95 mg (0.21 mmol) of **11** in 3 mL of THF was cooled to -78 °C and treated with 0.15 mL (0.33 mmol) of 2.2 M vinyllithium in THF. The yellow mixture was stirred for 5 min at -78 °C and then for 10 min at 0 °C whereupon 31 μL (0.5 mmol) of methyl iodide was added. The yellow color of the vinyllithium adduct was discharged in approximately 1 min whereupon the mixture was warmed to 20 °C and stirred for an additional 2 min. Solvent was removed under reduced pressure, and the residue was treated with water and extracted with dichloromethane. The extract was washed with water and dried over Na_2SO_4. The residue obtained upon solvent removal was purified by PTLC (silica gel, 20:1 CH_2Cl_2–EtOAc, two developments) giving 73 mg (73%) of a mixture of diastereomers (approximately 9:1). The more mobile major 4*R**,5*R** isomer, **12**, could be obtained as an oil free of the minor isomer **13** by careful PTLC: IR ($CHCl_3$) 3070, 3000, 1656, 1648, 1550, 1437, 1376, 1290, 1100, 1090 cm^{-1}; ^1H NMR (90 Mhz, $CDCl_3$) δ 0.64 (t, 3 H, OCH_2CH_3, J = 7.1 Hz), 1.01 (d, 3 H, 4-Me, J = 6.8 Hz), 1.56 (d, 3 H, $C{=}C(CH_3)_2$, J = 1.2 Hz), 1.69 (d, 3 H, $C{=}C(CH_3)_2$, J = 1.2 Hz), 3.22 (m, 1 H, 4-H), 3.71 (q, 2 H, OCH_2, J = 7.1 Hz), 3.6–4.1 (m, 1 H, 4-H), 4.7–5.1 (m, 3 H, vinyl protons), 5.55–5.93 (m, 1 H, $HC{=}CH_2$), 7.2–7.8 (m, 15 H, PhH). The spectrum of the 4*S**,5*R** isomer, **13**, is very similar with vinyl methyl resonances at δ 1.69 and 1.36. ^{13}C NMR ($CDCl_3$, 22.5 Mhz) of **12**: δ 13.8 (CH_3), 16.0 (4-Me), 18.2 (7-Me), 26.0 (C-8), 44.4 (d, C-4, $^3J_{CP}$ = 6.7 Hz), 45.9 (C-5), 58.3 (OCH_2), 72.0 (d, C-2, $^1J_{CP}$ = 108.8 Hz), 113.0 ($C{=}CH_2$), 126.1 (C-6); PPh_3 127.5 (d, $^1J_{CP}$ = 94.0 Hz), 128.3 (d, $^2J_{CP}$ = 12.1 Hz), 131.3 (d, $^4J_{CP}$ = 2.7 Hz), 133.2 (d, $^3J_{CP}$ = 9.4 Hz); 131.9 (C-7), 141.2 ($CH{=}CH_2$), 167.5 (d, C-1, $^2J_{CP}$ = 14.8 Hz), 200.0 (d, C-3 $^2J_{CP}$ = 2.7 Hz).

Methyl (2*R,3*R**)-2,5-Dimethyl-3-ethenyl-4-hexenoate (Methyl *epi*-Santolinate, 14).** A solution containing 300 mg (0.6 mmol) of **12** and **13** from above in 4.0 mL of acetonitrile was treated with 270 μL of 4 N NaOH and then cooled with an ice bath. A solution of 0.82 N NaOCl (1.8 mL, 1.48 mmol) was added over 30 min (approximately 0.5-mL portions every 7 min) followed by stirring at 0 °C for 2.5 h. The mixture was warmed to 20 °C, stirred for 0.5 h, and then treated with an additional 400 μL of 4 N NaOH followed by continued stirring for an additional 2.5 h. Small portions of $NaHSO_3$ were added until excess NaOCl was consumed (negative acidic starch–iodide paper test), and the acetonitrile was removed in vacuo. The remaining aqueous phase was brought to 4-mL volume and pH ≥10 by the addition of water and 4 N NaOH, respectively, and the mixture was extracted thrice with 10-mL portions of Et_2O to remove triphenylphosphine oxide and a small amount of unreacted **12** and **13**. The aqueous phase was acidified with aqueous HCl to pH 1 and extracted with 15 mL of pentane. Concentration of this extract (25 °C, 15 mmHg) gave 72 mg (71%; 77% based on 25 mg of **12** and **13** recovered by chromatography of the neutral extracts) of *epi*-santolinoic acid containing a small amount of santolinoic acid which was used without further purification; ^1H NMR ($CDCl_3$, 90 Mhz) δ 1.12 (d, 3 H, CH_3, J = 7.0 Hz), 1.63 (d, 3 H, $C{=}CCH_3$, J = 1.2 Hz), 1.73 (d, 3 H, $C{=}CCH_3$, J = 1.2 Hz), 2.43 (m, 1 H, CH_3CH), 3.21 (m, 1 H, allylic CH), 4.83–5.95 (m, 4 H, vinyl protons), 11.73 (s, 1 H, COOH).

The crude acid (65 mg, 0.39 mmol) in 3 mL of diethyl ether was treated portionwise with CH_2N_2 in diethyl ether until the yellow color of CH_2N_2 persisted for 1 min. Solvent and excess CH_2N_2 were removed by distillation, and the residue was dissolved in 5 mL of pentane. This solution was washed with saturated $NaHCO_3$ and then with water and dried over Na_2SO_4. Solvent removal gave 65 mg (92%) of the isomeric esters **14** and **15** shown by GLC (10% UCW-98, 135 °C) to consist of 91% **14** and 8% diasteromer **15**. The major less mobile component in our sample corresponded to authentic methyl *epi*-santolinate in a 1:1 mixture of the two diastereomers kindly provided by Professor Epstein.[9] An analytical sample was obtained by PTLC (silica gel, dichloromethane) followed by bulb-to-bulb distillation (160 °C, 13 mmHg); IR (neat) 2983, 1735, 1640, 1452, 1432, 1350, 1258, 1203, 1160, 912 cm^{-1}; ^1H NMR ($CDCl_3$), 90 Mhz) δ 1.09 (d, 3 H, 2-Me, J = 6.8 Hz), 1.63 (d, 3 H, $C{=}CCH_3$, J = 1.0 Hz), 1.73 (d, 3 H, $C{=}CCH_3$, J = 1.5 Hz), 2.43 (m, 1 H, CH_3CH), 3.18 (m, 1 H, allylic CH), 3.63 (s, 3 H, OCH_3), 4.84–5.90 (m, 4 H, vinyl protons) (the presence of the minor isomer is evidenced by a doublet at δ 1.12 (3 H, CH_3CH) and a singlet at δ 3.62 (3 H, OCH_3)); ^{13}C NMR ($CDCl_3$) δ 14.6 (2-Me), 18.1 (5-Me), 25.9 (C-6), 44.8 (C-2), 46.0 (C-3), 114.4 (CH_2), 123.6 (C-4), 134.0 (C-5), 139.3 ($CH{=}CH_2$, 176.0 (C-1). Additionally, resonances from the minor isomer (methyl santolinate) were found at δ 17.9, 44.5, 46.3, 115.2, 124.1, 133.3, and 138.6. Peak positions for both isomers correspond to those in the spectrum of the authentic mixture.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.58; H, 9.97.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Registry No. **4** (Z = $C(PPh_3)COOEt$), 83269-72-1; **4** (Z = OH), 142-62-1; **5** (Z = $C(PPh_3)COOEt$), 84454-74-0; **5** (Z = OH), 501-52-0; **6** (Z = $C(PPh_3)COOEt$), 1474-31-3; **6** (Z = OH), 65-85-0; **7** (Z = $C(PPh_3)COOEt$), 83269-74-3; **7** (Z = OH), 5636-65-7; **8** (Z = $C(PPh_3)COOEt$), 72449-05-9; **8** (Z = OH), 4541-43-9; **9** (Z = $C(PPh_3)COOEt$), 62251-85-8; **9** (Z = OH), 149-57-5; **10** (Z = $C(PPh_3)COOEt$), 84454-75-1; **10** (Z = OH) (isomer 1), 84454-72-8; **10** (Z = OH) (isomer 2), 84454-73-9; (*E*)-**11** (Z = $C(PPh_3)COOEt$), 84454-76-2; (±)-**12** (Z = $C(PPh_3)COOEt$), 84454-77-3; (±)-**13** (Z = $C(PPh_3)COOEt$), 84454-78-4; (±)-**14**, 61009-02-7; (±)-**15**, 61009-01-6; 3-Methyl-2-butenal, 107-86-8; diethyl 2,4-dioxo-4-ethoxy-3-(triphenylphosphoranylidene)butanephosphonate, 78980-76-4; (±)-episantolinic acid, 61009-00-5; (±)-santolinic acid, 61008-99-9; Methyl 5-methoxy-4-hexenoate, 84454-79-5.

A Convenient Route to *N*-(*p*-Tolylsulfonyl)phenanthren-9,10-imine and Related Compounds

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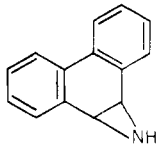
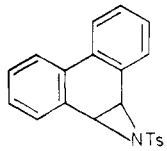
Received August 12, 1982

Because of their relationship to the carcinogenic epoxides of certain polynuclear aromatic hydrocarbons the corresponding imines have been the object of several synthetic studies.[1-9] The first such unsubstituted imine **1** was reported in 1978 by Blum and co-workers.[1] Subsequently a number of reports on this and related compounds appeared.[4-9] A number of *N*-alkyl and *N*-acyl derivatives had been reported earlier.[2,3] The *N*-tosyl derivative **2** was reported by Shudo and Okamoto[4] who obtained it by a tedious procedure starting from phenanthrene 9,10-oxide. Blum and co-workers[5] recently described the preparation of **2** via reaction of the *N*-trimethylsilyl derivative of **1** with *p*-toluenesulfonyl chloride. Direct tosylation of **1** led to ring opening.



1



2

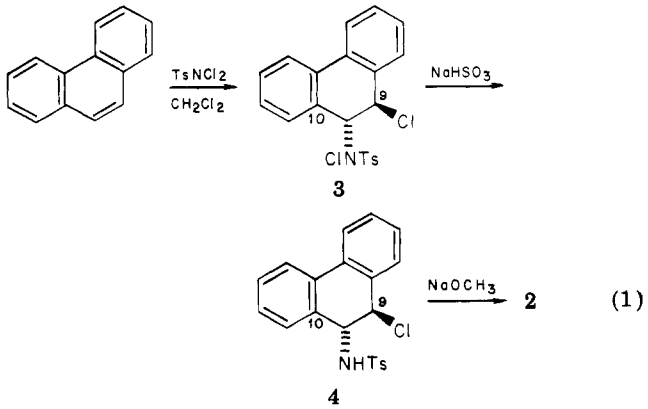
The Japanese and Israeli workers appear to have been unaware of the previous report in the Russian patent literature[10] of a prior claim for the preparation of **2**. Un-

(1) Ittah, Y.; Sasson, Y.; Shahak, I.; Tsaroom, S.; Blum, J. *J. Org. Chem.* **1978**, *43*, 4271.
(2) Ittah, Y.; Shahak, I.; Blum, J. *J. Org. Chem.* **1978**, *43*, 397.
(3) Blum, J.; Ittah, Y.; Shahak, I. *Tetrahedron Lett.* **1975**, 4607.
(4) Shudo, K.; Okamoto, T. *Chem. Pharm. Bull.*, **1976**, *24*, 1013.
(5) Weitzberg, M.; Aizenshtat, Z.; Blum, J. *J. Heterocycl. Chem.* **1981**, *18*, 1513.
(6) Weitzberg, M.; Aizenshtat, Z.; Jerushalmy, P.; Blum, J. *J. Org. Chem.* **1980**, *45*, 4252.
(7) Yona, I.; Blum, J. *J. Heterocycl. Chem.* **1981**, *18* , 1473.
(8) Blum, J.; Yona, I.; Tsaroom, S.; Sasson, Y. *J. Org. Chem.* **1979**, *44*, 4178.
(9) Denis, J. N.; Krief, A. *Tetrahedron* **1979**, *35*, 2901.

0022-3263/83/1948-0746$01.50/0

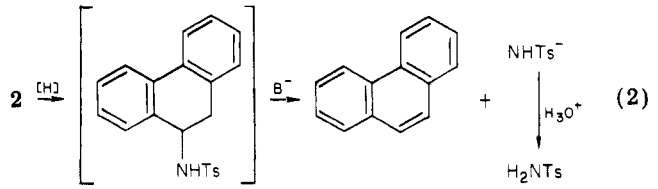
fortunately the abstract available provides no experimental details or physical constants except to state that **2** was obtained by treatment of phenanthrene with *N,N*-dichloro-*p*-toluenesulfonamide followed by stirring with alkaline sodium bisulfite. Recognizing this as a potentially simple general method[11] that would be especially valuable as a route to **1** if it became possible to remove the tosyl group without opening the three-membered ring, we have investigated this method in some detail. Although no information was available regarding structural evidence for **2**, the existence of a second patent[12] by the same group of investigators claiming the preparation of 9-*p*-toluenesulfonamidophenanthrene implied that this isomer, and by inference the tautomeric ketone *p*-toluenesulfonimide,[13] had been excluded.

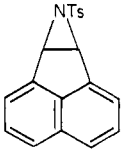
We have confirmed these results and by careful isolation procedures were able to stop the reaction at the stage of two intermediate precursors, **3** and **4**. The first intermediate **3** was obtained by carrying out the initial reaction in methylene dichloride at room temperature (eq 1).



Reduction of **3** by means of aqueous sodium bisulfite at 0 °C gave **4**. In the ^1H NMR spectrum the C-10 proton of **3** showed the expected[14] shift on conversion to **4**.

Confirmatory evidence for structure **2**, in addition to that cited by Shudo and Okamoto[4] and Blum and coworkers, is the appearance of an aziridine ring carbon signal at 44.7 ppm in the ^{13}C NMR spectrum.[15] Upon heating compound **2** underwent isomerization to 9-*p*-toluenesulfonamidophenanthrene.[4] Attempted deblocking of the tosyl group of **2** by means of the sodium–naphthalene radical anion in 1,2-dimethoxyethane[16] gave none of the free aziridine **1** but rather a mixture of phenanthrene and *p*-toluenesulfonamide. This suggests reductive ring opening to give **5** followed by elimination of *p*-toluenesulfonamide anion (eq 2). The present method was also shown to be applicable to the conversion of acenaphthylene to aziridine **6**.





Experimental Section

9-Chloro-10-(*N*-chloro-*p*-toluenesulfonamido)-9,10-dihydrophenanthrene (3). A solution of 2.4 g of Cl_2NTs[18] in 30 mL of CH_2Cl_2 was added dropwise to a stirred solution of 1.78 g of phenanthrene in 10 mL of CH_2Cl_2 cooled in an ice bath. After complete addition the solution was allowed to come to room temperature and stirred for 24 h. Removal of CH_2Cl_2 followed by trituration of the residue with 5 mL of ether and cooling in an ice bath gave 2.25 g of yellow solid, which was shown by TLC and NMR analysis to be a mixture of **3** and **4**. Fractional crystallization from 20 mL of ether gave 1.2 g of **3** and 0.4 g of **4** (combined yield 40.7%). The title compound had the following: mp 137–139 °C ether; IR ($CHCl_3$) 1160, 1360 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.47 (s, 3, CH_3), 5.30 (d, 1, ClCH), 5.66 (d, 1, ClNCH), 6.9–8.1 (m, 12, aryl).

Anal. Calcd for $C_{21}H_{17}Cl_2NO_2S$: C, 60.29; H, 4.09; N, 3.35. Found: C, 60.41; H, 4.40; N, 3.19.

9-Chloro-10-*p*-toluenesulfonamido-9,10-dihydrophenanthrene (4). To a stirred solution of 2.09 g of **3** in 50 mL of CH_2Cl_2 cooled to 0 °C in an ice–salt bath was added a solution of 1.58 g of $NaHSO_3$ in 75 mL of H_2O. Stirring was continued for 30 min. The organic layer was separated and the aqueous layer extracted with 30 mL of CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and evaporated in vacuo to give a pale-yellow solid, which upon recrystallization from ether gave 1.57 g (82%) of **4** as a white solid: mp 135–137 °C; IR ($CHCl_3$) 3350 (NH), 1330, 1160 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.42 (s, 3, CH_3), 4.60 (m, 2, HNCH), 5.22 (br s, 1, ClCH), 7.15–8.05 (m, 12, aryl).

Anal. Calcd for $C_{21}H_{18}ClNO_2S$: C, 65.79; H, 4.69; N, 3.65. Found: C, 65.72; H, 4.78; N, 3.69.

***N*-(*p*-Tolylsulfonyl)phenanthren-9,10-imine (2).** To a stirred solution of 1.27 g of **4** in 40 mL of CH_3OH was added a solution of 0.8 g of $NaOCH_3$ in 40 mL of CH_3OH over a period of 3 min. Stirring was continued until all the solid had dissolved (ca. 30 min) and the resulting solution was evaporated at room temperature to give a pale-yellow solid, which was triturated and washed with four 20-mL portions of H_2O. Recrystallization from 40 mL of CCl_4 gave 0.82 g (86%) of **2** as a white solid, mp 148–149 °C. The analytical sample had the following: mp 150–151 °C[19] (CCl_4); IR ($CHCl_3$) 1150, 1315 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.32 (s, 3, CH_3), 4.42 (s, 2, CHN), 7.15–8.10 (m, 12, aryl); ^{13}C NMR ($CDCl_3$) δ 21.5 (CH_3), 44.7 (CHN); MS (80 eV), *m/e* 347 (M^+, 84),

(10) Markov, V. I.; Kremlev, M. M.; Danileiko, D. A.; Baranovskaya, V. F. *Otkrystiya Izobret., Prom. Obraztsy, Tovarnye* Znaki **1972**, *49*, 87; *Chem. Abstr.* **1972**, *77*, 88166.

(11) Recently a number of closely related reactions have been examined as routes to *N*-arenesulfonylaziridines from simple olefins. See (a) Barton, D. H. R.; Britten-Kelly, M. R.; Ferreira, D. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1091. (b) Terauchi, H.; Takemura, S. *Chem. Parm. Bull.* **1975**, *23*, 2410. (c) Ueno, Y.; Takemura, S.; Ando, Y.; Terauchi, H. *Ibid.* **1967**, *15*, 1193, 1198, 1322. (d) Takemura, S.; Otsuki, K.; Okamoto, K.; Ueno, Y. *Ibid.* **1968**, *16*, 1881, 1885. (e) Terauchi, H.; Takemura, S.; Ueno, Y. *Ibid.* **1975**, *23*, 640. (f) Terauchi, H.; Kowata, K.; Minematsu, T.; Takemura, S. *Ibid.* **1977**, *25*, 556.

(12) Markov, V. I.; Kremlev, M. M.; Danileiko, D. A.; Baranovskaya, V. F. *Otkrystiya Izobret., Prom. Obraztsy, Tovarnye Znaki* **1973**, *50*, 63; *Chem. Abstr.* **1973**, *80*, 27026.

(13) Compare Zalkow, L. H.; Calhoun, R. M. *Tetrahedron Lett.* **1975**, 2149.

(14) Compare Daniher, F. A.; Butler, P. E. *J. Org. Chem.* **1968**, *33*, 4336.

(15) Levy, G. C. "^{13}C-Nuclear Magnetic Resonance for Organic Chemistry"; Wiley-Interscience: New York, 1972; p 52.

(16) Ji, S.; Gortler, L. B.; Waring, A.; Battisti, A.; Bank, S.; Closson, D. W.; Wriede, P. *J. Am. Chem. Soc.* **1967**, *89*, 5311. In this connection see also ref 11b and 11e.

(17) Melting points and boiling points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 727 instrument and ^1H NMR spectra on Perkin-Elmer R-12 and Varian A-60 instruments with Me_4Si as internal standard. The ^{13}C NMR spectra were taken on a Bruker HX-90 spectrometer with chemical shifts given relative to Me_4Si. Elemental analyses were carried out by the University of Massachusetts Microanalytical Laboratory under the direction of Greg Dabkowski.

(18) Soper, F. G. *J. Chem. Soc.* **1924**, *125*, 1899.

(19) Shudo and Okamoto[4] report a double melting point: 95–101 and 170–171 °C; Blum and co-workers[5] report mp 168–171 °C. Our form is presumably a polymorphic modification. Our spectral data correspond with those of the previous workers.

192 (97), 193 (26), 166 (37), 165 (100), 91 (18).

Anal. Calcd for $C_{21}H_{17}NO_2S$: C, 72.62; H, 4.90; N, 4.03. Found: C, 72.45; H, 4.78; N, 4.02.

1-Chloro-2-(*N*-chloro-*p*-toluenesulfonamido)-acenaphthene. To a well-stirred cold (0–2 °C) solution of 2.01 g of acenaphthylene in 15 mL of CH_2Cl_2 was added dropwise (10 min) a solution of 3.2 g of Cl_2NTs in 15 mL of CH_2Cl_2. Workup as described above followed except that CCl_4 at −30 °C was used in place of ether at 0–2 °C to triturate the crude solid. The insoluble portion (0.9 g, mp 149–152 °C) was identified as 1-chloro-2-*p*-toluenesulfonamidoacenaphthene (see below). The CCl_4 filtrate was evaporated and the residue was triturated with 15 mL of ether. Cooling to −30 °C (dry ice–acetone bath) gave a light-yellow solid, which was washed with two 3-mL portions of cold (−20 °C) ether to give 2.1 g (59.2%) of the *N*-chloro compound, mp 115–117 °C. The analytical sample had the following: mp 117–119 °C (ether); IR ($CHCl_3$) 1340, 1160 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.47 (s, 3, CH_3), 5.50 (d, 1, ClCH), 6.37 (d, 1, CHN), 7.30–8.20 (m, 10, aryl).

Anal. Calcd for $C_{19}H_{15}Cl_2NO_2S$: C, 58.16; H, 3.83; N, 3.57. Found: C, 58.26; H, 3.86; N, 3.22.

1-Chloro-2-*p*-toluenesulfonamidoacenaphthene. The *N*-chloro sulfonamide (2.09 g) was reduced with $NaHSO_3$ (1.58 g) as described for the phenanthrene derivative. The crude product was recrystallized from CCl_4 to give 1.35 g (75.8%) of the title compound, mp 152–154 °C. The analytical sample had the following: mp 154.5–155.5 °C (CH_2Cl_2–ligroin, bp 67–71 °C); IR ($CHCl_3$) 3375 (NH), 1340, 1160 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.47 (s, 3, CH_3), 5.10 (d, 1, NH), 5.35 (d, 1, CHN), 5.40 (s, 1, CHCl), 7.10–8.05 (m, 10, aryl).

***N*-(*p*-Tolylsulfonyl)acenaphthylenimine (6).** A solution of 1.79 g of 1-chloro-2-*p*-toluenesulfonamidoacenaphthene in 50 mL of CH_3OH was treated with 0.8 g of $NaOCH_3$ as described for the corresponding phenanthrene derivative. Recrystallization from ether–ligroin (bp 67–71 °C; 2/1, v/v) gave 1.5 g (94.7%) of the imine as a white solid: mp 140–142 °C; IR ($CHCl_3$) 1325, 1160 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.42 (s, 2, CH_3), 4.82 (s, 2, CHN), 7.27–7.95 (m, 10, aryl); ^{13}C NMR ($CDCl_3$) δ 21.7 (CH_3), 47.5 (CHN); MS (80 eV), *m/e* 321 (M^+, 27), 167 (55), 166 (100), 144 (29), 139 (35), 91 (30).

Anal. Calcd for $C_{19}H_{15}NO_2S$: C, 71.00; H, 4.67; N, 4.36. Found: C, 71.05; H, 4.62; N, 4.35.

Acknowledgment. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and in part by the National Science Foundation.

Registry No. 2, 60883-97-8; 3, 84195-16-4; 4, 84195-17-5; 6, 84195-18-6; Cl_2NTs, 473-34-7; phenanthrene, 85-01-8; 1-chloro-2-(*N*-chloro-*p*-toluenesulfonamido)acenaphthene, 84195-19-7; acenaphthylene, 208-96-8; 1-chloro-2-*p*-toluenesulfonamidoacenaphthene, 84195-20-0.

Activation Parameters and Location of the Transition State in the Retro-Diels–Alder Reaction of a 7-Oxabicyclo[2.2.1]hept-5-ene Derivative

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Received September 17, 1982

Retro-Diels–Alder thermolyses are thermally allowed ($_\pi4_s + _\pi2_s$) processes. The study of their mechanism cannot be dissociated from the corresponding one of the forward reaction for which the concerted pathway seems to be the most compatible with the experimental and theoretical results, at least for good donor–acceptor partners.[1]

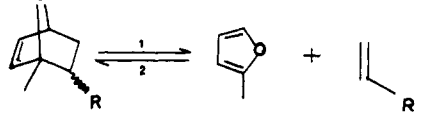
Table I. Temperature and Pressure Effect on the Rate Constant *k* in Thermolysis Reaction 1[a]

		10^4k,[b] s^{-1}		
P, bar	*T*, K	cyclohexane[c]	dichloromethane	acetonitrile
1	342.9		1.13	0.97
	343.1	0.665		
	353.2	2.07	3.30	2.37
	363.0	5.20		
	364.1		10.40	7.76
	374.8		26.39	21.10
1	353.2	2.07	3.30	2.37
225		2.19		
260				2.53
290			3.43	
445			3.46	2.57
465		2.15		
750		2.22	3.46	2.50
930		2.23		
945			3.47	2.62
1930				3.01

[a] Adduct composition (endo/exo ratio of 2:3). [b] Averaged value. Precision (5%); *P*, ±5 bar; *T*, ±0.1 K. [c] The miscibility of adduct and cyclohexane is ensured with the addition of 500 mg of CH_2Cl_2 (standard) in each run.

Numerous (4 + 2) cycloadditions have been investigated in the light of activation volume $\Delta V^{\ddagger}$.[2] It was found invariably that for a given reaction $\Delta V^{\ddagger}$ is very close[3] to the reaction volume $\overline{\Delta V}$, suggesting a late transition state in terms of nuclear positions. To our knowledge, no $\Delta V^{\ddagger}$ value has been reported yet for the reverse reaction.[4]

We observed some time ago[5] that, in the condensation of furans, the retrodiene cleavage 1 regenerating the



starting materials occurs at moderate temperatures in contrast to common retro-Diels–Alder reactions which require much more drastic conditions.[6] The instability of the bridged bicyclic adducts was attributed to the aromatic character of the furan system[7] and the ring strain.[8]

The pressure effect was investigated in some condensations of 2-methylfuran and typical dienophiles. As an example, in the reaction (R = CN) it was found that for the forward reaction $2\ \Delta V^{\ddagger}_2 = -30.3$ cm^3/mol (at 37.2 °C).[5] The comparison of $\Delta V^{\ddagger}$ with the reaction volume ΔV (−28.7 cm^3/mol) suggests a quasicyclic and tight transition state.[9] According to the principle of microscopic reversibility, the mechanism of the reverse reaction should in-

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