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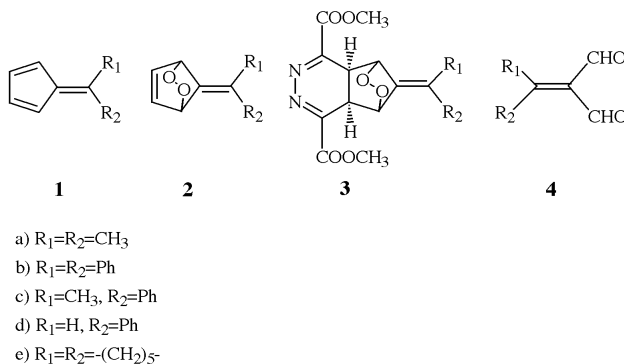
Reaction of unsaturated fulvene endoperoxides with dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate gave saturated fulvene endoperoxides containing the 1,2-dihydropyridazine ring. Treatment of dihydropyridazine endoperoxides with water followed by phenyliodosyl bis(trifluoroacetate) oxidation provided acrylic acid derivatives and dimethyl pyridazine-3,6-dicarboxylate.

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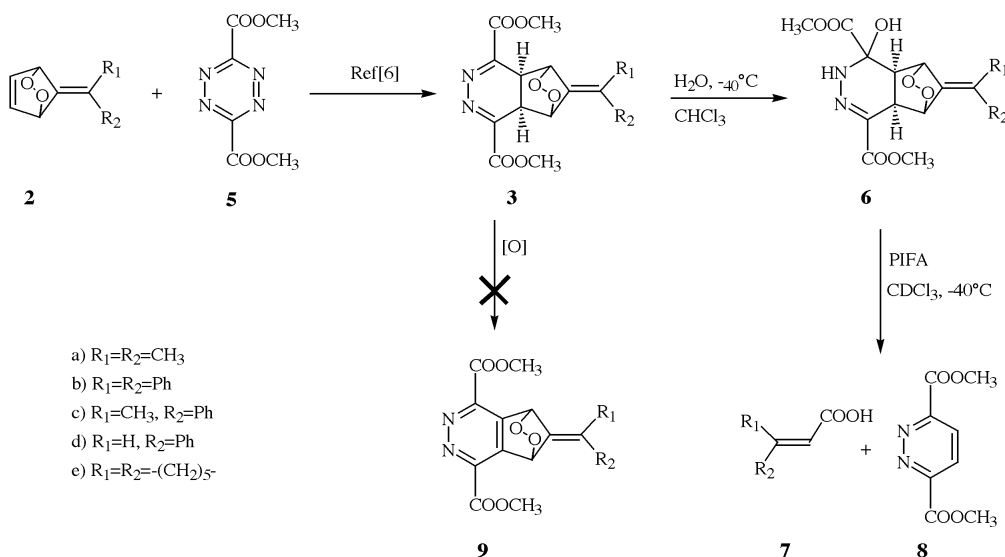
### Introduction.

Bicyclic endoperoxides obtained by [4+2] cycloaddition of singlet oxygen to various cyclic 1,3-dienes have become increasingly significant in a variety of chemical [1] and biochemical transformations [2]. On the other hand, the low chemical stability of the endoperoxides can be taken advantage of to perform selective transformations giving important compounds. Fulvenes **1** have been favorite substrates for singlet oxygenation. Sensitized photooxygenation of 6-substituted fulvenes has led to a number of interesting oxygenated derivatives [3]. Unstable fulvene endoperoxides **2** can be conveniently and selectively reduced to their respective stable saturated fulvene endoperoxides [4a]. Erden *et al.* [3d,4] have shown that functionalized 1,5-dicarbonyl compounds and tetrahydrofurans can be obtained by a relatively simple protocol involving thermolysis of saturated fulvene endoperoxides in the presence of acetic acid. Also, saturated fulvene endoperoxides derived from 6-vinylfulvene proved to be excellent precursors of 5-propylal-substituted 2-cyclopentenones [4].

Recently, we reported [5] the trapping of highly reactive fulvene endoperoxides **2** [4], obtained by photooxygenation of the appropriate fulvenes in the presence of tetraphenyl porphyrine (TPP), with dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate (**5**). The treatment of the trapping products **3** with cobalt (II) tetraphenylporphyrine gave alkylidene- and arylidenemalonaldehydes **4** [6]. In this paper, we report a new fragmentation of the fulvene



Scheme 1



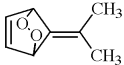
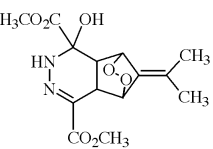
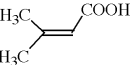
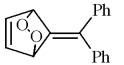
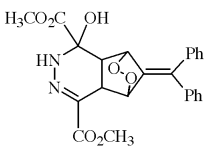
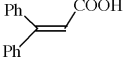
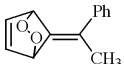
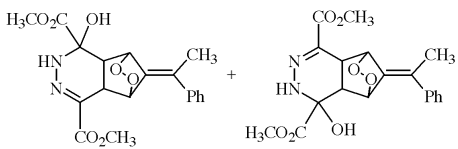
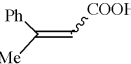
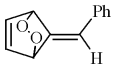
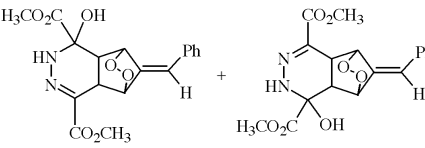
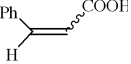
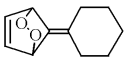
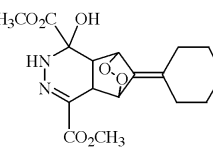
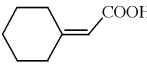
endoperoxides **3** with phenyliodosyl bis(trifluoroacetate) (PIFA) [7] to give the corresponding acrylic acid derivatives. This methodology may serve as an alternative route for the synthesis of substituted acrylic acid derivatives.

### Results and Discussion.

In the course of studying the trapping reactions of the unsaturated fulvene endoperoxides **3** we noticed that water adds to the 1,2-dihydropyridazine ring. Therefore, we investigated the reaction of the trapping products **3a-e** with water. Two equivalents of water was added to a cold solution ( $-40 \pm 5$  °C) of trapping products **3a-e** in  $\text{CHCl}_3$ . Compounds **6a-e** were formed by 1,2-addition of water as the sole products (Scheme 1). However, in the case of asymmetrical substitution at the fulvene ring, two isomeric addition products of **6c** and **6d** were formed as expected (Scheme 1).

The structures of **6a-e** were assigned by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR. The most conspicuous feature in the  $^1\text{H}$ -NMR spectra of **6a-e** was an AB system, which corresponds to vicinal protons in the 1,2-dihydropyridazine ring. The A-part, as well as the B-part of the AB system in **6a** resonate as a doublet of doublets at 3.46 ppm ( $J = 9.3, 1.5$  Hz) and 3.06 ppm ( $J = 9.3, 2.5$  Hz), respectively. The peroxide-bridgehead protons appear as a singlet at 4.68 ppm and a doublet at 5.08 ppm ( $J = 1.5$  Hz). There was no measurable coupling between protons in the dihydropyridazine ring and the bridgehead protons at 4.68 ppm due to a nearly  $90^\circ$  dihedral angle. Inspection of Drieding models confirmed this angle. On the other hand, the 14-line  $^{13}\text{C}$ -NMR spectrum of **6a** supports strongly the proposed asymmetrical structure. The stereochemistry of -OH group was not determined.

Table 1  
Acrylic Acids Obtained from some Unsaturated Fulvene Endoperoxides

Fulvene Endoperoxide	Water Addition Product	Product	Yield, %
 <b>2a</b>	 <b>6a</b>	 <b>7a</b>	82 [a] 57 [b]
 <b>2b</b>	 <b>6b</b>	 <b>7b</b>	67 [a] 13 [b]
 <b>2c</b>	 <b>6c</b> + <b>6c'</b>	 <b>7c</b> and <b>7c'</b>	78 [a] Z isomer 70 [c] E isomer 30 [c]
 <b>2d</b>	 <b>6d</b> + <b>6d'</b>	 <b>7d</b> and <b>7d'</b>	51 [a] Z isomer 47 [c] E isomer 53 [c]
 <b>2e</b>	 <b>6e</b>	 <b>7e</b>	58 [a] 46 [b]

[a] Total crude crystalline yield; [b] Crystalline yield; [c] According to  $^1\text{H}$ -NMR.

The quantitative addition of water to the six-membered ring at lower temperatures (-40 °C) indicates that the six-membered ring must be highly strained due to the planarity of ring and annelation of a strained five-membered ring. This ring strain can be partially released by the addition of water to the six-membered ring. Walls *et al.* have observed similar results. They reported easy addition of methanol to the dihydropyridazine ring [8].

Finally, the bicyclic endoperoxides **6a-e** were treated with phenyliodosyl bis(trifluoroacetate) in  $\text{CHCl}_3$  at -40 °C, that resulted in the formation of the corresponding acrylic acid derivatives **7a-e** and diazine **8** (Table 1). The structures were confirmed by means of spectroscopic methods. The formation mechanism of the acrylic acid derivatives is unclear. However, we assume that PIFA first attacks alcohol group [9] and causes an oxidative fragmentation of the fulvene endoperoxide ring. Consequently, the iodobenzene which is probably formed under the given reaction conditions acts as an oxygen-atom transfer agent and causes an oxidative decarboxylation [10] to give the corresponding acrylic acid derivatives **7a-e** [11]. The bicyclic endoperoxides **4** have been treated directly with PIFA. However, the expected aromatic compound **9** was not formed.

In conclusion, the unexpected reaction of phenyliodosyl bis(trifluoroacetate) with fulvene endoperoxide is demonstrated. The intriguing feature of this reagent is its versatility and broad application to a large number of compounds containing different functional groups. Furthermore, this method may be applied to the synthesis of highly functionalized acrylic acids.

## EXPERIMENTAL

### General.

Solvents were concentrated at reduced pressure. Melting points were determined on a Thomas-Hoover capillary melting apparatus. Infrared spectra were obtained from solution in 0.1 mm cells or KBr pellets for solids on a Perkin-Elmer 337 infrared recording spectrophotometer.  $^1\text{H}$  nmr spectra were recorded on Varian 60 and 200 MHz and  $^{13}\text{C}$  nmr spectra on a 50 MHz spectrometer and are reported in  $\delta$  units with  $\text{SiMe}_4$  as internal standard.

### Photooxygenation of Fulvenes [4].

To a solution of fulvene (1 mmol) in 5 mL of  $\text{CHCl}_3$  was added 5-10 mg of TPP. The resulting mixture was irradiated with a projection lamp (150 W) while dry oxygen was being passed through solution and the mixture was stirred for 1 h at -50±5 °C.

Trapping of Fulvene Endoperoxides **2** with Dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate [6].

To a stirred solution of fulvene endoperoxide **2** (1 mmol) prepared as described above in 5 mL of  $\text{CHCl}_3$  was added 1 mmol of dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate [12] at -50±5 °C. After complete addition (1-2 min), the mixture was stirred for 1 day at -50±5 °C. The resulting mixture was used to subsequent procedure.

### Addition of Water to Trapping Products.

To a stirred solution of the trapping product (1 mmol) prepared as described above in 5 mL of  $\text{CHCl}_3$  cooled to -40±5 °C was added 1 mmol of water during 1 min. After stirring for 1 day at -40±5 °C, the solution was slowly warmed to room temperature. The solvent was removed under reduced pressure. The water addition products were obtained in quantitative yield and the crude product was recrystallized from an appropriate solvent.

Dimethyl 6-Hydroxy-11-(1-methylethylidene)-9,10-dioxo-4,5-diazatricyclo[6.2.1.0<sup>2,7</sup>]undec-5-ene-3,6-dicarboxylate (**6a**).

The compound was obtained as white crystals from  $\text{CH}_2\text{Cl}_2$ /ether (80%), mp 110-112°; ir (potassium bromide): OH 3361, CO 1753, 1727  $\text{cm}^{-1}$ .  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  6.98 (d, J = 2.5 Hz, 1H, NH), 5.08 (d, J = 1.5 Hz, 1H, H1), 4.68 (s, 1H, H8), 4.23 (m, 1H, OH), 3.90 (s, 3H,  $\text{OCH}_3$ ), 3.82 (s, 3H,  $\text{OCH}_3$ ), 3.46 (dd, A-part of AB system, J = 9.3, 1.5 Hz, 1H, H2), 3.06 (dd, B-part of AB system, J = 9.3, 2.5 Hz, 1H, H7), 1.68 (s, 3H,  $\text{CH}_3$ ), 1.63 (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  171.5, 166.1, 140.9, 136.3, 128.9, 80.5, 79.6, 77.3, 55.4, 54.6, 51.9, 42.3, 24.0, 23.8.

Anal. Calcd. for  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_7$ : C, 51.53; H, 5.56; N, 8.59. Found: C, 51.17; H, 5.48; N, 8.78.

Dimethyl 6-Hydroxy-11-(diphenylmethylene)-9,10-dioxo-4,5-diazatricyclo-[6.2.1.0<sup>2,7</sup>]undec-5-ene-3,6-dicarboxylate (**6b**).

The compound was obtained as white crystals from  $\text{CH}_2\text{Cl}_2$ /ether (73%), mp 133-135°; ir (potassium bromide): OH 3390, CO 1759, 1738  $\text{cm}^{-1}$ .  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  7.35-7.17 (m, 10H, phenyl), 7.07 (d, J = 2.5 Hz, 1H, NH), 5.05 (d, J = 1.7 Hz, 1H, H1), 4.85 (bs, 1H, H8), 3.70 (s, 3H,  $\text{OCH}_3$ ), 3.68 (s, 3H,  $\text{OCH}_3$ ), 3.58 (dd, A-part of AB system, J = 9.5, 1.7 Hz, 1H, H2), 3.23 (dd, B-part of AB system, J = 9.5 Hz, 2.5 Hz, 1H, H7);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  171.4, 165.8, 142.0, 141.8, 141.0, 140.7, 138.3, 131.2, 130.9, 130.5, 130.2, 130.1, 129.9, 82.0, 79.4, 78.6, 55.2, 54.4, 52.3, 42.4.

Anal. Calcd. for  $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_7$ : C, 63.99; H, 4.92; N, 6.22. Found: C, 64.32; H, 5.08; N, 6.34.

Dimethyl 6-Hydroxy-11-[(E) and (Z)-1-Phenylethylidene]-9,10-dioxo-4,5-diazatricyclo[6.2.1.0<sup>2,7</sup>]undec-5-ene-3,6-dicarboxylate (**6c** and **6c'**).

The mixture was not stable toward column material. Yield 68%, white powder from  $\text{CH}_2\text{Cl}_2$ /ether.  $^1\text{H}$  nmr (deuteriochloroform) of the mixture:  $\delta$  7.31-7.03 (m, 12H, 2 phenyl and 2 NH), 5.27 (d, J = 1.5 Hz, 1H), 4.84 (bs, 2H), 4.61 (s, 1H), 3.94 (s, 3H,  $\text{OCH}_3$ ), 3.87 (s, 3H,  $\text{OCH}_3$ ), 3.59 (s, 6H, 2x $\text{OCH}_3$ ), 3.56 (dd, J = 9.3, 1.5 Hz, 2H, H2), 3.15-3.05 (m, 2H, H7), 2.05 (s, 3H,  $\text{CH}_3$ ), 2.03 (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  171.6, 171.2, 166.1, 165.6, 143.1, 143.0, 141.1, 140.6, 139.0 (2C), 133.3, 133.2, 130.2, 130.1 (2C), 129.5, 129.3, 129.2, 81.71, 80.7, 79.7, 79.3, 78.4, 77.6, 55.5, 55.1, 54.6, 54.2, 52.2, 51.8, 42.4, 42.3, 24.0, 23.6.

Anal. Calcd. for  $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_7$  (mixture): C, 59.31; H, 4.99; N, 7.01; Found: C, 58.76; H, 5.19; N, 7.21.

Dimethyl 6-Hydroxy-11-[(E) and (Z)-1-Phenylmethylidene]-9,10-dioxo-4,5-diazatricyclo[6.2.1.0<sup>2,7</sup>]undec-5-ene-3,6-dicarboxylate (**6d** and **6d'**).

The  $^1\text{H}$  NMR spectrum showed that the reaction mixture consisted of a mixture of **6d/d'** (1:1). Reaction mixture was

unstable toward column materials. Yield 68%;  $^1\text{H}$  nmr (deuteriochloroform) of the mixture:  $\delta$  7.32-7.09 (m, 12H), 6.58 (s, 1H, =CH), 6.56 (s, 1H, =CH), 5.48 (bs, 1H), 5.07 (s, 1H), 5.00 (s, 1H), 4.66 (s, 1H), 3.89 (s, 3H, OCH<sub>3</sub>), 3.84 (s, 3H, OCH<sub>3</sub>), 3.82 (s, 3H, OCH<sub>3</sub>), 3.74 (s, 3H, OCH<sub>3</sub>), 3.7-3.6 (m, 2H, H<sub>2</sub>), 3.21-3.11 (m, 2H, H<sub>7</sub>).  $^{13}\text{C}$  nmr of the mixture (deuteriochloroform)  $\delta$  171.4, 171.3, 166.1, 166.0, 142.5, 141.8, 141.3, 139.9, 137.3, 137.2, 130.5, 130.4, 130.1, 130.0, 124.7, 124.5, 84.4, 81.0, 79.7, 79.6, 79.4, 76.9, 55.4, 55.3, 54.6, 54.4, 52.4, 51.3, 42.7, 42.5.

Anal. Calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>7</sub> (mixture); C, 57.75; H, 4.85; N, 7.48; Found: C, 58.81; H, 5.04; N, 7.31.

Dimethyl 6-Hydroxy-11-cyclohexylidene-9,10-dioxo-4,5-diazatricyclo[6.2.1.0<sup>2,7</sup>]-undec-5-ene-3,6-dicarboxylate (**6e**).

Yield 81%, white crystals from CH<sub>2</sub>Cl<sub>2</sub>/ether, mp 90-91 °C; ir (potassium bromide): OH 3420, CO 1760, 1740 cm<sup>-1</sup>.  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  7.04 (bd, J = 2.4 Hz, 1H, NH), 5.12 (d, J = 1.1 Hz, 1H, H<sub>1</sub>), 4.69 (s, 1H, H<sub>8</sub>), 3.89 (s, 3H, OCH<sub>3</sub>), 3.81 (s, 3H, OCH<sub>3</sub>), 3.43 (dd, A-part of AB system, J = 9.3, 1.1 Hz, 1H, H<sub>2</sub>), 3.05 (dd, B-part of AB system J = 9.3, 2.4 Hz, 1H, H<sub>7</sub>), 2.07-2.01 (m, 4H, =C(CH<sub>2</sub>)), 1.57-1.34 (m, 6H (CH<sub>2</sub>)<sub>3</sub>);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  171.6, 166.1, 140.4, 136.0, 133.1, 80.1, 79.5, 76.7, 55.3, 54.5, 51.6, 42.2, 35.0 (2C), 29.0, 28.5, 28.0;

Anal. Calcd. for C<sub>17</sub>H<sub>22</sub>N<sub>2</sub>O<sub>7</sub>; C, 55.73; H, 6.05; N, 7.65; Found: C, 55.45; H, 6.00; N, 7.89.

Oxidation of Addition Products **6a-e** with Phenyliodosyl Bis(trifluoroacetate).

To a solution of **6a-e** (1 mmol) in 10 mL of CHCl<sub>3</sub>, prepared as described above was added phenyliodosyl bis(trifluoroacetate) (Merck) (1 mmol) at -40±5 °C and the resulting mixture was stirred for 1-2 min. The reaction mixture was allowed to warm-up slowly to room temperature. The solvent was removed under reduced pressure and 50 mL of ether was added. Addition of ether precipitated the diazine **8** as yellow crystals (70-80%). Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/ether of residue gave pure diazine **8**. The organic layer was washed with NaOH (1 N, 2x25 mL). The aqueous layer was acidified to pH 1 with concentrated hydrochloric acid and extracted with ether (2x50 mL). The ether extract was dried (CaCl<sub>2</sub>) and evaporated at reduced pressure. The crude product was the corresponding acrylic acid derivatives **7a-e**.

Dimethyl Pyridazine-3,6-dicarboxylate (**8**) [13].

This compound has mp 195-196°; ir (potassium bromide): CO 1770, 1746 cm<sup>-1</sup>;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  8.31 (s, 2H, aromatic), 4.06 (s, 6H, OCH<sub>3</sub>);  $^{13}\text{C}$  nmr (CDCl<sub>3</sub>):  $\delta$  165.9, 154.7, 130.23, 55.5.

3-Methylbut-2-enoic Acid (**7a**) [14].

The crude product (155 mg, 82%) was crystallized from CCl<sub>4</sub>/hexane, 108 mg (57%); mp 63-65 °C;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  10.18 (bs, 1H, COOH), 5.69 (h, J = 1.2 Hz, 1H, =CH), 2.17 (d, J = 1.2 Hz, 3H, CH<sub>3</sub>), 1.93 (d, J = 1.2 Hz, 3H, CH<sub>3</sub>);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  174.2, 162.0, 117.6, 29.6, 22.5.

3,3-Diphenylacrylic Acid (**7b**).

The crude product (150 mg, 67%) was crystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane, mp 150-152° (mp [11c], 158-160°);  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  7.39-7.19 (m, 10H, phenyl), 6.33 (s, 1H, =CH);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  172.4, 160.8, 142.8, 140.4, 131.7, 131.2, 130.5, 130.4 (2C), 129.9, 118.4.

(*E*)- and (*Z*)-3-Phenylbut-2-enoic Acids (**7c** and **7c'**).

These compounds were obtained in a combined yield of 78% [11a,15] (207 mg). Integration of  $^1\text{H}$ -NMR of the isomers mixture showed that *E*- and *Z*-isomers were present in the ratio 30:70. **7c**:  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  8.5-9.0 (br. s. 1H, COOH), 7.6-7.2 (m, 5H, aromatic), 5.95 (q, J = 1.0 Hz, 1H, =CH), 2.2 (d, J = 1.0 Hz, 3H, CH<sub>3</sub>). **7c'**:  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  8.5-9.0 (br. s. 1H, COOH), 7.5-7.2 (m, 5H, phenyl), 6.2 (q, J = 1.5 Hz, 1H, =CH), 2.62 (d, J = 1.5 Hz, 3H, CH<sub>3</sub>).

(*E*)- and (*Z*)-3-Phenylpropenoic Acids (**7d** and **7d'**).

These compounds were obtained in a combined yield of 51% [11a]: (117 mg). Integration of  $^1\text{H}$ -NMR of the isomers mixture showed that *E*- and *Z*-isomers were present in a ratio of 53:47. **7d**:  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  10.0 (bs, 1H, COOH), 7.80 (d, A-part of AB system, J = 16.0 Hz, 1H, H<sub>3</sub>) 7.30-7.64 (m, 5H, phenyl), 6.46 (d, B-part of AB system, J = 16.0 Hz, 1H, H<sub>2</sub>). **7d'**:  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  10.0 (bs, 1H, COOH), 7.30-7.64 (m, 5H, phenyl), 7.09 (d, A-part of AB system, J = 12.8 Hz, 1H, H<sub>3</sub>) 6.00 (d, B-part of AB system, J = 12.8 Hz, 1H, H<sub>2</sub>).

2-Cyclohexylideneacetic Acid (**7e**).

This compound was obtained in 58% yield (81 mg), and was crystallized from ether/hexane, 64 mg (46%); mp 89-90° (mp [11c], 90-91.5°);  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  10.71 (bs, 1H, COOH), 5.62 (s, 1H, =CH), 2.82 (m, 2H, CH<sub>2</sub>), 2.24 (m, 2H, CH<sub>2</sub>), 1.62 (m, 6H, CH<sub>2</sub>);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  174.5, 168.8, 114.5, 40.2, 32.1, 30.6, 29.8, 28.2; IR (KBr, cm<sup>-1</sup>) 3029, 2953, 2876, 1702, 1651, 1446, 1421, 1319, 1293, 1268, 1242, 1217, 1191, 1012, 961, 859.

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