# Synthesis and Reactions of 2,3-Diphenyl-2,5-dihydro-2-furanol

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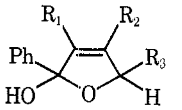
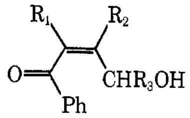
The unstable title compound 1 is the first example of a C-5 unsubstituted 2,5-dihydro-2-furanol to be prepared. In solution furanol 1 rapidly equilibrates between its cyclic and acyclic forms and slowly dehydrates to 2,3-diphenylfuran. The method of preparation of furanol 1 is general and can be adapted to positionally specific syntheses of other 2,5-dihydro-2-furanols.

In connection with our studies of the epoxidation of cyclopropenes,[2] a synthesis of 2,3-diphenyl-2,5-dihydro-2-furanol (**1**) was sought since it was a possible product of the *m*-chloroperbenzoic acid oxidation of 2,3-diphenyl-1-(hydroxymethyl)-2-cyclopropene. Several 5,5-disubstituted 2,5-dihydro-2-furanols[3] have been prepared and extensively studied, but relatively little is known about the 5-monosubstituted 2,5-dihydro-2-furanols[4] and no 5-unsubstituted 2,5-dihydro-2-furanols are known. The reported 5-monosubstituted 2,5-dihydro-2-furanols[4] were prepared by an unselective partial reduction of unsaturated 1,4 diketones to yield metastable furanols which readily dehydrated to furans, either spontaneously or under the influence of catalysts. In the monosubstituted C-5 case, **3**, most thoroughly studied,[4b] no trace of the acylic form **4** was detected, although its presence was indicated by cis–trans epimerization of furanol **3**.



**1**, $R_1$ = Ph; $R_2$ = $R_3$ = H

**3**, $R_1$ = $R_2$ = Cl; $R_3$ = Ph

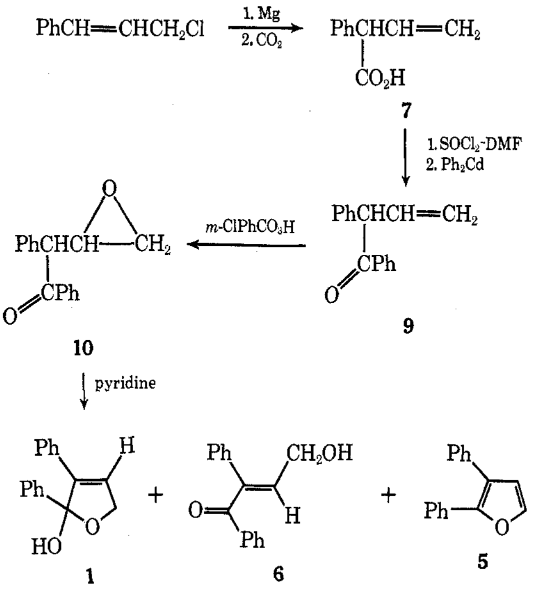


**2**, $R_1$ = Ph; $R_2$ = $R_3$ = H

**4**, $R_1$ = $R_2$ = Cl; $R_3$ = Ph

**Synthesis.**—Several straightforward routes were tried to prepare furanol **1**. Many of the simple routes which are given in the Experimental Section failed in part because of aromatization to 2,3-diphenylfuran (**5**). We, therefore, turned to the synthetic route shown in Scheme I which as expected also produced the trans isomer **6** in addition to furanol **1**. Reaction of cinnamyl chloride with magnesium followed by carbonation with Dry Ice gave an 84% yield of known phenylvinylacetic acid (**7**).[5] Thionyl chloride–dimethylformamide (DMF)[6] converted acid **7** quantitatively into acid chloride **8**, which was allowed to react with diphenylcadmium to afford the $\beta,\gamma$-unsaturated ketone **9** in 78% yield. Epoxidation of keto olefin **9** with *m*-chloroperbenzoic acid yielded 71% of epoxide **10** as apparently one single diasteriomer.

SCHEME I



The pyridine-catalyzed rearrangement of epoxide **10** was followed by nmr spectroscopy. The results presented in Table I show that trans–cis isomerization occurred under the reaction conditions with a slow formation of furan **5**, which after 96 hr accounted for 35% of the mixture. The trans–cis isomerization presumably occurs *via* reversible 1,4 addition of some unknown nucleophile to keto olefin **6**.[7] No epimerization of epoxide **10** was observed, which prevented the isolation

TABLE I

PYRIDINE-CATALYZED REARRANGEMENT OF 1,2-DIPHENYL-3,4-EPOXY-1-BUTANONE (10)[a]

| Time, hr | 10, % | 6, %[b] | 1–2, %[b] |
|---|---|---|---|
| 2.0 | 41 | 73 | 27 |
| 4.0 | 16 | 64 | 36 |
| 6.5 | 2 | 61 | 39 |
| 9.5 | <1 | 54 | 46 |
| 23.5 | 0 | 27 | 73 |
| 28.0 | 0 | 22 | 78 |
| 96.0 | 0 | 15 | 85 |

[a] At 50° employing 5 ml of pyridine per 1 g of epoxide. [b] Normalized so that the sum of compounds 6 and 1–2 equals 100.

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[1] To whom correspondence should be addressed. Financial support for this work came in part from the National Science Foundation, Grants GP-8878 and GP-20368.

[2] L. E. Friedrich and R. A. Cormier, *J. Org. Chem.*, **35**, 450 (1970).

[3] (a) V. I. Serkova, E. A. Basina, and E. D. Venus-Danilova, *J. Gen. Chem. USSR*, **37**, 1369 (1967), and preceding papers by Venus-Danilova; (b) A. Fabrycy and K. Kozlowski, *Rocz. Chem.*, **41**, 251 (1967); *Chem. Abstr.*, **67**, 33822*f* (1967); (c) A. N. Orlova and V. S. Lineva, *Zh. Org. Khim.*, **3**, 748 (1967); *Chem. Abstr.*, **67**, 43606*c* (1967); (d) C. S. Foote, M. J. Wuesthoff, S. Wexler, I. G. Burstain, R. Denny, G. O. Schenck, and K. H. Schulte-Elte, *Tetrahedron*, **23**, 2583 (1967); (e) A. Fabrycy and R. Dobrzeniecka, *J. Gen. Chem. USSR*, **37**, 53 (1967); (f) *Zesz. Nauk. Politech. Szczecin. Chem.*, **6**, 23 (1965); *Chem. Abstr.*, **65**, 13639*h* (1966); (g) A. Fabrycy and K. Kozlowski, *J. Gen. Chem. USSR*, **33**, 3702 (1963); (h) R. E. Lutz, C. L. Dickerson, and W. J. Welstead, Jr., *J. Org. Chem.*, **27**, 3062 (1962); (i) Yu. S. Zalkind and V. K. Teterin, *J. Prakt. Chem.*, **133**, 195 (1932); *Chem. Abstr.*, **26**, 2977 (1932); (j) A. Lowenbein and G. Ulich, *Chem. Ber.*, **58B**, 2662 (1925).

[4] (a) H. H. Freedman and G. A. Doorakian, *Tetrahedron*, **20**, 2181 (1964); (b) W. K. Hankins, R. E. Lutz, E. L. Anderson, M. G. Hankins, and D. W. Boykin, Jr., *J. Org. Chem.*, **35**, 2934 (1970).

[5] A. Iliceto and G. Gaggia, *Gazz. Chim. Ital.*, **90**, 262 (1960).

[6] H. H. Bosshard, R. Mory, H. Schmid, and H. Zollinger, *Helv. Chim. Acta*, **42**, 1653 (1959).

[7] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 344; F. M. Menger and J. H. Smith, *J. Amer. Chem. Soc.*, **91**, 4211 (1969).

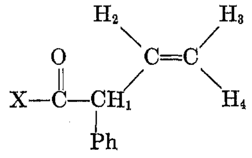
of the other diastereomer. It is therefore unknown if the two possible diastereomers may fragment to different ratios of compounds **6** and **1**–**2**. Graphical extrapolation of the **6**:**1**–**2** ratio to zero time gives a kinetic ratio of 76:24. In a typical preparative run the yield of isolated furanol **1** was 22% with large accompanying amounts of furan due to partial aromatization under the work-up conditions.

The crystalline furanol could be stored indefinitely at 0° without detectable decomposition, but at room temperature the material dehydrated to 2,3-diphenylfuran (**5**) in a week. Acetone–chloroform solutions of furanol **1** showed no dehydration after 15 hr at room temperature or after heating at 60° for *ca.* 30 min. Heating at 70° for *ca.* 30 min, however, resulted in nearly 80% dehydration. An attempt to obtain an nmr spectrum of furanol **1** in dimethyl sulfoxide solution showed only furan **5**. Similarly, attempts to chromatograph the furanol on Florisil or silica gel columns led to quantitative dehydration, whereas the reported 5-monosubstituted furanols[4b] were stable to Florisil chromatography.

**Nmr Spectra.**—The nmr spectra of acid **7**, its acid chloride **8**, and ketone **9** were sufficiently resolved that the straightforward use of LAOCOON III[8] gave the best values of the chemical shifts and coupling constants for these three compounds (see Table II). Similarly, computer-calculated values for epoxide **10** and furanol **1** are given in Tables III and IV, respectively.

TABLE II

COMPUTER-CALCULATED NMR VALUES FOR COMPOUNDS **7**, **8**, AND **9**[a]



| Proton or coupling | X = OH, **7**[b] | X = Cl, **8**[c] | X = Ph, **9**[d] |
|---|---|---|---|
| $H_1$ | 253.5 | 276.5 | 309.9 |
| $H_2$ | 368.4 | 368.0 | 377.8 |
| $H_3$ | 308.8 | 316.8 | 306.4 |
| $H_4$ | 305.1 | 310.1 | 299.9 |
| $J_{1,2}$ | 8.1 | 7.7 | 7.4 |
| $J_{1,3}$ | 1.0 | 0.9 | 1.0 |
| $J_{1,4}$ | 1.0 | 0.8 | 1.4 |
| $J_{2,3}$ | 10.9 | 10.6 | 10.3 |
| $J_{2,4}$ | 15.5 | 16.1 | 17.2 |
| $J_{3,4}$ | −1.3 | −1.4 | −1.4 |

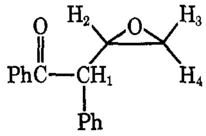
[a] All values in hertz. Shifts measured downfield from TMS. [b] Root mean square error = 0.3, degrees of freedom = 13. [c] Root mean square error = 0.1, degrees of freedom = 15. [d] Root mean square error = 0.2, degrees of freedom = 8.

**Equilibration of Furanol 1.**—The solid-phase ir spectrum of furanol **1** in Nujol showed no carbonyl band the same as reported for furanol **3**.[4b] In chloroform solution, however, the ir spectrum showed a strong absorption at 1664 cm$^{-1}$ corresponding to the carbonyl stretch of the open-form hydroxy ketone **2**.

The nmr spectrum of furanol **1** in $CDCl_3$ showed two broad singlets at δ 2.51 and 3.78 for alcohols **2** and **1**, respectively (relative area 1:4), which disappeared on exchange with $D_2O$. In addition, the allylic protons of furanol **1** appeared as a seven-peak multiplet at δ 4.51–5.05, whereas the allylic protons of alcohol **2** appeared as a broad doublet at δ 4.10 which sharpened to to a ringing doublet after $D_2O$ exchange. The vinyl protons of alcohols **1** and **2** were not clearly separated and appeared as a five-peak multiplet at δ 6.21–6.42. Finally, a multiplet at δ 7.77–7.94 which was downfield from the main phenyl absorptions was assigned to the benzoyl ortho protons of alcohol **2**.

TABLE III

COMPUTER-CALCULATED NMR VALUES FOR EPOXIDE **10**



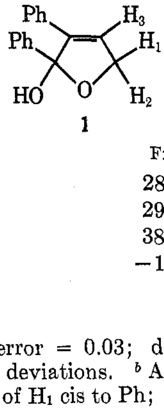
**10**

| Proton or coupling | Frequency, Hz[a] |
|---|---|
| $H_1$ | 257.23 ± 0.06 |
| $H_2$ | 225.62 ± 0.04 |
| $H_3$[b] | 169.25 ± 0.05 |
| $H_4$[b] | 155.25 ± 0.05 |
| $J_{1,2}$ | 7.75 ± 0.07 |
| $J_{1,3}$ | 0.78 ± 0.17[c] |
| $J_{1,4}$ | 0.02 ± 0.14 |
| $J_{2,3}$ | 3.98 ± 0.07 |
| $J_{2,4}$ | 2.77 ± 0.07 |
| $J_{3,4}$ | 4.95 ± 0.08 |

[a] Root mean square error = 0.07; degrees of freedom = 8; all errors are standard deviations. [b] Relative assignment based on expected larger cis coupling to $H_2$ than trans; see L. M. Jackman and S. Sternhell in "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, London, 1969, p 287. [c] For large coupling across four bonds, see reference in footnote *b*, p 334.

TABLE IV

COMPUTER-CALCULATED NMR VALUES FOR FURANOL **1**



**1**

| Proton or coupling | Frequency, Hz[a] |
|---|---|
| $H_1$[b] | 285.94 ± 0.03 |
| $H_2$[b] | 292.83 ± 0.10 |
| $H_3$ | 385.47 ± 0.03 |
| $J_{1,2}$ | −15.00 ± 0.03 |
| $J_{1,3}$ | 1.68 ± 0.04 |
| $J_{2,3}$ | 1.92 ± 0.13 |

[a] Root mean square error = 0.03; degrees of freedom = 4; all errors are standard deviations. [b] Assignment based on expected higher field shift of $H_1$ cis to Ph; see reference in footnote *b* of Table III, p 234.

The equilibration of compounds **1** and **2** was firmly established by variable-temperature nmr studies in a 9:1 v/v $CDCl_3$–acetone-$d_6$ solution. The values of the calculated equilibrium constants ($K$ = **1**/**2**) are given in Table V. The calculated values of the associated thermodynamic parameters are $\Delta H = -1.25 \pm 0.06$ kcal/mol; $\Delta S = -1.41 \pm 0.21$ cal/(deg mol).

The equilibrium appears also to be strongly dependent on the solvent. When the nmr spectrum of furanol **1** was run in pure acetone-$d_6$, the ratio of **1**/**2** was *ca.* 16. The origin of this solvent effect is presently un-

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(8) A. A. Bothner-By and S. M. Castellano in "Computer Programs for Chemistry," Vol. 1, D. F. DeTar, Ed., W. A. Benjamin, New York, N. Y., 1968, p 10.

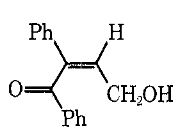
TABLE V

EQUILIBRIUM CONSTANTS FOR FURANOL 1 AND KETOL 2[a]

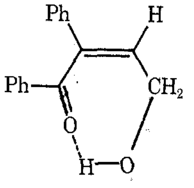
| Temp, °K[b] | $K = 1/2$[c] | DF[d] |
|---|---|---|
| 218 | $8.91 \pm 0.28$ | 28 |
| 229 | $7.45 \pm 0.22$ | 31 |
| 246 | $6.72 \pm 0.16$ | 15 |
| 254 | $5.74 \pm 0.08$ | 18 |
| 299 | $4.12 \pm 0.04$ | 10 |
| 333 | $3.20 \pm 0.08$ | 8 |

[a] In $CDCl_3$–acetone-$d_6$ solution, 9:1. [b] Error ±2°. [c] Errors are standard deviations from repetitive integration of nmr signals. [d] Degrees of freedom.

known, but presumably is not related to the possibility that ketol 2 exists primarily in an intramolecularly hydrogen bonded form, **2b**. Not only does the hydroxyl



**2a**



**2b**

proton of ketol 2 absorb at a higher nmr field strength than the hydroxyl proton of furanol 1, but both the *cis*-ketol 2 and *trans*-ketol 6 have similar ir carbonyl stretches at 1664 and 1658 $cm^{-1}$, respectively, in $CHCl_3$ solution. Furthermore, both the nmr hydroxyl hydrogen absorptions of furanol 1 and ketol 2 were strongly temperature dependent (see Table VI). Both

TABLE VI

CHEMICAL SHIFTS[a] OF HYDROXYL PROTONS OF FURANOL 1 AND KETOL 2

| Temp, °C | Furanol 1[b] | Ketol 2[c] |
|---|---|---|
| 26 | 262 | 132 |
| −19 | 309 | 162 |
| −27 | 316 | 166 |
| −44 | 334 | 179 |
| −55 | 354 | 194 |

[a] In hertz downfield from TMS in $CDCl_3$–acetone-$d_6$ solution (9:1). [b] Slope = −1.04 Hz/deg. [c] Slope = −0.66 Hz/deg.

temperature shifts were linear as observed in other cases.[9]

These data unequivocally establish furanol 1 to be the first which exists in thermal equilibration with a measurable concentration of its open ketol form 2. Whether this feature is due to the fact that furanol 1 is also the first to be unsubstituted at C-5 is unknown. The method of synthesis *via* keto olefin 9, however, will permit other furanols to be specifically synthesized without the attending problems of other preparations.[4]

## Experimental Section

**General.**—Nmr spectra were recorded with a Jeolco Model C60-HL spectrometer using tetramethylsilane as an internal standard. A Perkin-Elmer Hitachi RMU6E spectrometer was used to obtain mass spectra; a direct inlet probe was employed. Ir spectra were obtained with a Perkin-Elmer Model 137 spectrometer. A Cary Model 11 MS spectrophotometer was used to record uv spectra. Melting points were obtained on a calibrated Fisher–Johns melting point apparatus. Computer calculations were performed on an IBM 360/65 computer at the Computing Center of the University of Rochester. Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill.

**Phenylvinylacetic Acid (7).**—The following improved preparation of cinnamylmagnesium chloride is based on a procedure reported by Young, *et al.*[10] A 72.9-g (3.00 g-atoms) portion of crushed and oven-dried magnesium turnings was placed in a 5-l., three-necked flask fitted with a dropping funnel, mechanical stirrer, reflux condenser, and nitrogen inlet. The magnesium was covered with 2.7 l. of anhydrous ether under a nitrogen atmosphere, and the reaction was initiated by addition of *ca.* 3 ml of freshly distilled cinnamyl chloride[11] and a crystal of iodine. The reaction mixture was stirred vigorously, and the remainder of the 45.9 g (0.300 mol) of cinnamyl chloride in 300 ml of anhydrous ether (total *ca.* 30.0 mol) was added at such a rate that the ether barely refluxed. The addition required 3.5 hr, and the resulting blue-gray mixture was cooled in a Dry Ice–acetone bath. The ethereal solution was decanted from the excess magnesium onto 2 kg of powdered Dry Ice contained in a 6-l. beaker. The mixture was stirred manually, and, when all of the Dry Ice had disappeared, the mixture was made strongly acidic with 400 ml of 6 *M* aqueous HCl. The aqueous layer was separated and extracted with three 200-ml portions of ether, and the combined ethereal solutions were extracted with four 200-ml portions of 10% aqueous $Na_2CO_3$. The combined basic extracts were washed with one 200-ml portion of ether and made strongly acidic with 400 ml of 3 *M* aqueous HCl. The resulting mixture was extracted with five 200-ml portions of ether, and the combined ethereal extracts were washed with one 200-ml portion of saturated aqueous NaCl. After drying over anhydrous $Na_2SO_4$ the solvent was evaporated on a rotary evaporator to yield 40.6 g (84%) of colorless, oily acid 7. This material could be used without purification. Crystallization from petroleum ether (bp 30–60°) afforded white prisms: mp 31–32° (lit.[5] mp 32–33°); uv max (95% EtOH) 249 nm ($\epsilon$ 850), 257 (sh, 720), and 263 (sh, 490); ir ($CHCl_3$) 2933 (broad, OH), 1704 (C=O) and 995, 930 $cm^{-1}$ ($CH{=}CH_2$); nmr ($CCl_4$) $\delta$ 4.21 (d, $J$ = 7.5 Hz, 1 H, -PhCH-), 4.94–5.23 (three-peak m, 2 H, $-CH{=}\mathbf{CH_2}$), 5.88–6.45 (m, 1 H, $-\mathbf{CH}{=}CH_2$), 7.21 (s, 5 H, aromatic protons), and 11.93 (s, 1 H, -OH). Exchange with $D_2O$ caused the disappearance of the hydroxyl singlet at $\delta$ 11.93.

When the reaction was carried out using 72.9 g (3.00 g-atoms) of magnesium, 91.5 g (0.600 mol) of cinnamyl chloride, and 3 l. of ether, 72.8 g (75%) of acid 7 was obtained.

**1,2-Diphenyl-3-buten-1-one (9).**—Phenylvinylacetyl chloride (8) was synthesized by the method of Bosshard, *et al.*,[6] from the corresponding acid. The yield of pale yellow acid chloride 8 was 17.8 g (99%). This material was sufficiently pure for use in the next step. Further purification could be achieved by distillation under reduced pressure to afford a colorless liquid: bp 62–63° (1 mm); ir ($CCl_4$) 1764 (C=O), 1325, 1224 and 987, 935 $cm^{-1}$ ($CH{=}CH_2$); nmr ($CCl_4$) $\delta$ 4.63 (d, $J$ = 7.5 Hz, 1 H, -PhCH-), 5.04–5.37 (four-peak m, 2 H, $-CH{=}\mathbf{CH_2}$), 5.89–6.47 (m, 1 H, $-\mathbf{CH}{=}CH_2$), and 7.26 (s, 5 H, aromatic protons).

The acid chloride was converted to enone 9 by treatment with diphenylcadmium according to the procedure of Cason.[12,13] The 90% yield of crude product was dissolved in 200 ml of pentane and cooled in ice to give a reddish oil. The mother liquor was decanted from this oil and slowly cooled to −78° to yield 15.6 g (70%) of pale yellow ketone 9, mp 66–69°. Concentrating the mother liquor to *ca.* 50 ml and cooling to −78° afforded an additional 1.7 g (8%) of pale yellow ketone 9. This material was satifactory for use without further purification. Two more recrystallizations afforded the analytical sample: mp 70–71°; uv max (95% EtOH) 247 nm ($\epsilon$ 11,000); ir ($CCl_4$) 1684 (C=O), 1323, 1300, 1211 and 994, 925 $cm^{-1}$ ($CH{=}CH_2$); nmr ($CCl_4$) $\delta$ 4.85–5.21 (m, 3 H, -PhCH-, $-CH{=}\mathbf{CH_2}$), 6.03–6.60 (m, H, $-\mathbf{CH}{=}CH_2$), 7.19–7.34 (m, 8 H, aromatic protons), and 7.79–7.95 (m, 2 H, benzoyl ortho protons).

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[9] C. P. Rader, *J. Amer. Chem. Soc.*, **88**, 1713 (1966); ref 4b; J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 400; N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day San Francisco, Calif., 1964, p 5; J. R. Merrill, *J. Phys. Chem.*, **65**, 2023 (1961).

[10] R. H. DeWolfe, D. E. Johnson, R. I. Wagner, and W. G. Young, *J. Amer. Chem. Soc.*, **79**, 4798 (1957).

[11] H. Gilman and S. A. Harris, *Recl. Trav. Chim. Pays-Bas*, **50**, 1052 (1931).

[12] J. Cason, *J. Amer. Chem. Soc.*, **68**, 2078 (1946).

[13] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

*Anal.* Calcd for $C_{16}H_{14}O$ (222.27): C, 86.46; H, 6.35. Found: C, 86.53; H, 6.47.

Attempted purification of the crude reaction product by vacuum distillation or silica gel chromatography afforded a colorless oil identical with an authentic sample of (*Z*)- and (*E*)-1,2-diphenyl-2-buten-1-one.[14]

Alternate approaches to the preparation of ketone **9** were also attempted. Examination of the nmr spectrum of the crude product obtained from reacting 1,2-diphenyl-2-buten-1-one with 10 equiv of potassium *tert*-butoxide in *tert*-butyl alcohol[15] at room temperature for 5 hr and quenching with 10% aqueous acetic acid indicated that less than 10% deconjugation had occurred. Treatment of a dimethyl sulfoxide solution of 1,2-diphenyl-2-buten-1-one with 10 equiv of sodium methoxide at room temperature for 20 hr and quenching with 2:1 benzene–acetic acid according to the procedure of Kruger[16] afforded a product whose nmr spectrum indicated a *ca.* 60% yield of ketone **9**, which could not be efficiently separated from the conjugated isomer.

**1,2-Diphenyl-3,4-epoxy-1-butanone (10).**—A 15.2-g (0.0750 mol) portion of 85% *m*-chloroperbenzoic acid (Aldrich Chemical Co.) was added to a solution of 16.7 g (0.0750 mol) of ketone **9** in 500 ml of methylene chloride. The reaction mixture was refluxed for 25 hr, when a starch–iodide test indicated that the peracid had been consumed. The resulting yellow solution was washed with three 100-ml portions of 5% aqueous $NaHCO_3$ and one 50-ml portion of saturated aqueous NaCl. After drying over anhydrous $Na_2SO_4$ the solvent was removed on a rotary evaporator to yield 17.0 g (95%) of a yellowish oil which solidified. Two recrystallizations from hexane afforded 12.6 g (71%) of white prisms: mp 104.5–106.5°; uv max (95% EtOH) 247 nm ($\epsilon$ 13,700); ir ($CHCl_3$) 1686 (C=O), 1325, 1300, 1015, 947, 886, and 837 $cm^{-1}$ (epoxide ring); nmr ($CDCl_3$) $\delta$ 2.51–2.88 (m, 2 H, -CHCH$_2$-), 3.63–3.87 (m, 1 H, -CHCH$_2$-), 4.29 (d, $J$ = 7.5 Hz, 1 H, -PhCH-), 7.27–7.42 (m, 8 H, aromatic protons), and 7.82–7.98 (m, 2 H, benzoyl ortho protons).

*Anal.* Calcd for $C_{16}H_{14}O_2$ (238.27): C, 80.65; H, 5.92. Found: C, 80.86; H, 6.06.

No evidence (melting point, nmr) was found for the presence of more than one of the two possible diastereomers of epoxide **10**.

**2,3-Diphenyl-2,5-dihydro-2-furanol (1) and (*E*)-1,2-Diphenyl-4-hydroxy-2-buten-1-one (6).**—The following rearrangement is based on the method of Crandall and coworkers[17] for the conversion of epoxides to allylic alcohols. A solution of 7.93 g (0.0333 mol) of epoxide **10** in 40 ml of pyridine was heated at 50° (bath temperature) under a nitrogen atmosphere for 7 hr. The solvent was distilled at 5 mm (bath temperature 35–40°). The residual pyridine was removed by repeatedly (*ca.* 4–5 times) dissolving the oily residue in 25 ml of benzene and distilling as before. The residue was dissolved in 450 ml of benzene–hexane (1:5) at 40° and slowly cooled to −50° to yield 1.93 g (24%) of a tan solid. Two additional recrystallizations from benzene–hexane (1:6) afforded 1.19 g (15%) of fluffy white needles of furanol **1**: mp 107.5–108.5°; uv max (95% EtOH) 248 nm ($\epsilon$ 14,800); ir (Nujol) 3333 (OH), 1238, 1093, 1057, 1031, 1014, 985, 901 (C=CH), and 755, 692 $cm^{-1}$; ir ($CHCl_3$) 3497, 3322 (OH), 1664 (C=O, **2**), 1229, 1176, 1063, 1011, 971, 951, and 900 $cm^{-1}$ (C=CH); nmr ($CDCl_3$) $\delta$ 2.51 (broad s, rel area 0.2, -OH, **2**), 3.78 (broad s, rel area 0.8, -OH, **1**), 4.10 (broad d, $J$ = 6.5 Hz, rel area 0.4, -CH$_2$OH, **2**), 4.51–5.05 (seven-peak m, rel area 1.6, -CH$_2$OH, **1**), 6.21–6.42 (five-peak m, rel area 1.0, -C=CH-, **1** and **2**), 7.05–7.56 (m, rel area 9.6, aromatic protons, **1** and **2**), and 7.77–7.94 (m, rel area 0.4, benzoyl ortho protons, **2**); exchange with $D_2O$ caused the disappearance of the hydroxyl absorptions at $\delta$ 2.51 and 3.78 and the collapse of the broad doublet at $\delta$ 4.10 to a ringing doublet; mass spectrum (20 eV) *m/e* (rel intentsity) 238 (23.2), 220 (100), 208 (9.9), 191 (27.7), 115 (24.6), and 105 (40.1).

*Anal.* Calcd for $C_{16}H_{14}O_2$ (238.27): C, 80.65; H, 5.92. Found: C, 80.56; H, 5.91.

The above mother liquors were combined and evaporated on a rotary evaporator to yield 6.62 g (83%) of a brownish oil. This oil was chromatographed on 250 g of silica gel (Will Scientific, Grade 950, 60–200 mesh), *d* 3.5 cm, prepared as a slurry in benzene. Application with benzene and elution gave the following (solvent, product): benzene (1 l.), 1.65 g (21%) of colorless, oily furan **5**; 15% ether in benzene (2 l.), 1.80 g (23%) of an orange, oily mixture of furan **5**, *trans*-ketol **6** and unidentified material(s); 25% ether in benzene (1 l.) and 50% ether in benzene (1 l.), 2.75 g (35%) of pale yellow, oil *trans*-ketol **6**. The course of the chromatography was followed by tlc and nmr. Thin layer plates were prepared by dipping microscope slides into a slurry of Merck silica gel G in chloroform. Benzene was used as eluent, and the plates were developed in an iodine chamber.

Data for 2,3-diphenylfuran (**5**) follow: bp 131–133° (0.5 mm) [lit.[18] bp 173–174° (8 mm)]; uv max (95% EtOH) 230 nm ($\epsilon$ 18,300), 288 (14,500); ir ($CCl_4$) 1236, 1159, 1059, 1025, 943, 917, and 893 $cm^{-1}$; nmr ($CCl_4$) $\delta$ 6.43 (d, $J$ = 2 Hz, 1 H, CH=CH) and 7.11–7.61 (m, 11 H, CH=CH and aromatic protons) [lit.[18] ir ($CCl_4$) 890 $cm^{-1}$; nmr ($CCl_4$) $\delta$ 6.37 (d, $J$ = 2 Hz, 1 H), 7.16 (m, 10 H), and 7.43 (d, $J$ = 2 Hz, 1 H)]; mass spectrum (20 eV) *m/e* (rel intensity) 220 (100) and 191 (31.8).

Data for (*E*)-1,2-diphenyl-4-hydroxy-2-buten-1-one (**6**) follow: uv max (95% EtOH) 243 nm ($\epsilon$ 15,600); ir ($CHCl_3$) 3623, 3460 (OH), 1658 (C=O), 1267, 1065, 1034, 1021, and 915 $cm^{-1}$ (C=CH); nmr ($CDCl_3$) $\delta$ 2.27 (broad s, 1 H, -OH), 4.36 (d, $J$ = 6 Hz, 2 H, -CH$_2$OH), 6.48 (t, $J$ = 6 Hz, 1 H, -C=CH-), 7.20–7.58 (m, 8 H, aromatic protons), and 7.80–7.95 (m, 2 H, benzoyl ortho protons); exchange with $D_2O$ effected the disappearance of the hydroxyl absorption at $\delta$ 2.27, mass spectrum (20 eV) *m/e* (rel intensity) 238 (74.8), 221 (41.1), 207 (44.2), and 105 (100).

*Anal.* Calcd for $C_{16}H_{14}O_2$ (238.27): C, 80.65; H, 5.92. Found: C, 80.60; H, 5.89.

A boiling point for (*E*)-1,2-diphenyl-4-hydroxy-2-buten-1-one (**6**) could not be obtained, since attempted distillation in a sublimation apparatus at 0.2 mm (bath temperature 150–160°) afforded a mixture of ketol **6** and furan **5** in a 2:1 ratio (nmr), respectively.

The yield of furanol **1** could be improved somewhat at the expense of ketol **6** by continuing the reaction beyond the time when all of epoxide **10** was consumed. After a reaction time of 27 hr the isolated yields of compounds **1**, **5**, and **6** were 22, 26, and 19%, respectively.

**Temperature Variation of the Equilibrium between 2,3-Diphenyl-2,5-dihydro-2-furanol (1) and (*Z*)-1,2-Diphenyl-4-hydroxy-2-buten-1-one (2).**—A solution of 100 mg of furanol **1** in 1 ml of 9:1 (v/v) chloroform-$d_1$–acetone-$d_6$ was prepared at room temperature in a sealed nmr tube. The equilibrium ratio was determined by a minimum of ten repetitive integrations of the methylene protons of either isomer, **1** and **2**. The nmr tube was kept at room temperature when not in the nmr probe. Methanol (−50–25°) and ethylene glycol (25–60°) were used for temperature calibration.

The most probable value of the equilibrium constant, $K = 1/2$, was determined by a weighted least squares regression analysis on the function, $K = y/x$, allowing the error in both $y$ and $x$ to be included. The results are given in Table V. The corresponding thermodynamic parameters were calculated by a weighted least squares regression analysis on the function, $\ln K = (\Delta S/R) - (\Delta H/RT)$, incorporating the errors determined for the equilibrium constants and the temperatures.

**Unsuccessful Approaches to the Synthesis of Furanol 1 and Ketols 2 and 6. A. From (*Z*)-$\beta$-Benzoylcinnamic Acid Ethyl Ester.**—According to the procedures of D'yakanov and Komendantov,[19] (*Z*)-$\beta$-benzoylcinnamic acid ethyl ester was prepared in 23% overall yield from diphenylacetylene. A 36% yield of the ester was also obtained from reaction of benzil with 1 equiv of triethyl phosphonoacetate in diglyme.[20]

Reduction of the ester with lithium monoethoxyaluminohydride,[21] aluminum hydride,[22] or lithium aluminum hydride afforded nearly quantitative yields of varying mixtures of (*Z*)-1,2-diphenyl-2-butene-1,4-diol and 1,2-diphenyl-4-hydroxy-1-butanone, which could not be separated by vacuum distillation or silver nitrate extraction.

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[14] A. Padwa and R. Gruber, *J. Amer. Chem. Soc.*, **92**, 100 (1970).

[15] H. J. Ringold and S. U. Malhotra, *Tetrahedron Lett.*, 669 (1962).

[16] G. Kruger, *J. Org. Chem.*, **33**, 1750 (1968).

[17] J. K. Crandall and L. H. Chang, *ibid.*, **32**, 435 (1967); J. K. Crandall and L.-H. C. Lin, *ibid.*, **33**, 2375 (1968).

[18] A. Padwa, *Tetrahedron Lett.*, 1049 (1965); A. Padwa and R. Hartman, *J. Amer. Chem. Soc.*, **88**, 1518 (1966).

[19] I. A. D'yakanov and M. I. Komendantov, *J. Gen. Chem. USSR*, **33**, 2387 (1963).

[20] W. S. Wadsworth, Jr., and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961).

[21] R. S. Davidson, W. H. H. Günther, S. W. Waddington-Feather, and B. Lythgoe, *J. Chem. Soc.*, 4907 (1964).

[22] M. J. Jorgenson, *Tetrahedron Lett.*, 559 (1962).

Attempted ketalization of the ester with a 10-mol excess of triethyl orthoformate in refluxing absolute ethanol was completely unsuccessful.

**B. From $\beta,\gamma$-Diphenyl-$\gamma$-chloro-$\Delta^{\alpha,\beta}$-butenolide [Pseudo-(*Z*)-$\beta$-benzoylcinnamoyl Chloride].**—Hydrolysis of (*Z*)-$\beta$-benzoylcinnamic acid ethyl ester with 5% methanolic KOH afforded a 71% yield of $\beta,\gamma$-diphenyl-$\gamma$-hydroxy-$\Delta^{\alpha,\beta}$-butenolide [pseudo-(*Z*)-$\beta$-benzoylcinnamic acid].[19] Reaction of the hydroxybutenolide with a 2-mol excess of thionyl chloride–dimethylformamide[6] in methylene chloride gave a 92% yield of $\beta,\gamma$-diphenyl-$\gamma$-chloro-$\Delta^{\alpha,\beta}$-butenolide. An 82% yield of the same chlorobutenolide was obtained from treatment of the hydroxybutenolide with 1 equiv of sodium methoxide followed by 3 equiv of oxalyl chloride.[23]

Attempted reduction of the pseudo acid chloride with lithium tri-*tert*-butoxyaluminohydride[24] or sodium borohydride[25] afforded only unreacted starting chloride.

**C. From $\alpha$-Phenyl-$\Delta^{\alpha,\beta}$-butenolide.**—Analogous to the preparation of $\Delta^{\alpha,\beta}$-butenolide from vinylacetic acid,[26] treatment of phenylvinylacetic acid with 1 equiv of performic acid followed by hydrolysis with 1.5 *M* aqueous HCl afforded a 69% yield of $\alpha$-phenyl-$\Delta^{\alpha,\beta}$-butenolide.[27] Reaction of the butenolide with a 10% excess of phenyllithium analogous to the work of Pablova and coworkers[28] afforded a 75% yield of a mixture containing (nmr) 74% 2,3-diphenylfuran, 10% unreacted butenolide, and 15% of unidentified material(s).

**D. From 1,2-Diphenyl-2-buten-1-one.**—1-Bromo-1-phenylpropene[29] was prepared in 56% yield by reaction of propylbenzene with a 2.5-mol excess of *N*-bromosuccinimide in refluxing carbon tetrachloride followed by dehydrobromination in 10% ethanolic KOH. Treatment of the bromide with magnesium in anhydrous ether followed by condensation with benzaldehyde gave 1,2-diphenyl-1-hydroxy-2-butene[14] in 50% yield. Oxidation of this alcohol with pyridinium dichromate[30] afforded a 65% yield of 1,2-diphenyl-2-buten-1-one.[14] Attempted allylic hydroxylation of this ketone with a 10-mol excess of $SeO_2$ in refluxing 95% ethanol for 96 hr resulted only in cis–trans isomerization. Treatment of the ketone with 1 equiv of *N*-bromosuccinimide in refluxing carbon tetrachloride afforded a quantitative yield of 1,2-diphenyl-4-bromo-2-buten-1-one.[14] Attempted hydrolysis of this bromide with a 2-mol excess of $Na_2CO_3$ in 80% aqueous acetone produced only 2,3-diphenylfuran (**5**) in 70% yield.

**E. From 1,2-Diphenyl-3,4-epoxy-1-butanone (10).**—Rearrangement of epoxide **10** with a 10-mol excess of potassium *tert*-butoxide in *tert*-butyl alcohol at room temperature produced a nearly quantitative yield of furan **5**. Treatment of the epoxide with a catalytic amount of triethylamine in benzene solution at room temperature for 5 hr gave no reaction.

**Registry No.**—**1**, 30953-21-0; **2**, 30953-22-1; **5**, 954-55-2; **6**, 30953-24-3; **7**, 30953-25-4; **8**, 30953-26-5; **9**, 30953-27-6; **10**, 30953-28-7.

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[23] R. Scheffold and P. Dubs, *Helv. Chim. Acta*, **50**, 798 (1967).

[24] H. C. Brown and R. F. McFarlin, *J. Amer. Chem. Soc.*, **80**, 5372 (1958); H. C. Brown and B. C. Subba Rao, *ibid.*, **80**, 5377 (1958).

[25] S. W. Chaiken and W. G. Brown, *ibid.*, **71**, 122 (1949).

[26] R. Palm, H. Ohse, and H. Cherdron, *Angew. Chem., Int. Ed. Engl.*, **5**, 994 (1966).

[27] G. Swain, A. R. Todd, and W. S. Warring, *J. Chem. Soc.*, 548 (1944).

[28] L. A. Pablova, V. V. Belogorodskii, and E. D. Venus-Danilova, *J. Gen. Chem. USSR.*, **36**, 1396 (1966).

[29] D. Y. Curtin and J. W. Crump, *J. Amer. Chem. Soc.*, **80**, 1922 (1958).

[30] W. M. Coates and J. R. Corrigan, *Chem. Ind. (London)*, 1594 (1969).

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# Photolysis of Stilbene and 1,1-Diphenylethylene in the Presence of 2-Methyl-4,5-dihydrofuran

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*trans*-Stilbene reacts with 2-methyl-4,5-dihydrofuran on photolysis to yield two cycloaddition products. The reaction proceeds *via* the excited singlet state of stilbene. The rate constant for the quenching of *trans*-stilbene fluorescence by 2-methyl-4,5-dihydrofuran is reported and approximates the diffusion-controlled rate constant. 1,1-Diphenylethylene reacts *via* its excited triplet with 2-methyl-4,5-dihydrofuran to form two cycloaddition products in contrast to the previously reported reaction with 2,3-dihydropyran in which one cycloaddition product and two other adducts are observed.

We recently reported the results of our investigations of the photochemistry of stilbene (**1**) and 1,1-diphenylethylene (**2**) in the presence of 2,3-dihydropyran (**3**).[1] We found that stilbene gave two cycloadducts (**4** and **5**) in addition to two dimers (**6** and **7**) (Scheme I) and that this reaction could not be sensitized with triplet sensitizers.[1a] The ratio of the cycloadducts **4** and **5** was independent of the initial stilbene isomer ratio. 1,1-Diphenylethylene reacted *via* its triplet state[1b] to give one cycloadduct (**8**) and two addition products (**9** and **10**) (Scheme II), which were presumably formed in consecutive reactions initiated by hydrogen abstraction by the triplet of **2** followed by free-radical coupling.[2]

In this paper we report our results for the photolysis of **1** and **2** in the presence of 2-methyl-4,5-dihydrofuran (**11**). This study was conducted for the purpose of observing the influence of ring size of the cyclic vinyl ether substrate on the reaction.

**Photolysis of Stilbene in 2-Methyl-4,5-dihydrofuran.**—Solutions of *cis*- and *trans*-stilbene in 2-methyl-4,5-dihydrofuran (**11**) were photolyzed at 2537 Å. The solutions were irradiated for 48 hr in quartz vessels exposed to the atmosphere. Glpc analysis indicated that stilbene was consumed and that four products were produced whose yields were virtually independent of the stilbene isomer reactant. Two products were identified

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[1] (a) H. M. Rosenberg, R. Rondeau, and P. Servé, *J. Org. Chem.*, **34**, 471 (1969); (b) P. Servé, H. M. Rosenberg, and R. Rondeau, *Can. J. Chem.*, **47**, 4295 (1969).

[2] For additional examples of hydrogen abstraction by the triplet excited state of 1,1-diphenylethylene, see H. M. Rosenberg and P. Servé, *J. Amer. Chem. Soc.*, **92**, 4746 (1970), and T. S. Cantrell, *Chem. Commun.*, 1633 (1970).