times from an ethanol–ether mixture to yield 0.19 (33%) of pure product: mp 142° dec; nmr (D_2O) δ 7.1 (multiplet, 10.0 H), 3.85 (quintet, J = 5.0 Hz, 1.08 H), 4.6 (doublet, J = 3.8 Hz, 1.1 H), 2.0 (singlet, 9.0 H), 1.0 (doublet, J = 2.6 Hz, 3.0 H).

erythro-**1,2-Diphenylpropyltrimethylammonium iodide** was prepared by the method of Cram, Greene, and DePuy:[3] mp 212° dec (lit.[3] mp 212–213° dec; nmr (D_2O) δ 7.1 (multiplet, 10.0 H), 3.85 (multiplet, 1.0 H), 4.6 (doublet, J = 3.7 Hz, 1.0 H), 2.0 (singlet, 9.0 H), 1.0 (doublet, J = 2.5 Hz, 3.0 H).

erythro-**1,2-Diphenyl-1-propanol-***1-d* was obtained by reduction of 1,2-diphenylpropanone with lithium aluminum deuteride, following the procedure of Cram and Elhafez[15] for the hydride reduction. After three recrystallizations from ether, 77% of material of mp 49–51° resulted (lit.[15] mp 50–51° for the undeuterated material), 0.93 D atom per molecule by mass spectrometry.

threo-**1,2-Diphenylpropyl-***1-d* **chloride** was prepared from *erythro*-1,2-diphenyl-1-propanol-*1-d* and thionyl chloride as described by Elhafez and Cram.[16]

erythro-**1,2-Diphenylpropyl-***1-d*-**trimethylammonium chloride** was prepared from the reaction of *threo*-1,2-diphenylpropyl-*1-d* chloride with trimethylamine as described above for the undeuterated compound. The product (32% yield) had mp 142–143° dec; nmr (D_2O) δ 7.1 (multiplet, 10.0 H), 3.85 (quartet, J = 5.5 Hz, 1.05 H), 4.6 (doublet, J = 3.7 Hz, 0.04 H), 2.0 (singlet, 9.1 H), 1.0 (doublet, J = 2.5 Hz, 3.0 H).

2-Phenylpropionaldehyde-*2-d* was obtained by refluxing with stirring a mixture of 54 g (0.40 mol) of 2-phenylpropionaldehyde and 40 g (2.0 mol) of deuterium oxide containing a few drops of 40% sodium deuteroxide in deuterium oxide. The aldehyde was recovered and the process was repeated twice. The final product contained 0.97 D atom per molecule by mass spectroscopy.

threo-**1,2-Diphenylpropanol-***2-d* was obtained by the reaction of 2-phenylpropionaldehyde-*2-d* with phenylmagnesium bromide and recrystallization of the *p*-nitrobenzoate of the product 16 times from ethyl acetate [final *p*-nitrobenzoate mp 143–144° (lit.[15] mp 143–144°)], followed by saponification to give a viscous, clear oil: bp 136–137° (1.4 mm); $n^{25}D$ 1.5715 (lit.[15] $n^{25}D$ 1.5718); nmr ($CDCl_3$) δ 1.02 (doublet, J = 5.0 Hz, 3.0 H), 2.25 (broad singlet, 1.1 H), 3.05 (multiplet, 0.9 H), 4.65 (doublet, J = 3.5 Hz, 0.9 H), 7.10 (multiplet, 10.0 H).

threo-**1,2-Diphenylpropyl-***2-d p*-**bromobenzenesulfonate** was obtained as previously described for the undeuterated compound.[17] It was kept in dry benzene because it decomposes in the neat state.[17]

erythro-**1,2-Diphenylpropyl-***2-d*-**dimethylamine** was obtained from *threo*-1,2-diphenylpropyl-*2-d p*-bromobenzenesulfonate and dimethylamine as described for the undeuterated compound.[3] Its mass spectrum indicated 0.97 D atom per molecule; nmr ($CDCl_3$) δ 7.1 (multiplet, 10.0 H), 4.75 (doublet, J = 0.8 Hz, 1.0 H), 3.4 (multiplet, 0.07 H), 2.1 (singlet, 6.0 H), 1.40 (doublet, J = 0.9 Hz, 3.0 H).

erythro-**1,2-Diphenylpropyl-***2-d*-**trimethylammonium iodide** was obtained from *erythro*-1,2-diphenylpropyl-*2-d*-dimethylamine and methyl iodide by the procedure for the undeuterated compound:[3] mp 212–213° dec; nmr (D_2O) δ 7.1 (multiplet, 10.0 H), 3.85 (multiplet, 0.07), 4.6 (doublet, J = 0.8 Hz, 1.0 H), 2.0 (singlet, 9.0 H), 1.0 (doublet, J = 0.9 Hz, 3.0 H).

Recovery of 1,2-Diphenylpropyltrimethylammonium Salts after Partial Reaction. The reactions were carried out with 5.3 × 10^{-4} M *erythro*-1,2-diphenylpropyltrimethylammonium salt, appropriately deuterated, in 0.057 M potassium *tert*-butoxide in *tert*-butyl alcohol at 35° for one half-life (5.8 hr). The mixture was chilled and worked up by the procedure used by Smith and Bourns[4] to recover 2-phenylethyltrimethylammonium bromide. Two recrystallizations of the crude material from ethanol–ether yielded crystals of 1,2-diphenylpropyltrimethylammonium bromide.

Stability of 1,2-Diphenyl-1-propene to Reaction Conditions. A 2.41 × 10^{-3} M solution of α-methylstilbene [Pfaltz and Bauer, Inc., λ_{max} 274 nm (lit.[15] 274 nm for trans isomer)] in *tert*-butyl alcohol was photolyzed for 3 hr in a Kimax test tube with a medium-pressure mercury lamp, using a potassium dichromate filter solution to isolate the 313-nm line. The resulting material was diluted 1:25 with 95% ethanol and the uv spectrum was determined. λ_{max} 264 nm, no shoulder near 255 nm (9-methylphenanthrene). For the cis olefin, λ_{max} 260 nm is reported;[18] so the photoisomerized mixture appears to contain an excess of cis over trans olefin. The photostationary state is reported to have a cis/trans ratio of 2.6 at 313 nm.[19] In contrast, the trans isomer predominates by at least 50:1 at equilibrium.

A solution containing the photoisomerized olefin mixture (4.82 × 10^{-4} M), potassium *tert*-butoxide (0.3 M), and tetra-*n*-butylammonium bromide (8 × 10^{-3} M) was placed in a bath at 30°. Samples were taken after 2 hr and 27 hr and diluted 1:5 with 95% ethanol, and the uv spectra were determined. For both samples λ_{max} 265–266 nm was observed, indistinguishable within experimental error from λ_{max} for the starting material. The half-life of the elimination reaction of 4.82 × 10^{-4} M 1,2-diphenylpropyltrimethylammonium iodide in 0.3 M potassium *tert*-butoxide can be calculated from the reported rate constant[3] at 30° to be 2 hr.

Registry No.—**1**, 42879-24-3; **2**, 42879-25-4; *erythro*-1,2-diphenylpropyltrimethylammonium chloride, 42879-26-5; *threo*-1,2-diphenylpropyl chloride, 7693-88-1; trimethylamine, 75-50-3; *erythro*-1,2-diphenylpropyltrimethylammonium iodide, 42879-28-7; *threo*-1,2-diphenylpropanol-*2-d*, 42879-29-8; *erythro*-1,2-diphenylpropyl-*2-d*-dimethylamine, 42879-30-1; *threo*-1,2-diphenylpropyl-*2-d p*-bromobenzenesulfonate, 42879-31-2.

References and Notes

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Stereospecific Synthesis of D-*threo*-Sphinganine

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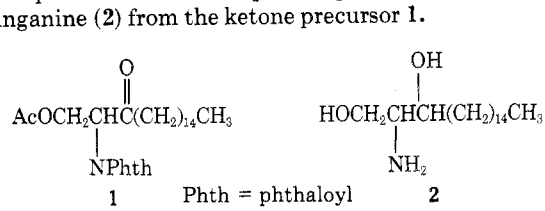
Received August 16, 1973

In the course of our studies on the synthesis of sphingolipid bases[1,2] we have uncovered a very interesting case of stereoelectronic control on the course of a reduction, which permits the stereospecific preparation of D-*threo*-sphinganine (**2**) from the ketone precursor **1**.

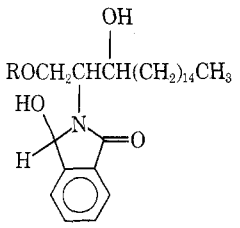


1 Phth = phthaloyl **2**

Heretofore, **2** has been available only by resolution of the DL mixture which was, in turn, obtained by separation

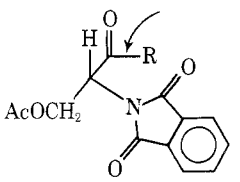
from its DL-erythro isomer with which it is formed in combination.[3,4]

Thus, treatment of chiral D-1 with lithium tri-*tert*-butoxyaluminum hydride resulted in the selective reduction of the ketone carbonyl to give *O*-acetyl-*N*-phthaloyl **2** exclusively, which was then deblocked (see below) to give **2**. Lithium aluminum hydride or sodium borohydride proved unsuitable; both led to concomitant reduction of one of the phthalimido carbonyls to give **3**. The lithium aluminum hydride reduction gave additionally the deacetylated product **4**.



3, R = Ac
4, R = H

The reaction observed is understandable in terms of the unique conformation A for **1** in which the ketone carbonyl

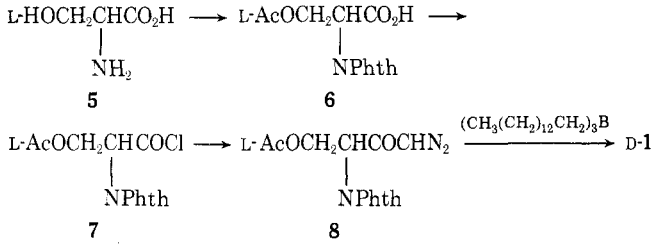


A

group is oriented antiparallel to the phthalimido substituent, thereby minimizing the dipole–dipole interaction between the two moieties.[5]

Exclusive attack of A by hydride from the sterically least hindered top side (see arrow) would then lead to the stereospecific formation of the threo isomer.

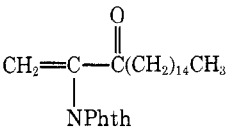
The ketone **1** was prepared according to our previously published method[2] in which a suitably protected serine derivative is elaborated to a diazo ketone and the latter is allowed to react with a trialkylborane. Thus, L-serine **5** was N-phthaloylated and then O-acetylated to give **6**, which was then converted to the acid chloride **7**. Treatment of the latter with diazomethane gave the diazo ketone **8**, which was converted to D-**1** with tritetradecylborane.[6]



Blocking group removal from *O*-acetyl-*N*-phthaloyl **2** was readily accomplished, preferentially in two steps:[7] acid-catalyzed methanolysis to remove the acetyl substituent followed by hydrazinolysis to remove the phthaloyl moiety.

An interesting aspect of the chemistry of **1** is the extreme ease with which it underwent loss of acetic acid to give the unsaturated ketone **9**; thick layer chromatography on silica gel was sufficient to effect this elimination.

In this connection, Weiss and Stiller[8] described a minor product which they obtained admixed with D-1-hydroxy-



9

2-acetamido-3-ketodecane from the chromic oxide–pyridine oxidation of N-acylated sphinganine which became the major product on repeated silicic acid column chromatography. They speculate that this product is a substituted oxazolidine. We would like to suggest the *N*-acetyl analog of the α,β-unsaturated ketone **9** as a likely possibility based on our observations on the chromatographic behavior of **1**.

Experimental Section

General. Evaporations were carried out on a rotary evaporator under reduced pressure. Melting points were taken with a Mel-Temp apparatus and are not corrected. The petroleum ether used boiled at 30–60° and magnesium sulfate was used for drying. Thin layer chromatograms were run on 250-μ silica gel plates (Analtech Inc., Newark, Del.); spots were developed with uv and/or phosphomolybdic acid spray (10% ethanolic phosphomolybdic acid). Nmr spectra were determined on either a Varian A-60 or HA-100 instrument using tetramethylsilane as an internal standard. Mass spectra were run on an AEI-MS-9 spectrometer at 70 eV. The 2-mm silica gel plates used for thick layer chromatography were also obtained from Analtech. Partition chromatographs were run on Celite 545 using heptane–Methyl Cellosolve for development; 1.5 ml of lower phase per gram of Celite was used. The letters w, m, and s following the infrared spectral absorptions denote weak, medium, and strong, respectively.

L-*O*-Acetyl-*N*-phthaloylserine (6). Commercially available L-serine (**5**) was first N-phthaloylated according to the procedure of Nefkin, *et al.*,[9] then O-acetylated. Thus, a mixture of 10.5 g (0.01 mol) of L-serine, 27.5 g (0.014 mol) of *N*-carbethoxyphthalimide (Aldrich), and 28.8 g (0.1 mol) of sodium carbonate decahydrate in 150 ml of water was vigorously stirred at room temperature for 45 min and then filtered to separate the small amount of insoluble material. The clear filtrate was acidified with 6 *N* HCl and the *N*-pathaloyl derivative, which separated as an oil, was extracted into ether. Drying and evaporating the ethereal solution left *ca.* 30 g of *N*-phthaloyl-L-serine as a colorless, viscous oil which was acetylated directly by stirring with 100 ml of acetyl chloride at room temperature for 30 min. Most of the excess acetyl chloride was evaporated with moderate heating and the residue was shaken well with ice–water for 10 min to decompose the remaining acetyl chloride. The water was decanted and the shaking was repeated with a fresh portion of ice–water for 5 min. After the water was decanted, the residue was dissolved in ether and the ethereal solution was dried and evaporated to leave 23 g of a pale yellow, oily solid. Trituration with benzene gave 6.5 g of L-*O*-acetyl-*N*-phthaloylserine, mp 151–153° (lit.[10] mp 151–153), which can be recrystallized from benzene with good recovery.

Dilution of the benzene filtrate with a large volume of petroleum ether caused a thick, opaque oil to separate. The supernatant was decanted, and the oil was washed again with petroleum ether. Removal of the last traces of solvent left 11.7 g of a pasty solid which was indicated by tlc ($CHCl_3$–EtOH–H_2O 40:20:4) to be very largely the desired **6** (R_f 0.55) along with a very minor faster running impurity; total yield 18.2 g (66%). The oily product obtained was of good enough quality to be used for further conversion to the acid chloride and then to the diazo ketone as outlined in the next experiment.

An improved yield of purer product can be obtained by modifying the work-up as follows. After most of the excess acetyl chloride was evaporated, the liquid residue was poured into ice–water and the suspended organic phase was frequently agitated. During the first 6 hr the water was changed at *ca.* 1.5-hr intervals, being separated each time by decantation. After it was kept in the water overnight (room temperature) the now solid, off-white product was collected and air dried. Recrystallization from benzene furnished **6**, mp 154–157°, in overall 40% yield from L-serine.

L-*O*-Acetyl-*N*-phthaloylseryldiazomethane (8). An 11.7-g (0.42 mol) portion of the oily fraction of L-*O*-acetyl-*N*-phthaloylserine (**6**) obtained in the previous experiment in 40 ml of anhydrous benzene was heated under reflux with 7.5 ml of thionyl chloride for 15 min (reaction mixture was inserted into a preheat-

ed bath), then evaporated. Repeating the evaporation twice more with fresh 100-ml portions of benzene gave the acid chloride as a dark orange oil. The crude acid chloride was dissolved in 125 ml of ether and added dropwise with stirring to a cold solution of ethereal diazomethane (from 30 g of *N*-methyl-*N*-nitrosourea) during 25 min. After the solution was stirred in the cold for an additional 1.5 hr, it was evaporated, leaving the diazo ketone **8** as a thick orange oil, λ_{max} (film) 4.73 (s, diazo), 5.70 (s, OAc), and 5.73 (vs) with a weak peak at 5.65 (phthaloyl) and 6.10 μ (s, ketone). The integrated ratio of the phthaloyl at δ 7.8 (multiplet), $-CHN_2$ at δ 5.5, and CH_3CO_2-protons at δ 2.0 in the nmr indicated the product to contain *ca.* 80% diazo ketone.

D-1-Acetoxy-2-phthalimido-3-ketooctadecane (1). A solution of 0.04 mol of tritetradecylborane in tetrahydrofuran was prepared by adding 24 g (0.12 mol) of neat tetradecene (Aldrich) to 40 ml of 1 *M* diborane in THF (Alpha Inorganics) during 5 min with cooling (ice-water) to moderate the strong exotherm accompanying the addition. The cooling bath was removed after the addition was completed and the solution was stirred at room temperature for 2.5 hr [R_f of tritetradecylborane on tlc (PhH-EtOAc 9:1) *ca.* 0.35].

A solution of the diazo ketone **8** in 40 ml of THF (Matheson Coleman and Bell, bp 65.5–66.5°, freshly opened bottle) was then added dropwise during 10 min at room temperature (gas evolution) and the mixture was stirred at room temperature for 2.5 hr. Water (*ca.* 40 ml) was added and the two-phase mixture was heated under vigorous reflux for 30 min. After cooling, ether was added and the aqueous phase (acidic) was separated. Washing, drying, and evaporating the organic phase left 34 g of an opaque yellow residue. After 2 days at room temperature the product was triturated with petroleum ether and filtered to separate insoluble solid. (Although not identified, its infrared spectrum, which showed only weak absorption in the carbonyl region, indicated it not to be any of the desired **1**.) The liquid residue obtained by evaporating the petroleum ether filtrate (*ca.* 23 g) separated into two phases on standing. The lower phase was rich in the desired **1** and the upper phase in unreacted tritetradecylborane (indicated by tlc). The entire residue was partition chromatographed and the desired **1** was eluted after *ca.* two holdback volumes. The product was a pale yellow solid (4.4 g, 22% based on starting acid **6**): mp 52–55° (shrinking 48°); λ_{max} (KBr) 5.7 (OAc), 5.8 μ (ketone + phthaloyl) (a weak 5.6-μ peak associated with the phthaloyl moiety was also present); $[\alpha]^{25}D$ −50.3° (*c* 0.83, EtOH); R_f on tlc (PhH-EtOAc 9:1) *ca.* 0.6.

Anal. Calcd for $C_{28}H_{41}NO_5$ (471.62): C, 71.30; H, 8.76; N, 2.97. Found: C, 71.63; H, 8.85; N, 3.13.

2-Phthalimido-3-ketooctadecene-1 (9). On attempted thick layer chromatography (PhH-EtOAc 9:1) the ketone **1** underwent elimination of acetic acid to give the olefinic ketone **9**: mp 67–70° (after trituration with petroleum ether); λ_{max} (KBr) 5.8 (s) and 5.6 (w, phthaloyl) and 5.9 (w-m, ketone). The nmr spectrum showed two one-proton doublets (J = 1.2 Hz) at δ 6.50 and 6.10 due to the terminal methylene.

Anal. Calcd for $C_{26}H_{37}NO_3$ (411.58): C, 75.87; H, 9.06; N, 3.40. Found: C, 76.19; H, 9.07; N, 3.78.

9 runs slightly faster than **1** on tlc (PhH-EtOAc 9:1).

D-1-Acetoxy-2-phthalimido-3-hydroxyoctadecane (*O*-Ac-*N*-phth-2). Three grams (0.0063 mol) of ketone **1** was added, neat, to a cooled (ice-water), stirred solution of lithium tri-*tert*-butoxyaluminum hydride (Ventron) in 100 ml of THF (Matheson Coleman and Bell, bp 65.5–66.5°) and the solution was stirred in the cold for 35 min, then diluted with ice-water and ether, and acidified with hydrochloric acid. The organic phase was separated, dried, and evaporated to yield 2.9 g of a pasty, ivory-colored solid whose tlc (PhH-EtOAc 9:1) showed very predominantly one spot at R_f 0.35. Purification of a 100-mg sample by thick layer chromatography (PhH-EtOAc 9:1) gave *O*-Ac-*N*-phth-**2**: mp 69–75°; λ_{max} (KBr) 5.72 (s, OAc), 5.86 (vs), 5.6 μ (w, phthaloyl); $[\alpha]^{25}D$ −16.9° (*c* 0.56, EtOH).

Anal. Calcd for $C_{28}H_{43}NO_5$ (473.63): C, 71.00; H, 9.15; N, 2.96. Found: C, 71.01; H, 9.15; N, 2.95.

The crude material was suitable for conversion to D-*threo*-sphinganine (**2**), as described in the next experiment.

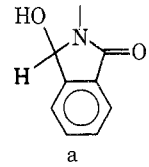
D-*threo*-Sphinganine (1,3-Dihydroxy-2-aminooctadecane) (2). *O*-Ac-*N*-phth-**2** (0.1 g) was heated under reflux in 2 ml of methanol containing 2 drops (Pasteur pipette) of concentrated hydrochloric acid for 30 min. Diluting with ice-water gave *N*-phthaloylsphinganine as a solid which, after drying for 2 hr (probably unnecessary), was heated under reflux with 1.5 ml of 10% ethanolic hydrazine hydrate for 1 hr. The reaction mixture was diluted with ice-water, made strongly basic by adding KOH pellets, and extracted with methylene chloride. Drying and evaporating the methylene chloride extracts left a solid residue which after trituration with ether furnished 25 mg (40%) of colorless, glistening plates: mp 107–109.5°; $[\alpha]^{25}D$ −12.9° (*c* 0.48, $CHCl_3$); R_f on tlc ($CHCl_3$-MeOH-2NNH_4OH 40:10:1)[11] *ca.* 0.35 (I_2 vapor). Grob, *et al.*,[12] report for D-*threo*-sphinganine mp 109°, $[\alpha]^{25}D$ −14.1 ± 2°.

Anal. Calcd for $C_{18}H_{39}NO_2$ (301.50): C, 71.70; H, 13.04; N, 4.65. Found: C, 71.56; H, 13.19; N, 4.60.

***N*-Acetyl Derivative.** Fifty milligrams of analytically pure D-*threo*-sphinganine was dissolved in 5 ml of methanol (with slight warming) and 1 ml of acetic anhydride was added.[13] After 15 hr at room temperature, ice-water was added and the colorless solid which separated was collected, washed with water, and air dried, yield 52 mg, mp 92–96° (shrinking *ca.* 75°). Recrystallization from methylene chloride furnished the analytical sample: mp 97–99.5°; λ_{max} (KBr) 6.05 μ (amide); $[\alpha]^{25}D$ +5.1° (*c* 0.39, $CHCl_3$); R_f on tlc ($CHCl_3$-MeOH 9:1) 0.65 (lit.[11b] mp 98–99°; $[\alpha]^{22.5}D$ +8.5°).

Lithium Aluminum Hydride Reduction of 1. Formation of 1-Acetoxy-2-dihydrophthalimido-3-hydroxyoctadecane (3) and 1,3-Dihydroxy-2-dihydrophthalimidooctadecane (4). A solution of 180 mg (0.44 mmol) of **1** in 3 ml of anhydrous ether was added during 1 min to a cooled (Dry Ice–methanol), stirred partial solution of 35 mg (0.9 mmol) of $LiAlH_4$ in 3 ml of anhydrous ether. After the solution was stirred in the Dry Ice–methanol bath for another 1 min, ice was added at that temperature followed by water, ether, and dilute hydrochloric acid. The ethereal phase was separated, washed with aqueous bicarbonate, dried, and evaporated to yield 140 mg of a pale yellow syrup which was indicated by tlc (PhH-EtOAc 1:1) to consist very largely of two components with R_f's of 0.55 and 0.25. These were separated by thick layer chromatography (PhH-EtOAc 1:1).

The faster running component (52 mg, yellow syrup) was indicated to be **3** by its infrared [3.1 (moderately broad, OH), 5.75 (OAc), and 6.0 μ (amide carbonyl)], mass [*m/e* 475 (M^+ for **3**), 457 (M − H_2O), 397 (M − HOAc)], and nmr spectra [δ 5.9 (bold-faced proton in a) and 3.0 (CH_3CO)].



a

The slower running component (waxy, colorless solid, mp 39–42°, 51 mg) was indicated to be **4** by its infrared [3.1 (moderately broad, OH) and 6.0 μ (amide carbonyl)], mass [*m/e* 433 (M^+ for **4**), 415 (M − H_2O)], and nmr spectra [δ 5.9 (bold-faced proton in a)].

Anal. Calcd for $C_{26}H_{43}NO_4$ (433.62) (**4**): C, 72.01; H, 10.00; N, 3.23. Found: C, 71.72; H, 10.05; N, 3.05.

Acknowledgments. Analyses were performed by Mr. L. Brancone and staff, nmr spectra and optical rotations by Messrs. W. Fulmor and G. Morton, partition chromatograms by Mr. J. Baker, and mass spectra by Dr. G. Van Lear.

Registry No. **1**, 42806-63-3; **2**, 15639-50-6; *O*-Ac-*N*-phth-**2**, 42806-65-5; *N*-Ac-**2**, 35301-25-8; **3**, 42806-67-7; **4**, 42806-68-8; **6**, 41765-22-4; **8**,42806-70-2; **9**, 42806-71-3.

References and Notes

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Photoreaction of 2,6-Diphenyl-4*H*-thiopyran-4-one 1,1-Dioxide with Arylacetylenes

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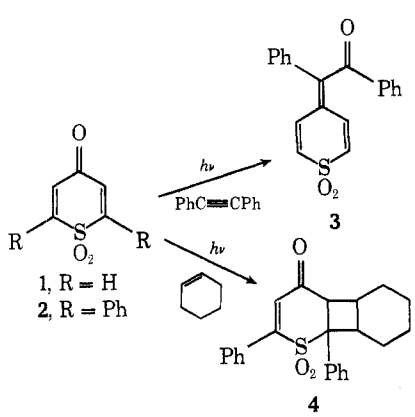
Received June 28, 1973

Photoaddition of *p*-quinones to olefins or acetylenes has attracted considerable attention.[2] Two major pathways are cycloaddition of the carbonyl function to the unsaturated carbon–carbon bond to give oxetanes[3] or their rearranged products[4,5] and cycloaddition of the ring double bond of *p*-quinone to a carbon–carbon double or triple bond to yield cyclobutane or cyclobutene derivatives.[6] Even though 4*H*-thiopyran-4-one 1,1-dioxides (**1** and **2**) are structurally similar to *p*-quinones,[7] only few photochemical studies have so far been reported on this project. Ultraviolet irradiation of **1** and diphenylacetylene yields **3**,[8] similar to the photoreaction of *p*-benzoquinone and diphenylacetylene.[4] Also **2** adds photochemically to cyclohexene to form **4**,[9] a reaction identical with the photoaddition of 2-methoxy-*p*-benzoquinone to acetylenes.[6]

The present research, photoaddition of 2,6-diphenyl-4*H*-thiopyran-4-one 1,1-dioxide (**2**) and arylacetylenes, is part of our continued studies on the photoreaction of *p*-quinones and unsaturated hydrocarbons.[5b,10]



A mixture of **2** and an arylacetylene (diphenylacetylene, methylphenylacetylene, or phenylacetylene) in benzene was irradiated with a medium-pressure mercury lamp using a Pyrex filter. Column chromatography of the reaction mixture in each case gave a single product in significant quantity. The infrared spectra of these photoproducts showed strong absorption bands at 1270–1285 and 1110–1125 cm^{-1}, characteristic of antisymmetric and symmetric stretch of the SO_2 group.[11] Absence of a carbonyl band in the infrared rules out structures similar to **3** or **4** as the structure of the photoproduct. The mass spectra obtained at 70 eV for the photoproducts from **2** and diphenylacetylene, methylphenylacetylene, or phenylacetylene displayed the base peak at the highest mass of *m/e* 382, 320, and 306, respectively, their magnitude corresponding to the expulsion of sulfur dioxide from their parent peaks ($M - SO_2$). Lowering the electron energy to 15 eV for the photoproduct of **2** and diphenylacetylene led to the appearance of a weak peak at *m/e* 446, indicative of its mass number. Molecular weights determined by osmometry were 450 and 370 for the products from **2** and diphenylacetylene and **2** and phenylacetylene. These results clearly indicate that the photoproducts are the decarbonylated compounds of the 1:1 adducts of **2** and arylacetylenes. The nmr spectra of the reaction products showed the olefinic and the aromatic protons at δ 6.8–8.0. The ultraviolet spectrum of the photoproduct from **2** and diphenylacetylene exhibited absorptions at 217 nm (ϵ 3.6 $\times 10^4$), 265 (2.6 $\times 10^4$), and 315 (5.4 $\times 10^3$). This spectrum appears to match that of tropone,[12] while the uv spectrum of the parent thiepin 1,1-dioxide[13] is similar to that of cycloheptatriene.[14] Naturally these spectral properties suggest that the photoproducts have the structure of thiepin 1,1-dioxide.[13,15,16]

Confirmation of the thiepin 1,1-dioxide structure was obtained by thermolysis and hydrogenation of the photoproduct from **2** and diphenylacetylene (Scheme I). Heat-

Scheme I

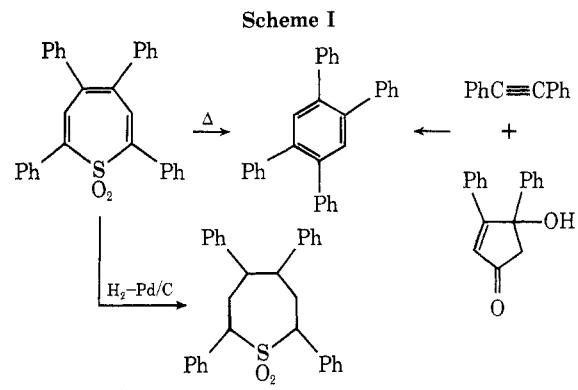


Table I
Spectral and Physical Data for the Photoproducts

Product	Yield, %	Mp, °C	Ir, cm^{-1} (KBr)	Uv (CH_2Cl_2) λ, nm	Uv (CH_2Cl_2) ε	Nmr, δ (acetone-d_6)	Mass spectra, *m/e* (rel intensity) (70 eV)	Mol wt	Anal. Calcd (found), % C	H	O	S
5	60[a]	224–225	1600, 1490, 1285, 1125, 755, 685	217 265 315	36,330 26,000 5,400	7.1–6.2 (m, 10 H) 7.3–7.6 (m, 10 H) 7.9–8.0 (m, 2 H)	496 (M^+, <1)[d], 383 (32), 382 (100), 381 (81), 367 (6), 305 (14), 304 (8), 291 (13), 290 (6), 289 (5)	450	80.54 (80.69)	4.85 (4.96)	7.01 (7.01)	7.07 (7.02)
6	26[b]	88–92	1490, 1445, 1285 1120, 760, 690			1.33 (s, 3 H) 6.87 (s, 1 H) 6.97 (s, 1 H) 7.0–7.8 (m, 15 H)	321 (28), 320 (100), 305 (33), 304 (22), 272 (21)		78.10 (77.92)	5.24 (5.01)		8.34 (8.35)
7	20[c]	172–174	1595, 1485, 1440 1120, 760, 690			7.0–7.3 (m, 11 H) 7.5–7.7 (m, 5 H) 7.9–8.0 (m, 2 H)	307 (25), 306 (100), 305 (20), 290 (20), 288 (21), 102 (33), 91 (20) 77 (29)	370	77.81 (78.07)	4.96 (5.01)		8.44 (8.44)

[a] Recovery of **2** was 11%. [b] Recovery of **2** was 35%. [c] Recovery of **2** was 27%. [d] At 15 eV.