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SO-Photoextrusion of 7-Thiabicyclo[2.2.1]hept-2-ene 7-Oxides[##]

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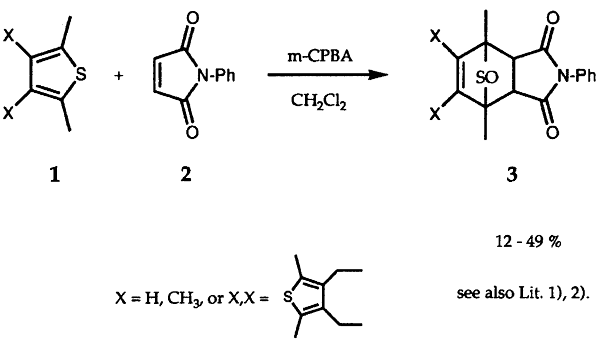
The photoextrusion of the SO-bridge of 7-thiabicyclo[2.2.1]hept-2-ene 7-oxides is discussed. An analysis of all the major by-products in the exemplary case of the photo reaction of **3a** is given. The existence of intermediate dienes **4** has been established. Data on a comparative photoextrusion of an epithio-bridge of 7-thiabicyclo[2.2.1]-hept-2-ene (**6**) are provided.

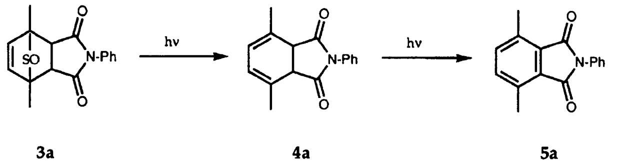
Oxidized thiabicyclo[2.2.1]heptene systems of type **3** can be easily obtained by the oxidative cycloaddition of thiophenes to maleimides(1) (Scheme 1). This mild cycloaddition reaction, which proceeds even at temperatures as low as 0 °C, has been recently applied to cyclothiophenophanes(2) and thiopheno crown ethers.(3) Especially from the viewpoint of the preparation of novel cyclophanes, it was of importance to find an effective method for extruding the sulfinyl-bridge at low temperatures, preferably with a concurrent oxidation step to yield the corresponding aromatic systems. The thermally induced extrusion of SO can be achieved only at higher temperatures of between 180 °C (for **3a**) and 250 °C (for **3b**).(2) Reports on photochemical SO-extrusion reactions at room temperature(4) prompted us to look at the photochemical behaviour of the thiabicyclo[2.2.1]heptene oxides, **3a**—**3c**.

Results and Discussion

When **3a** is irradiated in either dichloromethane or benzene with or without a sensitizer, two products are formed (Scheme 2). One is the arene **5a**, which can easily be isolated from the reaction mixture. The other is not as easily separable from the irradiated solution, since its concentration decreases with the irradiation time. From the NMR-spectrum of the reaction mixture we deduced this latter product to be the diene **4a**. The diene can be synthesized independently from **3a** by treating **3a** with tributyltin hydride in refluxing benzene (Scheme 3). This method is known to reduce sulfoxides to sulfides;(5) in this case, however, no sulfide was observed. The synthesized product proved to be identical with the second photoproduct.

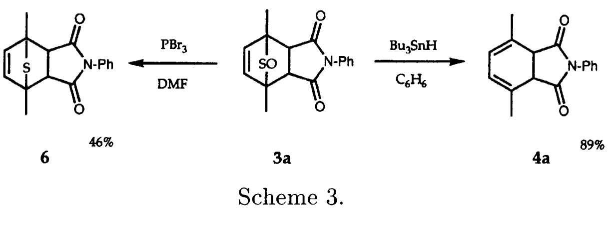


Scheme 1.



Scheme 2.

It is believed that the diene **4a** is an intermediate in the photoextrusion/oxidation reaction and that the extruded sulfur monoxide (SO) oxidizes the diene **4a** to the arene **5a**. The ground electronic state of SO is a triplet ($X^3\Sigma^-$) and the molecule has electronic excited states, ($a^1\Delta$) and ($b^1\Sigma^+$), 17.6 and 30.0 kcal mol^{-1} above its ground state.(6) Work on the photochemical dissociation of thietane S-oxide has shown that direct photolysis produces SO ($a^1\Delta$), while sensitizing the reaction [with Hg($^3P_1$)] produces the ground electronic state SO ($X^3\Sigma^-$).(7) On the other hand, the mercury lamp used in our photoreaction would also provide a suitable energy for the transition of SO ($X^3\Sigma^-$) to SO ($a^1\Delta$) (5862 cm^{-1}). SO ($a^1\Delta$), however, is rapidly deactivated to SO ($X^3\Sigma^-$) through collisions.(8) Due to its reactivity/deactivation only chemical experiments of SO ($a^1\Delta$) in a rare-gas matrix have been carried out.(9) While SO ($X^3\Sigma^-$) is also known to have only a very short lifetime in solution, SO ($X^3\Sigma^-$) generated in solution by the thermolysis of thiirane S-oxide(10,11) has



Scheme 3.

[##] Part of this work was presented at the 66th Annual Spring Meeting of the Chemical Society of Japan (Abstr., No. 3P 79, March 1993).

been used in cycloadditions; further, SO has been introduced as a ligand in a metal complex by the photoirradiation of thiirane S-oxide.[12] Nevertheless, in the present case no definite conclusion can be reached as to whether SO ($X^3\Sigma^-$) or SO ($a^1\Delta$) is responsible for the transformation of **3a** to **5a**.[13] The diene **4a** without an additional oxidizing agent also yields some arene upon photoirradiation; this reaction, however, in the case of the diene alone, is more complex and does not account for the selective transformation of **3a** to **5a**.

The influence of the solvent polarity, sensitization and excitation wavelength on the yield and nature of the photo-products was investigated. Figures 1, 2, 3, and 4 show the results of the photoirradiation of **3a** in different solvents and in the presence of sensitizers using different glass-types. When **3a** is irradiated directly at $\lambda > 300$ nm (dichloromethane as solvent), no SO-extrusion takes place, which is not surprising, since **3a** shows no appreciable absorption at $\lambda > 300$ nm ($\lambda_{\max}$ (**3a**)=228 nm). When benzophenone is added as a sensitizer, **3a** does react to give the arene **5a** and the diene **4a** (Fig. 1). In this case the diene is quite stable and no side products are formed. The photolysis of **3a** in dichloromethane ($\lambda > 222$ nm, Fig. 2) leads to a good turnover of the starting material, giving **5a** in high yield. In this case the concentration of the diene as an intermediate is lower than that found in the irradiation of **3a** at $\lambda > 300$ nm (dichloromethane as solvent) with a sensitizer. No other products were formed in the photolysis of **3a** in dichloromethane with or without a sensitizer, even after a long irradiation time ($t > 16$ h). Using benzene as a solvent in direct irradiation (Fig. 3) leads to a smaller amount of the aromatized product and to the formation of side products (vide infra). These side products can be suppressed when a solution of **3a** in

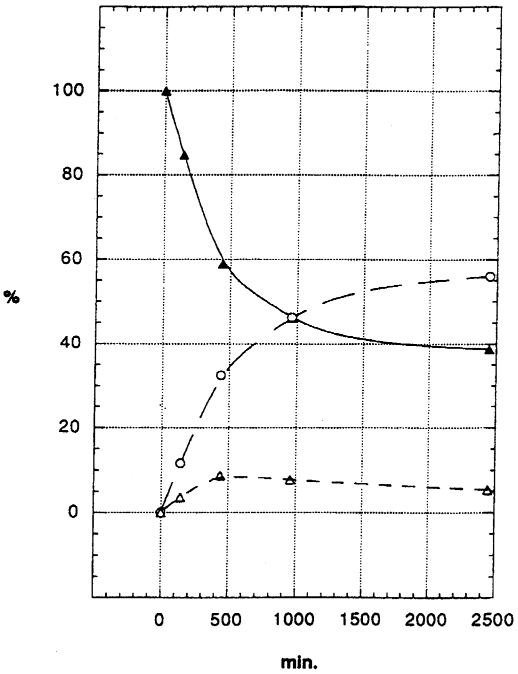


Fig. 1. Photochemical SO-extrusion of **3a**. Distribution of products as a function of reaction time. CD_2Cl_2, sensitizer: benzophenone, $\lambda > 300$ nm. -▲- **3a**; -△- **4a**; -O- **5a**.

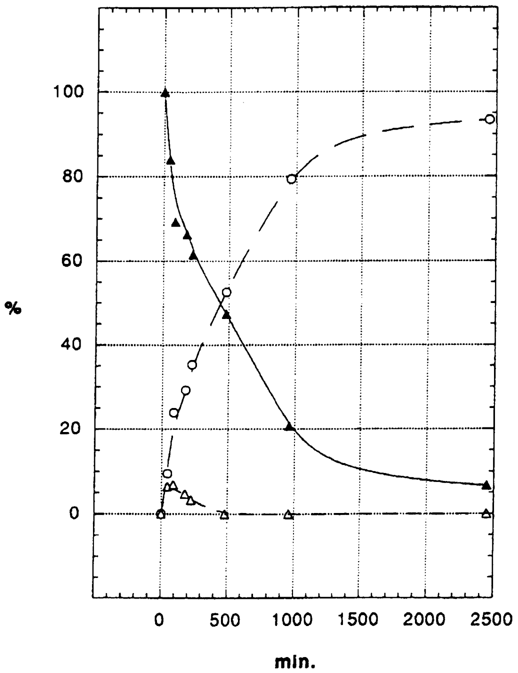


Fig. 2. Photochemical SO-extrusion of **3a**. Distribution of products as a function of reaction time. CD_2Cl_2, no sensitizer, $\lambda > 222$ nm. -▲- **3a**; -△- **4a**; -O- **5a**.

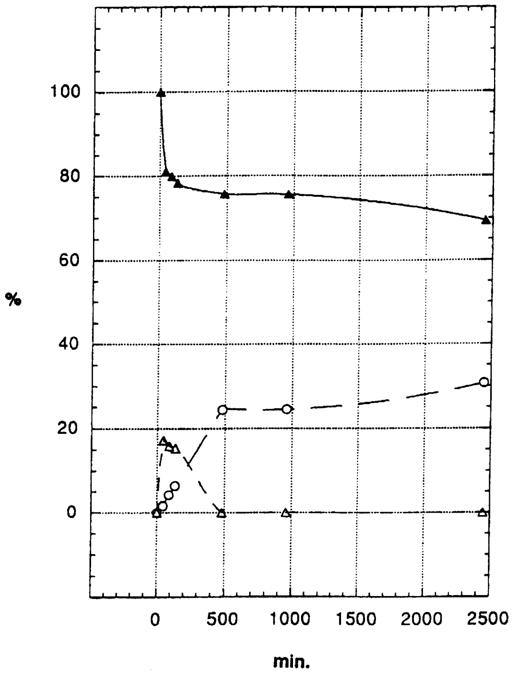


Fig. 3. Photochemical SO-extrusion of **3a**. Distribution of products as a function of reaction time. C_6D_6, no sensitizer, $\lambda > 222$ nm. -▲- **3a**; -△- **4a**; -O- **5a**.

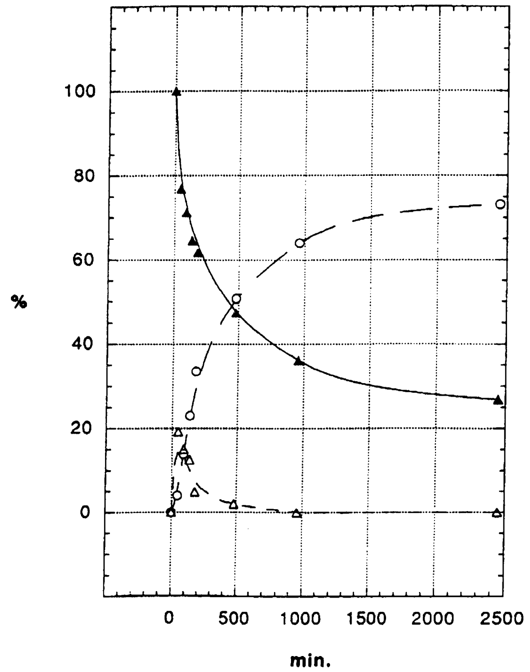


Fig. 4. Photochemical SO-extrusion of **3a**. Distribution of products as a function of reaction time. C_6D_6, sensitizer: benzophenone, $\lambda > 222$ nm. -▲- **3a**; -△- **4a**; -○- **5a**.

benzene is irradiated in the presence of benzophenone as a sensitizer. In this case (Fig. 4) the yield of **5a** is higher than in the direct photolysis of **3a** in the same solvent, but lower than in photolysis without a sensitizer, using dichloromethane as a solvent. This 'heavy-atom-effect' is a hint that **5a** is formed via a triplet-state.[14)]

The optimal condition for the preparation of **5a** is therefore the photolysis of **3a** in dichloromethane at wavelengths greater than 222 nm (80% yield of **5a** after 16 h irradiation).

A long irradiation time (16 h), using benzene as a solvent, resulted in the formation of several minor photo products, which by the end of the reaction comprised about 25 per cent of the total amount of product. Since the diene was present in the reaction mixture throughout the photolysis, albeit in low concentration, and some of the sulphur monoxide may have been lost during the reaction, we deduced that these side-products must have originated from the diene, which was less readily oxidized to **5a** during the later stages of photolysis.

Upon irradiation (minimum irradiation time 3 h $\lambda >$ 222 nm, benzene) pure diene **4a**, itself, yields 6 major products, which are identical with the minor products formed in the photolysis of **3a** for long reaction times (16 h, $\lambda > 222$ nm, benzene). The photochemical behavior of similar structures as **3a**, such as dihydrophthalimides,[15,16)] dihydrophthalic anhydrides,[17)] and thioanhydrides,[18)] has already been the object of intensive study. Photoproducts **7a/b** (stereochemistry was not assigned), **9**, and **11** with corresponding, differing substitution patterns and/or functionalities have already been observed in some cases (Scheme 4). In the photolysis of **4a** we found two additional products, **8** and **10**. The photolysis of the diene with benzophenone in benzene leads to a smaller amount of side products, as compared to direct irradiation in benzene.

From the ^{1}H and ^{13}C NMR spectra it could be deduced that **10** most probably is of C_2-symmetry, having only half a set of signals, thus, for example, exhibiting only one signal for both methyl groups. The mass spectrum showed **10** to be a monomer. On the other hand, some of the protons ($H_{1,4}$, $H_{6,8}$) exhibited a very complicated coupling behavior. The ^{1}H COSY spectrum of **10** revealed that, despite the complexity of the signal, $H_{6,8}$ has only one coupling partner ($H_{1,4}$), apart from showing a long-range coupling with the methyl groups. This, along with mechanistic considerations, which are given below, led to a 3-aza-bicyclo[3.2.2]nonane structure for **10**. $H_{1,4}$ thus couples with $H_{6,8}$ via a ^3J- and a ^4J-coupling. The structure of **10** was later confirmed by X-ray crystallography (Fig. 5)(Table 1).

The structure of the cyclopropane-containing compound **8** was ascertained with the help of an ^{1}H COSY experiment. One of the cyclopropyl-protons showed a coupling to the olefinic proton; the other cyclopropyl-proton coupled with the proton of C-2. No cross-peak was observed for coupling ($J \geq 1.5$ Hz) between (C-2)–H and the olefinic proton, thus ruling out another possible cyclopropane-containing structure that would have been formed by mechanism route 2 (see Scheme 5).

The mechanistic pathways to such products as **5,7/b**, **9**, and **11** have been previously elaborated.[16)] The bond between the imido carbonyl and the bridge-head carbon in the phthalimide moiety is cleaved homolytically. The ensuing carbonyl radical can then add to either end of the two double bonds of the cyclohexadiene moiety; four ways of addition thus become possible (marked 1—4 in Scheme 5). Two modes of addition formally lead to 1,3-biradicals, which upon combination generate a cy-

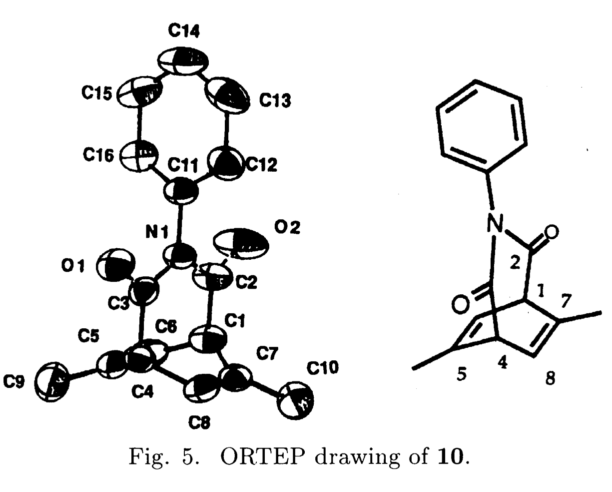
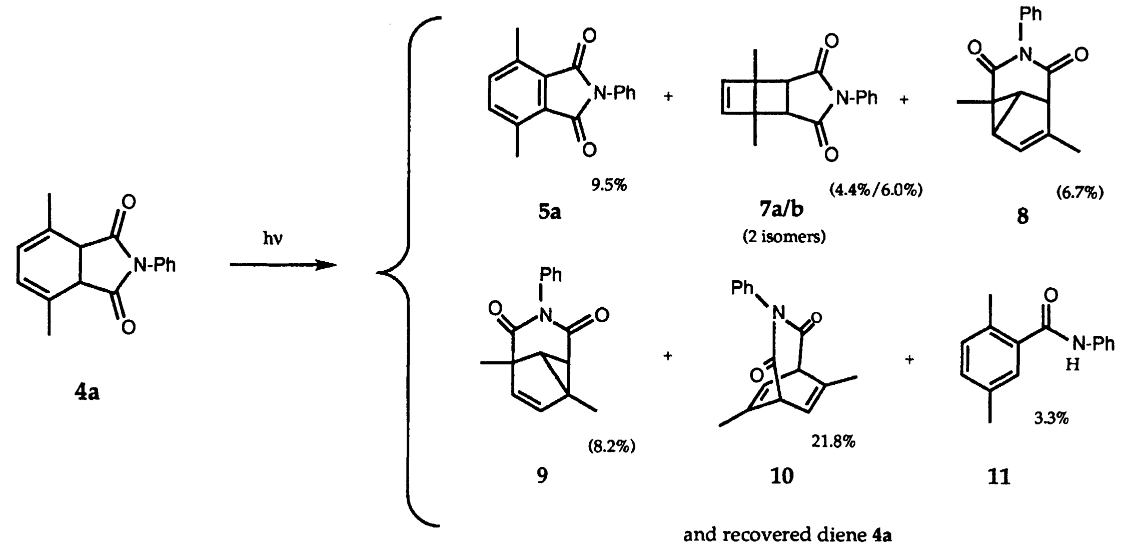


Fig. 5. ORTEP drawing of **10**.



Scheme 4.

Table 1. Selected Bond Length (l/Å) and Bond and Dihedral Angles (ϕ/°) of **10**

C(1)–C(2)	1.521(4)
C(1)–C(6)	1.498(5)
C(1)–C(7)	1.518(3)
C(5)–C(6)	1.309(4)
C(7)–C(10)	1.480(4)
C(2)–N(1)	1.410(3)
C(1)–C(6)–C(5)	118.4(3)
C(1)–C(7)–C(10)	119.0(2)
C(2)–C(1)–C(7)	107.9(2)
C(6)–C(1)–C(7)	110.8(2)
C(8)–C(7)–C(10)	126.6(2)
C(7)–C(1)–C(6)–C(5)	43.94(0.36)
C(2)–C(1)–C(7)–C(8)	77.70(0.29)
C(2)–N(1)–C(11)–C(12)	−88.40(0.30)
C(3)–N(1)–C(2)–C(1)	6.27(0.40)

clopropyl substructure (products **8** and **9** of which could be isolated); one addition formally leads to a 1,4-diradical (**13**), the direct combination product of which has not been found; the other addition formally leads to a 1,2-biradical, which combines to give the cyclohexadiene **10**.

Irradiation of the tetramethyl-substituted **3b** and the orthocyclophane **3c**[2)] in the presence of benzophenone (dichloromethane, $\lambda>300$ nm) gives the corresponding aromatized products, **5b** and **5c** (Figs. 6 and 7). In both cases, the formation of dienes could be observed during the photolysis. Arenes **5b** and **5c** were the only reaction products after long irradiation (Scheme 6). Of the three starting materials (**3a**, **3b**, and **3c**), the tetramethyl substituted **3b** extrudes SO most readily, while the cyclophane **3c** extrudes SO only very slowly.

The sulfoxide **3a** can easily be reduced to the sulfide **6** with PBr_3[19)] in dry DMF (Scheme 3). Upon photo irradiation of **6** in benzene the sulfide-bridge is ex-

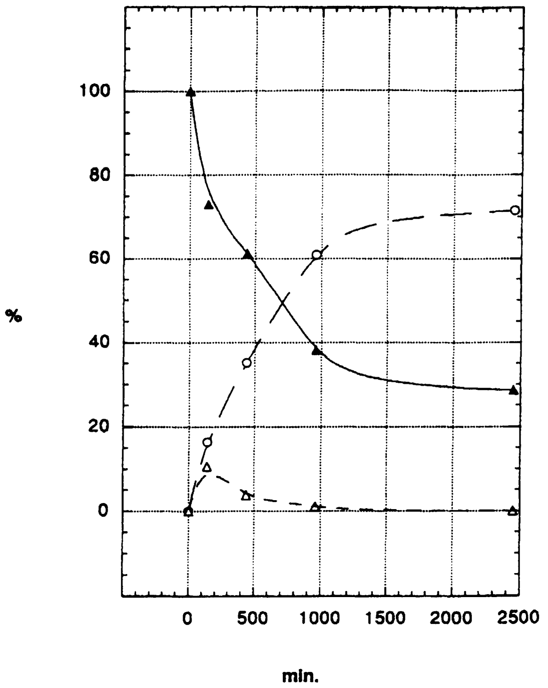
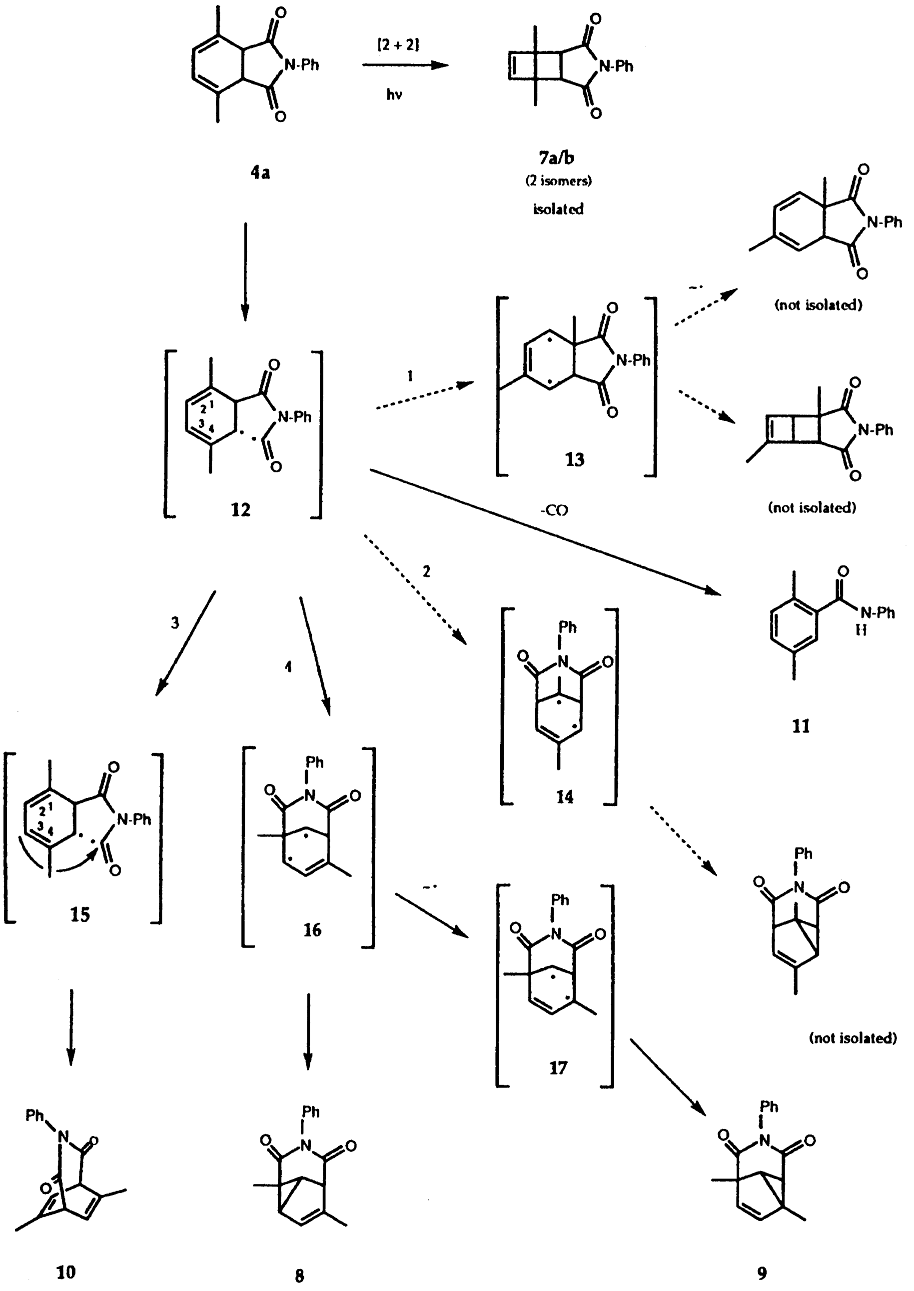


Fig. 6. Photochemical SO-extrusion of **3b**. CD_2Cl_2, sensitizer: benzophenone, $\lambda>300$ nm. –▲– **3b**; –△– **4b**; –○– **5b**.

Table 2. Product Distribution in the Photoextrusion of Sulfide **6**[a)]

Time (min)	**6** (%)	**4a** (%)	**5a** (%)
0	100	0.00	0.00
45	31.80	57.24	10.96
90	11.63	61.63	26.74
135	2.35	57.65	40.00

a) C_6D_6, no sensitizer, quartzglass.



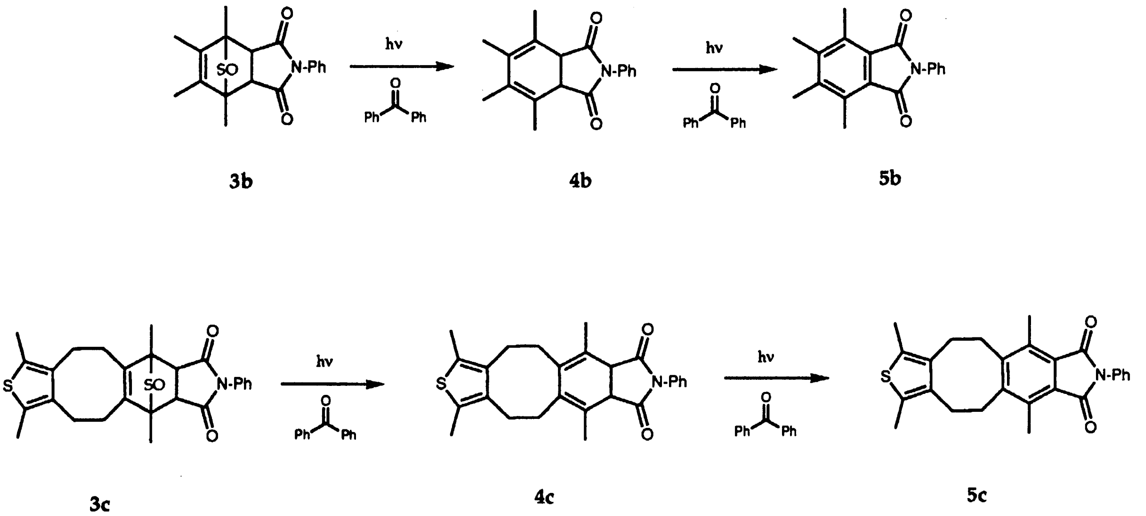
Scheme 5. Proposed mechanism of photoproducts of **4a**.

truded and diene **4a** and the phthalimide **5a** are formed (Table 2). Comparative irradiation of the sulfoxide **3a** and the sulfide **6** shows that the sulfide-bridge is extruded more readily than the sulfinyl-bridge.

In conclusion, the sulfinyl-bridges of the 7-thiabicyclo[2.2.1]hept-2-en-7-oxides **3a**—**3c** can be extruded photochemically. This extrusion goes concurrent with oxidation. Although more than one pathway may be operating, especially in the oxidation step, dienes **4a**—**4c** are intermediates in at least one major pathway. These dienes are also the starting points of side products in the reaction, which can be isolated and identified. The photochemical SO-extrusion at room temperature presents a mild alternative to the thermal or oxidative SO-extrusion[2,3] of such systems.

Experimental

General. All of the melting points were determined on a Mitamurariken MELT THERMO and are uncorrected. The IR spectra were measured on a JASCO-102. The NMR spectra were recorded at 270 MHz (proton) and at 69.7 MHz (carbon-13) with a JEOL GSX-270 using TMS as an internal standard. The UV-spectra were measured on a Hitachi 220 A spectrophotometer. The mass spectra were obtained on a JEOL JMS-O1SG-2 mass spectrometer at 70 ev using a direct inlet system (for compounds **3b** and **11**) or on a JEOL-AM20 GC/MS linkage (fused silica capillary column: Quadrex corporation, 007-1-25-0.25F, 0.25 mm i.d.×25 m, liquid phase: Methyl Silicone). Col-



Scheme 6.

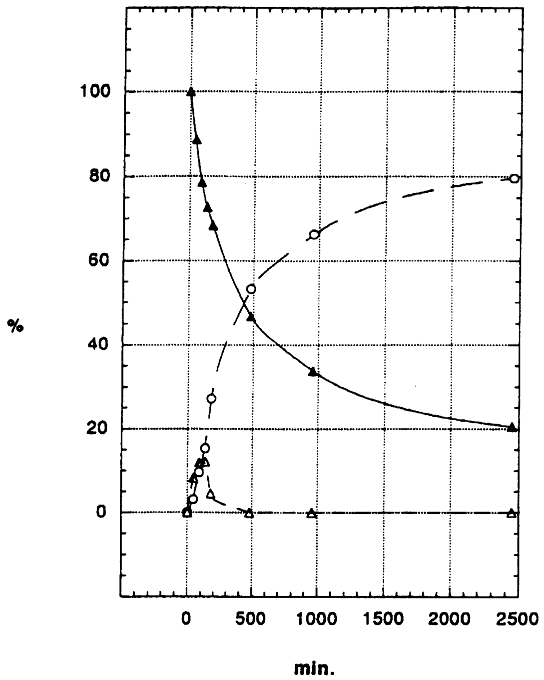


Fig. 7. Photochemical SO-extrusion of **3b**. Distribution of products as a function of reaction time. CD_2Cl_2, no sensitizer, $\lambda > 222$ nm. -▲- **3b**; -△- **4b**; -○- **5b**.

umn chromatography was carried out on silica gel (Wako gel, C-300). Analytical vapor-phase chromatography was performed on a Yanagimoto Gas Chromatograph G-2800 instrument equipped with a fused-silica capillary column (Quadrex corporation, 007-1-25-0.25F, 0.25 mm i.d.×25 m, liquid phase: Methyl Silicone).

Photochemical Equipment. All photo irradiations were carried out in an ice-water cooled pyrex well. A medium pressure mercury lamp (Riko UVL-100HA) was used. Some irradiations were monitored by ^{1}H NMR using either pyrex or quartz NMR-tubes. For the preparative photolysis of the diene, quartz tubes (0.8×19 cm) were chosen. All of the solutions were 0.1 molar. All of the solvents were degassed and were of UV-grade.

Oxidative Cycloaddition of Tetramethylthiophene (1b) with *N*-Phenylmaleimide. To solution of 2,3,4,5-tetramethylthiophene (**1b**)[20] (1.0 g, 7.1 mmol) and *N*-phenylmaleimide (1.24 g, 7.1 mmol) in dichloromethane (20 ml) was added *m*-chloroperbenzoic acid (70 w%, 3.7 g, 15.0 mmol) within 2.5 h and at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred for 20 h. Saturated aq $NaHCO_3$ (10 ml) was added, the layers separated, and the aqueous layer extracted with dichloromethane (2×10 ml). The organic phases were collected, washed with water (2×10 ml), dried over $MgSO_4$, and concentrated in vacuo. The residue was separated by column chromatography on silica gel (ether/hexane 1 : 2) to give fraction 1, *N*-phenyltetramethylphthalimide **5b** (220 mg, 12%) as colorless needles; mp 172—173 °C, and fraction 2, *N*-phenyl-1,2,3,4-tetramethyl-7-thiabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide 7-oxide **3b** (220 mg, 10%) as colorless crystals; mp 225—226 °C; IR 3150, 2950, 1770, 1710, and 1590 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=1.75$ (6H, s), 1.80 (6H, s), 3.75 (2H, s), 7.10 (2H, d, $J=7.43$ Hz), and 7.35—7.55 (3H, m); ^{13}C NMR ($CDCl_3$) 11.89, 12.97, 50.94, 73.22, 126.36, 128.91, 129.05, 131.59, and 174.50; MS *m/z* (%) 329 (M$^+$, 4.6), 281 (76.4), and 134 (100); UV (CH_2Cl_2) $\lambda_{\max}=230$ nm ($\log\varepsilon=3.77$). Found: C, 65.65; H, 5.78; N, 4.26%. Calcd for $C_{18}H_{19}O_3NS$: C, 65.57; H, 5.90; N, 4.19%.

Preparation of *N*-Phenyl-3,6-dimethyl-1,2-dihydrophthalimide 4a. A solution of **3a** (100 mg, 0.33 mmol), tributyltin hydride (0.40 ml, 1.48 mmol), and azoisobutyronitrile (20 mg) in dry benzene (15 ml) were refluxed for 30 min. The reaction mixture was then cooled and hydrolysed (15 ml water). Ether (20 ml) was added and the resultant two layers were separated. The aqueous phase was extracted with ether (2×10 ml). The organic phases were combined, washed with water and brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was separated by column chromatography on silica gel (hexane/ether 3 : 2) to yield **4a** (75 mg, 89%) as a colorless powder; mp 114.0—115.5 °C; IR (KBr) 2950, 1770, 1705, 1600, 1500, 1420, 1350, 1280, 1150, 810, 780, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=2.01$ (6H, s), 3.75 (2H, s), 5.75 (2H, s), 7.27—7.28 (2H, m), and 7.29—7.30 (3H, m); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ=21.85, 46.40, 120.75, 126.71, 126.79, 128.55, 129.13, 132.06, and 176.03; UV (CH_2Cl_2) λ_{max1}=276 nm (log ε=3.58), λ_{max2}=231 nm (log ε=3.73). Found: C, 75.69; H, 5.93; N, 5.60%. Calcd for $C_{16}H_{15}NO_2$: C, 75.89; H, 5.93; N, 5.53%.

Deoxygenation of 3a with PBr_3: To **3a** (500 mg, 1.66 mmol) in dry DMF (14 ml) was slowly added PBr_3 (1.29 ml). After stirring the solution for 30 min the reaction mixture was slowly hydrolysed with water (2 ml) and poured into a two-phase mixture of water and ether. The water phase was extracted with ether (2×10 ml). The organic phases were combined, dried over $MgSO_4$ and concentrated in vacuo. The resulting chromatography of the residue (ether/hexane 1 : 1) gave *N*-phenyl-1,4-dimethyl-7-thiabicyclo[2.2.1]hept-2-ene-5,6-dicarboximide **6** (223 mg, 46%) as colorless needles (ether/hexane): Mp 126.5—127.5 °C; IR 1700, 1385, 1185, 755, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.02 (6H, s 2×CH_3), 3.83 (2H, s), 6.32 (2H, s), 7.10—7.15 (2H, m), and 7.33—7.46 (3H, m); ^{1}H NMR (C_6D_6) δ=1.81 (6H, s 2×CH_3), 3.31 (2H, s), 5.92 (2H, s), and 7.00—7.39 (5H, m); ^{13}C NMR ($CDCl_3$) δ=18.31, 57.82, 65.68, 126.39, 128.73, 129.11, 131.52, 141.20, and 173.69; MS *m/z* (%) 285 (M^+, 9), 203 (24), 121 (13), and 112 (100); UV (CH_2Cl_2) λ_{max}=229 nm (log ε=3.84). Found: C, 67.36; H, 5.23; N, 4.92%. Calcd for $C_{16}H_{15}O_2NS$: C, 67.34; H, 5.29; N, 4.90%.

Photoirradiation of 3a, 3b, and 3c. The same procedure was used for the photolysis of **3a**, **3b**, and **3c**. The photolysis of **3a** is described below as an example.

Compound **3a** (30.1 mg, 0.1 mmol) was placed into an NMR-tube (Pyrex or quartz) and dissolved in a deuteriated solvent (1 ml, either dichloromethane or benzene). Argon was bubbled through the solution for 5 min and the tube sealed under argon. The sealed tube was irradiated for 41 h. In the case of a sensitization experiment an equimolar amount of benzophenone (19.8 mg, 0.10 mmol) was added to the solution.

The samples were monitored by ^{1}H NMR spectroscopy; the values are given in Figs. 1, 2, 3, 4, 5, 6, and 7.

Fig. 1: **3a** in CD_2Cl_2, with benzophenone as a sensitizer, λ>300 nm.

Fig. 2: **3a** in CD_2Cl_2, no sensitizer, λ>222 nm.

Fig. 3: **3a** in C_6D_6, no sensitizer, λ>222 nm.

Fig. 4: **3a** in C_6D_6, with benzophenone as a sensitizer λ>222 nm.

Fig. 6: **3b** in CD_2Cl_2, with benzophenone as a sensitizer λ>300 nm.

Fig. 7: **3b** in CD_2Cl_2, no sensitizer, λ>222 nm.

During the first part of the photolysis (up to 3 h) the samples were measured every 45 min; in later stages they were measured after 3, 8, 16, and 41 h, respectively.

Preparative Photoirradiation of the Diene 4a. Compound **4a** (699.5 mg, 2.76 mmol) was dissolved in 110 ml benzene and divided equally among four quartz tubes. The samples were simultaneously irradiated for 8 h at 18—19 °C. The samples were then combined and concentrated in vacuo. A ^{1}H NMR spectrum of the resulting crude material was taken to insure that the isolated compounds (see below) were not artifacts of secondary reactions during the column chromatography. The residue was then chromatographed on silica gel to give the following products:

Fraction 1, R_f=0.69 (CH_2Cl_2): *N*-Phenyl-3,6-dimethylphthalimide **5a** (23.9 mg, 9.5%).

Fraction 2, R_f=0.57 (CH_2Cl_2): *N*-Phenyl-3,6-dimethyl-1,2-dihydrophthalimide **4a** (183.1 mg 26.2%).

Fraction 3, R_f=0.48 (CH_2Cl_2): *N*-Phenyl-6,8-dimethyl-3-azabicyclo[3.2.2]nona-6-8-diene-2,4-dione **10** (153.2 mg, 21.8%) as colorless plates (ether/hexane), mp 133.5—134.5 °C; IR 3000, 2950, 1718, and 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$, ^{1}H COSY) δ=2.05 (6H, d, *J*=1.32 Hz), 4.16 (2H, dd, *J*=1.98 and 6.77 Hz), 6.16 (2H, m), 6.96 (2H, m), and 7.25—7.46 (3H, m); ^{1}H NMR (C_6D_6) δ=1.73 (6H, d, *J*=1.65 Hz), 4.05 (2H, dd, *J*=1.98 and 6.60 Hz), 5.70 (2H, m) and 7.05—7.34 (5H, m); ^{13}C NMR ($CDCl_3$, DEPT$^\#$ 135, DEPT 90) δ=20.18 (CH_3), 56.50 (CH), 121.87 (CH), 128.07 (CH), 128.18 (CH), 128.99 (CH), 136.42 (C_{quat}), 139.75 (C_{quat}), and 169.86 (C_{quat}); a C–H correlation NMR-experiment was performed to ensure the position of the olefinic carbons C_5, C_6 and C_7, C_8; GC/MS *m/z* (%) 253 (M^+, 9.2), 106 (100), and 91 (90.8). Found: C, 75.25; H, 6.05; N, 5.46%. Calcd for $C_{16}H_{15}O_2N$: C, 75.87; H, 5.97; N, 5.33%.

And further fractions, which were collected and subjected to a second column chromatography on silica gel to give:

Fraction 4, R_f=0.43 (ether/hexane 1 : 2): *N*-Phenyl-2,4-dimethylbenzamide **11** (22.1 mg, 3.3%) as colorless needles, mp 137 °C; IR (KBr) 3245, 3130, 3060, 2930, 1640, 1595, 1530, and 1500 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.35 (3H, s), 2.46 (3H, s), and 7.12—7.63 (9H, m); ^{13}C NMR ($CDCl_3$) δ= 19.32, 20.85, 124.47, 127.21, 129.09, 130.98, 131.20, 133.19, 135.54, 136.30, 138.02, and 168.18; MS *m/z* (%) 225 (M^+, 4.2), 133 (73.2), 77 (100). Found: C, 79.76; H, 7.03; N, 6.01%. Calcd for $C_{15}H_{15}ON$: C, 79.97; H, 6.71; N, 6.22%.

Fraction 5, R_f=0.21 (ether/hexane 1 : 2): *N*-Phenyl-1,4-dimethylbicyclo[2.2.0]hex-5-ene-2,3-dicarboximide **7a** (stereochemistry was not assigned) (31.1 mg, 4.4%); IR (neat) 1770 and 1722 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.24 (6H, s), 3.33 (2H, s), 6.38 (2H, s), and 7.27—7.55 (5H, m); ^{13}C NMR ($CDCl_3$) δ=13.59, 47.28, 53.48, 126.41, 128.19, 129.05 (2C), 143.50, and 176.17; GC/MS *m/z* (%) 253 (M^+, 11.8), 225 (16.3), 106 (89.6), 91 (100).

Fraction 6, R_f=0.19 (ether/hexane 1 : 2): *N*-Phenyl-3,6-dimethylbicyclo[3.1.0]hex-3-ene-2,6-dicarboximide **8** (47.2 mg, 6.7%); IR (neat) 2975, 2930, 1725, and 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.48 (3H, s), 1.75 (3H, s), 2.34 (2H, m), 3.82 (1H, d, *J*=7.26 Hz), 5.81 (1H, d, *J*=1.32 Hz), 6.96 (1H, m), and 7.30—7.50 (4H, m); ^{1}H NMR (C_6D_6) δ=1.41 (3H, s), 1.73 (3H, d, *J*=0.66 Hz), 1.76 (1H, m), 1.91 (1H, m), 3.72 (1H, d, *J*=7.59 Hz), 5.57 (1H, m), 7.24—7.46 (5H, m); ^{13}C NMR ($CDCl_3$, DEPT$^\#$ 135, DEPT 90) δ=13.94 (CH_3), 20.25 (CH_3), 31.57 (C_{quat}), 32.06 (CH), 42.08 (CH), 55.40 (CH), 127.81 (CH), 127.94 (CH), 128.21 (CH), 128.66 (CH), 135.85 (C_{quat}), 141.29 (C_{quat}), 172.88 (C_{quat}, C=O), and 173.74 (C_{quat}, C=O); ^{13}C NMR (C_6D_6, DEPT$^\#$ 135, DEPT 90) δ=137.79 (CH_3), 20.06 (CH_3), 31.45 (C_{quat}), 31.74 (CH), 41.57 (CH), 55.75 (CH), 127.10 (CH), 128.00 (CH), 129.06 (CH), 129.35 (CH), 137.15 (C_{quat}), 141.36 (C_{quat}), 172.02 (C_{quat}, C=O), and 172.69 (C_{quat}, C=O); GC/MS *m/z* (%) 253 (M^+, 36.1), 118 (83.0), 106 (100).

Fraction 7, R_f=0.14 (ether/hexane 1 : 2): *N*-Phenyl-

#DEPT = Distortionless Enhancement of Polarisation Transfer; (C_{quat}) denotes quaternary, (CH) tertiary, (CH_3) primary carbons.

2,5-dimethylbicyclo[3.1.0]hex-3-ene-2,6-dicarboximide **9** (57.7 mg, 8.2%); IR (KBr) 2980, 1720, and 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=1.48$ (3H, s), 1.56 (3H, s), 2.02 (1H, d, $J=7.59$ Hz), 2.29 (1H, d, $J=7.26$, Hz), 5.51 (1H, dd, $J=1.32$, 5.28 Hz), 6.00 (1H, d, $J=5.27$ Hz), 6.99 (2H, m), and 7.30—7.50 (3H, m); ^{1}H NMR (C_6D_6) $\delta=1.07$ (3H, s), 1.34 (1H, d, $J=7.59$ Hz), 1.42 (3H, s), 1.93 (1H, d, $J=7.59$ Hz), 5.19 (1H, d, $J=5.27$ Hz), 5.57 (1H, d, $J=5.28$ Hz), and 7.00—7.32 (5H, m); ^{13}C NMR $\delta=19.19$, 20.33, 33.34, 36.62, 44.19, 55.38, 127.92, 128.19, 129.15, 134.72, 135.71, 136.41, 169.25, and 175.74; ^{13}C NMR (C_6D_6, DEPT$^{\#}$ 135, DEPT 90) $\delta=18.66$ (CH_3), 20.92 (CH_3), 33.55 (CH), 36.18 (CH), 43.19 (C_{quat}), 55.37 (C_{quat}), 127.64 (CH), 128.00 (CH), 128.36 (CH), 134.43 (CH), 135.39 (CH), 137.16 (C_{quat}), 168.23 (C_{quat}, C=O), and 174.88 (C=O); GC/MS m/z (%) 253 (M^+, 21.6), 106 (100), and 91 (73.7).

Fraction 8, $R_f=0.30$ (ether/Hexane 1:1): *N*-Phenyl-1,4-dimethylbicyclo[2.2.0]hex-2-ene-5,6-dicarboximide **7b** (stereochemistry was not assigned) (42.1 mg, 6.0%); IR (neat) 3000, 2975, 1778, and 1718 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=1.36$ (6H, s), 3.17 (2H, s), 6.30 (2H, s), and 7.20—7.50 (5H, m); ^{13}C NMR ($CDCl_3$) $\delta=17.54$, 42.52, 53.01, 126.85, 128.07, 128.86, 129.10, 140.90, and 176.37; GC/MS m/z (%) 251 (M^+-2H, 100) and 222 (14.7).

X-Ray Analysis of 10. Crystallographic Section. Monoclinic, space group $P2_1/a$, $a=14.588(5)$, $b=8.561(1)$, $c=11.381(8)$ Å, $\beta=104.87(6)^\circ$, $D_{calcd}=1.22(5)$ g cm^{-3}, $V=1373.9$ Å^3, $Z=4$.

Data Collection. Diffractometer: CAD 4 (ENRAF-NONIUS), crystal size: 0.2×0.15×0.3 mm, radiation: Cu $K\alpha$ (1.54184 Å), monochrometer: graphite, data collecting mode: $\omega-2\theta$ scan, number of reflections: 2337 (observed), temperature, 298 K.

Structure Analysis. Solution: SIR, $R=0.067$, $R_w=0.096$, software: MOLEN.

Supplementary Material Available. The tables of bond distances (2 pages), bond angles (3 pages), structure factors (43 pages), positional parameters and their estimated standard deviations (5 pages), refined displacement parameter expressions (4 pages), and general displacement parameter expressions (4 pages) of the X-ray crystallography of **10** are deposited as Document No. 67040 at the Office of the Editor of the Bull. Chem. Soc. Jpn..

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