on completion of the photolysis to give an oil. The 220-MHz ^1H NMR spectrum of this material showed only a trace of photocyclization has occurred.

Transesterification of 105 mg of this oil was carried out by heating it for 1 h at reflux in HCl-saturated anhydrous ethanol. The products were isolated by using an identical procedure with that employed earlier. After separation of the ester fraction from the pyridone fragment[22] by preparative TLC as before, the mixed esters were quantitated by high-pressure LC. The composition of the ester mixture was found to be 98.4 ± 0.5 mol % percent (*E*) and (*Z*)-ethyl cinnamate, 1.6 ± 0.5 mol % diethyl δ-truxinate, and a trace of diethyl β-truxinate.

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for support of this work. The mass spectrometry equipment used in this work was provided by a grant from the National Institutes of General Medical Sciences (GM 27029) to the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois.

(22) Under these conditions the methoxypyridine functionality is cleaved to the pyridone.

Registry No. (*E,E*)-1, 75949-27-8; (*E,Z*)-1, 75949-28-9; (*Z,E*)-1, 75949-29-0; (*Z,Z*)-1, 75949-30-3; 2, 75949-31-4; (*E,E*)-3, 75961-49-8; (*E,Z*)-3, 76022-94-1; (*Z,E*)-3, 76022-95-2; (*Z,Z*)-3, 76022-96-3; (*E,E*)-4, 76022-97-4; (*E,Z*)-4, 76022-98-5; (*Z,E*)-4, 76022-99-6; (*Z,Z*)-4, 76023-00-2; 5, 75961-50-1; 6, 76023-01-3; 7, 76023-02-4; 8, 76023-03-5; 9, 76023-04-6; 10, 76023-05-7; 11, 76023-06-8; 12, 76023-07-9; 13, 75949-32-5; 14a, 75992-52-8; 15, 75949-33-6; 16, 75949-34-7; 17, 70863-80-8; 18, 16695-31-1; 19, 75949-35-8; 20, 75949-36-9; methyl 9-hydroxynonanoate, 34957-73-8; dihydropyran, 110-87-2; 1-cyanopyrrolidine, 1530-88-7; cinnamoyl chloride, 102-92-1; (*E*)-ethyl cinnamate, 4192-77-2; (*Z*)-ethyl cinnamate, 4610-69-9.

Notes

Diels–Alder Reactions of 2-(Phenylthio)cyclopentenone. Synthesis of Dihydro-1-indanones

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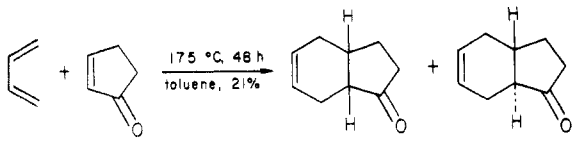
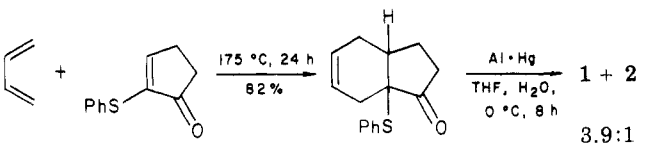
Diels–Alder reactions of simple cyclic enones are fraught with problems of yield, reaction rate, and isomerization of the product.[2,3] Cyclopentenone, as an example, reacts with butadiene in a sealed tube at 175 °C to give in 21% yield a mixture of two tetrahydroindanones (1:2 = 1.3:1).[3,4]



1 1.3:1 2

We intended to modify the cyclic enone to improve its cycloaddition reaction and, coincidentally, the versatility of its adduct. To this end we have prepared 2-(phenylthio)cyclopent-2-en-1-one (**3**)[5] and studied its reactions with simple dienes. The results are displayed in Table I.

Butadiene reacts with **3** to give the adduct **4a** in 82% yield. The rate of disappearance of **3** is about twice that



3 **4a**

of cyclopentenone under the same conditions. The phenylthio group therefore exerts a small accelerating effect on the Diels–Alder reaction despite its larger steric bulk compared with hydrogen.

The adducts in Table I are amenable to further useful transformations.[6] Oxidation to the corresponding sulfoxides was achieved under standard conditions.[7] Subsequent elimination to the dihydro-1-indanones occurred between 25 and 50 °C in carbon tetrachloride. The results are displayed in Table II. The predominance of elimination toward the angular hydrogen is in accord with the recent explanation[7] invoking a repulsion between the negative ends of the carbon–oxygen and sulfur–oxygen dipoles. The oxidative elimination reactions also prove the stereochemistry and regiochemistry of the piperylene adducts **4b** and **5b**.

The phenylthio group of **4a** was reductively removed under mild conditions, giving **1** and **2** in the ratio 3.9:1. This two step procedure is thus the best way to minimize the isomerization of **1** to **2**.

These reactions allow the preparation of a variety of tetrahydro- and dihydroindanones not readily available by other methods. For the Diels–Alder reaction, 2-(phenylthio)cyclopentanone (**3**) is the synthetic equivalent of *cyclopentynone*, since the derived dihydroindanones **6** are formally the [4 + 2] adducts of the latter. We are currently investigating the use of these compounds as intermediates for the synthesis of cyclopentanoid natural products, such

(1) Henry Rutgers Undergraduate Scholar, 1978–1979.

(2) (a) A. S. Onischenko, "Diene Synthesis", Israel Program of Scientific Translations, Jerusalem, 1964, p 100. (b) A. Ichihara, R. Kimura, K. Moriyasu, and S. Sakamura, *Tetrahedron Lett.*, 4331 (1977).

(3) Recently, however, Wenkert and co-workers have reported the use of aluminum chloride catalysis for improving the Diels–Alder reactions of cycloalkenones. F. Fringuelli, F. Pizzo, A. Taticchi, and E. Wenkert, *Synth. Commun.*, **9**, 391 (1979).

(4) (a) E. Dane and K. Eder, *Justus Liebigs Ann. Chem.*, **539**, 207 (1939). (b) R. Granger, P. F. G. Nau, and C. Francois, *Bull. Soc. Chim. Fr.*, 1902 (1962).

(5) Compound **3** is available in 50% yield from cyclopentanone by the method of H. J. Monteiro, *J. Org. Chem.*, **42**, 2324 (1977). See also S. Iriuchijima, K. Tanokuchi, K. Takokoro, and G. Tsuchihashi, *Agric. Biol. Chem.*, **40**, 1031 (1976); H. J. Monteiro and A. L. Gemal, *Synthesis*, 437 (1975); T. Mukaiyama, T. Adachi, and T. Kunamoto, *Bull. Chem. Soc. Jpn.*, **44**, 3155 (1971).

(6) For leading references on the uses of α-phenylthio ketones see T. Cohen, D. Kuhn, and J. R. Falck, *J. Am. Chem. Soc.*, **97**, 4749 (1975).

(7) B. M. Trost, T. N. Salzmann, and K. Hiroi, *J. Am. Chem. Soc.*, **98**, 4887 (1976).

(8) H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **28**, 27 (1963).

0022-3263/81/1946-0624$01.00/0

Table I. Reactions of 3 with Dienes

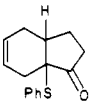
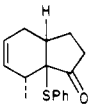
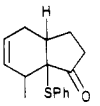
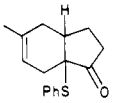
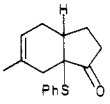
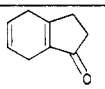
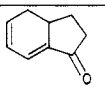
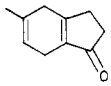
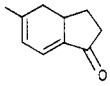
reaction	diene	conditions	major adduct 4	minor adduct 5	isolated % yield	4:5
a		175 °C, 24 h		-	82	-
b		170 °C, 16 h			81	7:1
c		180 °C, 24 h			81	1.4:1
c		$AlCl_3$ (0.2 equiv), CH_2Cl_2, 18 °C, 15 h	as above	as above	93	18:1

Table II. Oxidative Elimination of Diels-Alder Adducts

reaction	adduct	major dihydroindanone 6 (isolated % yield)		minor dihydroindanone 7 (isolated % yield)	
e	4a		72		14
f	4b		72		18
g	5b	as above	49	-	
h	4c		71		24

as steroids and fungal metabolites.

Experimental Section

Gas chromatography (GC) was performed on a Varian Aerograph Model 90-P instrument using helium as the carrier gas. A 10% OV-101 column (Chromsorb W, 80–100 mesh, 200 cm × 3.2 mm) was used for analytical GC; a 20% SE-30 column (Chromsorb A, 45–60 mesh, 6.5 ft × $^3/_8$ in.) for preparative GC. E. Merck silica gel plates (0.25-mm thickness) and silica gel (70–230 mesh) were used for analytical thin-layer chromatography (TLC) and column chromatography, respectively. Petroleum ether (30–60 °C)/ether mixtures were used as eluant (mixture ratio appears in parentheses). Proton nuclear magnetic resonance (NMR) spectra were taken on a Varian Associates Model T-60. Chemical shifts are reported in parts per million downfield from tetramethylsilane in deuteriochloroform solution and coupling constants are reported in hertz. Infrared (IR) spectra were taken on a Perkin-Elmer Model727-B spectrophotometer, using a thin film between salt plates or chloroform solution. Mass spectra were taken on a Hitachi Perkin-Elmer Model RMU-7 instrument at 70 eV. Microanalyses were performed by Galbraith Laboratories. Homogeneity (≥95%) of isolated isomeric compounds was verified by NMR and GC analysis.

Diels–Alder Reaction of Cyclopentenone and Butadiene.[4] A solution of 0.82 g (10 mmol) of cyclopentenone and 0.020 g of hydroquinone in 3 mL of butadiene and 3 mL of toluene was heated in a sealed tube at 175 °C. GC analysis indicated the formation of 1 and 2 (retention times 18.4 and 15.5 min, respectively, at 110 °C, 14 mL/min) whose ratio decreased from 7:1 after 1 h to 1.3:1 after 48 h. Chromatography of the reaction mixture on 20 g of silica gel (9:1) gave 0.301 g (21%) of the adducts.[4] The cis and trans isomers were separated by preparative GC (retention times 20.5 and 17.8 min, respectively, at 110 °C, 54 mL/min). **1**: IR (neat) 3040, 2950, 2850, 1745, 1660, 1440, 1410, 1170, 1150, 1120, 660 cm^{-1}. **2**: IR (neat) 3040, 2940, 2855, 1745, 1640, 1440, 1410, 1365, 1195, 1170, 1140, 665 cm^{-1}.

Competitive Diels–Alder Reaction of 3 and Cyclopentenone. A mixture of 0.380 g (2 mmol) of **3**, 0.164 g (2 mmol) of cyclopentenone, 0.067 g (0.5 mmol) of butylbenzene as standard, 0.099 g (0.5 mmol) of benzyl ether as standard, butadiene (2.41 g, 45 mmol), and 2 mL of toluene was heated at 175 °C in a sealed Carius tube. Aliquots were taken about every 3 h for 21 h and examined by GC. Disappearance of **3** and cyclopentenone followed pseudo-first-order kinetics during this period, affording half-lives of 6.2 and 13.0 h, respectively, by least-squares analysis.

General Procedure for Thermal Diels–Alder Reactions of 3. A solution of **3** (2 mmol) and hydroquinone (0.010 g) in the appropriate diene (30 mmol) was sealed in a Carius tube and heated in an electric oven. Progress of reaction was monitored by GC or TLC. After the disappearance of **3**, the reaction mixture was concentrated and chromatographed on 5 g of silica gel.

4a: R_f (9:1) 0.33; NMR 1.5–2.8 (m, 9 H), 5.4–5.8 (m, 2 H), 7.2–7.7 (m, 5 H); IR (neat) 3040, 2925, 2840, 1730, 1660, 1470, 1440, 1165, 915, 730 cm^{-1}; mass spectrum, *m/e* 244 (76, M^+), 188 (21), 135 (100), 110 (97), 91 (86).

4b: mp 36–38 °C (petroleum ether); R_f (9:1) 0.34; NMR 1.14 (d, 3 H, J = 7), 1.2–2.8 (m, 8 H), 5.63 (br s, 2 H), 7.20–7.65 (m, 5 H); IR ($CHCl_3$) 3000, 2975, 2900, 1740, 1680, 1590, 1475, 1440, 1400, 1270, 1160, 1120, 880 cm^{-1}; mass spectrum, *m/e* 258 (24, M^+), 190 (86), 149 (53), 105 (60). Anal. Calcd for $C_{16}H_{18}OS$: C, 74.38; H, 7.02; S, 12.41. Found: C, 74.48; H, 7.14; S, 12.49.

5b: R_f (9:1) 0.30; NMR 1.20 (d, 3 H, J = 7), 1.2–2.8 (m, 8 H), 5.60 (br s, 2 H), 7.3–7.8 (m, 5 H); IR ($CHCl_3$) 3000, 2960, 1730, 1700, 1590, 1470, 1435, 1260, 1020, 690 cm^{-1}.

4c: mp 88–89 °C (petroleum ether); R_f (1:1) 0.62; NMR 1.60 (br s, 3 H), 1.4–2.7 (m, 9 H), 5.30 (br s, 1 H), 7.2–7.6 (m, 5 H); IR ($CHCl_3$) 3000, 2975, 2920, 2840, 1730, 1440, 1140, 1025, 690 cm^{-1}; mass spectrum, *m/e* 258 (15, M^+), 149 (100), 105 (77), 91 (31). Anal. Calcd for $C_{16}H_{18}OS$: C, 74.37; H, 7.04; S, 12.41. Found: C, 74.49; H, 7.19; S, 12.06.

5c: R_f (1:1) 0.62; retention time (preparative, 170 °C, 70 mL/min) 66 min; NMR 1.58 (br s, 3 H), 1.4–2.8 (m, 9 H), 5.35 (br s, 1 H), 7.3–7.7 (m, 5 H); IR ($CHCl_3$) 3040, 3000, 2960, 2930, 1730, 1440, 1260, 1080, 1025, 810 cm^{-1}.

Aluminum Chloride Catalyzed Reaction of 3 with Isoprene. Preparation of 4c and 5c. A solution of 0.380 g (2 mmol) of **3** and 0.054 g (0.4 mmol) of freshly sublimed aluminum chloride in 8 mL of dichloromethane was stirred at 18 °C in the refrigerator. Isoprene (0.544 g, 8 mmol) was added and the mixture was monitored by TLC until **3** was consumed, about 15 h. The reaction was diluted with ether, filtered through Celite, and distilled bulb to bulb at 120 °C (1 mm) to give 0.483 g (93%) of adduct. GC analysis indicated the adduct to consist of an 18:1 mixture of **4c** and **5c** (retention times 5.5 and 4.6 min, respectively, at 200 °C, 17 mL/min). Pure **4c** was obtained by crystallization from petroleum ether. Adduct **5c** was purified by preparative GC.

Desulfurization of 4a.[9] A mixture of 0.244 g (1 mmol) of **4a**, 1 g of aluminum foil strips, and 25 mL of 9:1 tetrahydro-

(9) M. S. Newman, *J. Org. Chem.*, **26**, 582 (1961).

furan–water was stirred at 0 °C. Mercuric chloride (0.027 g, 0.1 mmol) was added, and the disappearance of **4a** was monitored by TLC. After 8 h the mixture was diluted with ether, filtered through celite, washed with saturated aqueous sodium bicarbonate, and concentrated. The product was purified by chromatography on 5 g of silica gel (19:1). GC analysis indicated that the product was a 3.9:1 mixture of *cis*- and *trans*-tetrahydroindanones (**1** and **2**).

A portion of the product (0.030 g, 0.2 mmol) was dissolved in 0.5 mL of tetrahydrofuran and treated with 0.030 mL of a 0.65 M solution of potassium *tert*-butoxide in *tert*-butyl alcohol (0.02 mmol). After 5 min, GC analysis indicated that the ratio of isomers had reached the equilibrium value of 1:2 = 1.1:1.

General Procedures for Oxidative Elimination. Syntheses of Dihydroindanones. A solution of the phenylthio ketone (1.5 mmol) in 15 mL of dichloromethane was treated with 1.5 mmol of *m*-chloroperoxybenzoic acid in 6 mL of dichloromethane at −78 °C. After 10 min the reaction was quenched with 10% aqueous sodium sulfite and warmed to room temperature. The organic layer was dried over magnesium sulfate and concentrated. If elimination was incomplete according to TLC, the residue was dissolved in 5 mL of carbon tetrachloride and heated at 50 °C for 1 h. The reaction mixture was purified by column chromatography on 20 g of silica gel.

6e: mp 75–76 °C (lit.[8] mp 76.5–77 °C); R_f (1:1) 0.29.

7e: R_f (1:1) 0.43; NMR 2.0–3.3 (m, 7 H), 6.0–6.4 (m, 2 H), 6.7–6.9 (m, 1 H).

6f: R_f (9:1) 0.05; NMR 1.27 (d, 3 H, J = 7), 2.2–2.8 (m, 4 H), 3.10 (br s, 3 H), 5.80 (br s, 2 H).

7f: R_f (9:1) 0.25; NMR 1.1–1.95 (m, 2 H), 1.95–3.0 (m, 8 H), 6.1 (br s, 2 H).

6h: mp 90.5–92 °C (petroleum ether); R_f (9:1) 0.12; NMR 1.67 (br s, 3 H), 2.46 (br s, 6 H), 2.85 (br s, 4 H), 5.53 (br s, 1 H); IR ($CHCl_3$) 3000, 2920, 2860, 1698, 1683, 1644, 1438, 1417, 1408, 1270, 1168, 991 cm^{-1}. Anal. Calcd for $C_{10}H_{12}O$: C, 81.05; H, 8.16. Found: C, 80.90; H, 8.18.

7h: R_f (9:1) 0.17; NMR 1.9 (br s, 3 H), 2.1–3.2 (m, 7 H), 5.8–6.1 (m, 1 H), 6.7–6.9 (m, 1 H); IR ($CHCl_3$) 3020, 2980, 2940, 1685, 1651, 1575, 1443, 1234, 1061, 1013, 822 cm^{-1}.

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Registry No. 1, 53921-54-3; **2**, 25050-74-2; **3**, 34780-08-0; **4a**, 75781-75-8; **4b**, 75781-76-9; **4c**, 75781-77-0; **5b**, 75781-78-1; **5c**, 75781-79-2; **6e**, 75781-80-5; **6f**, 75781-81-6; **6h**, 75781-82-7; **7e**, 75781-83-8; **7f**, 75781-84-9; **7h**, 75781-85-0; 1,3-pentadiene, 504-60-9; cyclopentenone, 930-30-3; butadiene, 106-99-0; isoprene, 78-79-5; aluminum chloride, 7446-70-0.

Syntheses of Selected ϵ-(2- or 9-Anthryl)alkanoic Acids and Certain Esters—Carbon-13 Spin-Lattice Relaxation Time Measurements of Methyl 5-(2-Anthryl)pentanoate and Methyl 7-(2-Anthryl)heptanoate

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Fluorescent probes have been widely applied in the study of microenvironments of large biological structures such as proteins and membranes.[1] Such probes with hydrophilic and hydrophobic properties have made it possible to study certain regions of membranes. Waggoner and Stryer[2] synthesized some fluorescent probes to study the hydrophilic regions of membranes. Since the above probes provided only a hydrolyzable fluorescent marker, Stoffel and Michaelis[3] developed a class of anthracene-labeled fatty acids and phospholipids. However, the bulky anthracene residue of the above probes was not transported through the membrane or used by fatty acid kinase or acyltransferase for the biosynthesis of membrane phospholipids of the *E. coli* mutant.[3] In connection with other studies concerned with biological mimics, we had occasion to prepare several ϵ-(2- and 9-anthryl)alkanoic acids and esters which have a general structural formula shown below.

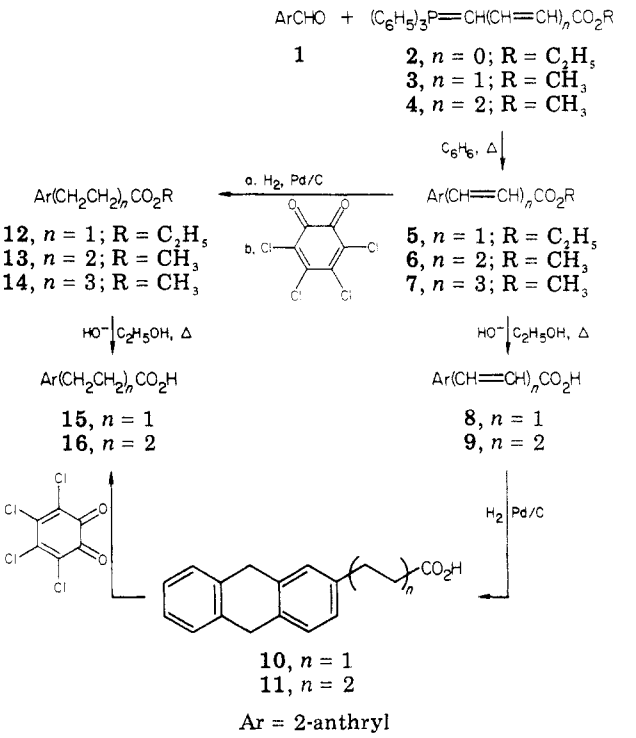
$$Ar(CH_2)_nCO_2R$$

Ar = 2-anthryl, 9-anthryl

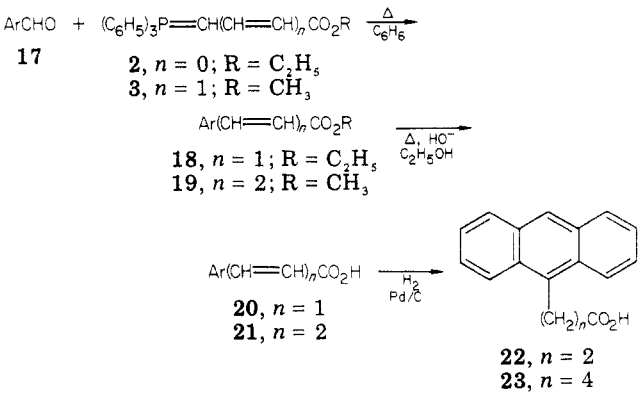
n = 2, 4, 6

R = H, CH_3, C_2H_5

Scheme I



Scheme II



(1) (a) W. W. Mantulin and H. J. Pownall, *Photochem. Photobiol.* **26**, 69 (1977); (b) A. Waggoner, *Enzymes Biol. Membr.* 1, 119 (1976); (c) L. Stryer, *Science*, **162**, 526 (1968).

(2) A. S. Waggoner and L. Stryer, *Proc. Natl. Acad. Sci. U.S.A.*, **67**, 579 (1970).

(3) W. Stoffel and G. Michaelis, *Z. Physiol. Chem.*, **357**, 7, 21 (1976).

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