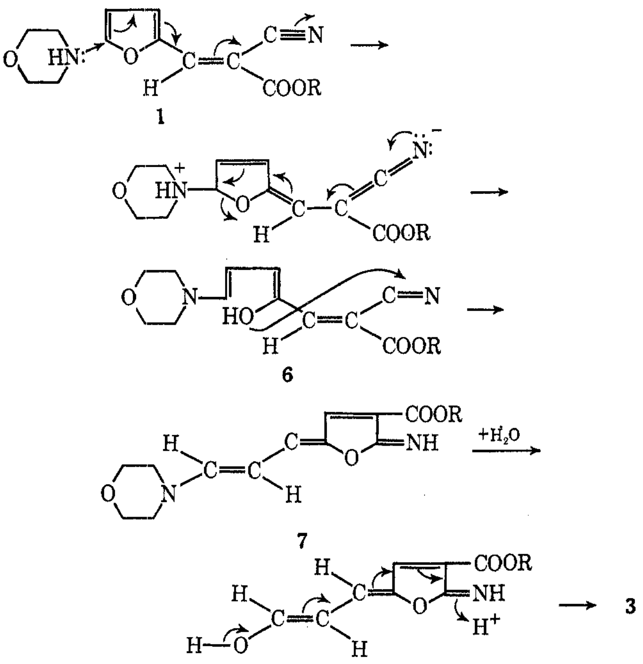
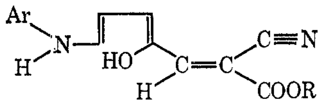
trum showed a fragment ion peak at m/e 163, which is considered to be generated by loss of C_2H_5OH from the parent ion peak by McLafferty rearrangement.[5]

A plausible reaction mechanism is postulated in Scheme I. It seems reasonable to assume that initially the base may attack the 5-position of the furan ring in **3**. Cyclization of the intermediate **6** may occur between the OH and CN groups to give the intermediate **7**, which then yields, when treated with water, the product **3**. When the primary arylamines are used as a base in the reaction, the resulting intermediate **8** similar to **6** would cyclize between the OH and NH groups to give the product **2**.

SCHEME I





8

Experimental Section

Nmr spectra were obtained on a JNM-C-60 high-resolution nmr spectrometer at a temperature of 19–20°. Tetramethylsilane (δ, 0) was used as an internal reference standard. Ir spectra were determined in the chloroform solution using a Perkin-Elmer 521 spectrophotometer. Mass spectra were measured with JMS-01S instrument operating at 75 eV.

Reaction of Ethyl α-Cyano-β-furylacrylate(1a) with Morpholine.—A mixture of 10 g (0.052 mol) of the ester and 40 ml of morpholine was stirred at room temperature for 30 min. The reaction was exothermic, and the solution immediately turned orange, then reddish brown, and finally dark red. After being allowed to stand overnight, the viscous solution was poured into 1.0 l. of water under vigorous stirring. The resulting solid matrial was recrystallized from chloroform to give 5.9 g (54% yield) of **3a** as yellowish green needles: mp 174–175°; uv max ($CHCl_3$) 284 mμ (ε 5200), 374 (34,000); (99.5% EtOH) 228 (10,100), 284 (7200), 387 (36,500); ir ($CHCl_3$) 3508, 3382 (NH_2), 2818, 2730 (aldehyde CH), 1685 (aldehyde C=O), 1672 (ester C=O), 1636 (C=C), 1612, 1378, 1312, and 985 cm^{-1} (furan ring); nmr (d_6-DMSO) δ 1.27, 4.23 ($COOCH_2CH_3$), 6.06 (quartet, H_β, $J_{\beta\gamma} = 15.0$ Hz, $J_{\alpha\beta} = 7.8$ Hz, $J_{\alpha\gamma} = ca. 0$), 7.30 (d, H_γ, $J_{\beta\gamma} = 15.0$ Hz), 9.78 (d, H_α, $J_{\alpha\beta}$, = 7.8 Hz), 7.14 (s, furan ring H), 7.82 (broad, NH_2).

Anal. Calcd for $C_{10}H_{11}NO_4$: C, 57.42; H, 5.26; N, 6.70. Found: C, 57.49; H, 5.17; N, 6.77.

The 2,4-dinitrophenylhydrazone (**4**) occurred as dark brown needles (from pyridine–methanol), mp over 250°.

Anal. Calcd for $C_{16}H_{15}N_5O_7$: N, 17.99. Found: N, 18.05.

The semicarbazone 5 occurred as yellow needles (from methanol), mp 203–204°.

Anal. Calcd for $C_{11}H_{14}N_4O_4$: N, 21.05. Found: N, 20.98.

Reaction of Benzyl α-Cyano-β-furylacrylate (1b) with Morpholine.—The reaction procedure was the same as described above. Recrystallizations of solid **3b** from chloroform and from glyme–ethanol gave brown needles: mp 188–189°; uv max ($CHCl_3$) 287 mμ (ε 5,100), 375 (30,600); (99.5% v/v EtOH) 227 (9400), 285 (7000), 385 (33,200); ir ($CHCl_3$) 3495, 3380 (NH_2), 2800, 2720 (aldehyde CH), 1685 (aldehyde C=O), 1672 (ester C=O), 1630 (C=C), 1613, 1382, 1303 cm^{-1} (furan ring); nmr (d_6-DMSO) δ 5.23 (s, $COOCH_2Ph$), 6.04 (quartet, H_β, $J_{\beta\gamma} = 15.0$ Hz, $J_{\alpha\beta} = 7.8$ Hz), 7.20 (s, furan ring H), 7.30 (d, H_γ, $J_{\beta\gamma} = 15.0$), 7.99 (broad, NH_2), 9.45 (d, H_α, $J_{\alpha\beta} = 7.8$); mass spectrum (75 eV) m/e 271 (molecular ion peak).

Anal. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.82; H, 4.74; N, 5.04.

Registry No.—**3a**, 23386-18-7; **3b**, 23386-19-8; **4**, 23386-20-1; **5**, 23386-21-2.

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Chromous Sulfate Reduction of 2-Methyl-3-hexyne-2,5-diol

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The reduction of nonterminal acetylenes by chromous sulfate[2] has been reported[3] to lead stereoselectively to *trans* olefins in high yields. Sterically hindered alkylacetylenes are found to react slowly or to be inert to chromous sulfate. Conversely, the presence of hydroxyl or carboxyl substituents near the acetylenic bond enhances reduction.

We have found that the reduction of 2-methyl-3-hexyne-2,5-diol with aqueous chromous sulfate, while proceeding readily at room temperature, does not produce the expected *trans*-2-methyl-3-hexene-2,5-diol. Rather the reaction leads to three isomeric reduction products (Scheme I) in which the hydroxyl group rather than the triple bond is reduced. The overall yield of products is 70%, the balance being recovered starting material.

The hydrogenolysis of a hydroxyl group under such mild conditions is unusual and seems to have been previously observed only in reductions with lithium aluminum hydride.[4,5]

The reduction products (**1**, **2**, and **3**) were isolated in pure form by preparative gas chromatography (glpc) (see Experimental Section).

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[1] To whom all correspondence should be directed: Chemistry Department, Stanford University, Stanford, California 94305.

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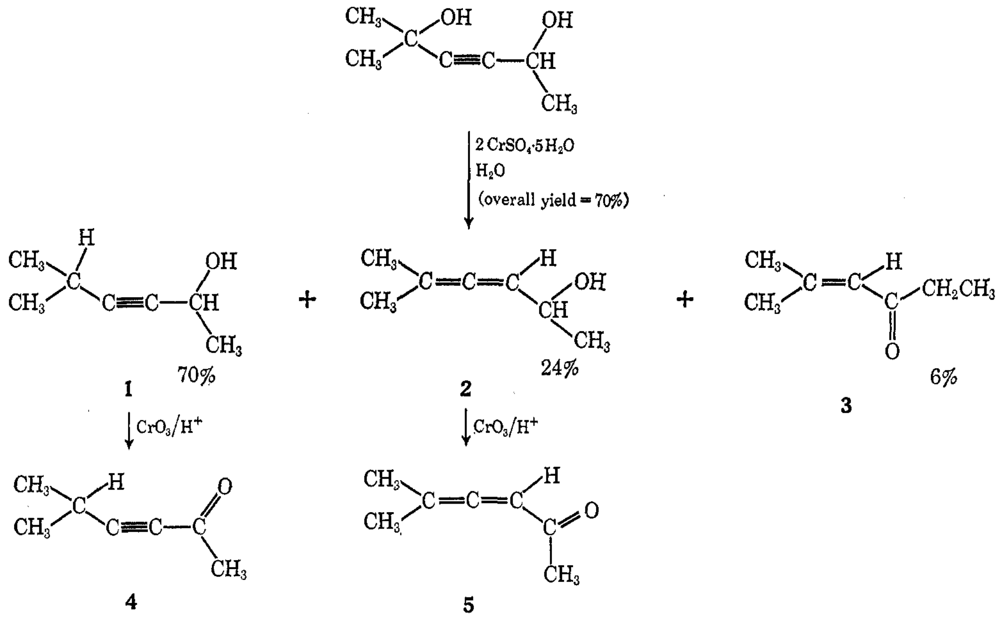
Scheme I



The previously known 5-methyl-3-hexyn-2-ol (**1**)[6] was identified by inspection of its ir and nmr spectra. The structural assignment was confirmed by Jones oxidation[7] of the alcohol to the corresponding ketone **4**,[6] identified as the 2,4-dinitrophenylhydrazone whose physical properties agreed with those reported.[6]

2-Methyl-2,3-hexadien-5-ol (**2**) was characterized by its ir[8] and nmr spectra, and elemental analysis. The structural assignment was more firmly established by oxidation[7] of the alcohol to the corresponding ketone **5** whose ir and nmr spectra were as expected for an allenic ketone (see Experimental Section).

2-Methyl-2-hexen-4-one (**3**) was identified by comparison of its ir and nmr spectra with those of authentic material (Aldrich Chemical Co.); the two sets of spectra were superimposable.

Experimental Section

Nmr spectra were recorded on a Varian A-60A instrument; samples were 50 vol. % solutions in chloroform-*d* with internal TMS as a reference. Infrared spectra were recorded on a Perkin-Elmer Model 237B instrument. Elemental analyses were performed by Mr. N. H. Tashinian at the University of California, Berkeley, Calif. Product separation was effected on a Varian-aerograph model A-90-P3 gas chromatograph with a 5 ft × $^3/_8$ in. aluminum column (packed with 60–80 mesh Chromosorb G coated with 6% Carbowax 20M) using a helium flow rate of 40 ml/min and a temperature of 128°.

2-Methyl-3-hexyne-2,5-diol was prepared as previously described[9] in 60% yield: bp 120–123° (10 mm); $n^{22}\mathrm{D}$ 1.4669 [lit.[9] bp 89–90° (3 mm), $n^{20}\mathrm{D}$ 1.4651]; nmr ($CDCl_3$) δ 1.44 (d, 3, J = 6.5 Hz, CH_3), 1.51 [s, 6, $(CH_3)_2C$], and 4.56 ppm (q, 1, J = 6.5 Hz, $CH(OH)CH_3$).

Oxidation of a small amount of the diol with activated magnesium dioxide by the method of Attenburrow[10] yielded 52% 2-methyl-2-hydroxy-3-hexyn-5-one: bp 76–79° (0.7 mm); $n^{25}\mathrm{D}$ 1.4593 [lit.[11] bp 60° (0.8 mm), $n^{20}\mathrm{D}$ 1.4619]: nmr (CCl_4) δ 1.56 [s, 6, $(CH_3)_2CH(OH)$] and 2.32 ppm (s, 3, $COCH_3$).

Cr(II) Reduction of 2-Methyl-3-hexyne-2,5-diol.—To 9.8 g (0.077 mol) of 2-methyl-3-hexyne-2,5-diol in 25 ml of nitrogen-purged (1 hr) water was added 37 g (0.16 mol) chromous sulfate pentahydrate [prepared (and handled) in a nitrogen atmosphere, in 47% yield, according to the method of Lux and Illman[12]] in 375 ml of nitrogen-purged (1 hr) water. The mixture was stirred to obtain a homogeneous solution and was then allowed to stand at room temperature in a glass-stoppered flask for 22 days. [Glpc analysis (FFAP at 230°) of aliquots of the reaction mixture showed that most of the conversion of starting material to products occurs within 48 hr.] The mixture was then extracted six times with 100-ml portions of ether, saturated with ammonium sulfate, and extracted twice more with 100-ml portions of ether. The combined extracts were dried ($MgSO_4$); the solvent was removed using a rotary evaporator. There was obtained 8.5 g of a colorless liquid, from which three compounds (70% of the mixture) in the ratio of 70:24:6 were isolated by preparative glpc as previously described (the remaining 30% of the mixture was largely starting material according to its glpc retention time). Each compound separated was rechromatographed (one or two times) to obtain the pure product and to demonstrate that isomerization did not occur during chromatography. Product **1** (5-methyl-3-hexyn-2-ol): nmr ($CDCl_3$) δ 1.15 (d, 6, J = 6.5 Hz, CH_3), 1.40 (d, 3, J = 6.5 Hz CH_3), 2.56 [m, 1, J = 6.5 and 1.5 Hz, $CH(CH_3)_2$], 4.51 [m, 1, J = 6.5 and 1.5 Hz, $CH(OH)CH_3$], and 3.4 ppm (s, 1, position concentration dependent, OH).

Oxidation of 1.—To 350 mg (3.12 mmol) of 5-methyl-3-hexyn-2-ol in 1 ml of acetone (redistilled over potassium permanganate) was added 0.8 ml of standard Jones reagent[7] (solution of 26.7 g of chromium trioxide in 23 ml of concentrated sulfuric acid diluted with water to a volume of 100 ml) at 0° over 1 hr. The resulting mixture was extracted four times with 50-ml portions of ether; combined extracts were washed once with water and dried overnight ($MgSO_4$). Solvent removal yielded 200 mg (58%) 5-methyl-3-hexyn-2-one (**4**): nmr ($CDCl_3$) δ 1.22 [d, 6, J = 6.5 Hz, $CH(CH_3)_2$], 2.29 (s, 3, CH_3), and 2.74 ppm [m, 1, J = 6.5 Hz, $(CH_3)_2CH$]; 2,4-dinitrophenylhydrazone,[13] mp 110–111° (recrystallized from 95% ethanol) (lit.[6] 110–110.5°). Product **2** (2-methyl-2,3-hexadien-5-ol): nmr ($CDCl_3$) δ 1.25 [d, 3, J = 6.0 Hz, $CH(OH)CH_3$], 1.70 [d, 6, J = 3.0 Hz, $=C(CH_3)_2$],

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3.0 (s, 1, concentration dependent position, OH), 4.27 [m, 1, J = 6.0 and 6.0 Hz, CH(OH)CH_3], and 5.11 ppm (m, 1, J = 3.0 and 6.0 Hz, =CH); ir (CCl_4)[8] 3613 (OH), 3352 (OH), and 1969 cm^{-1} (C=C=C).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 75.30; H, 11.02.

Oxidation of 2.—Oxidation of 198 mg (1.77 mmol) of **2** by the method described above yielded 80 mg (41%) of 2-methyl-2,3-hexadien-5-one (**5**): nmr ($CDCl_3$) δ 1.84 [d, 6, J = 3.0 Hz, $(CH_3)_2C$=], 2.18 (s, 3, $COCH_3$), and 5.60 ppm (m, 1, J = 3.0 Hz, =$CHCOCH_3$); ir ($CDCl_3$) 1957 (C=C=C) and 1676 cm^{-1} (=C—C=O). Product **3** (2-methyl-2-hexen-4-one): nmr ($CDCl_3$) 1.06 (t, 3, J = 7.0 Hz, CH_2CH_3), 1.88 (d, 3, J = 1.0 Hz, CH_3), 2.14 (d, 3, J = 1.0 Hz, CH_3), and 2.42 (q, 2, J = 7.0 Hz, CH_2CH_3), and 6.08 ppm (q, 1, J = 1.0 Hz, =CHCO). The ir spectrum was identical with that of a commercial sample.

Registry No.—Chromous sulfate pentahydrate, 13825-86-0; 2-methyl-3-hexyne-2,5-diol, 5111-43-3; **1**, 23293-50-7; **2**, 2425-47-0; **3**, 13905-10-7.

A New Route to the 2-Oxabicyclo[3.2.0]hept-6-ene Ring System

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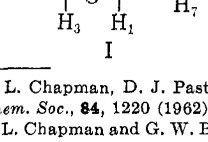
The valence-bond isomerizations of various substituted 1,3-heptadienes to the corresponding bicyclo[3.2.0]hept-6-enes is a well-documented reaction.[1,2] Paquette and coworkers[3] extended this reaction to compounds containing heteroatoms when they photolyzed 2,3-dihydrooxepin and recovered the valence isomer 2-oxabicyclo[3.2.0]hept-6-ene (I). Paquette utilized the parent compound and deuterated analogs to unravel a number of the many coupling constants present in the nmr spectra of the molecule, to which unusual interest had been attached. However, because of the long-range couplings present in the cyclobutene ring, the hydrogen-labeled H_5 was reported merely as a complex multiplet.

In order to elucidate the coupling constants of H_5 with H_4 and $H_{4'}$ and at the same time attempt to extend to the bicyclo[3.2.0]hept-6-ene system the reaction reported earlier, whereby an acetylene was photocycloadded to a cyclic vinyl ether,[4] a solution of diphenylacetylene in 2-methyl-4,5-dihydrofuran was photolyzed at 2537 Å. At the end of 24 hr, only one product and no diphenylacetylene could be detected by glpc. The product isolated by column chromatography was identified as 1-methyl-6,7-diphenyl-2-oxabicyclo[3.2.0]hept-6-ene (II) based on spectral evidence presented in the Experimental Section.



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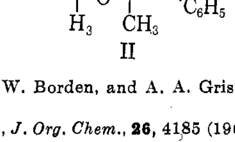

II

Because of the substitution pattern on II, all the cyclobutene couplings with H_5 are eliminated, and H_5 can couple its spin only with H_4 and $H_{4'}$. The nmr spectra for II was correspondingly simplified and showed H_5 to be a pair of doublets with J = 3.5 and 4.0 Hz. This would imply that the dihedral angles between the planes containing the hydrogen H_4 and H_5 and $H_{4'}$ and H_5 are nearly equal and not 90°.[5] In the 2-oxabicyclo[4.2.0]oct-7-ene system III the coupling constant for H_6–H_5 was found to be 0 Hz; this was attributed to a 90° dihedral angle between H_6–C_6 and H_5–C_5.

Sensitization and quenching experiments were performed in order to gain information regarding the reactive excited species involved in the reaction between 2-methyl-4,5-dihydrofuran and diphenylacetylene. It was found that pyrene [E_T = 48.7 kcal/mol[6]] inhibited the reaction between diphenylacetylene (E_T = 51 kcal/mol)[7] and 2-methyl-4,5-dihydrofuran. Equimolar concentration of diphenylacetylene and quencher were used. Since their molar extinction coefficients are about equal at the excitation wavelength (log ε 4.1 at 2437 Å), the quenching effect was due to triplet energy transfer rather than absorption of the exciting light by pyrene. However, the use of triphenylene (E_T = 66.6 kcal/mol)[6] as a sensitizer for the reaction run on a degassed sample in a Pyrex vessel at 3500 Å proved successful. The unsensitized reaction does not occur upon photolysis at this wavelength. Therefore, we conclude that the reaction proceeds through the first excited triplet state of diphenylacetylene.[8]

Finally, we would like to point out that this is only the second reported example of cyclobutene formation from the photocycloaddition of an acetylene to an olefin which is not part of an α,β-unsaturated carbonyl system, and the first example of this type of photocycloaddition in the bicyclo[3.2.0]hept-6-ene system.

Experimental Section

Melting points are uncorrected. Photolyses were conducted in a Rayonet photochemical reactor at 2537 or 3500 Å as indicated. The infrared spectra were obtained on a Perkin-Elmer Model 621 spectrophotometer. High resolution mass spectra were obtained on a CEC-21-110 instrument. Glpc were performed on a Varian Aerograph Model 1200 HYFI. Nmr spectra were taken on a Varian DP-60-IL instrument.

Reaction of Diphenylacetylene with 2-Methyl-4,5-dihydrofuran.—In a quartz vessel, a solution of diphenylacetylene (4 g, 0.022 mol) in 2-methyl-3,4-dihydrofuran (25 g, 0.3 mol) was irradiated at 2537 Å in a Rayonet photochemical reactor for 48 hr. After removal of the unreacted dihydrofuran under reduced pressure, the remaining liquid was subjected to column chromatography on alumina (80–200 mesh). Elution with petroleum ether (bp 30–60°) gave 1-methyl-6,7-diphenyl-2-oxabicyclo[3.2.0]hep-6-ene: 4.8 g, 82%; mp 52–54; parent peak 260.1487 ($C_{19}H_{18}O$); ir (thin film) 3035 (aromatic CH), 2920 (aliphatic CH), 1600, 1500 (aromatic C=C), 1090 (COC), and 745, 690 cm^{-1} (monosubstituted phenyl); nmr (C_6D_6) δ^{TMS} 7.5–7 (10 H, multiplet, aromatic CH), 3.9 (2 H, multiplet H_3, H_3), 3.15 (1 H, 2 doublets J = 3.5, 4.0 Hz), 1.6 (3 H, singlet, CH_3), 1.45 (2 H multiplet, H_4 and $H_{4'}$).

Registry No.—II, 23385-99-1; diphenylacetylene, 501-65-5; 2-methyl-4,5-dihydrofuran, 1487-15-6.

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