrothermal IA 9100 apparatus. ^{1}H and ^{13}C NMR: Bruker DRX-500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, $CDCl_3$, δ, ppm, calibrated to the residual resonance of the solvent, s = singlet, d = doublet, t = triplet, m = multiplet). FT-IR spectra: Nicolet 205 and Nicolet Avatar 360 spectrometer (ν, cm^{-1}, s = strong, m = middle, w = weak, br = broad). Mass spectra: HP 1100 – Bruker Esquire Ion Trap (ESI/APCI, m/z, U = 10–50 V). Elemental analysis: Carlo Erba Instruments EA 1108 and Hekatech EA 3000. Hofer high-pressure apparatus (hydraulic press) up to 1400 MPa. Microwave apparatus CEM Discover System, model 908010.

3.2. *X-ray crystallography*

The data set for sultone **1** was collected with a Nonius KappaCCD diffractometer equipped with a molybdenum fine-focus sealed tube. Programs used: COLLECT (*21*) for the data collection; Dirax/lsq (*22*) for the cell refinement; EvalCCD (*23*) for the data reduction; SHELXS-97 (*24*) for the structure solution; SHELXL-97 (*25*) for the structure refinement; Schakal-99 (*26*) for graphics.

3.3. *Crystal data for sultone* **1**

$C_{16}H_{12}O_3S$, M = 284.32, colorless crystal 0.65 × 0.26 × 0.12 mm, triclinic, space group *P1bar*, $a = 9.075(1)$, $b = 9.416(1)$, $c = 9.799(1)$ Å, $\alpha = 80.37(1)$, $\beta = 62.55(1)$, $\gamma = 63.41(1)°$, $V = 663.6(1)$ Å^3, $Z = 2$, $D_{calc} = 1.423\,g\,cm^{-3}$, $\mu = 2.47\,mm^{-1}$, $T = 195\,K$, $\lambda = 0.71073$ Å, 22459 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\Theta)/\lambda] = 0.70$ Å^{-1}, 3758 independent ($R_{int} = 0.020$), 3229 observed reflections [$I \geq 2\sigma(I)$], 193 refined parameters, $R = 0.035$, $wR_2 = 0.096$, maximal residual electron density 0.34 $(-0.33)e$ Å^{-3}, hydrogen calculated and refined as riding atoms.

3.4. *Diels-Alder/retro-Diels-Alder reaction of 4,6-diphenyl-[1,2]oxathiine 2,2-dioxide* **1** *with dimethyl acetylenedicarboxylate* **2** *under microwave activation*

Sultone **1** (100 mg, 0.352 mmol) was placed into a microwave test tube, and the respective amount of dimethyl acetylenedicarboxylate **2** was added. The resulting suspension was placed in a microwave apparatus and exposed to the radiation according to the conditions listed in Table 1 with 5 min starting time and external cooling with nitrogen gas. The resulting red-brown highly viscous crude product mixture was purified by flash chromatography (silica gel, pentane/ethyl acetate 5:1 for product **4**, 2:1 for product **3**) under TLC control. CAUTION: Product **3** can be easily confused with sultone **1** on TLC.

3.5. *Diels-Alder/retro-Diels-Alder reaction of 4,6-diphenyl-[1,2]oxathiine 2,2-dioxide* **1** *with dimethyl acetylenedicarboxylate* **2** *under high-pressure activation*

A solution of sultone **1** (100 mg, 0.352 mmol) in dichloromethane (10 mL) was transferred to a Teflon® high-pressure test tube, and dimethyl acetylenedicarboxylate **2** (390 mg, 2.75 mmol) was added. The test tube was closed, inserted into the high-pressure apparatus, and subjected to a pressure of 1300 MPa at room temperature for 72 h. Then the high pressure was relieved, and the solvent was removed at reduced pressure. Product **3** was isolated from the resulting red-brown highly viscous mixture by flash chromatography with pentane/ethyl acetate (5:1 → 2:1) under TLC control.

3.6. *Diels-Alder/retro-Diels-Alder reaction of 4,6-diphenyl-[1,2]oxathiine 2,2-dioxide* **1** *with dimethyl acetylenedicarboxylate* **2** *under thermal activation*

Sultone **1** (100 mg, 0.352 mol) was placed into a 5 mL round bottom flask, and dimethyl acetylenedicarboxylate **2** (390 mg, 2.75 mmol) was added. The resulting suspension was stirred for 18 h at 150 °C oil-bath temperature under an argon atmosphere. The resulting red-brown highly viscous mixture solidified when it was cooled to room temperature. It was purified by flash chromatography with pentane/ethyl acetate (5:1 for product **4**, 2:1 for product **3**) under TLC control.

3.6.1. *[1,1′;3′,1″]Terphenyl-4′,5′-dicarboxylic acid dimethyl ester* **3**

A $R_f = 0.26$ (pentane/ethyl acetate 5:1), slowly crystallizing light yellow oil, mp 75–77 °C (lit. (*14*): light yellow oil). ^{1}H NMR: 3.70 (s, 3H), 3.84 (s, 3H), 7.39–7.45 (m, 6H), 7.46–7.49 (m, 2H), 7.64–7.66 (m, 2H), 7.78 (d, $J = 1.8$ Hz, 1H), 8.24 (d, $J = 1.8$ Hz, 1H). ^{13}C NMR: 52.23 (CH_3), 52.65 (CH_3), 127.18 (CH), 127.44 (CH), 127.95 (CH), 128.26 (CH), 128.31 (CH), 128.56 (CH), 128.73 (C), 128.97 (CH), 132.65 (CH), 133.32 (C), 139.01 (C), 139.22 (C), 141.14 (C), 142.17 (C), 166.15 (CO), 166.22 (CO). MS (ESI): 347 $[M + H]^+$, 710 $[2M + NH_4]^+$, 715 $[2M + Na]^+$. IR: 636 (m), 697 (s), 744 (s), 760 (s), 781 (m), 794 (m), 844 (w), 896 (m), 973 (m), 1000 (w), 1058 (m), 1070 (s), 1118 (s), 1199 (s), 1237 (s, br), 1266 (s, br), 1341 (m), 1372 (w), 1429 (m), 1463 (m), 1497 (w), 1598 (m), 1724 (s, br), 2849 (w), 2950 (w), 3033 (w), 3062 (w). Elemental analysis, %: calcd. for $C_{22}H_{18}O_4$: C 76.29, H 5.24; found: C 76.19, H 5.36.

3.6.2. *[1,1′;3′,1″]Terphenyl-4′,5′-dicarboxylic acid anhydride* **4**

A $R_f = 0.44$ (pentane/ethyl acetate 5:1), pale yellow solid, mp 172–173 °C (lit. (*27*): mp 176–177 °C). ^{1}H NMR: 7.49–7.56 (m, 6H), 7.62–7.64 (m, 2H), 7.68–7.71 (m, 2H), 8.03 (d, $J = 1.5$ Hz, 1H), 8.19 (d, $J = 1.5$ Hz, 1H). ^{13}C NMR: 122.63 (CH), 125.09 (C), 127.49 (CH), 128.56 (CH), 129.23 (CH), 129.42 (CH), 129.49 (CH), 129.62 (CH), 133.37 (C), 135.01 (C), 136.16 (CH), 137.93 (C), 143.64 (C), 149.46 (C), 161.90 (CO), 162.95 (CO). MS (ESI): 301 $[M + H]^+$, 318 $[M + NH_4]^+$. IR: 637 (m), 684 (s), 697 (s), 735 (s), 762 (s), 848 (m), 891 (s), 907 (s), 1025 (m), 1078 (m), 1130 (m), 1185 (m), 1206 (m), 1230 (s), 1257 (m), 1356 (m), 1387 (w), 1443 (m), 1453 (m), 1466 (m), 1496 (w), 1575 (m), 1614 (m), 1765 (s, br), 1801 (m), 1843 (m), 2853 (w, br), 2922 (w, br), 3033 (w), 3058 (w, br). Elemental analysis, %: calcd. for $C_{20}H_{12}O_3$: C 79.99, H 4.03; found: C 79.49, H 4.31.

Acknowledgements

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Note

1. Crystallographic data for the structure **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 693463.

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