of toluene was refluxed for 6 hr with a gentle sweep of nitrogen through the solution. The toluene was removed under reduced pressure leaving a semicrystalline solid which was recrystallized three times from acetonitrile.

3-Phenyl-1H-pyrano[3,2-*f*]quinoline (13).—This compound was obtained from 5-[(dimethylamino)methyl]-6-quinolinol in analogy to **12** after 2 hr of refluxing and crystallization from ethanol or ethyl acetate.

Hydrolysis of 3.—A solution of 10 ml of 10% NaOH and 2 g of **3** in 40 ml of 95% ethanol was refluxed for 2 hr and concentrated under reduced pressure. The aqueous residue was diluted with 50 ml of water and washed several times with chloroform in order to remove triphenylphosphine oxide. The aqueous portion was chilled and acidified with 5 *N* HCl. The precipitated solid was recrystallized from benzene. The physical and analytical properties of the product were identical with those of indole-3-propionic acid: mp 132–133° (lit.[14] mp 132–133°); ν_{max}^{Nujol} 1697 cm^{-1} (-COOH).

Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.83; H, 5.89; N, 7.34.

Hydrolysis of 8.—A mixture of 1 g of **8** and 1 g of KOH was refluxed in 100 ml of 75% ethanol for 6 hr. The clear solution was concentrated under reduced pressure, and the aqueous residue was diluted with 75 ml of water. The resulting oily precipitate which solidified on standing was identified as triphenylphosphine oxide.[15] The aqueous filtrate was acidified with concentrated HCl, and the crystalline precipitate was filtered off and recrystallized from ethanol. The physical and analytical properties of the product were identical with those of 3-(*p*-hydroxyphenyl)-propiophenone: mp 118.5–120.5° (lit.[16] mp 116–117°); ν_{max}^{Nujol} 3400 (-OH), 1675 cm^{-1} (>CO).

Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.69; H, 6.24. Found: C, 79.66; H, 6.27.

The Wittig Reaction (Compounds of Table II).—The following procedures are illustrative of the methods employed for the preparation of the acids, esters, and lactones of Table II.

Ethyl α-(4-Pyridylmethylene)indole-3-propionate (14).—A solution of 30.5 g of **3** and 6.9 g of 4-pyridinecarboxaldehyde in 250 ml of dioxane was refluxed for 21 hr and evaporated under reduced pressure. The residual gum was dissolved in 200 ml of ether, and the solution was extracted with three 50-ml portions of 4 *N* HCl. The acid solution was made basic with 5% NaOH solution and extracted with chloroform to afford 22 g of crude product upon evaporation. Crystallization from 100 ml of ether followed by recrystallization from 50% aqueous ethanol gave analytical material: ν_{max}^{Nujol} 740 (ms), 1070 (m), 1202 (ms), 1257 (ms), 1600 (w), 1710 (s), 3150 (m) cm^{-1}.

Ethyl α-(2-Hydroxy-3-methoxybenzylidene)indole-3-propionate (17).—A solution of 1.52 g of 2-hydroxy-3-methoxybenzaldehyde and 4.77 g of **3** in 75 ml of dioxane was refluxed for 18 hr. The dioxane was removed under reduced pressure, and the residual gum was extracted with five 25-ml portions of Skellysolve B. The remaining gum was dissolved in ethyl acetate and chromatographed on a column of 300 g of Florisil. Concentration of the first few fractions gave crystalline material. The crystals were combined, and recrystallized from ethanol: ν_{max}^{Nujol} 730 (m), 750 (m), 960 (m), 1020 (m), 1185 (ms), 1225 (ms), 1250 (s), 1575 (mw), 1610 (mw), 1690 (ms), 3375 (m), 3395 (ms) cm^{-1}.

2-(*p*-Hydroxybenzyl)-5-phenyl-2,4-pentadienoic Acid (21).—A solution of 5.28 g of cinnamaldehyde and 18 g of **7** in 300 ml of dioxane was refluxed for 24 hr. The dioxane was removed under reduced pressure, and the residue was taken up in 100 ml of 50% ethanol. The solution was treated with 8 g of KOH and refluxed for 4 hr. The ethanol was removed under reduced pressure, and the concentrate was diluted to *ca.* 100 ml with H_2O. The aqueous mixture was extracted with four 50-ml portions of ether. The aqueous phase was made strongly acidic with concentrated HCl, and the precipitated product was filtered, washed with cold H_2O, and recrystallized from absolute ethanol: ν_{max}^{Nujol} 730 (m), 785 (mw), 985 (m), 1100 (mw), 1165 (m), 1215 (ms), 1275 (ms), 1280 (ms), 1515 (ms), 1590 (s), 1610 (ms), 1665 (ms), 3400 (m) cm^{-1}.

α-(4-Biphenylmethylene)-α-oxoindole-3-valeric Acid (22).—A solution of 10.38 g of **9** and 3.64 g of 4-biphenylcarboxaldehyde in 150 ml of dioxane was refluxed for 24 hr. The dioxane was removed under reduced pressure, and the residue was taken up in 50 ml of 50% ethanol. After addition of 4 g of KOH and refluxing for 4 hr, the ethanol was removed under reduced pressure, and the aqueous concentrate was diluted to *ca.* 50 ml with H_2O. The mixture was washed with four 50-ml portions of ether, followed by four extractions, each with 25 ml of ethyl acetate. The combined ethyl acetate extracts were dried over Na_2SO_4 and concentrated to a gum under reduced pressure. The gum was crystallized from ethanol: ν_{max}^{Nujol} 690 (m), 750 (m), 970 (mw), 1150 (mw), 1230 (m), 1520 (m), 1580 (m), 1610 (ms), 1675 (ms), 3150 (ms) cm^{-1}.

2-(Hydroxy)-α-(*p*-hydroxybenzyl)-1-naphthalene Acrylic Acid δ-Lactone-(24).—A solution of 1.72 g of 2-hydroxy-1-naphthaldehyde and 4.54 g of **7** in 75 ml of dioxane was refluxed for 18 hr and evaporated under reduced pressure. The partially crystalline residue was extracted with three 25-ml portions of boiling Skellysolve B and recrystallized from ethanol: ν_{max}^{Nujol} 740 (m), 820 (ms), 1070 (m), 1170 (mw), 1230 (m), 1515 (m), 1580 (m), 1680 (s), 3300 (ms), cm^{-1}.

3-(4-Biphenylylmethylene)-3,4-dihydro-2H,5H-pyrano[3,2-*c*][1]-benzopyran-2,5-dione (25).—A solution of 4.7 g of **10** and 1.82 g of 4-biphenylcarboxaldehyde in 25 ml of dioxane was refluxed for 24 hr. The dioxane was removed under reduced pressure, leaving a semicrystalline residue. This was triturated with five 50-ml portions of boiling ether. The residue was recrystallized from CH_3CN: ν_{max}^{Nujol} 760 (m), 960 (mw), 1040 (mw), 1110 (mw), 1575 (mw), 1645 (m), 1725 (s), 1745 (m), cm^{-1}.

Mannich bases used as starting materials are either commercially available[17] or were prepared by standard methods.[18] The previously undescribed **5-[(dimethylamino)methyl]-6-quinolinol** was obtained from a solution of 6-hydroxyquinoline (7.25 g), dimethylamine (2.7 g), and 37% formaldehyde (4.25 ml) in ethanol (150 ml). The solution was brought to reflux, allowed to stand for 2 days at room temperature, and concentrated under reduced pressure. The oily residue crystallized on standing. The analytical sample was prepared by recrystallizations from ethyl acetate and ethanol with the aid of charcoal: mp 106–107.5°; yield 55%; λ_{max} 239 mμ (ε 33,800), 285 (2900), 336 (3800).

Anal. Calcd for $C_{12}H_{14}N_2O$: C, 71.26; H, 6.98; N, 13.85. Found: C, 71.23; H, 7.07; N, 13.55.

Registry No.—**3**, 17791-03-6; **4**, 17791-04-7; **5**, 17791-05-8; **6**, 17791-06-9; **7**, 17791-07-0; **8**, 17818-06-3; **9**, 17791-08-1; **10**, 17791-09-2; **11**, 17791-10-5; **12**, 14271-36-4; **13**, 17791-12-7; **14**, 17791-13-8; **15**, 17791-14-9; **16**, 17791-15-0; **17**, 17791-16-1; **18**, 17791-17-2; **19**, 17791-18-3; **20**, 17791-19-4; **21**, 17791-20-7; **22**, 17791-21-8; **23**, 17791-22-9; **24**, 17791-23-0; **25**, 5807-40-9; 3-(*p*-hydroxyphenyl)propiophenone, 17791-25-2; 5-[(dimethylamino)methyl]-6-quinolinol, 17791-26-3.

(14) M. R. Snyder, C. W. Smith, and J. M. Stewart, *J. Amer. Chem. Soc.*, **66**, 200 (1944).

(15) A. Michaelis, *Ann.*, **229**, 306 (1885).

(16) V. A. Zasosov, E. I. Metel'kova, and S. N. Milovanova, *Zh. Obshch. Khim.*, **26**, 2499 (1956); *Chem. Abstr.*, **51**, 4994*d* (1956).

(17) Aldrich Chemical Co., Inc.

(18) H. Hellmann and G. Opitz, "α-Aminoalkylierung," Verlag Chemie, Weinheim, 1960.

The Geometrical Isomers of 1,5-Diphenylpentadien-3-ol

J. GRAY DINWIDDIE, JR., AND HAROLD M. WHITE

Department of Chemistry and Geology, Clemson University, Clemson, South Carolina 29631

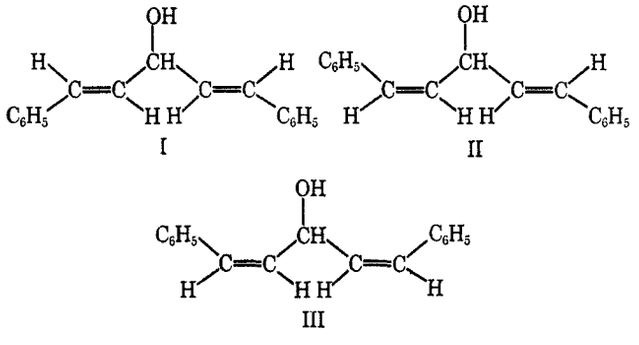
Received March 25, 1968

In a previous report[1] we described the preparation of the geometrical isomers of dibenzalacetone (1,5-diphenyl-1,4-pentadien-3-one). This paper describes

(1) J. G. Dinwiddie, Jr., H. M. White, and W. J. Day, *J. Org. Chem.*, **27**, 327 (1962).

the preparation of the geometrical isomers of 1,5-diphenyl-1,4-pentadien-3-ol and attempts to resolve the *cis,trans* isomer. At the time this work was started there were no known examples of optical isomerism where the asymmetry of the molecule was due to differences in the geometrical isomerism of otherwise identical groups. The resolution of compounds exhibiting such *cis,trans* asymmetry has recently been reported by Riemschneider.[2]

The preparation of 1,5-diphenyl-*trans*-1-*trans*-4-pentadien-3-ol (I) by the sodium borohydride reduction of the *trans,trans* isomer of dibenzalacetone has been reported by Huls and Simon,[3] and this method was used in this work. The *cis,trans* (II) and *cis,cis* (III) isomers were prepared by hydrogenation over Lindlar catalyst of 1,5-diphenylpent-1-yn-*trans*-4-en-3-ol (IV) and 1,5-diphenyl-1,4-pentadiyn-3-ol (V), respectively. IV was prepared by the reaction of phenylacetylene-magnesium bromide with cinnamaldehyde in 62% yield. This preparation was subsequently reported by Iwai and coworkers[4] in somewhat poorer yield. Compound V was prepared by the method of Liang.[5] An attempted preparation of II by sodium borohydride reduction of 1,5-diphenyl-*cis*-1-*trans*-4-pentadien-3-one gave only polymeric material with a molecular weight about twice that of the desired product.



I II

III

The infrared spectrum of each isomer showed the characteristic absorption of *cis*- and/or *trans*-substituted double bonds.[6] The melting points and ultraviolet absorption data are included in Table I. The uv absorption of I is in agreement with the values reported in the literature.[2g,7,8]

TABLE I
PROPERTIES OF THE ISOMERS OF 1,5-DIPHENYL-1,4-PENTADIEN-3-OL

Isomer	Mp, °C	λ_{max}, mμ	ϵ_{max}
trans,trans (I)	64	263	33,100
cis,trans (II)	57	258	20,600
cis,cis (III)	71	236	18,350

The *trans,trans* isomer was found to be sensitive to light. Molecular weight determinations indicated that a dimer was formed initially on exposure to light, followed by more extensive polymerization. The *cis,trans* alcohol was also sensitive, polymerizing very rapidly in the presence of light and over a period of 2–3 days in the absence of light.

Each of the isomeric alcohols yielded the *trans,trans*-dibenzalacetone when oxidized by stirring over manganese dioxide in an organic solvent. The oxidation proceeded most rapidly with the all-*trans* isomer, being quantitative in 6 hr, whereas the all-*cis* isomer was not completely oxidized after 72 hr. The indications are that the steric requirements for proper contact with the surface of the heterogeneous oxidizing agent require the isomerization of the *cis* double bonds.

The chemical instability of II precluded the possibility of effecting a practical resolution. It was decided to resolve the starting material, IV and then produce the enantiomeric *cis,trans* alcohols by catalytic reduction of the triple bond. The biphthalate of IV was prepared in the usual manner, converted into the strychnine salt and crystallized from benzene. Successive fractions of the salt gave no change in optical rotation and this method was abandoned.

The Δ^5-3-β-acetoxyetiocholenate ester of IV (VI) was prepared and resolved by recrystallization from hexane.[9,10] The Δ^5-3-β-acetoxyetiocholenyl chloride was prepared from pregnenolone acetate by a modification of the procedure of Djerassi and Staunton.[9] Thirty per cent formalin solution was used to destroy the excess sodium hypobromite used in the oxidation to the acid, and oxalyl chloride was used to convert the acid into the acid chloride. When thionyl chloride was used, following the published procedure, good yields of the acid anhydride were obtained rather than the acid chloride.

After three recrystallizations, the specific rotation of the ester in chloroform at 25° decreased and reached a value of −10.46°. Further recrystallizations produced no additional change.

Alkaline hydrolysis of VI to yield optically active IV was attempted, but the only product was an intractable tar. During the original purification of VI by chromatography on acid-washed alumina, one column had been allowed to stand overnight before being eluted. The major fraction obtained from this column was an alcohol with an ir spectrum almost identical with that of IV. This method was investigated as a practical method of obtaining the alcohol from the ester.

A sample of optically active ester (VI) was placed on a column of acid-washed alumina and allowed to stand for 52 hr before elution. The alcohol (VII) obtained from this column was optically active and was hydrogenated over Lindlar catalyst to the corresponding *cis,trans* alcohol (VIII) which was also optically active. Examination of the ir spectrum of VIII showed that it was not identical with that of the racemic *cis,trans* alcohol (II). Apparently rearrangement had occurred on the alumina column. While moisture was not scrupulously avoided, the alumina used was Merck acid washed, and the solvents used were believed to be

(2) (a) R. Riemschneider and K. Brendel, *Angew. Chem.*, **73**, 655 (1961). (b) R. Riemschneider and A. Rook, *Naturwisschaften*, **48**, 500 (1961). (c) R. Riemschneider and A. Rook, *Monatsch. Chem.*, **92**, 1197, 1227 (1961). (d) R. Riemschneider and H. Kampfer, *Z. Naturforsch.*, **16b**, 704 (1961). (e) R. Riemschnedier and D. Kirstein, *ibid.*, **17b**, 522 (1962). (f) R. Riemschneider and H. Kampfer, *Ann.*, **665**, 35 (1963). (g) R. Riemschneider, K. Brendel, and J. Takei, *ibid.*, **665**, 43 (1963).

(3) R. Huls and Y. Simon, *Bull. Soc. Roy. Sci. Liege*, **25**, 89 (1956).

(4) I. Iwai, Y. Yura, T. Konotsune, and K. Tomita, *Yakugaku Zasshi*, **80**, 156 (1960).

(5) C. K. Liang, *Bull. Soc. Chim. Fr.*, **53**, 33 (1933).

(6) N. Sheppard and D. M. Simpson, *Quart. Rev.* (London), **6**, 1 (1952).

(7) F. Bohlman, *Chem. Ber.*, **85**, 1144 (1952).

(8) G. Hesse and P. Thieme, *Ann.*, **686**, 64 (1965).

(9) C. Djerassi and J. Staunton, *J. Amer. Chem. Soc.*, **83**, 736 (1961).

(10) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

dry. This rearrangement certainly does not require the conditions reported by Herz and Caple, who found that it was necessary to saturate the eluting solvent with water to effect the rearrangement of an unsaturated ester.[11]

The acetylenic alcohol (VII) was oxidized to the corresponding ketone (IX) with the Kiliani reagent.[12] The same ketone was prepared by the base-catalyzed condensation of acetophenone with phenylpropargylaldehyde. The ir spectrum, analytical data, and method of preparation indicated that IX was 1,5-diphenylpent-1-yn-3-en-5-one. The acetylenic alcohol, VII, was therefore 1,5-diphenylpent-1-yn-3-en-5-ol, and the hydrogenated alcohol, VIII, was 1,5-diphenyl-*cis*-1-*trans*-3-pentadien-5-ol.

Iwai[13] has reported the preparation of IX by the Meyer–Schuster rearrangement of V. The compound reported by Iwai melts at 124° and has carbonyl absorption at 1692 cm^{-1}. The ketone to which we have assigned the same structure melts at 97° and shows carbonyl absorption at 1650 cm^{-1}. Our method of synthesis and the physical properties of the product agree well with the work of Stetter and Reischl.[14] On the basis of the evidence cited we believe that our structural assignment is correct. One attempt to duplicate Iwai's results yielded only starting material.

A sample of partially resolved VI with a specific rotation in chloroform of −17.1° was hydrogenated over Lindlar catalyst to yield 1,5-diphenyl-*cis*-1-*trans*-4-pentadien-3-(Δ^5-3-β-acetoxyetiocholenate) (X). X was allowed to stand on a column of acid-washed alumina as before. The alcohol eluted from the column was optically active, and was shown to be 1,5-diphenyl-*trans*-1-*trans*-3-pentadien-5-ol (XI) by comparison with an authentic sample prepared by the method of Bohlman.[7] The occurrence of optical activity in the rearranged alcohol demands that the parent alcohol (II) must have been asymmetric and requires a stereospecific pathway for the rearrangement.

Experimental Section[15]

***cis,trans*-1,5-Diphenylpentadien-3-ol (II).**—A solution of 2 g of 1,5-diphenylpent-1-yn-4-en-3-ol in 50 ml of methanol was stirred over 1 g of Lindlar catalyst in an atmosphere of hydrogen until 1 mol of hydrogen had been absorbed. The solution was filtered, and the solvent was removed under reduced pressure. The residue was recrystallized from petroleum ether (bp 30–60°) yielding 1.8 g (90%) of white needles: mp 58°; ir 3330, 1005, and 970 cm^{-1}.

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.28; H, 6.66.

***cis,cis*-1,5-Diphenylpentadien-3-ol (III).**—This compound was prepared by the hydrogenation of 1,5-diphenylpentadiyn-3-ol over Lindlar catalyst in methanol. After the absorption of 2 mol of hydrogen, the catalyst was filtered off, and the solvent was removed under reduced pressure. The residue was recrystallized from petroleum ether (bp 30–60°) to give a quantitative yield of white needles: mp 70.5–71.5°; ir 3390, 1030, and 1005 cm^{-1}.

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.28; H, 6.64.

Oxidation of the Isomeric 1,5-Diphenylpentadien-3-ols.—A solution of 2.0 g of *trans,trans*-1,5-diphenylpentadien-3-ol in 25 ml of acetone and 30 ml of petroleum ether (bp 30–60°) was stirred over 10 g of manganese dioxide for 6 hr. The manganese dioxide was removed by filtration; the solvent was removed on a steam bath; and the residue was recrystallized from methanol to give 1.8 g of *trans,trans*-1,5-diphenylpentadien-3-one, which was identified by comparison with an authentic sample.

When a solution of 0.5 g of *cis,trans*-1,5-diphenylpentadien-3-ol in 10 ml of acetone and 25 ml of petroleum ether (bp 30–60°) was stirred over 5 g of manganese dioxide for 12 hr the product was shown to be *trans,trans*-1,5-diphenylpentadien-3-one.

Similar treatment of 0.5 g of *cis,cis*-1,5-diphenylpentadien-3-ol yielded after 12 hr a residue that showed both hydroxyl and carbonyl ir bands. Additional oxidation for 60 hr did not completely remove the alcohol. Recrystallization from methanol gave 0.2 g of the *trans,trans* ketone.

1,5-Diphenylpent-1-yn-4-en-3-(Δ^5-3-β-acetoxyetiocholenate) (VI).—A solution of 5 g of Δ^5-3-β-acetoxyetiocholenic acid in 15 ml of oxalyl chloride was allowed to stand for 8 hr at room temperature. The excess oxalyl chloride was removed under reduced pressure (oil pump) leaving a yellow crystalline residue of the acid chloride. The acid chloride was dissolved in 25 ml of pyridine (freshly distilled from barium oxide), and a solution of 3.2 g of 1,5-diphenylpent-1-yn-4-en-3-ol in 25 ml of pyridine was added. The flask was tightly stoppered and allowed to stand for 8 hr. The reaction mixture was poured into excess ice-cold dilute hydrochloric acid, filtered, and air dried, yielding 5.5 g of crude ester. The crude ester was chromatographed on acid-washed alumina. The benzene eluent yielded 2 g of material which crystallized from petroleum ether as white needles, mp 145–149°. Three additional crystallizations from *n*-hexane afforded 1.03 g of ester: mp 162°; $[\alpha]^{25}D$ −10.46° ($CHCl_3$). The rotation and melting point were unchanged by further crystallizations.

Anal. Calcd for $C_{39}H_{44}O_4$: C, 81.21; H, 7.69. Found: C, 81.32; H, 7.56.

Hydrolysis and Rearrangement of 1,5-Diphenylpent-1-yn-4-en-3-(Δ^5-3-β-acetoxyetiocholenate).—A solution of 1.25 g of VI in 25 ml of benzene was placed on a column (2.5 × 30 cm) of acid-washed alumina. The column was washed with two 5-ml portions of benzene, closed, and allowed to stand for 52 hr. The column was eluted with 500 ml of benzene followed by 400 ml of 10% ether–benzene. The solvent was removed from the ether–benzene fraction, leaving 0.4162 g of 1,5-diphenylpent-1-yn-3-en-5-ol. Recrystallization from petroleum ether (bp 30–60°) gave white needles: mp 57°; $[\alpha]^{25}D$ −6.45° ($CHCl_3$); ir 3390, 2240, and 950 cm^{-1}.

Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.31; H, 5.93.

1,5-Diphenyl-*cis*-1-*trans*-3-pentadien-5-ol (VIII).—A solution of 0.1586 g of optically active 1,5-diphenylpent-1-yn-3-en-5-ol in 25 ml of methanol was stirred over 0.5 g of Lindlar catalyst in an atmosphere of hydrogen until uptake of hydrogen ceased. The catalyst was filtered off, and the solvent was removed under reduced pressure, leaving 0.1362 g of 1,5-diphenyl-*cis*-1-*trans*-3-pentadien-5-ol: $[\alpha]^{25}D$ −14.05° (CH_3OH); ir 3636, 3390, 1060, and 985 cm^{-1}.

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.47; H, 7.00.

Reduction, Hydrolysis, and Rearrangement of 1,5-Diphenylpent-1-yn-4-en-3-(Δ^5-3-β-acetoxyetiocholenate).—A solution of 1.215 g of partially resolved VI, $[\alpha]^{25}D$ −17.1°, in 30 ml of methanol was stirred over 0.5 g of Lindlar catalyst in an atmosphere of hydrogen until 66 ml (1 mol) of hydrogen had been taken up. The solvent was removed under reduced pressure, the residue dissolved in 10 ml of benzene and placed on a column of acid-washed alumina. The column was closed and allowed to stand for 70 hr. The column was developed with benzene followed by 10% benzene–ether.

The solvent was removed from the ether–benzene fraction leaving 0.1017 g of *trans,trans*-1,5-diphenylpentadien-5-ol, $[\alpha]^{25}D$ −5.00° ($CHCl_3$). The identity of the alcohol was established by comparison of its ir spectrum with that of an authentic sample.

Oxidation of 1,5-Diphenylpent-1-yn-3-en-5-ol (VII).—Kiliani reagent[12] was added dropwise to a stirred solution of 0.5 g of 1,5-diphenylpent-1-yn-3-en-5-ol in 25 ml of acetone until the orange

(11) W. Herz and G. Caple, *J. Amer. Chem. Soc.*, **84**, 3518 (1962).
(12) Y. Sato and N. Ikekawa, *J. Org. Chem.*, **24**, 1367 (1959).
(13) I. Iwai and Y. Okahima, *Yakugaku Zasshi*, **79**, 1284 (1959).
(14) H. Stetter and A. Reischl, *Chem. Ber.*, **93**, 1253 (1960).
(15) All analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were taken on Perkin-Elmer Model 137 Infracord either as liquid films or potassium bromide disks. All melting points are uncorrected and were taken on a Scientific Glass Melt meter. Optical rotations were taken on a Rudolph Model 70 polarimeter. Ultraviolet spectra were taken in chloroform solution on a Perkin-Elmer Model 4000A spectrophotometer.

color of the reagent persisted. The reaction mixture was extracted with ether. The ether extract was washed with water and dried over sodium sulfate, and the ether was removed on a steam bath. The residue was recrystallized from methanol to give 0.3 g (60%) of 1,5-diphenylpent-1-yn-3-en-5-one as yellow needles, mp 97°. The ir spectrum was identical with that of a sample prepared by an unambiguous route.

Preparation of 1,5-Diphenylpent-1-yn-3-en-5-one (IX).—A mixture of 1.3 g of phenylpropargylaldehyde and 1.2 g of acetophenone was added dropwise to a stirred solution of 2.5 g of sodium hydroxide in 20 ml of water and 16 ml of methanol. The temperature of the reaction was maintained below 20° by an ice bath. The mixture was stirred for 0.5 hr after addition was completed and filtered, yielding 0.6 g of light yellow solid. Recrystallization from methanol gave 0.5 g of lemon yellow needles, mp 97° (lit.[14] mp 101.5°).

Anal. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21. Found: C, 88.04; H, 5.23.

Registry No.—I, 17791-55-8; II, 17791-56-9; III, 17791-57-0; VI, 17791-58-1; VIII, 17791-59-2; 1,5-diphenylpent-1-yn-3-en-5-ol, 17791-60-5.

The Reductive Cyclization of 4-Tosyloxybicyclo[5.2.1]decan-10-one[1]

J. W. BAUM[2] AND C. DAVID GUTSCHE

Department of Chemistry, Washington University, St. Louis, Missouri 63130

Received June 5, 1968

The photolysis of bicyclo[5.2.1]decan-10-one (**7**) yields octamethyleneketene[3] rather than the tricyclic alcohol **8**, a product which might have been anticipated on the basis of the reported photoisomerization of monocyclic ketones to bicyclic alcohols.[4] This compound has now been synthesized by the sequence of reactions depicted in Scheme I. Employing a bis-homologation ring-expansion procedure,[5] 4-hydroxycyclohexanone (**1**) was converted in 54% yield into a mixture comprised of approximately equal parts of the epimers **2** and **3**, one of which was stable in the keto alcohol form (*i.e.*, **2**) and one of which was stable in the hemiketal form (*i.e.*, **10**). Unfortunately, the hemiketal proved to be so resistant to ring opening that carbonyl derivatives could not be prepared; its utility as a synthesis intermediate being thereby limited, attention was directed to the keto alcohol **2**. This compound, isolated *via* its tosylate **4**, was shown to be epimerically related to **3** (and **10**) by acetolysis to a mixture of the olefin **5** and the actate **6** followed by methanolysis of **6** to the hemiketal **10**. Reductive cyclization of **4** with lithium in ammonia–dimethoxyethane yielded a complex mixture of products, the volatile portion of which was shown by vpc to contain two major components. One of these possesses an analysis compatible with a $C_{10}H_{16}O$ formula and has an nmr and mass spectrum interpretable in terms of the tricyclic alcohol **8**. The other material possesses an analysis compatible with a $C_{10}H_{16}O_2$ formula, has an nmr spectrum which indicates that the two oxygens are present as tertiary hydroxyl groups, and gives a periodate test which indicates the hydroxyl groups to be vicinal. The most reasonable structure commensurate with these data is the diol **9**.

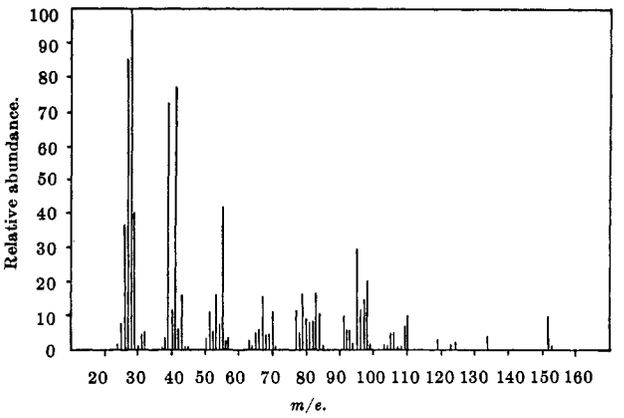


Figure 1.—Mass spectrum of tricyclo[5.2.1.$0^{4,10}$]decan-10-ol (**8**).

No attempt to unravel the details of the mechanism of the reductive cyclization was undertaken. The formation of the alcohol **8** is reasonably explained as an addition of one (or two) electrons to the carbonyl group to yield a radical anion (or a dianion) which then effects a transannular displacement of the tosyl group, a reaction having some resemblance to the reductive cyclization of keto esters which has been investigated in this laboratory.[6]

Experimental Section[7]

10-Oxatricyclo[5.2.1.$1^{4,11}$]undecan-11-ol (10).—A 34.2-g (0.300 mol) sample of 4-hydroxycyclohexanone[8] in 120 ml of methanol, cooled in an ice–salt bath, was mixed with 1.0 g of powdered, anhydrous potassium carbonate. To the stirred suspension 87.0 g (0.300 mol) of N,N′-dinitroso-N,N′-dicarbethoxybutanediamine[5] in 120 ml of methylene chloride was added dropwise over a period of 70 min at a rate such that the temperature was maintained at 5–10°. After an additional 30 min 99% of the theoretical amount of nitrogen had been evolved, and the reaction mixture was processed. The combined crude product from two reactions was distilled through a 20-cm Vigreux column to give (A) 8.1 g, bp 25–96° (0.3 mm); (B) 27.5 g, bp 96–111° (0.1 mm), mainly at 109–111° (0.1 mm); (C) 34.2 g, bp 111–130° (0.15 mm); and (D) 6.1 g bp 130–145° (0.15 mm). Vpc analysis on column 1[7] of fractions A and B indicated that they contained mainly a single component, and by preparative-scale vpc separation on column 3[7] a pure sample of 10-oxatricyclo[5.2.1.$1^{4,11}$]undecan-11-ol (**10**) was obtained as a colorless solid: mp 109–111° (after three melting–solidifying cycles the melting point rose to 111–113°); ν^{KBr}, in cm^{-1}, 3006 (hydroxyl), no absorption in carbonyl region; nmr (CCl_4), in ppm, 14-proton multiplet at 1.17–2.50, one-proton multiplet at 4.06–4.50 (O–C**H** at C-4), one-proton singlet at 4.35 (O**H**).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.03; H, 9.53.

Attempts to make hydroxyl derivatives (benzoate and *p*-toluenesulfonate) and carbonyl derivatives (semicarbazone and

(1) This work was supported, in part, by Grant No. DA ARO(D)-31-124-G533 from the U. S. Army Research Office.

(2) National Institutes of Health Predoctoral Fellow, 1963–1966.

(3) C. D. Gutsche and J. W. Baum, *J. Amer. Chem. Soc.*, **90**, 5862 (1968).

(4) M. Barnard and N. C. Yang, *Proc. Chem. Soc.*, 302 (1958).

(5) C. D. Gutsche and T. D. Smith, *J. Amer. Chem. Soc.*, **82**, 4067 (1960).

(6) C. D. Gutsche, I. Y. C. Tao, and J. Kozma, *J. Org. Chem.*, **32**, 1782 (1967).

(7) All melting points and boiling points are uncorrected. The infrared (ir) spectra were measured on a Perkin-Elmer Infracord instrument. The nmr spectra were measured on Varian HA-60 and A-60A spectrometers; the resonances are expressed in parts per million downfield shift from tetramethylsilane, present as an internal reference. Microanalyses were performed by Dr. Josef Zak, Mikroanalytisches Laboratorium, Vienna, Austria. Vpc analyses were performed on units containing thermistor detectors and using the following columns: (1) a 1/4 in. × 16 ft column packed with 15% w/w neopentylglycol sebacate polymer on 40-50 mesh type ABS Anakrom (a product of Analytical Engineering Laboratory, Inc., Hamden, Conn.); (2) a 1/4 in. × 6 ft column packed with 5% w/w Dow No. 710 silicone oil on 40-50 mesh type ABS Anakrom; (3) a 1/2 in. × 9 ft column packed with 15% w/w Dow No. 710 silicone oil on 40-50 mesh type ABS Anakrom.

(8) E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 615 (1949).