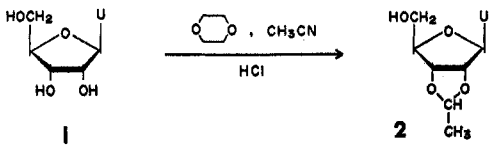
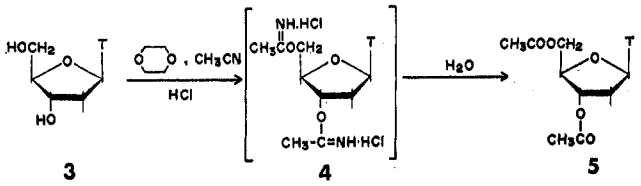
SCHEME II





(S_2) 0.7, (S_3) 0.59; nmr (CD_3SOCD_3 + D_2O) δ 7.74 (d, 1 H, H_6), 5.69 (two overlapping doublets, 2 H, $H_{1'}$ + H_5), 5.18 (d, 1 H, CH, acetal), 4.74 (m, 2 H, $H_{2'}$ + $H_{3'}$), 4.10 (poorly resolved, overlapped with HDO signal, 1 H, $H_{4'}$), 3.62 (d, 2 H, $H_{5'}$) 1.40 (d, 3 H, CH_3).

Anal. Calcd for $C_{11}H_{14}N_2O_6$: C, 48.89; H, 5.22; N, 10.37. Found: C, 48.75; H, 5.37; N, 10.58.

3′,5′-Di-*O*-acetylthymidine (5).—Thymidine (**3**, 0.12 g, 0.5 mmol) was shaken with acetonitrile (5 ml) and a 6.5 *M* solution of anhydrous hydrogen chloride in dioxane (0.5 ml) for 48 hr at room temperature. Only after 3 hr did the reaction mixture become homogeneous. The solution was added dropwise to an excess of sodium acetate in water and the mixture was extracted with chloroform. The dried organic layer was evaporated to dryness. The syrupy residue solidified after drying at 0.1 mm to give 90 mg (56%) of chromatographically pure solid **5**: mp 123–125° (crystallized from benzene–carbon tetrachloride 2:1 mixture) (lit.[7] mp 123–125°); R_f (S_1) 0.76, (S_4) 0.81. Ammonolysis of **5** gave thymidine as found by paper chromatography (S_1).

Anal. Calcd for $C_{14}H_{18}N_2O_7$: C, 51.53; H, 5.56; N, 8.59. Found: C, 51.52; H, 5.56; N, 8.38.

Reaction of Uridine with Acetonitrile and Anhydrous Hydrogen Chloride.—A suspension of uridine (**1**, 0.12 g, 0.5 mmol) in acetonitrile (10 ml) was saturated with hydrogen chloride, and the solution, which contained a small amount of undissolved solid, was held overnight at room temperature. The reaction mixture was evaporated to dryness; a portion of the crude product was dissolved in 1 *M* triethylammonium acetate (pH 6), and chromatographed in S_1. Authentic samples of **1**, 5′-*O*-acetyluridine, and 2′,3′,5′-tri-*O*-acetyluridine were run simultaneously. Five spots were detected, which were eluted with water and the amount of uv-absorbing material was determined spectrophotometrically at 260 nm (Table I).

TABLE I

Compound	R_f	%[a]
Uridine (1)	0.15	1
5′-*O*-Acetyluridine	0.26	46
Unidentified	0.37	14
Unidentified	0.51	16
2′,3′,5′-Tri-*O*-acetyluridine	0.74	23

[a] Based on sum of the uv absorbances of the five eluted spots.

Registry No.—2, 29765-28-4; **5**, 6979-97-1.

Acknowledgments.—Thanks are due to Dr. Jerome P. Horwitz for valuable comments and to Mr. N. Cvetkov for measuring the nmr spectrum.

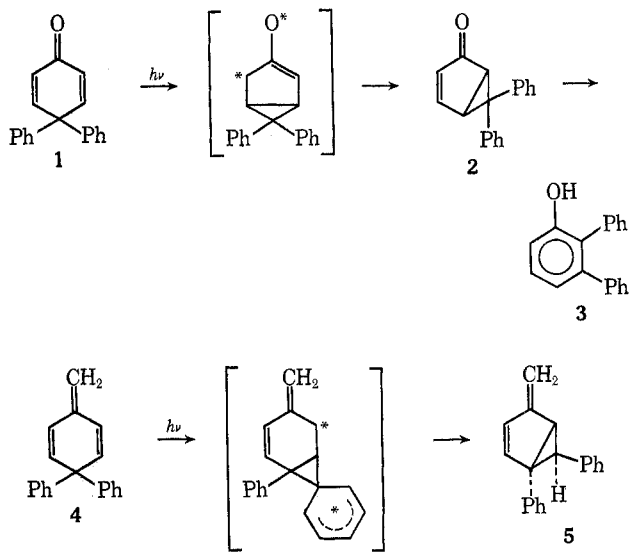
A Novel Photochemical Rearrangement–Elimination of an Allylic Alcohol Having a Di-π-methane Structure[1]

WILLIAM G. DAUBEN,* WAYNE A. SPITZER,[2] AND RICHARD M. BODEN

Department of Chemistry, University of California, Berkeley, California 94720

Received November 30, 1970

In the course of a study of the di-π-methane rearrangement, the photochemistry of a variety of compounds having a geminal phenyl group allylic to two double bonds has been examined. Generally, compounds having this chromophoric structural feature rearrange to give cyclopropyl products either by 1,3-vinyl–vinyl interaction such as in **1** to **2**,[3] and ultimately **3**, or by 1,3-vinyl–aryl interaction such as in **4** to **5**.[4]



In contrast, when 1-hydroxy-4,4-diphenyl-2,5-cyclohexadiene (**6**) was irradiated in an ethanolic solution with a Vycor filter (λ >210 nm), the only low molecular weight photoproduct was an aromatic hydrocarbon. The product was identified as *o*-terphenyl (**7**) by comparison of its spectra with those of the known compound. A dark control, run parallel with the irradiation, showed no reaction. When the reaction was followed using thin layer chromatography, no buildup of an intermediate could be detected.

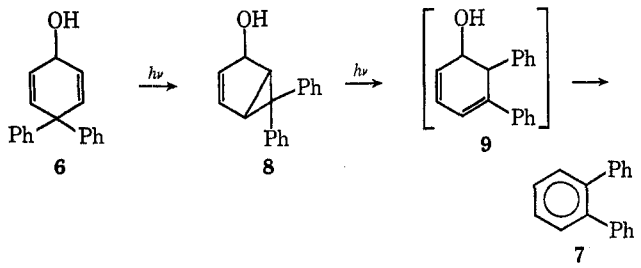
The 1,2-phenyl migration in such a system is a common process, but the elimination of water is quite distinctive. Of two possible mechanisms involving intermediates related to structures **2** and **5**, only the alcohol **8** related to the former type has been evaluated owing to synthetic difficulties leading to an alcohol related to **5**, *i.e.*, 1,6-diphenylbicyclo[3.1.0]hex-2-en-4-ol. An intermediate such as **8** could photochemically rearrange

(1) This work was supported, in part, by Grant No. AM-00709, National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service, and the Hoffmann-La Roche Foundation.

(2) National Institute of Health Predoctoral Fellow, 1967–1970.

(3) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962).

(4) H. E. Zimmerman, P. Hackett, D. F. Juers, and B. Schroder, *ibid.*, **89**, 5973 (1967).



to a second intermediate **9** which, in turn, could dehydrate to the observed product. The alcohol **8** was prepared from the ketone **2** by lithium aluminum hydride reaction. The alcohol was unstable upon silica gel and alumina and so was characterized by spectral properties; oxidation of it gave back the starting ketone.

Direct irradiation of **8** in ethanol with a Vycor filter yielded the expected *o*-terphenyl. A dark control reaction yielded no *o*-terphenyl. The rate of photoinduced disappearance was three times as rapid as that of **6**; such a result is required since no buildup of an intermediate had been detected. Thus, the involvement of the cyclopropane alcohol **8** is not only feasible but possible. As with other related compounds with the 4,4-diphenyl-2-cyclohexenyl chromophore,[5] the reaction of **8** proceeds *via* the triplet state, the reaction being sensitized by acetophenone.

Experimental Section

Preparation of 4,4-Diphenyl-2,5-cyclohexadienone (1).—2,3-Dichloro-5,6-dicycano-1,4-benzoquinone (DDQ, 5.8 g, 0.026 mol) and 4,4-diphenyl-2-cyclohexanone[3] (5.8 g, 0.024 mol) were dissolved in 50 ml of dioxane and refluxed for 15 hr. After work-up, the product was recrystallized from a methylene chloride–hexane solution to give 3.1 g (48%) of 1, mp 122–123° (lit.[3] mp 121–123°).

Preparation of 1-Hydroxy-4,4-diphenyl-2,5-cyclohexadiene (6).—4,4-Diphenyl-2,5-cyclohexadienone (1.35 g) and sodium borohydride (0.2 g) were dissolved in 50 ml of ethanol and stirred overnight at room temperature. Upon work-up, the residue (1.05 g, 78%) crystallized on standing. Compound **6** has the following properties: mp 82–84°; uv max (95% EtOH) 260 nm (ε 420); ir (CCl_4) 3430 and 695 cm^{-1}; nmr (CCl_4) δ 6.97 (s, 10, phenyl), 5.6–6.0 (m, 4, CH=CH), 4.23 (s, 1, CHOH), 2.92 (s, 1, CHOH); mass spectrum *m/e* 248, 231, 230, 229, 228, 215, and 202.

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 86.85; H, 6.53.

Irradiation of 1-Hydroxy-4,4-diphenyl-2,5-cyclohexadiene (6).—A solution of 235 mg of 1-hydroxy-4,4-diphenyl-2,5-cyclohexadiene (1) in 235 ml of absolute ethanol was irradiated under a nitrogen atmosphere using a 450-W Hanovia lamp and a Vycor filter (λ >210 nm). The progress of the irradiation was followed by thin layer chromatography. After 30 min the irradiation was halted, the solvent was removed by rotary evaporation, and the photomixture was separated by silica gel column chromatography. Two fractions were isolated, 31 mg of starting alcohol and 81 mg (43% based on reacted alcohol) of an aromatic hydrocarbon. The remainder of the photomixture was high molecular weight. The photoproduct was identified as *o*-terphenyl by comparison of spectra with those of the known compound. A dark control run parallel with the photoreaction showed no reaction.

Preparation of 6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-ol (8).—A solution of 100 mg of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**2**)[3] in 100 ml of anhydrous ether was added, dropwise, to a suspension of 128 mg of lithium aluminum hydride in 150 ml of anhydrous ether. The reaction mixture was stirred for 1 hr, water was carefully added, and the ethereal layer was separated and dried. The solvent was rotary evaporated. The crude **8** had the following properties: ir (CCl_4) 3420 and 1120 cm^{-1}; nmr (CCl_4) δ 7.12–7.17 (m, 10, phenyl), 6.02 (m, 2, CH=CH), 4.7 (m, 1, CHOH), 3.68 (s, 1, CHOH), 2.0–2.6 (m, 2, cyclopropyl); mass spectrum *m/e* 248, 230, 215, 202. Oxidation of the alcohol with chromic acid in pyridine[6] yielded the starting ketone.

Irradiation of 6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-ol (8).—A solution of 100 mg of **8** in 235 ml of absolute ethanol was irradiated under a nitrogen atmosphere using a 450-W Hanovia lamp and a Vycor filter. After 30 min, the irradiation was stopped, the solvent was rotary evaporated, and the photomixture was separated by silica gel column chromatography. *o*-Terphenyl (79 mg) was isolated and identified by comparison with an authentic sample.

Sensitized Irradiation of 6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-ol (8).—A solution of 370 mg of **8** in 230 ml of benzene, 15 ml of methanol, and 7 ml of acetophenone was irradiated under a nitrogen atmosphere using a 450-W Hanovia lamp and a Nonex filter (λ >310 nm). After 20 min, the irradiation was stopped, the benzene and methanol were rotary evaporated, and the acetophenone was distilled at reduced pressure. The residue was chromatogaphed on 70 g of basic Woelm alumina (activity III) and 84 mg of *o*-terphenyl eluted with 5% ethyl acetate–hexane. A dark control reaction showed no reaction.

Registry No.—**6**, 29765-37-5; **8**, 29765-38-6.

(5) W. G. Dauben and W. A. Spitzer, *J. Amer. Chem. Soc.*, **92**, 5817 (1970).

(6) R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).

Synthesis of 5,6-Dihydropyrido[2,3-*d*]pyrimidine Derivatives Directly from Acyclic Precursors

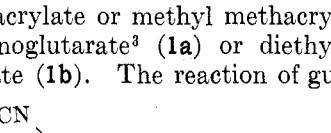
ALLEN M. SCHOFFSTALL

Department of Chemistry, University of Colorado, Colorado Springs, Colorado 80907

Received December 31, 1970

Existing methods for the synthesis of 5,6-dihydropyrido[2,3-*d*]pyrimidines involve several steps including production and isolation of one or more pyrimidine[1] or piperidine[1a,2] derivatives and subsequent ring closure. We wish to report a method by which several members of this class of compounds may be prepared in a single synthetic step starting with acyclic precursors.

Ethyl cyanoacetate sodium salt was caused to react with methyl acrylate or methyl methacrylate forming diethyl 2-cyanoglutarate[3] (**1a**) or diethyl 2-cyano-4-methylglutarate (**1b**). The reaction of gunaiidne with



1a, R = H
b, R = CH_3

1a and **1b** in ethanol afforded 2-amino-5,6-dihydropyrido[2,3-*d*]pyrimidine-4,7(3*H*,8*H*)-dione (**2a**) and its 6-methyl analog **2b**, respectively. A similar reaction of **1a** with benzamidine afforded **3**. The pmr spectrum of

(1) (a) W. J. Irwin and D. G. Wibberley, *Advan. Heterocycl. Chem.*, **10**, 149 (1969); (b) J. Biggs and P. Sykes, *J. Chem. Soc.*, 1849 (1959); (c) L. Suranyi and L. Schuler, German Patent 1,100,030 (1961); *Chem. Abstr.*, **57**, 2231 (1962); (d) B. R. Baker and P. I. Almaula, *J. Heterocycl. Chem.*, **1**, 263 (1964); (e) V. Papesch, U. S. Patents 3,235,554 and 3,235,555 (1966); *Chem. Abstr.*, **64**, 14198 (1966); (f) B. Blank and W. T. Caldwell, *J. Org. Chem.*, **24**, 1137 (1959).

(2) J. DeGraw and L. Goodman, *Can. J. Chem.*, **41**, 3137 (1963).

(3) (a) C. F. Koelsch, *J. Amer. Chem. Soc.*, **65**, 2458 (1943); (b) L. Ruzicka, A. Borgesde Almeida, and A. Brack, *Helv. Chim. Acta*, **17**, 183 (1934); (c) P. C. Guha and D. D. Gupta, *J. Indian Inst. Sci., Sect. A*, **22**, 255 (1939); (d) L. Barthe, *C. R. Acad. Sci.*, **118**, 1268 (1894).

(4) C. K. Ingold, *J. Chem. Soc.*, **119**, 329 (1921).