# Communications

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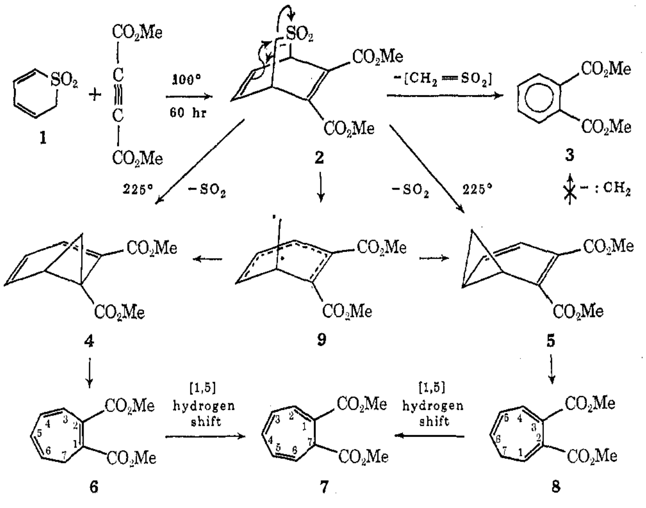
## Cycloheptatriene Derivatives from a 2,2-Dioxido-2-thiabicyclo[2.2.2]-octa-5,7-diene

*Summary:* Thermolysis of dimethyl 2,2-dioxido-2-thiabicyclo[2.2.2]octa-5,7-diene-5,6-dicarboxylate at 220° provides in a sulfur dioxide extrusion–rearrangement reaction a mixture of dimethyl cycloheptatriene-1,2-, -2,3-, -1,7-dicarboxylates and, in a retro Diels–Alder reaction under the loss of sulfene, dimethyl phthalate.

*Sir:* The generation of sulfene ($CH_2{=}SO_2$) by dehydrohalogenation of methanesulfonyl chloride with tertiary amines has the disadvantage that, in the absence of reactive partners such as strongly nucleophilic olefins[1,2] or diazoalkanes,[1,3,4] the components form sulfonyl chloride–amine adducts[5,6] or sulfene–trialkylamine adducts.[7] We considered as a possible route for the formation of a nonstabilized sulfene thermolysis of dimethyl 2,2-dioxido-2-thiabicyclo[2.2.2]octa-5,7-diene-5,6-dicarboxylate (**2**) which in a retro Diels-Alder reaction was expected to liberate sulfene and dimethyl phthalate as the only coproduct.



Recently, King and Lewars[8] reported the thermolysis of the 4-phenyl derivative of **2** to give dimethyl biphenyl-2,3-dicarboxylate and sulfene which was detected by trapping experiments with an enamine and amine. Thermolysis of the bicyclic sulfone without a reaction partner also gave high yields of dimethyl biphenyl-2,3-dicarboxylate and sulfur dioxide. The authors discussed as a possible route initial formation of sulfene and subsequent reactions leading to sulfur dioxide and unidentified methylene fragments. The present communication describes preliminary results on the thermolysis of sulfone **2** which undergoes a sulfur dioxide extrusion–rearrangement. The reaction represents a useful extension of the thermal rearrangement of allylic sulfones[9] to bicyclic analogs.

Heating of α-thiopyran 1,1-dioxide (**1**)[10] with dimethyl acetylenedicarboxylate at 100° for 60 hr gave 60% **2**: mp 108–110°; $\lambda_{\max}^{\mathrm{MeOH}}$ 239 nm ($\epsilon$ 3.86 × $10^3$); $m/e$ 272 ($M^+$), 149 (base peak); $\nu_{\max}^{\mathrm{KBr}}$ 1755, 1652, 1656, 1305, 1155 cm$^{-1}$; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 2.76 (m, 2 H, $CH_2SO_2$), 3.85 (s, 6 H, $CO_2Me$), 4.32 (br dq, 1 H, $J$ = 3.0, 5.5 Hz, $CHCH_2SO_2$), 5.06 (dd, 1 H, $J$ = 2.0, 5.5 Hz, $CHSO_2$), 6.67 (m, 2 H, CH=CH). Thermolysis of **2** at 230° for 10 min with 1-morpholinocyclohexene gave <5% sulfene cycloaddition product.[1,8] Thermolysis of **2**, neat or in THF, for 10 min at 220–225° resulted in a mixture of several compounds. Samples from the gas phase of the thermolysis tube showed on gas chromatographic–mass spectral (gc–ms) analysis (8-ft Porapak S column) only one component with major peaks at $m/e$ (rel intensity) 66 (4.9), 64, (100), 48 (49), and 38 (11); the mass spectrum was identical with that of sulfur dioxide. The gc–ms analysis of the crude oil on a 12-ft SE-30 column isothermal at 200° gave one well-resolved peak followed by a minor and a major broad peak. The mass spectrum (70 eV) [$m/e$ (rel intensity) 194 (10), 77 (100)] of the first eluted component was identical with that of dimethyl phthalate (**3**). The other two gc bands exhibited highly similar mass spectral patterns showing parent peaks at $m/e$ 208 ($C_{11}H_{12}O_4^+$) and intense peaks at $m/e$ 149 (base peak) and 91. The mass spectral fragments at $m/e$ 149 and 91 indicated methyltropylium carboxylate ions ($C_9H_9O_2^+$) and tropylium ions ($C_7H_7^+$), respectively.

Column chromatography (silica gel–benzene) of the crude mixture resulted in a partial separation and an enrichment of the different components. Purified samples[11] which were essentially free of **3** showed uv absorptions at $\lambda_{\max}^{\mathrm{MeOH}}$ 211 and 275 nm and ir bands at 2945 (m), 1725 (s), 1620 (m), 1440 (s), 1260 (s), 1125 (s), and 1060 (s) cm$^{-1}$. The above uv and ir spectral parameters are in good agreement with data reported in the literature[12,13] for cycloheptatrienecarboxylates, strongly suggesting dimethyl cycloheptatrienedicarboxylates in the thermolysis mixture obtained from **2**.

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[8] J. F. King and E. G. Lewars, *J. Chem. Soc., Chem. Commun.*, 700 (1972).

[9] E. M. LaCombe and B. Stewart, *J. Amer. Chem. Soc.* **83**, 3457 (1961).

[10] E. Molenaar and J. Strating, *Recl. Trav. Chim. Pays-Bas.*, **86**, 1047 (1967).

[11] A mixture of **6**, **7**, and **8** gave elemental analyses satisfactory for $C_{11}H_{12}O_4$.

[12] H. Prinzbach and R. Schwesinger, *Angew. Chem. Int. Ed. Engl.*, **11**, 940 (1972).

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Structural assignments and compositional analyses of the components were made by inspection of increasing and decreasing nmr signals in spectra obtained from different column chromatography fractions. The nmr structural assignments[14] were verified by double irradiation experiments. Initial fractions contained a mixture of dimethyl phthalate (**3**) and dimethyl cycloheptatriene-1,2-dicarboxylate (**6**): $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 2.52 (d, 2 H, $J$ = 7.0 Hz, C-7 protons), 3.79 (s, 3 H, $CO_2Me$), 3.81 (s, 3 H, $CO_2Me$), 5.48 (dt, 1 H, $J$ = 8.8, 7.0 Hz, C-6 proton), 6.33 (dt, 1 H, $J$ = 8.8, 3.0 Hz, C-5 proton), 6.82 (br d, 2 H, $J$ = 3.0 Hz, C-3 and C-4 protons). Subsequent fractions provided increasing amounts of dimethyl cycloheptatriene-1,7-dicarboxylate (**7**) [$\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.61 (s, 3 H, $CO_2Me$), 3.81 (s, 3 H, COOMe), 4.18 (d, 1 H, $J$ = 8.0 Hz, C-7 proton), 5.91 (br dd, 1 H, $J$ = 8.0, 10 Hz, C-6 proton), 6.42 (br dd, 1 H, $J$ = 10, 6 Hz, C-5 proton), 6.64 (br dd, 1 H, $J$ = 10, 6.0 Hz, C-3 proton), 6.84 (dd, 1 H, $J$ = 10, 6 Hz, C-4 proton), 7.38 (br d, 1 H, $J$ = 6.0 Hz, C-2 proton)] and dimethyl cycloheptatriene-2,3-dicarboxylate (**8**) [$\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 2.45 (dd, 2 H, $J$ = 6.5, 7.5 Hz, C-7 protons), 3.74 (s, 3 H, $CO_2Me$), 3.82 (s, 3 H, $CO_2Me$), 5.86 (dt, 1 H, $J$ = 9.5, 7 Hz, C-6 proton), 6.35 (dd, 1 H, $J$ = 9.5, 5.5 Hz, C-5 proton), 6.52 (t, 1 H, $J$ = 7.5 Hz, C-1 proton), 7.65 (d, 1 H, $J$ = 5.5 Hz, C-4 proton)]. The fourth possible isomer, dimethyl cycloheptatriene-3,4-dicarboxylate,[12] was not detected. Integration of the carbomethoxy region in the nmr spectrum of the crude thermolysis mixture of **2** showed the following composition: **3** (24%), **6** (18%), **7** (27%), and **8** (31%). Thermolysis of a mixture of **3** (28%), **6** (33%), **7** (29%), and **8** (10%) at 220–225° for 1 hr resulted in an increase of **8** (33%) at the expense of compound **6** (7%) whereas the amount of **7** (30%) and **3** (30%) remained practically constant. Heating of a mixture of **3** (11%), **6** (19%), **7** (29%), and **8** (44%) gave a similar relative ratio of cycloheptatriene derivatives as in the previous reaction, indicating that the **6**, **7**, and **8** readily interconvert at 220°. In all cases, equilibrium was already established after 20 min at 220°.

The formation of compounds **3**, **6**, **7**, and **8** from **2** is of considerable mechanistic interest. A possible formation of the cycloheptatriene derivatives **6–8** from **2** could proceed under extrustion of sulfur dioxide to give first diradical **9** followed by a collapse to the norcaradiene derivatives **4** and **5**. The reaction could also involve initial formation of dimethyl norborna-2,5-diene-2,3-dicarboxylate. When the latter was thermolyzed under the same conditions as described for **2**, the starting material was recovered exclusively, thus excluding dimethyl norborna-2,5-diene-2,3-dicarboxylate as an intermediate in the formation of compounds **6** to **8**. Another attractive mechanism would be a linear $[{}_{\pi}2_{a} + {}_{\sigma}2_{a} + {}_{\sigma}2_{s}]$ or nonlinear $[{}_{\pi}2_{s} + {}_{\sigma}2_{a} + {}_{\sigma}2_{a}]$ cheletropic sulfur dioxide extrustion–rearrangement reaction (shown for conversion of **2** to **5**) also leading to the norcaradiene intermediates **4** and **5**. From the latter, cycloheptatriene derivatives **6** and **8** would be derived by skeletal rearrangements followed by [1,5]-hydrogen shifts to give **7**.

The formation of **3** may be formulated either as a sulfene extrusion reaction from **2** or possibly as a carbene extrusion reaction of intermediates **4** and **5**. Examples for the loss of carbene from cycloheptatriene derivatives *via* norcaradienes have been described in the literature.[15] Thermolysis of **2** in the presence of cyclododecene as a carbene acceptor as well as prolonged heating of a mixture of **3**, **6**, **7**, and **8** did not result in an increase of **3**. Thus, formation of **3** from intermediates **4** and **5** by a carbene transfer reaction seems to be an unlikely route. The experimental data indicate that in the thermolysis of **2** two independent processes are competing: sulfur dioxide extrusion leading to cycloheptatrienes **6**, **7**, and **8** represents the predominant route, whereas retro Diels–Alder reaction which liberates sulfene from **2** is energetically less favored at 220°. The presence of a phenyl group at C-4 in the thermolysis of the bicyclic sulfone can essentially suppress norcaradiene formation and force the reaction to proceed *via* the sulfene route exclusively.[8] The fate of methylene fragments, possibly derived from sulfene, is not clear. Minor nmr signals typical for cyclopropane ring protons at about δ 0.5 were observed in a short-time thermolysis of **2** at 220°, but were not detected in the 10-min reactions. These signals could be due to thermally labile, sulfene-derived, methylene transfer products. Present investigations are oriented toward the study of the electronic and/or steric influence of different substituents on the two competing processes as well as synthetic aspects of the previously described sulfur dioxide extrustion–rearrangement reaction.

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[14] The chemical shifts for compounds **7** and **8** which were determined in $CDCl_3$ differ by 0.05 to 0.15 ppm from the reported parameters[12] which were obtained in $CCl_4$.

[15] A. P. Ter Borg, E. Razenberg, and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas.*, **85**, 774 (1966).

[16] Detailed experimental data on the synthesis of α-thiopyran 1,1-dioxide will be described in a coauthored full paper.

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## The Preparation of Enamines by Addition of Grignard Reagents to *N,N*-Dialkylformamides

*Summary:* The reaction of *N,N*-dialkylformamides with alkylmagnesium bromides, unlike the corresponding reaction with lithium alkyls, gives a primary addition product which undergoes spontaneous elimination forming an enamine in preparatively useful yield.

*Sir:* We have found that the reaction of Grignard reagents with readily available *N,N*-dialkylformamides affords a method of wide applicability for the preparation of aldehyde enamines (Scheme I). The reaction is particularly suited for the preparation of enamines **4** where R′ = alkyl, R″ = H, and R is a bulky substituent such as secondary alkyl. Enamines of this