



# Synthesis of Normorphan Derivatives from Norbornadiens

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# Synthesis of Normorphan Derivatives from Norbornadienes

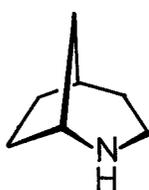
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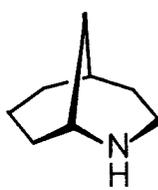
A convenient synthetic method for the preparation of 2-azabicyclo [3.2.1] oct-3, 6-diene derivatives from norbornadienes has been developed by employing three reactions of 1,3-dipolar cycloadditions, the decomposition of triazoline compounds, and the thermal rearrangement of tricyclic aziridines.

## 1. Introduction

Normorphan derivatives are important intermediary substances for the synthesis of the functionalized morphan compounds with potential analgetic activity,<sup>1)</sup> since the five-membered ring of the normorphan derivatives can be enlarged to the six-membered ring by a relatively facile method. The literatures report only few syntheses of the normorphan system.<sup>2-4)</sup> Recently we have proposed the reaction mechanism for valence isomerization of the tricyclic aziridines **3** to the normorphan derivatives **4**.<sup>5)</sup> This reaction was applied to the synthesis of the normorphan derivatives. In this paper, we will describe the synthetic method for the preparation of normorphans **4** and **5** from norbornadienes **la-c** under mild conditions.



normorphan  
skeleton



morphan  
skeleton

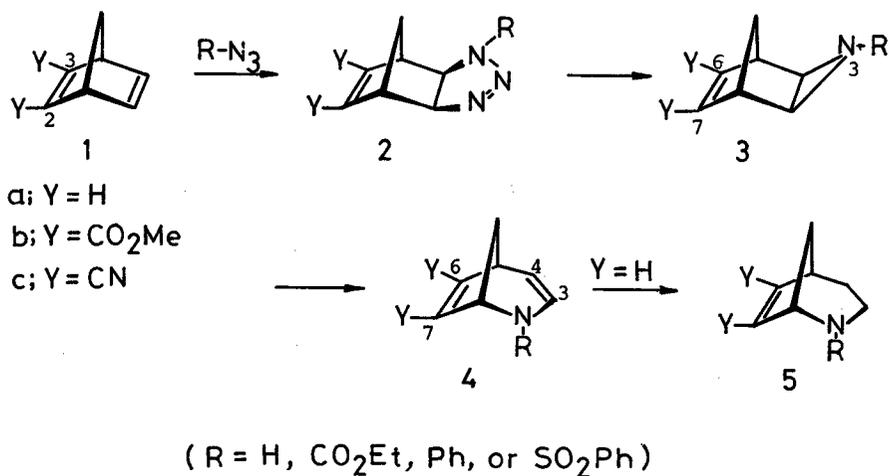
## 2. Results and Discussion

### Preparation of Unsaturated Tricyclic Aziridines **3** from Norbornadienes **la-c**

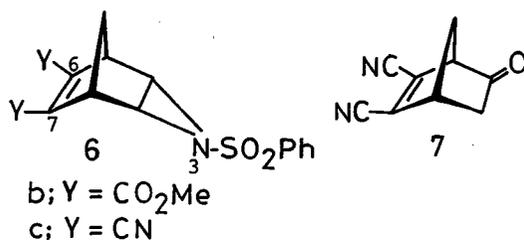
The unsaturated tricyclic aziridines were prepared from norbornadienes **la-c** and various azides. The data are collected in Table 1 and the results are summarized as follows.

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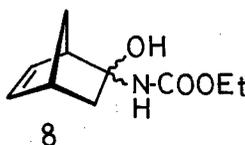
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1) The reaction of **1a** with benzenesulfonyl azide gave **4a** ( $R=SO_2Ph$ ) via the formation of **3a** ( $R=SO_2Ph$ ) in higher yield than that described previously.<sup>6)</sup> When the substituents such as methoxycarbonyl and cyano groups exist at the  $C_2$  and  $C_3$  positions of norbornadiene, however, prolonged heating was necessary for forcing this reaction (Entries 1, 2, and 3). The products were mainly **3b, c** ( $R=SO_2Ph$ ) and their endo isomers **6b, c**. Only in the case of **1c**, 2, 3-dicyano-bicyclo[2.2.1]hept-2-en-5-one **7** was produced as another by-product (Entry 3). In these reactions, **4b, c** ( $R=SO_2Ph$ ) were not obtained at all. Thus, it was found that the electron-withdrawing substituents at the  $C_2$  and  $C_3$  positions cause the lowering of the yields of **3** and **4**.



2) In the cases of ethyl azidoformate and phenyl azide, the triazoline compounds **2a** ( $R=COOEt$  and  $Ph$ ), which are precursors of **3a** ( $R=COOEt$  and  $Ph$ ), were isolated as the reaction products, as shown in the literatures<sup>7), 8)</sup> (Entries 4 and 5). Compound **2a** ( $R=COOEt$ ) was decomposed to **3a** ( $R=COOEt$ ) by adding **2a** to ethanol at  $10^\circ C$ . When a solution of **2a** ( $R=COOEt$ ) in toluene was heated at  $110^\circ C$  for 13 h, however, **4a** ( $R=COOEt$ ) was obtained in 41% yield with 5-ethoxycarbonylamino-5-hydroxy-bicyclo[2.2.1]hept-2-ene **8** in 37% yield. In the case of **2a** ( $R=Ph$ ), we found that **3a** ( $R=Ph$ ) is produced by



irradiating a solution of **2a** (**R=Ph**) in cyclohexane for 22 h, but not by the thermal decomposition of **2a** (**R=Ph**). Thus, this fact indicates that the electron-withdrawing substituent **R** is necessary for the preparation of compounds **3**.

Table 1. The yields of the products in the reactions of norbornadienes with azides

| Entry | Norbornadienes | Azides                           | Molar <sup>a)</sup> ratio | Conditions                 | Product                                 | Yield, %              |
|-------|----------------|----------------------------------|---------------------------|----------------------------|---|-----------------------|
| 1     | <b>1a</b>      | PhSO <sub>2</sub> N <sub>3</sub> | 3:1                       | benzene, rt, 24h           | <b>4a</b> ( <b>R=SO<sub>2</sub>Ph</b> ) | 86 (62) <sup>b)</sup> |
| 2     | <b>1b</b>      | PhSO <sub>2</sub> N <sub>3</sub> | 3:1                       | benzene, 50°C, 48h         | <b>3b</b> ( <b>R=SO<sub>2</sub>Ph</b> ) | 74                    |
|       |                |                                  |                           |                            | <b>6b</b>                               | 10                    |
| 3     | <b>1c</b>      | PhSO <sub>2</sub> N <sub>3</sub> | 3:1                       | benzene, 80°C, 68h         | <b>3c</b> ( <b>R=SO<sub>2</sub>Ph</b> ) | 19                    |
|       |                |                                  |                           |                            | <b>6c</b>                               | 21                    |
|       |                |                                  |                           |                            | <b>7</b>                                | 12                    |
| 4     | <b>1a</b>      | EtOOCN <sub>3</sub>              | 2.5:1                     | hexane, rt, 3day           | <b>2a</b> ( <b>R=COOEt</b> )            | 72 <sup>c)</sup>      |
| 5     | <b>1a</b>      | PhN <sub>3</sub>                 | excess                    | cyclo- 60°C, 2h<br>hexane, | <b>2a</b> ( <b>R=Ph</b> )               | 67 <sup>d)</sup>      |

a) Molar ratio = Norbornadienes : Azides. b) Ref. 6. c) Ref. 7. d) Ref. 8.

### Preparation of Normorphan Derivatives **4** from Tricyclic Aziridines **3**

The normorphan derivatives **4** were prepared from the tricyclic aziridines by the thermal rearrangement. The reactions were carried out by heating a solution of **3** in various solvents in the range of 78 to 179°C. The data are collected in Table 2 and the results are summarized as follows.

1) The exo aziridines **3a-c** (**R=SO<sub>2</sub>Ph**) were converted quantitatively into the corresponding normorphan derivatives **4a-c** (**R=SO<sub>2</sub>Ph**) by valence isomerization (Entries 6, 7, and 8). In the cases of **3b, c** (**R=SO<sub>2</sub>Ph**), however, it was necessary to raise the reaction temperature to 139 - 179°C. Thus, this fact indicates that the valence isomerization becomes difficult owing to the existence of the electron-withdrawing substituent **Y**.

2) Compounds **3a** (**R=H** and **Ph**) underwent no isomerization under the similar conditions described in Table 2 (Entries 10 and 11). This fact means that it is preferable to have an electron-withdrawing group at the 3-position for the preparation of normorphan derivatives.

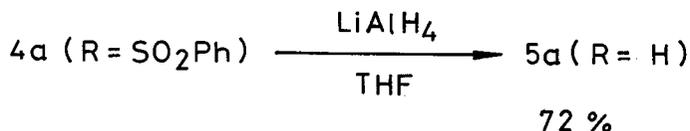
3) The protic solvent promoted significantly valence isomerization of **3**, as Table 2 shows (Entry 9).

Table 2. The Yields of normorphan derivatives in the thermal rearrangements of tricyclic aziridines 3

| Entry | Aziridines                | Conditions                                 | Product                   | Yield, % |
|-------|---------------------------|--|---------------------------|----------|
| 6     | 3a (R=SO <sub>2</sub> Ph) | benzene, 80°C, 5 h                         | 4a (R=SO <sub>2</sub> Ph) | 98       |
| 7     | 3b (R=SO <sub>2</sub> Ph) | xylene, 139°C, 11 h                        | 4b (R=SO <sub>2</sub> Ph) | 99       |
|       |                           | o-dichloro- 179°C, 0.2 h<br>benzene,       | 4b (R=SO <sub>2</sub> Ph) | 100      |
| 8     | 3c (R=SO <sub>2</sub> Ph) | o-dichloro- 179°C, 7 h<br>benzene,         | 4c (R=SO <sub>2</sub> Ph) | 100      |
| 9     | 3a (R=COOEt)              | toluene, 110°C, 13 h<br>ethanol, 78°C, 2 h | 4a (R=COOEt)              | 99<br>95 |
| 10    | 3a (R=Ph)                 | benzene, 80°C, 10 h                        | polymeric<br>material     |          |
| 11    | 3a (R=H) <sup>a)</sup>    | benzene, 80°C, 10 h                        | polymeric<br>material     |          |

a) The 3a (R=H) was prepared according to the method described in the literature.<sup>7)</sup>

The above results demonstrate that the choice of azides and solvents is important for the synthesis of normorphan derivatives from norbornadienes. Using benzenesulfonyl azide, it is possible to prepare quantitatively the normorphan derivatives from norbornadienes. Further conversion of 4a (R=SO<sub>2</sub>Ph) into 5a (R=H) was achieved by Barraclough's method<sup>9)</sup> using LiAlH<sub>4</sub> as a reducing agent.



### 3. Experimental

Melting points were uncorrected. IR, NMR, and mass spectra were obtained on a Hitachi 216 grating infrared spectrometer, a Hitachi R-24A spectrometer, and a Hitachi RMU-6E mass spectrometer, respectively. Elemental analyses were recorded on a Yanaco CHN corder MT-2. The spectral data of 3a-c (R=SO<sub>2</sub>Ph), 3a (R=Ph), 6b, c, 4b, c (R=SO<sub>2</sub>Ph), and 4a (R=COOEt) are summarized in Tables 3 and 4.

*3-Phenylsulfonyl-2, 4-exo-3-azatricyclo [3.2.1.0<sup>2,4</sup>] oct-6-ene 3a (R=SO<sub>2</sub>Ph)*: A solution of a mixture of 15 g (0.163 mol) of norbornadiene and 7 g (0.038 mol) of benzenesulfonyl azide in 55 ml of dry benzene was stirred at 5°C for 42 h. After the removal of benzene *in vacuo*, 120 ml of (10 : 1) hexane-benzene was added into the residue and the mixture was stirred at 10°C for 8 h. The supernatant solution was taken out of the apparatus and was allowed to stand overnight at -14°C to give 1.7 g (18%) of 3a (R=SO<sub>2</sub>Ph) as colorless prisms: mp 75 - 76°C; MS, m/e, 247 (M<sup>+</sup>). Found: C; 63.17, H; 5.42, N; 5.56%. Calcd for C<sub>13</sub>H<sub>13</sub>NO<sub>2</sub>S: C; 63.16, H; 5.26, N; 5.67%.

Table 3. Spectral data of compounds 3a-c (R=SO<sub>2</sub>Ph), 3a (R=Ph), and 6b, c

| Compound                  | IR (cm <sup>-1</sup> )   | NMR (δ values from TMS, Solvent; CDCl <sub>3</sub> )   |
|---------------------------|--|--|
| 3a (R=SO <sub>2</sub> Ph) | 1620 (ν <sub>C=C</sub> )<br>1345 (ν <sub>SO<sub>2</sub></sub> )<br>1160 (ν <sub>SO<sub>2</sub></sub> ) | 7.38 - 8.11 (m, 5H, aromatic), 6.35 (t, 2H, J=1.6Hz, 6-H, 7-H),<br>3.17 (s, 2H, 2-H, 4-H), 3.00 (m, 2H, 1-H, 5-H), 1.16 (d, 1H,<br>J=8.3Hz, 8-H <sub>β</sub> ), 1.72 (d, 1H, J=8.3Hz, 8-H <sub>α</sub> ) |
| 3b (R=SO <sub>2</sub> Ph) | 1740 (ν <sub>CO</sub> )<br>1345 (ν <sub>SO<sub>2</sub></sub> )   | 7.30 - 8.00 (m, 5H, aromatic), 3.80 (s, 6H, OCH <sub>3</sub> ), 3.45 (brs, 4H,<br>1-H, 2-H, 4-H, 5-H), 1.83 (d, 1H, J=8.7Hz, 8-H <sub>β</sub> ), 1.41 (d, 1H,<br>J=8.7Hz, 8-H <sub>α</sub> )             |
| 3c (R=SO <sub>2</sub> Ph) | 2240 (ν <sub>CN</sub> )<br>1335 (ν <sub>SO<sub>2</sub></sub> )   | 7.46 - 8.16 (m, 5H, aromatic), 3.50 (brs, 2H, 1-H, 5-H), 3.43 (s,<br>2H, 2-H, 4-H), 2.03 (d, 1H, J=10.7Hz, 8-H <sub>β</sub> ), 1.55 (d, 1H,<br>J=10.7Hz, 8-H <sub>α</sub> )                              |
| 3a (R=Ph)                 | 1600 (ν <sub>C=C</sub> )   | 6.58 - 7.30 (m, 5H, aromatic), 6.22 (brs, 2H, 6-H, 7-H), 2.96 (m,<br>2H, 1-H, 5-H), 2.40 (s, 2H, 2-H, 4-H), 1.82 (d, 1H, J=8.0Hz,<br>8-H <sub>β</sub> ), 1.12 (1H, d, J=8.0Hz, 8-H <sub>α</sub> )        |
| 6b                        | 1730 (ν <sub>CO</sub> )<br>1325 (ν <sub>SO<sub>2</sub></sub> )   | 7.40 - 8.00 (m, 5H, aromatic), 3.72 (brs, 2H, 2-H, 4-H), 3.66 (s,<br>6H, OCH <sub>3</sub> ), 3.38 (m, 2H, 1-H, 5-H), 1.98 (brs, 2H, 8-CH <sub>2</sub> )  |
| 6c                        | 2230 (ν <sub>CN</sub> )<br>1325 (ν <sub>SO<sub>2</sub></sub> )   | 7.50 - 8.30 (m, 5H, aromatic), 3.81 (m, 2H, 2-H, 4-H), 3.45 (m,<br>2H, 1-H, 5-H), 2.15 (s, 2H, 8-CH <sub>2</sub> )   |

Table 4. Spectral data of compounds 4b,c (R=SO<sub>2</sub>Ph) and 4a (R=COOEt)

| Compound                  | IR (cm <sup>-1</sup> )   | NMR (δ values from TMS, Solvent; CDCl <sub>3</sub> )  |
|---------------------------|--|---|
| 4b (R=SO <sub>2</sub> Ph) | 1730 (ν <sub>CO</sub> )<br>1350 (ν <sub>SO<sub>2</sub></sub> ) | 7.30 - 8.00 (m, 5H, aromatic), 6.49 (dd, 1H, J=7.0Hz, J=1.0Hz,<br>3-H), 5.35 (m, 1H, 1-H), 3.82 (s, 3H, OCH <sub>3</sub> ), 3.68 (s, 3H, OCH <sub>3</sub> ),<br>3.08 (m, 1H, 5-H), 1.95 (m, 1H, 8-H <sub>α</sub> ), 1.29 (d, 1H, J=11.0Hz, 8-H <sub>β</sub> )   |
| 4c (R=SO <sub>2</sub> Ph) | 2230 (ν <sub>CN</sub> )<br>1360 (ν <sub>SO<sub>2</sub></sub> ) | 7.50 - 8.15 (m, 5H, aromatic), 6.68 (dd, 1H, J=1.3Hz, J=8.0Hz, 3-H),<br>5.33 (t, 1H, J=8.0Hz, J=6.0Hz, 4-H), 5.10 (m, 1H, 1-H), 3.20 (m,<br>1H, 5-H), 2.02 (m, 1H, 8-H <sub>α</sub> ), 1.43 (d, 1H, J=11.8Hz, 8-H <sub>β</sub> )  |
| 4a (R=COOEt)              | 1710 (ν <sub>CO</sub> )<br>1622 (ν <sub>C=C</sub> )            | 6.49 (dd, 1H, J=8.3Hz, J=1.6Hz, 3H), 6.20 (dd, 1H, J=2.7Hz,<br>J=5.7Hz, 6-H), 5.51 (dd, 1H, J=5.7Hz, J=2.3Hz, 7-H), 5.10 (m, 2H,<br>1-H, 4-H), 4.20 (q, 2H, -OCH <sub>2</sub> CH <sub>3</sub> ), 2.69 (m, 1H, 5-H), 1.80 (m, 1H,<br>8-H <sub>α</sub> ), 1.25 (t, 4H, -OCH <sub>2</sub> CH <sub>3</sub> , 8-H <sub>β</sub> ) |

6, 7-Bis(methoxycarbonyl)-3-phenylsulfonyl-2,4-exo-3-azatricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene 3b (R=SO<sub>2</sub>Ph): A solution of a mixture of 3.7 g (0.0178 mol) of 2,3-bis(methoxycarbonyl) norbornadiene and 1.1 g (0.006 mol) of benzenesulfonyl azide in 20 ml of dry benzene was stirred at 50°C for 48 h. After the removal of benzene *in vacuo*, the residue was chromatographed on silica gel. Elution with (12 : 1) benzene-acetone gave 1.16 g (74%) of 3b (R=SO<sub>2</sub>Ph) and 0.23 g (10%) of 6b (R=SO<sub>2</sub>Ph). The 3b (R=SO<sub>2</sub>Ph) was recrystallized from methanol to give colorless prisms: mp 127 - 128°C; MS, m/e, 363 (M<sup>+</sup>). Found: C; 56.05, H; 4.70, N; 3.98%. Calcd for C<sub>17</sub>H<sub>17</sub>NO<sub>6</sub>S: C; 56.20, H; 4.68, N; 3.86%. The 6b

was recrystallized from methanol to give colorless cubic crystals: mp 100 - 100.5°C; MS, m/e, 363 ( $M^+$ ). Found: C; 56.17, H; 4.68, N; 4.09%. Calcd for  $C_{17}H_{17}NO_6S$ : C; 56.20, H; 4.68, N; 3.86%.

**6,7-Dicyano-3-phenylsulfonyl-2,4-exo-3-azatricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene 3c (R=SO<sub>2</sub>Ph):** A solution of a mixture of 5.0 g (0.0352 mol) of 2,3-dicyanonornbornadiene<sup>10)</sup> and 2.2 g (0.012 mol) of benzenesulfonyl azide in 20 ml of dry benzene was stirred at 80°C for 68 h and then benzene was removed *in vacuo*. The residue was chromatographed on silica gel. Elution with (12 : 1) benzene-ethyl acetate gave 0.68 g (19%) of 3c (R=SO<sub>2</sub>Ph), 0.74 g (21%) of 6c, and 0.23 g (12%) of 7. The 3c (R=SO<sub>2</sub>Ph) was recrystallized from ethanol to give colorless plates: mp 182 - 183°C; MS, m/e, 297 ( $M^+$ ). Found: C; 60.72, H; 3.68, N; 14.01%. Calcd for  $C_{15}H_{11}N_3O_2S$ : C; 60.61, H; 3.70, N; 14.14%. The 6c was recrystallized from methanol to give colorless plates: mp 188 - 189°C; MS, m/e, 297 ( $M^+$ ). Found: C; 60.63, H; 3.72, N; 13.90%. Calcd for  $C_{15}H_{11}N_3O_2S$ : C; 60.61, H; 3.70, N; 14.14%. The 7 was recrystallized from (5 : 1) hexane-chloroform to give colorless needles: mp 119 - 121°C; NMR (CDCl<sub>3</sub>)  $\delta$  = 3.66 (m, 1H, 1-H), 3.51 (1H, m, 4-H), 2.68 (1H, d, J=11.3Hz, 6-H<sub>exo</sub>), 1.98-2.45 (m, 3H, 6-H<sub>endo</sub>, 7-CH<sub>2</sub>); IR (KBr) 2220 ( $\nu_{CN}$ ), 1750 ( $\nu_{CO}$ ); MS, m/e, 158 ( $M^+$ ). Found: C; 68.60, H; 3.78, N; 17.67%. Calcd for  $C_9H_6N_2O$ : C; 68.35, H; 3.80, N; 17.72%.

**3-Phenyl-2,4-exo-3-azatricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene 3a (R=Ph):** A solution of 4.4 g (0.021 mol) of the 2a (R=Ph) in 35 ml of dry cyclohexane placed in pyrex-tube was irradiated for 22 h from a 100 W-mercury lamp. After the removal of cyclohexane *in vacuo*, the residue was distilled at 106 - 107°C (0.4 mmHg) to obtain 1.38 g (36%) of 3a (R=Ph): MS, m/e, 183 ( $M^+$ ). Found: C; 85.50, H; 7.18, N; 7.41%. Calcd for  $C_{13}H_{13}N$ : C; 85.24, H; 7.10, N; 7.65%.

**Decomposition of triazoline compound 2a (R=COOEt):** A solution of 5.72 g (0.028 mol) of 2a (R=COOEt) in 56 ml of dry toluene was refluxed for 13 h and then toluene was removed *in vacuo*. The residue was chromatographed on silica gel. Elution with benzene gave 2.02 g (41%) of 4a (R=COOEt) and 2.02 g (37%) of 8. The 4a (R=COOEt) was distilled at 85 - 86°C (0.4 mmHg): MS, m/e, 179 ( $M^+$ ). Found: C; 67.30, H; 7.41, N; 7.95%. Calcd for  $C_{10}H_{13}NO_2S$ : C; 67.02, H; 7.26, N; 7.82%. The 8 was recrystallized from (2 : 1) hexane-benzene to give colorless prisms: mp 77 - 78.5°C; NMR (CDCl<sub>3</sub>)  $\delta$  = 6.29 (dd, 1H, J=5.3 Hz, J=3.0Hz, 2-H), 6.03 (dd, 1H, J=5.3Hz, J=3.3Hz, 3-H), 5.67 (m, 1H, OH), 4.62 (m, 1H, NH), 4.11 (q, 2H, -OCH<sub>2</sub>CH<sub>3</sub>), 3.18 (m, 1H, 4-H), 2.87 (m, 1H, 1-H), 1.40 - 2.23 (m, 4H, 6-CH<sub>2</sub>, 7-CH<sub>2</sub>), 1.22 (t, 3H, -OCH<sub>2</sub>CH<sub>3</sub>); IR (KBr) 3290 ( $\nu_{OH}$ ,  $\nu_{NH}$ ) and 1730 ( $\nu_{CO}$ )  $cm^{-1}$ ; MS, m/e, 180. Found: C; 60.69, H; 7.90, N; 7.06. Calcd for  $C_{10}H_{15}NO_3$ : C; 60.91, H; 7.61, N; 7.11%.

**2-Phenylsulfonyl-2-azabicyclo[3.2.1]oct-3,6-diene 4a (R=SO<sub>2</sub>Ph):** A solution of 6.53 g (0.026 mol) of 3a (R=SO<sub>2</sub>Ph) in 50 ml of dry benzene was refluxed for 5 h and then benzene was removed *in vacuo*. The residue was chromatographed on silica gel. Elution with benzene gave 6.40 g (98%) of 4a (R=SO<sub>2</sub>Ph). The spectral data and elemental analysis agreed with the data described in the literature.<sup>6)</sup>

**2-Ethoxycarbonyl-2-azabicyclo[3.2.1]oct-3,6-diene 4a (R=COOEt):** Use of toluene as

a solvent; A solution of 3.64 g (0.02 mol) of 3a (R=COOEt) in 20 ml of dry toluene was refluxed for 13 h. Use of dry ethanol as a solvent; A solution of 3.64 g of 3a (R=COOEt) in 20 ml of dry ethanol was refluxed for 2 h. In both cases, the solution after the reaction was treated as follows. After the removal of the solvent *in vacuo*, the residue was chromatographed on silica gel. Elution with benzene gave 3.46 - 3.60 g (95 - 99%) of 4a (R=COOEt).

*6,7-Bis(methoxycarbonyl)-2-phenylsulfonyl-2-azabicyclo[3.2.1]oct-3,6-diene* 4b (R=SO<sub>2</sub>Ph): Use of dry xylene as a solvent; A solution of 1.09 g (0.003 mol) of 3b (R=SO<sub>2</sub>Ph) in 20 ml of xylene was refluxed for 11 h. Use of dry o-dichlorobenzene as a solvent; A solution of 1.09 g (0.003 mol) of 3b (R=SO<sub>2</sub>Ph) in 20 ml of o-dichlorobenzene was refluxed for 0.2 h. In both cases, the solution after the reaction was treated as follows. After the removal of the solvent *in vacuo*, the residue was chromatographed on silica gel. Elution with (12 : 1) benzene-acetone gave 1.08 - 1.09 g (99 - 100%) of 4b (R=SO<sub>2</sub>Ph). The 4b (R=SO<sub>2</sub>Ph) was recrystallized from 95% ethanol to give colorless prisms: mp 83 - 84°C; MS, m/e, 363 (M<sup>+</sup>). Found: C; 55.96, H; 4.78, N; 3.70%. Calcd for C<sub>17</sub>H<sub>17</sub>NO<sub>6</sub>S: C; 56.20, H; 4.68, N; 3.86%.

*6,7-Dicyano-2-phenylsulfonyl-2-azabicyclo[3.2.1]oct-3,6-diene* 4c (R=SO<sub>2</sub>Ph): A solution of 1.19 g (0.004 mol) of 3c (R=SO<sub>2</sub>Ph) in 10 ml of dry o-dichlorobenzene was refluxed for 7 h and then o-dichlorobenzene was removed *in vacuo*. The residue was chromatographed on silica gel. Elution with (12 : 1) benzene-acetone gave 1.18 g (100%) of 4c (R=SO<sub>2</sub>Ph). The 4c (R=SO<sub>2</sub>Ph) was recrystallized from 95% ethanol to give colorless prisms: mp 116 - 118°C; MS, m/e, 297 (M<sup>+</sup>). Found: C; 60.84, H; 3.61, N; 13.99%. Calcd for C<sub>15</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>S: C; 60.61, H; 3.70, N; 14.14%.

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