

3.0 (s, 1, concentration dependent position, OH), 4.27 [m, 1, $J = 6.0$ and 6.0 Hz, $\text{CH}(\text{OH})\text{CH}_3$], and 5.11 ppm (m, 1, $J = 3.0$ and 6.0 Hz, $=\text{CH}$); ir (CCl_4)⁹ 3613 (OH), 3352 (OH), and 1969 cm^{-1} ($\text{C}=\text{C}=\text{C}$).

Anal. Calcd for $\text{C}_7\text{H}_{12}\text{O}$: 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, $(\text{CH}_3)_2\text{C}=\text{C}$], 2.18 (s, 3, COCH_3), and 5.60 ppm (m, 1, $J = 3.0$ Hz, $=\text{CHCOCH}_3$); ir (CDCl_3) 1957 ($\text{C}=\text{C}=\text{C}$) and 1676 cm^{-1} ($=\text{C}-\text{C}=\text{O}$). 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, $=\text{CHCO}$). 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

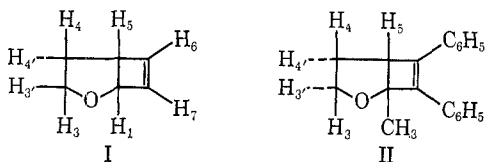
M. P. SERVÉ AND H. M. ROSENBERG

Department of Chemistry, Wright State University,
Dayton, Ohio 45431

Received July 22, 1969

The valence-bond isomerizations of various substituted 1,3-heptadienes to the corresponding bicyclo[3.2.0]hept-6-ene is a well-documented reaction.^{1,2} Paquette and coworkers³ 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,⁴ 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.



(1) O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Amer. Chem. Soc.*, **84**, 1220 (1962).

(2) O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26**, 4185 (1961).

(3) L. A. Paquette, J. H. Barrett, R. P. Spitz, and R. Pitcher, *J. Amer. Chem. Soc.*, **87**, 3417 (1965).

(4) H. M. Rosenberg and P. Servé, *J. Org. Chem.*, **33**, 1653 (1968).

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_5-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/mol⁶] 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 ($\log \epsilon$ 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]hept-6-ene: 4.8 g, 82%; mp 52–54; parent peak 260.1487 ($\text{C}_{19}\text{H}_{18}\text{O}$); ir (thin film) 3035 (aromatic CH), 2920 (aliphatic CH), 1600, 1500 (aromatic $\text{C}=\text{C}$), 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.

(5) F. A. L. Onet, *J. Amer. Chem. Soc.*, **84**, 671 (1962).

(6) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 453 (1965).

(7) M. Beer, *J. Chem. Phys.*, **25**, 745 (1956).

(8) There is evidence that the presence of oxygen is required for efficient generation of the triplet state of diphenylacetylene. See R. C. Herson and E. D. Owen, *Chem. Commun.*, 153 (1967).