H, 7.56; N, 16.58. Found: C, 51.91; H, 7.63; N. 16.51.

Reaction of 15 with 2. Compound **15** (2.08 g, 8.2 mmol) and 1.43 g (8.2 mmol) of **2** were dissolved in 70 mL of acetonitrile. After 2 h, the red color disappeared, and 10 mL of methanol was added. Volatile compounds were removed on a rotary evaporator, and the residual solids were purified by column chromatography (silica gel; 3.3% ethanol in chloroform as eluent). Compound **6** (826 mg, 46% yield) was isolated as pure crystals. The residue was found to contain **18** and dimer of **19** by NMR analysis, both NCH_3 and NC_6H_5 proton signals being observed in **18** and the NC_6H_5 proton signals being absent in the disiloxane derived via hydrolysis of **19**.

Acknowledgment. This work was supported in part by the Polymer Program, Division of Materials Research of the National Science Foundation, under Grant No. DMR-7723437, for which we are grateful.

Registry No. 1, 762-72-1; **2**, 4233-33-4; **3**, 1113-12-8; **4**, 75782-33-1; **5**, 58263-25-5; **6**, 73970-92-0; **7**, 13274-43-6; **8**, 75782-34-2; **9**, 75782-35-3; **10**, 75782-36-4; **13**, 75782-37-5; **15**, 75782-38-6; **16**, 75782-39-7; **18**, 75790-44-2; **19**, 75781-13-4; propylene, 115-07-1.

Molecular Organization by Hydrogen Bonding: Juxtaposition of Remote Double Bonds for Photocyclization in a 2-Pyridone Dimer

Peter Beak* and John M. Zeigler

Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801

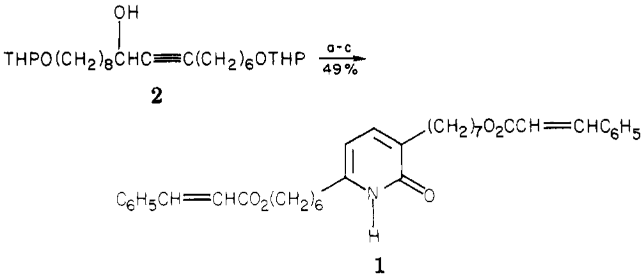
Received September 9, 1980

Irradiation of the hydrogen bonded dimer of 3-[7-(cinnamoyloxy)heptyl]-6-[6-(cinnamoyloxy)hexyl]-2-pyridone (**1**) provides the δ-truxinic acid ester **3** and the β-truxinic acid ester **4**, respectively. The photocyclization occurs via a 25-membered ring in yields which are significantly greater than those achieved in the absence of dimerization as shown by photolysis of a monomeric model system.

Study of hydrogen bonded substrates which have pendant groups suitably disposed for subsequent reaction is of interest because of the advantages which this facile entropic activation could provide over conventional methodology.[1,2] Ten years ago Breslow and Scholl used this approach to achieve 87.5% functionalization at the C-10 to C-15 positions in a hexadecyl chain by photolysis of *n*-hexadecyl hemisuccinate in the presence of benzophenone-4-carboxylic acid.[2] Our recent studies, which have shown that hydrogen-bonding associations of pyridones dramatically perturb the hydroxypyridine–pyridone equilibria in a variety of solvents,[3] suggest that the dimerization of 2-pyridones could provide an anchor which would bring otherwise distant groups into juxtaposition for reaction. In a severe test of this proposition we have investigated the photocyclization of the cinnamate moieties of 3-[7-(cinnamoyloxy)heptyl]-6-[6-(cinnamoyloxy)hexyl]-2-pyridone (**1**). Our results show that the δ- and β-truxinic acid esters, expected for interaction between double bonds which are separated by 25 atoms, are formed in the hydrogen bonded dimer of **1** in yields which are significantly greater than those expected from the corresponding monomer.[4]

Results

The elegant methodology of Overman and co-workers[5] was used to prepare **1** from 1,17-bis(2-tetrahydropyranyloxy)heptadec-7-yn-9-ol (**2**). A highly convergent



$$THPO(CH_2)_8\overset{OH}{\underset{}{C}}HC{\equiv}C(CH_2)_6OTHP \xrightarrow[49\%]{a-c}$$

2

1

a, (1) NaH, Et_2O, (2) 1-cyanopyrrolidine, Et_2O;
b, (1) xylene, 137 °C, (2) CH_3OH, $TsOH{\cdot}H_2O$;
c, (1) $C_6H_5CH{=}CHCOCl$, pyridine, Δ, (2) H_2O, pyridine, Δ

synthesis of **2** from methyl 9-hydroxynonanoate and 8-(2-tetrahydropyranyloxy)-1-octyne is detailed in the Experimental Section. Vapor-pressure osmometry of **1** in benzene establishes that this material is completely dimerized at a 0.00516 M concentration in benzene. At the same concentration in chloroform, **1** is 35% dimerized, consistent with previous observations on related systems.[3]

Irradiation of 0.005 M **1** in benzene with light from a sunlamp for 36 h provides material which could be seen by ^1H NMR to be a mixture of **1** bearing (*Z*)- and (*E*)-

---

[1] S. N. Vinogradov and R. H. Linnell, "Hydrogen Bonding", Van Nostrand-Reinhold, New York, 1971; M. D. Joesten and L. J. Schaad, "Hydrogen Bonding", Marcel Dekker, New York, 1973. For a general summary of amide hydrogen bonding see R. B. Homer and C. D. Johnson, "The Chemistry of the Amides", J. Zabricky, Ed., Interscience, New York, 1970, pp 223-7.

[2] R. Breslow and P. C. Scholl, *J. Am. Chem. Soc.*, **93**, 2331 (1971). The selectivity increased to 38% of a single product when a more rigid steroid was used as the alcohol substrate in the half-ester.

[3] P. Beak, J. B. Covington, S. G. Smith, J. M. White, and J. M. Zeigler, *J. Org. Chem.*, **45**, 1354 (1980).

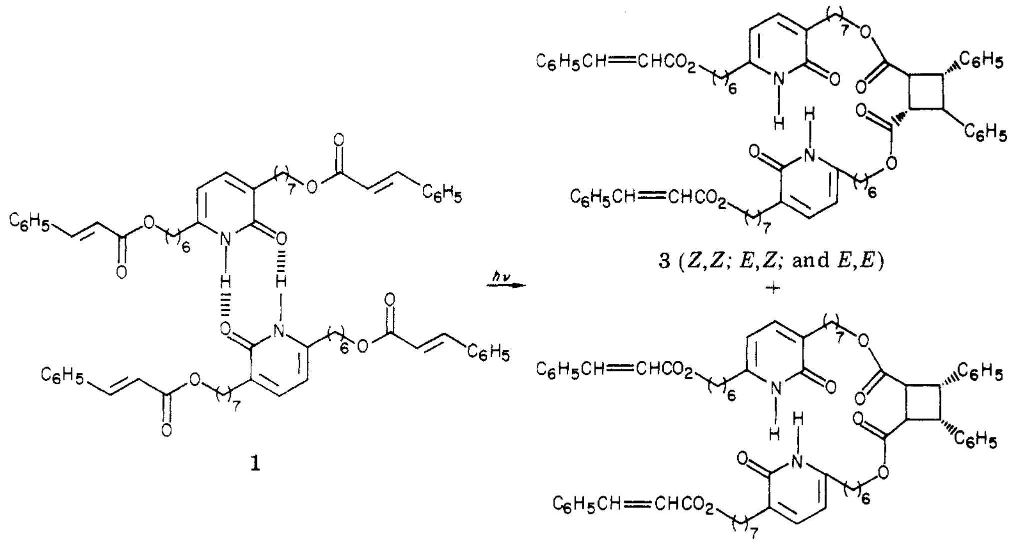
[4] The reaction has been used to close large rings of covalently bound cinnamates. J. A. Ors and R. Srinivasan, *J. Am. Chem. Soc.*, **100**, 316 (1978); J. A. Ors and R. Srinivasan, *J. Chem. Soc., Chem. Commun.*, 400 (1978), and references cited therein.

[5] L. E. Overman and S. Tsuboi, *J. Am. Chem. Soc.*, **99**, 2813 (1977); L. E. Overman, S. Tsuboi, J. P. Roos, and G. F. Taylor, *ibid.*, **102**, 747 (1980).

[6] Efforts to prepare the more suitable *N*-methyl-2-pyridone model compound were not successful. Investigation of the ultraviolet spectrum of 3-(7-acetoxyheptyl)-6-(6-acetoxyhexyl)-2-pyridone prepared from **20** established the pyridone form to be the only detectable protomer.

0022-3263/81/1946-0619$01.00/0 © 1981 American Chemical Society

Scheme I



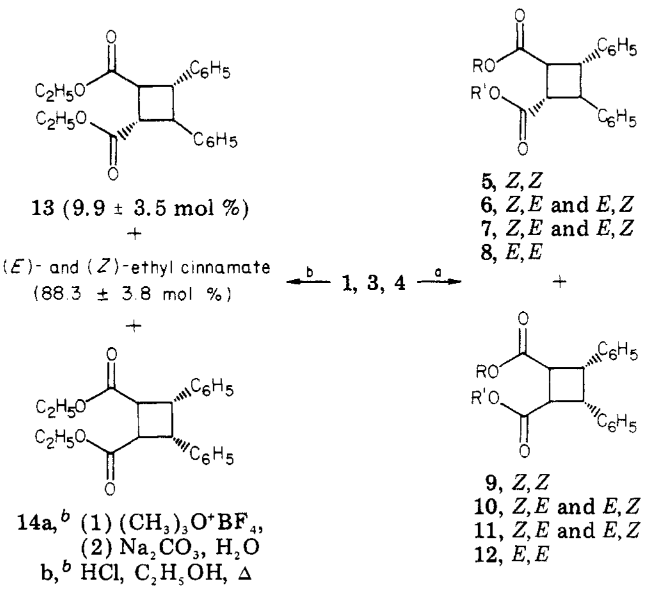
1

3 (*Z,Z*; *E,Z*; and *E,E*)

+

4 (*Z,Z*; *E,Z*; and *E,E*)

Scheme II[a]



13 (9.9 ± 3.5 mol %)

+

(*E*)- and (*Z*)-ethyl cinnamate (88.3 ± 3.8 mol %)

+

14a,[b] (1) $(CH_3)_3O^+BF_4^-$, (2) Na_2CO_3, H_2O

b,[b] HCl, C_2H_5OH, Δ

1, 3, 4

5, *Z,Z*
6, *Z,E* and *E,Z*
7, *Z,E* and *E,Z*
8, *E,E*

+

9, *Z,Z*
10, *Z,E* and *E,Z*
11, *Z,E* and *E,Z*
12, *E,E*

[a] R = 2-methoxy-3-(7-heptyl)-6-(6-cinnamoyloxy)pyridine; R′ = 2-methoxy-3-(7-cinnamoyloxy)-6-(6-hexyl)pyridine. [b] Total of 1.9 ± 0.3 mol %.

cinnamate groups[7] and photocyclized 3 and 4 as a mixture of Z and E isomers. These results are shown in Scheme I. The combined yields of 3 and 4 as determined by ^1H NMR and the weight of crude products were was 37 ± 5%.

Isolation of pure materials could be achieved only after methylation of the product mixture to the corresponding methoxypyridines and a series of careful medium- and high-pressure chromatographies. Separation of the *Z,Z* and *E,E* isomers, 5 and 8, respectively, from a mixture of the *Z,E* and *E,Z* isomers 6 and 7, all with the δ-truxinate regiochemistry of 3, was thus achieved. The structures of the methoxypyridines shown in Scheme II were confirmed by high-resolution and field-desorption mass spectrometry and 220 mHz ^1H NMR spectral comparisons with authentic diethyl esters of ε- and α-truxillic acid β- and δ-truxinic acids. The signals due to the cyclobutane protons as well as those attributable to the *Z* and *E* olefins are characteristic. In addition, a small amount of a mixture of 2-methoxypyridine photodimers having the β-truxinic geometry of 4 was isolated. The structures 9–12 shown in Scheme II were assigned on the basis of 220 MHz ^1H NMR spectral comparisons and mass spectral data on the purified mixture.

Further confirmation of the stereochemistry of the truxinic acid products was obtained by transesterification of the product mixture to diethyl δ-truxinate (13, 9.9%), diethyl-β-truxinate (14, 1.9%), and (*Z*)- and (*E*)-ethyl cinnamate (88.3%) as shown in Scheme II. The mole percent values given represent an average of duplicate runs.

In order to determine if the photochemistry of the dimer of 1 is, in fact, different from that of an unassociated species, we carried out the photolysis of 2-methoxy-3-[7-(cinnamoyloxy)heptyl]-6-[6-(cinnamoyloxy)hexyl]pyridine (15) under conditions identical with those of the photolysis of 1.[6] The ^1H NMR spectrum of the crude product showed that less than 5% photocyclization had occurred. Treatment of the products with ethanolic hydrogen chloride, as for the case of the photoproducts in Scheme II, provided 1.6 ± 0.5% diethyl δ-truxinate. Field-desorption mass spectrometry of the crude reaction product showed the photocyclized material to have a molecular weight corresponding to the expected dimer of 15.

The ultraviolet absorption spectra of 1 and 15 differ somewhat with the former, showing a long-wavelength tailing. To investigate the possibility that absorption differences could account for the results, we carried out the photolyses in a quartz apparatus with a medium-pressure Hanovia mercury lamp. Under these conditions the difference in the absorption of light between 1 and 15 is small. The results of photocyclization are comparable to those previously obtained; transesterification provides 11.3 ± 1.1% δ-truxinate and 1% β-truxinate from 1 and ~1% δ-truxinate from 15.

Discussion

Photolysis of the hydrogen bonded dimer of 1 results in the formation of photodimers 3 and 4 between complementary cinnamate moieties despite separation of the reactive double bonds by 25 atoms. Interpretation of the

---

[7] B. K. Vaidya, *Proc. R. Soc. London, Ser. A*, **129**, 299 (1930); M. Freedman, Y. Mohadger, J. Rennert, S. Soloway, and I. Waltcher, *Org. Prep. Proced.*, 1, 267 (1969); J. Rennert, S. Soloway, J. Waltcher, and B. Leong, *J. Am. Chem. Soc.*, **94**, 7242 (1972); M. D. Cohan and G. H. J. Schmidt in "Reactivity of Solids", J. H. DeBoer, Ed., Elsevier, Amsterdam, 1961, p 556.

greater extent of photocyclization for dimerized **1** over that of **15**, a model for the monomer of **1**, requires assessment of the photochemical as well as the entropic differences between these systems.

Since the triplet state is strongly implicated in the solution photodimerization of cinnamates,[7] selective triplet quenching by the 2-methoxypyridine chromophore of **15** should be considered. However, phosphorescence spectra show energy transfer from the triplet of cinnamic acid to 2-methoxypyridine or 2-pyridone would be endoenergetic by 18.9 and 4.0 kcal/mol so this possibility can be discounted.[8,9] Singlet quenching prior to intersystem crossing is only slightly endoenergetic for (*E*)-cinnamic acid relative to 2-methoxypyridine, but it is exoenergetic by 10 kcal/mol relative to 2-pyridone.[9] Accordingly, if this process affects photocyclization in **1** and **15**, the yields from **1** will be reduced while those from **15** would be unaffected. The operation of such quenching would make the entropic contribution seem smaller than it might be in fact.

The alternative possibility of selective sensitization for **1** is more difficult to evaluate. Which the triplet energy differences between the chromophores in **1** and **15** are such that energy transfer would occur on each encounter, the extent of intersystem crossing for the 2-pyridone and 2-methoxypyridine systems would also be important. If the phosphorescence efficiencies of 2-pyridone and 2-methoxypyridine are assumed to be comparable, then the tenfold lesser phosphorescence quantum yield of 2-pyridone can be taken to suggest that such sensitization would be less for **1** than for **15**.[9]

It appears that the most economical explanation for the increase in photocyclization in the dimer of **1** relative to that of the unassociated model **15** is that the hydrogen bonding association of **1** increases the probability of the necessary encounter of the excited- and ground-state cinnamate moieties.[4,7,10] While the increase is not dramatic, this reaction occurs via a 25-membered ring, and the difference could be increased by carrying out the reactions at still higher dilutions. This demonstration of the control of a remote reaction in a 2-pyridone cyclic dimer can be taken to encourage further development of similar systems on the basis of the principle of designed juxtaposition of pendant reactive groups by hydrogen bonding of appropriate anchor functions.

Experimental Section[11]

Materials. Reagents and solvents were purified by standard methods.[12]

Molecular Weights. Osmometric molecular weight measurements were made by using a Mechrolab 301A vapor-pressure osmometer or a Knauer vapor-pressure osmometer. The instrument was calibrated with 0.01–0.05 M solutions of highly purified benzil. Calculations of the solution molecular weights of the nonassociating solute, triphenylmethane, by using the above calibrations typically gave values within 1% of the formula weight. It was also demonstrated that 1-methyl-2-pyridones were unassociated at the working concentrations employed for the measurements on associating species.

Chromatography. The medium-pressure liquid chromatographic system employed for preparative separations was a modified version of the system recently described by Meyers et al.[13] Included in the system was an Isco Model UA-5 absorbance monitor for UV detection and a Fluid Metering Inc. PD-60-LF mechanical pulse dampener, with Gyrolok stainless-steel fittings being used throughout. Analytical and semipreparative high-pressure LC separations were carried out on 4 mm × 30 cm μ-Porasil or μ-Bondapak C_{18} prepacked columns (Waters Associates). The pump used as a Waters Model 6000 solvent delivery system. Sample injection was accomplished by means of a commercial stopped-flow injector system. The detector was either the Isco Model UA-5 UV absorbance monitor or the Waters R-401A differential refractometer.

Photolyses. Commerical solvents were used without further purification. Photolyses were conducted in Pyrex reaction vessels by using sunlamp irradiation. The reaction vessel was cooled externally with water, and all solutions were deoxygenated prior to irradiation by bubbling N_2 through them for at least 30 min. The inert atmosphere was maintained throughout the course of the photolysis.

Methyl 9-(2-tetrahydropyranyloxy)nonanoate (16). To neat methyl 9-hydroxynonanoate[14] (34.87 g, 0.185 mol) cooled to 0 °C were added 5 drops of concentrated HCl, followed by dropwise addition of dihydropyran (18.69 g, 0.222 mol). After completion of the addition, the mixture was allowed to warm and was stirred at ambient temperature for 22 h. Extractive workup with ether, washings with 5% aqueous NaOH and saturated NaCl solution, and drying over solid K_2CO_3 followed by removal of solvent at reduced pressure afforded an oil which was distilled at 0.1 mmHg to give 38.0 g (75%) of **16**: bp 135–137; ^1H NMR (CCl_4) δ 1.0–1.9 (br m, 18 H, $THPOCH_2(C\mathbf{H}_2)_6$ and $OCHOCH_2(C\mathbf{H}_2)_3$, 2.20 (t, J = 6 Hz, 2 H, $C\mathbf{H}_2CO_2CH_3$), 3.10–3.85 (m, 4 H, $OCHOC\mathbf{H}_2$ and $C\mathbf{H}_2OTHP$), 3.60 (s, 3 H, CO_2CH_3), 4.46 (br s, 1 H, $OC\mathbf{H}OCH_2$); IR (neat) 1748 cm^{-1} (C=O). Anal. ($C_{15}H_{28}O_4$): C, H.

9-(2-Tetrahydropyranyloxy)nonanal (17). A solution of 36.26 g (0.133 mol) of **16** in 800 mL of 1:1 toluene/pentane at −78 °C under an N_2 atmosphere was treated dropwise with neat diisobutylaluminum hydride (Ventron; 18.88 g, 0.140 mol). Stirring was continued at −78 °C for 2 h, the mixture was allowed to warm to room temperature, and water as added cautiously. Extractive workup, washings with 2% aqueous NaOH and saturated NaCl solution, and drying over Na_2SO_4 followed by removal of the solvent at reduced pressure gave an oil which wa purified by distillation in a Kugelrohr apparatus at 0.45 mmHg to provide 28.2 g (87%) of the aldehyde **17**: bp 145 °C (0.45 mmHg); ^1H NMR (CCl_4) δ 1.1–1.9 (br m, 18 H, $(C\mathbf{H}_2)_6CH_2CHO$ and $OCHOCH_2(C\mathbf{H}_2)_3$, 2.35 (dt, J = 6, 1.8 Hz, 2 H, $C\mathbf{H}_2CHO$), 3.1–3.9 (m, 4 H, $C\mathbf{H}_2OTHP$ and $OCHOC\mathbf{H}_2$), 4.48 (br s, 1 H, $OC\mathbf{H}OCH_2$) 9.67 (t, J = 1.8 Hz, 1 H, CHO), IR (neat) 2717 (aldehyde CH), 1724 cm^{-1} (C=O). Anal. ($C_{14}H_{26}O_3$): C, H.

8-(2-Tetrahydropyranyloxy)-1-octyne (18). 8-(2-Tetrahydropyranyloxy)-1-octyne, prepared by the method of Green et al.,[15] with substitution of the bromide[16] for the corresponding chloride employed by the previous workers, had satisfactory physical and spectral properties and analytical data.

1,17-Bis(2-Tetrahydropyranyloxy)heptadec-7-yn-9-ol (2). A dry THF solution of 8.01 g (38.1 mmol) of the alkyne **18** was cooled to −78 °C under an N_2 atmosphere and treated dropwise

---

(8) Details are available from University Microfilms, Ann Arbor, MI; J. M. Zeigler, Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1979.

(9) The pertinent energies in kilocalories/mole are as follows. E_T: (*E*)-cinnamic acid, 57.5; 2-pyridone, 61.5; 2-methoxypyridine, 76.4. E_S: (*E*)-cinnamic acid, 104.8; 2-pyridone, 94.4; 2-methoxypyridine, 105.0. S. Hotchandani and A. C. Testa, *J. Chem. Phys.*, **67**, 5201 (1977); K. Nakamura and S. Kikuchi, *Bull. Chem. Soc. Jpn.*, **41**, 1977 (1968). The effect of dialkyl substitution on the triplet energies of the parent systems would be a few kilocalories/mole.[8] Similar arguments can be used to discount the selective involvement of singlets.

(10) M. A. Winnick, *Acc. Chem. Res.*, **10**, 173 (1977), and references cited therein.

(11) Melting points and boiling points are uncorrected. Elemental analyses were performed by Dr. J. Nemeth and associates. Chemical shifts for the ^1H NMR spectra are reported in parts per million downfield from tetramethylsilane as internal standard. Mass spectra were run by J. Carter Cook and associates on Varian MAT CH-5 and Varian MAT 731 spectrometers.

(12) J. A. Riddick and W. A. Bunger "Organic Solvents", 3rd ed., Interscience, New York, 1970; L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1–6, Wiley, New York, 1967.

(13) A. I. Meyers, J. Slade, R. K. Smith, E. D. Mihelich, F. M. Hershenson, and C. D. Liang, *J. Org. Chem.*, **44**, 2247 (1979).

(14) W. H. Lycan and R. Adams, *J. Am. Chem. Soc.*, **51**, 625 (1929). The ester was obtained in 95% yield by reduction of methyl azelate with $BH_3 \cdot THF$ (Ventron).

(15) N. Green, M. Jacobsen, T. J. Henneberry, and A. N. Kishaba, *J. Med. Chem.*, **10**, 533 (1967).

(16) H. E. Henderson and F. L. Warren, *J. S. Afr. Chem. Inst.*, 9 (1970).

with 15.92 mL (38.9 mmol) of 2.44 M *n*-butyllithium in hexane. After the resulting solution was allowed to stir at −78 °C for 45 min, a THF solution of 9.24 g (38.1 mmol) of the aldehyde **17** was introduced in a single portion and the reaction mixture allowed to stir at −78 °C for 30 min. After the reaction was allowed to warm to room temperature and quenched with water, a little pentane was added prior to the extractive workup. Washing with saturated aqueous NaCl, drying over K_2CO_3, and removal of the solvent at reduced pressure afforded 17.0 g (99%) of the alcohol **2** as a colorless oil. The ^{1}H NMR of this material indicated it to be essentially pure. Because of its high molecular weight and sensitive functionality, **2** was not purified further: ^{1}H NMR (CCl_4) δ 1.0–2.3 (m, 34 H, $\mathrm{THPOCH_2(C\mathbf{H}_2)_6CH(OH)C{\equiv}CCH_2(C\mathbf{H}_2)_4CH_2OTHP}$ and $\mathrm{OCHOCH_2(C\mathbf{H}_2)_3}$), 2.11 (br m, 2 H, $\mathrm{C{\equiv}CCH_2}$), 3.1–3.8 (m, 8 H, $\mathrm{C\mathbf{H}_2OTHP}$ and $\mathrm{OCHOC\mathbf{H}_2}$), 4.10 (br s, 1 H, $\mathrm{C\mathbf{H}OH}$), 4.43 (br s, 2 H, $\mathrm{OC\mathbf{H}OCH_2}$); IR (neat) 3425 (OH), 2222 cm^{-1} (w, $C{\equiv}C$).

1,17-Bis(2-tetrahydropyranyloxy)heptadec-7-yn-9-yl 1-Pyrrolidinecarboximidate (19). A dry etheral solution of 1-cyanopyrrolidine[5,17] (3.12 g, 32.5 mmol) was cooled to −10 °C under an N_2 atmosphere and treated dropwise with an ethereal solution of 14.02 g (31.0 mmol) of crude alcohol **2** to which had been added 0.421 g of 57% sodium hydride dispersion (10 mmol). Upon completion of the addition, the mixture was allowed to warm to ambient temperature and stirred for 16 h. The ethereal solvent was then removed and replaced by an equal volume of hexane. To this solution was added 10 mmol of glacial acetic acid in 10 mL of hexane. After the resulting mixture was allowed to stand for a few minutes, the precipitated sodium acetate was removed by filtration and the hexane solvent removed in vacuo to give 17.22 g of material which was shown by ^{1}H NMR to be 62% of **19**. This material was highly sensitive to moisture and was not purified further: ^{1}H NMR (CCl_4) δ 1.0–2.3 (m, 34 H, $\mathrm{THPOCH_2(C\mathbf{H}_2)_6CH(OH)C{\equiv}CCH_2(C\mathbf{H}_2)_4CH_2OTHP}$ and $\mathrm{OCHOCH_2(C\mathbf{H}_2)_3}$, 1.88 (m, 4 H, $\mathrm{N(CH_2(C\mathbf{H}_2))}\mathbf{2}$), 2.20 (m, 2 H, $\mathrm{C{\equiv}CCH_2}$), 3.25 (m, 4 H, $\mathrm{NCH_2}$), 3.1–3.8 (m, 8 H, $\mathrm{C\mathbf{H}_2OTHP}$ and $\mathrm{OCHOC\mathbf{H}_2}$), 4.17 (s, 1 H, NH), 4.48 (br s, 2 H, $\mathrm{OC\mathbf{H}OCH_2}$), 5.23 (m, 1 H, $\mathrm{C\mathbf{H}OCH{=}NH}$); IR (neat) 1634 cm^{-1} (C=N).

3-(7-Hydroxyheptyl)-6-(6-hydroxyhexyl)-2-pyridone (20). Cyclization of the pseudourea **19** (17.23 g of ca. 65% pure material, 20.21 mmol) was accomplished by heating it in 800 mL of refluxing xylene[5] for 31 h under an N_2 atmosphere. The xylene solvent was removed at reduced pressure, the residual orange oil taken up in 200 mL of methanol, 100 mg of toluenesulfonic acid monohydrate added, and the resulting mixture stirred at ambient temperature for 24 h. The methanolic solvent was then removed, replaced with dichloromethane, and extractive work up with saturated sodium bicarbonate solution, saturated aqueous NaCl, drying over $MgSO_4$, and the subsequent removal of the solvent afforded an oil which crystallized on standing. Two crystallizations of this material from acetonitrile/chloroform and two from ethanol/ethyl acetate afforded 3.3 g (35% overall from **18**) of analytically pure **20** as a colorless solid: mp 84.5–85.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.1–1.8 (br m, 18 H, $\mathrm{CH_2(C\mathbf{H}_2)_4CH_2OH}$ and $\mathrm{CH_2(C\mathbf{H}_2)_5CH_2OH}$), 2.51 (overlapping t, J = 6 Hz, 4 H, $\mathrm{C\mathbf{H}_2pyr}$), 3.60 (t, J = 6 Hz, 4 H, $\mathrm{C\mathbf{H}_2OH}$), 5.96 (d, J = 8 Hz, 1 H, H_5), 7.16 (d, J = 8 Hz, 1 H, H_4); IR (Nujol mull) 3330 (br, OH), 1658 cm^{-1} (C=O). Anal. ($C_{18}H_{31}NO_3$): C, H, N.

3-[7-(Cinnamoyloxy)heptyl]-6-[6-(cinnamoyloxy)hexyl]-2-pyridone (1). A dry pyridine solution of 850 mg (2.75 mmol) of the pyridone diol **20** was heated for 3 h at reflux with 1.46 g (8.79 mmol) of cinnamoyl chloride. The brown mixture was then allowed to cool, and selective hydrolysis of the initially formed 2-cinnamoyloxypyridine was effected by addition of water to the point of turbidity and heating to reflux for 3 h. Extractive workup with dichloromethane with washes with water, aqueous HCl, saturated aqueous $NaHCO_3$, and saturated NaCl solution, followed by drying over $MgSO_4$ and removal of the organic solvent at reduced pressure, afforded crude **1** as a brown, highly crystalline solid. Two recrystallizations of this mixture from acetonitrile/chloroform gave 1.31 g (84%) of analytically pure **1** as a white solid: mp 74–75; ^{1}H NMR (CCl_4) δ 1.25–1.90 (br m, 18 H, $\mathrm{CH_2(C\mathbf{H}_2)_5CH_2OOCR}$ and $\mathrm{CH_2(C\mathbf{H}_2)_4CH_2OOCR}$), 2.41 (t, J = 6 Hz, 2 H, $\mathrm{C\mathbf{H}_2(CH_2)_5CH_2OOCR}$), 2.52 (t, J = 6 Hz, 2 H, $\mathrm{C\mathbf{H}_2(CH_2)_4CH_2OOCR}$), 4.11 (t, **J** = 6 Hz, 4 H, $\mathrm{C\mathbf{H}_2OOCR}$), 5.83 (d, J = 8 Hz, 1 H, H_5), 6.33 (d, J = 15 Hz, 2 H, $\mathrm{C\mathbf{H}{=}CHPh}$), 7.04 (d, J = 8 Hz, 1 H, H_4), 7.20–7.60 (m, 10 H, Ar H), 7.56 (d, **J** = 15 Hz, 2 H, $\mathrm{CH{=}C\mathbf{H}Ph}$), 9.32 (br s, 1 H, NH). IR (Nujol mull) 1712 (ester C=O), 1642 (lactam C=O), 989, 979 (trans olefinic CH deformation); mass spectrum (70 eV), *m/e* (relative intensity) 570 (2.16), 569 ($M^{+}\cdot$) (4.82), 438 (10.8), 339 (22.9), 131 (100); UV (cyclohexane): λ_{max} 219 nm (ϵ 35 000), 224 (33 000), 245 (s), 278 (44 500), 295 (s), 301 (s). Anal. ($C_{36}H_{43}NO_5$): C, H, N.

2-Methoxy-3-[7-(cinnamoyloxy)heptyl]-6-[6-(cinnamoyloxy)hexyl]pyridine (15). A dry dichloromethane solution of 324 mg (0.569 mmol) of **1** was stirred at room temperature for 24 h with 101 mg (0.682 mmol) of trimethyloxonium tetrafluoroborate. After addition of 10% aqueous Na_2CO_3, extractive workup, washing with saturated aqueous NaCl, and drying over K_2CO_3, subsequent removal of solvent at reduced pressure afforded a slightly yellow oil which was then subjected to medium-pressure liquid chromatography on silica gel with 20% ether in pentane as eluent. Removal of solvent from the product fractions at reduced pressure gave **15** as a colorless oil which was heated in vacuo at 100 °C for 4 h. This procedure yielded analytically pure **15** (290 mg, 88%) as a colorless oil: bp ~205 °C (0.5 mmHg); ^{1}H NMR (CCl_4) δ 1.23–1.81 (br m, 18 H, $\mathrm{CH_2(C\mathbf{H}_2)_5CH_2OOCR}$ and $\mathrm{CH_2(C\mathbf{H}_2)_4CH_2OOCR}$), 2.48 (t, J = 6 Hz, 2 H, $\mathrm{C\mathbf{H}_2(CH_2)_5CH_2OOCR}$), 2.60 (t, J = 6 Hz, 2 H, $\mathrm{CH_2(C\mathbf{H}_2)_4CH_2OOCR}$), 3.88 (s, 3 H, OCH_3), 4.11 (t, J = 6 Hz, 4 H, CO_2CH_2), 6.33 (d, J = 16 Hz, 2 H, $\mathrm{PhCH{=}C\mathbf{H}}$), 6.50 (d, J = 8 Hz, 1 H, H_5), 7.14 (d, J = 8 Hz, 1 H, H_4), 7.30–7.50 (m, 10 H, Ar H), 7.57 (d, J = 16 Hz, 2 H, $\mathrm{PhC\mathbf{H}{=}CH}$); IR (neat) 1720 (C=O), 1650 cm^{-1} (ring C=N); UV (cyclohexane) λ_{max} 219 nm (ϵ 36 000), 224 (36 000), 278 (45 500), 299 (s); mass spectrum (70 eV), *m/e* (relative intensity) 584 (21.46), 583 ($M^{+}\cdot$, 52.9), 552 (20.96), 452 (23.1), 436 (48.6), 367 (44.0), 131 (100.0). Anal. ($C_{37}H_{45}NO_5$): C, H, N.

Photolysis of the Pyridone Dicinnamate 1. The pyridone (569.7 mg, 1.00 mmol) was dissolved in 200 mL of benzene and irradiated with a 275-W sunlamp placed 5 in. from the Pyrex flask. An equilibrium solution temperature of 18 °C was reached after about 10 min, and photolysis was continued for 36 h. Removal of the solvent under reduced pressure followed by repeated dissolution in and evaporation of CCl_4 gave a yellow oil. This material was protected from room light in foil-wrapped vessels. this oil exhibited a UV spectrum identical with that of **1** except for a decrease in the extinction coefficient for the cinnamate absorption at 278 nm. The 220 MHz ^{1}H NMR spectrum of this material showed new signals at δ 3.20 and 3.75 which can be attributed to the formation of ca. 35% δ-truxinate and β-truxinate **3** and **4**, respectively.[4,7] The well-precedented photoisomerization of the cinnanate double bond was confirmed by a new doublet at δ 6.85.[4,7]

Methylation of photoproduct Mixture and Chromatographic Separation of the Methoxypyridine Photodimers. It proved necessary to methylate the photoproduct mixture above in order to obtain a separable mixture. This was accomplished by allowing 284.9 mg (0.5 mequiv) of the photoproduct mixture to react with 96.2 mg (0.65 mmol) of trimethyloxonium fluoborate in dichloromethane solution. After an extractive workup analogous to that used **15**, a yellow oil was obtained which was subjected to medium-pressure LC separation on an E. Merck size B silica gel 60 prepacked Lobar column.

The initial solvent, 20% ether in pentane, eluted a band containing several comonents which were assigned on the basis of ^{1}H NMR spectroscopy to be a mixture of 2-methoxypyridines derived from the four possible (*E,E*, *E,Z*, *Z,E* and *Z,Z*) noncyclized photoisomerized olefins from **1**. The isolated yield of this "noncyclized" fraction was 69 mg (24%).

Elution with 30% ether in pentane provided a second group of components. The ^{1}H NMR spectrum of this material clearly showed it to be a mixture of products having an overall 2:1 ratio of olefin to cyclobutane moieties. The *E/Z* ratio of the olefins was the same as for the "noncyclized" fraction above. Thus, this band contained those methylated photoproducts in which one photocyclization had occurred per mole of the original hydrogen bonded pyridone dimer of **1**. The isolated yield of this "monocyclized fraction" was 90 mg (32%).

---

(17) W. L. Garbrecht and R. M. Herbst, *J. Org. Chem.*, 18, 1003 (1953).

The remainder of the material, eluted from the column with neat ethyl acetate, on evaporation of the solvent provided a yellow oil which was indicated by ^1H NMR to be a mixture of partially methylated materials somewhat enriched in photocyclized products relative to the original mixture. A total of 96 mg (34%) of this "polar" fraction was obtained.

Upon remethylation of the "polar" fraction with 125 mg (0.85 mmol, 5 equiv) of trimethyloxonium fluoborate in dichloromethane at room temperature for 72 h followed by chromatography as described above, the isolated yields of the noncyclized and monocyclized fractions were increased to 29% and 39%, respectively, while the amount of the polar fraction was reduced to 15%. The photoproduct from a duplicate photolysis run, after a single methylation with 1.2 equiv of trimethyloxonium fluoborate and chromatographic separation, gave isolated yields of 28%, 23%, and 39%, respectively, of the same noncyclized, monocyclized, and polar fractions described above.

The monocyclized fraction was further resolved by medium-pressure LC using the above Lobar size B solumn with 30% ether in pentane as the mobile phase. Six individual components of the monocyclized fraction could be observed on the medium-pressure LC trace, and three major components separated from three minor components which had a somewhat larger retention volume. The fractions containing the three major components were, thus, combined, and solvent was removed at reduced pressure to afford a colorless oil.

The reduction in bandwidth brought about by splitting the monocyclized fraction into two groups of three components each made the application of recycling high-pressure LC feasible. Thus, the band containing the three major components was subjected to high-pressure LC on a 4 mm × 30 cm μ-Porasil (Waters Associates) prepacked analytical column employing as mobile phase 8% ethyl acetate in hexane at a flow rate of 4.0 mL/min. By overloading the column, it was possible to separate approximately 6 mg/run and thereby separate all the material in 5 runs. On the first pass through the column, small amounts of contaminating materials of higher and lower retention volume were the column effluent containing the three components of interest was recyclized back onto the column. On the third pass through the column, sufficient separation had taken place that it was possible to collect pure products from the leading and trailing edges of the least and most highly retained bands, respectively. The still partially mixed center portion of the original band was recycled. After continuing this procedure through five more passes, the component of intermediate retention volume was obtained free from isomers. High-resolution mass spectral analysis of each of these three components confirmed the elemental formula of $C_{74}H_{90}N_2O_{10}$. Examination of each of the three components thus isolated by 220-MHz ^1H NMR allowed assignment of the dimeric structures **5**, **6** and **7**, and **8** to the components of lowest, intermediate, and highest retention volumes. In addition to the signals reported below, a triplet at 1.0 ppm attributable to hexane is observed in the NMR spectra of these oils.

For **5**: ^1H NMR (CCl_4) δ 1.25–1.90 (br m, 18 H, $CH_2(C\mathbf{H}_2)_5CH_2OOCR$ and $CH_2(C\mathbf{H}_2)_4CH_2OOCR$), 2.45 (br t, 2 H, $C\mathbf{H}_2(CH_2)_5CH_2OOCR$), 2.52 (br t, 2 H, $C\mathbf{H}_2(CH_2)_4CH_2OOCR$), 3.38 (m (A′BB′), 2 H, CHPh), 3.60 (m (AA′BB′), 2 H, $CHCO_2$), 3.95 (s, 3 H, OCH_3), 4.12, 4.15 (2 t, *J* = 6 Hz, 4 H, CH_2OOCR), 6.37 (d, *J* = 15 Hz, 2 H, $C\mathbf{H}{=}CHPh$), 6.51, 6.55 (2 d, *J* = 8 Hz, 2 H, H_5), 7.00–7.70 (m, 13 H, Ar H).

For **6** and ,**7**: ^1H NMR: δ 1.23–1.81 (br m, 18 H, $CH_2(C\mathbf{H})_2)_5CH_2OOCR$ and $CH_2(C\mathbf{H}_2)_4CH_2OOCR$), 2.44 (br t, 2 H, $C\mathbf{H}_2(CH_2)_5CH_2OOCR$), 2.56 (br t, 2 H, $C\mathbf{H}_2(CH_2)_4CH_2OOCR$), 3.30 (m (AA′BB′), 2 H, CHPh); 3.63 (m (AA′BB′), 2 H, $CHCO_2$), 3.68 (s, 3 H, OCH_3), 4.05–4.09 (2 t, *J* = 6 Hz, 4 H, CO_2CH_2), 5.83 (d, *J* = 12 Hz, 1 H, $PhCH{=}C\mathbf{H}$), 6.33 (d, *J* = 15 Hz, 1 H, $PhCH{=}C\mathbf{H}$), 6.49, 6.51 (2 d, *J* = 8 Hz, 2 H, H_5), 6.79 (d, J = 12 Hz, 1 H, $PhC\mathbf{H}{=}CH$), 7.13–7.53 (m, 13 H, Ar H, $PhC\mathbf{H}{=}CH$).

For **8**: ^1H NMR (CCl_4) δ 1.23–1.81 (br m, 18 H, $CH_2(C\mathbf{H}_2)_5CH_2OOCR$ and $CH_2(C\mathbf{H}_2)_4CH_2OOCR$), 2.48 (t, *J* = 6 Hz, 2 H, $C\mathbf{H}_2(CH_2)_5CH_2OOCR$), 2.60 (t, *J* = 6 Hz, 2 H, $C\mathbf{H}_2(CH_2)_4CH_2OOCR$), 3.33 (m (AA′BB′), 2 H, CHPh), 3.63 (m (AA′BB′), 2 H, $CHCO_2$), 3.87 (s, 3 H, OCH_3), 4.02, 4.07 (2 t, *J* = 6 Hz, 4 H, CO_2CH_2), 5.83 (d, *J* = 12 Hz, 2 H, $PhCH{=}C\mathbf{H}$), 6.49 (d, *J* = 8 Hz, 2 H, H_4), 6.84 (d, *J* = 12 Hz, 2 H, $PhC\mathbf{H}{=}CH$), 7.14 (d, *J* = 8 Hz, 1 H, H_4), 7.20–7.80 (m, 12 H, Ar H).

The assignment of cinnamate geometry follows from the coupling constants for the olefinic protons. The assignment of δ-truxinic geometry to these materials is based on direct comparison of the distinctive ^1H NMR signals of the cyclobutane protons with those of authentic diethyl esters of α- and ϵ-truxillic and β- and δ-truxinic acids.

The three minor components were not separated by this recycle procedure. However, 220-MHz ^1H NMR analysis of center cuts of each of the three components from the second medium-pressure LC run showed these products to have the *z,Z*, *Z,E*, *E,Z*, and *E,E* olefinic linkages analogous to **9–12**, respectively, but different, probably β-truxinic, cyclobutane geometry. High-resolution mass spectral analysis of these materials confirmed the elemental formula of $C_{74}H_{90}N_2O_{10}$.

Transesterification of the Photoproducts from 1. Transesterification of 142 mg (0.25 mmol) of the crude photoproduct from **1** was accomplished by heating it for 1 h at reflux in 15 mL of HCl-saturated anhydrous ethanol, followed by cautious addition of the cooled solution to excess 10% aqueous Na_2CO_3 solution. Extraction with dichloromethane, followed by washings with water and saturated NaCl solution, drying over $MgSO_4$, and concentration gave a solution which was applied to a preparative silica gel TLC plate. Development with 1:1 pentane/ether gave two bands. Elution with ethyl acetate of the broad band at high R_f gave 63 mg of oil which was shown by ^1H NMR to be a mixture of isomeric ethyl cinnamates and photodimerized diesters. The band which remained at the origin, upon elution with methanol, gave material with a ^1H NMR spectrum essentially identical with that of pyridonediol **20**.

High-Pressure LC Quantitation of the Ester Mixture from Transesterification of the Crude Photoproduct from 1. Authentic samples of the ethyl esters of the four possible photodimers of cinnamic acid, diethyl α-truxillate,[18] diethyl ϵ-truxillate,[19] diethyl β-truxinate (**13**)[20] and diethyl δ-truxinate (**14**),[21] were prepared. Their chromatographic retention volumes and that of (*E*)-ethyl cinnamate were then determined on the same μ-Porasil analytical column described earlier by using as mobile phase 80/18/2 hexane/chloroform/ether at a flow rate of 2.0 mL/min with refractive index detection. Determination of the refractive index response factors allowed determination of the composition of the ester mixture from the transesterification of the photoproduct to be 87.1 ± 1.4 mol % ethyl cinnamate, 10.6 ± 1.3 mol % diethyl δ-truxinate, and 2.3 ± .1 mol % diethyl β-truxinate. These values were calculated from 5–7 independent determinations each of the δ-truxinate/cinnamate ratio and the β-truxinate/δ-truxinate ratio. All error limits represent three standard deviations. A duplicate photolysis run gave 89.4 ± 2.4, 9.2 ± 2.2, and 1.4 ± 0.2 mol % yields of the same products. Confirmatory identification of the products was carried out by collection of the materials as they eluted from the column and comparison of the 220-MHz Fourier transform ^1H NMR spectra of the materials isolated with those of the corresponding authentic material.

Other Photolyses of 1 and 15. Short-wavelength photolysis of **1** was carried out in benzene at 30 °C for 36 h in a quartz vessel under N_2 with a Hanovia medium-pressure mercury lamp surrounded by a Corex No. 9700 glass filter sleeve. The extent of photocyclization was determined by transesterification and subsequent analysis of the esters thus produced as heretofore mentioned. The composition thus determined was 87.7 ± 1.5, 11.3 ± 1.1, and ~1 mol % of mixed (*E*)- and (*Z*)-ethyl cinnamate, diethyl δ-truxinate, and diethyl β-truxinate, respectively.

Similar photolysis of **15** provided less than 3% photocylized material as judged by 220-MHz NMR.

Photolysis of **1** under the sunlamp in the presence of 10 mol % benzophenone using the same procedures as heretofore mentioned gives 85.0 ± 2.4 % (*Z*)- and (E)-ethyl cinnamate, 15 ± 2.4% diethyl δ-truxinate, and a trace of diethyl β-truxinate.

Photolysis of 15. The 2-methoxypyridine **15** (210 mg, 0.360 mmol) was irradiated in 72 mL of benzene under conditions identical with those employed for **1**. The solvent was removed

---

[18] C. Liebermann, *Ber. Dtsch. Chem. Ges.*, **21**, 2342 (1888).

[19] R. Stoermer and E. Emmel, *Etsch. Chem. Ges.*, **53**, 497 (1920).

[20] C. Liebermann, *Dtsch. Chem. Ges.*, **21**, 2342 (1888).

[21] R. Stoermer and F. Scholtz, *Dtsch. Chem. Ges.*, **54**, 85 (1921).

on completion of the photolysis to give an oil. The 220-MHz ^{1}H 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.

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.

---

[22] Under these conditions the methoxypyridine functionality is cleaved to the pyridone.

Notes

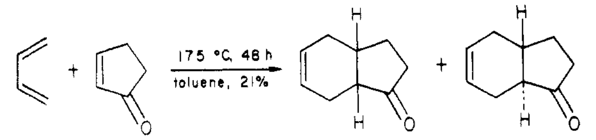
Diels–Alder Reactions of 2-(Phenylthio)cyclopentenone. Synthesis of Dihydro-1-indanones

Spencer Knapp,* Randall Lis,[1] and Paul Michna[1]

Department of Chemistry, Rutgers University, New Brunswick, New Jersey 08903

Received July 17, 1980

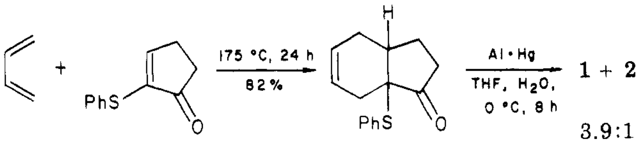
Diels–Alder reactions of simple cyclic enones are fraught with problems of yield, reaction rate, and isomerization of the product.[2,3] Cyclopentenone, as an example, reacts with butadiene in a sealed tube at 175 °C to give in 21% yield a mixture of two tetrahydroindanones (1:2 = 1.3:1).[3,4]



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 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.



3 **4a**

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