D-Xylose-*2-^{3}H* was converted to I in acidified water in 33% yield. An aliquot of I was converted to the crystalline phenylhydrazone which contained 13% the activity of the starting sugar. Conversion of a further aliquot of I to 2-furoic acid which was radiochemically inert showed that all of the radiochemical activity was located on the aldehyde carbon of I.

The data collected established that intramolecular C-2 → C-1 hydrogen transfers occur during dehydration reactions, probably as a result of conversion of aldoses to ketoses as was established for the D-glucose to D-fructose conversion. It is noteworthy that analogous transfers in proceeding from 2-ketoses to aldoses have not yet been established in the case of chemical catalysis, and, for a complete assessment of the role and importance of reaction pathways involving intramolecular hydrogen shifts *vis-à-vis* 1,2-enediols, substantially more data will be required.

Experimental Section

Materials and Methods. Radiochemical activities were determined on a Packard Tri-Carb scintillation counter using a scintillant composed of two parts of a solution composed of 2 l. of toluene, 8.25 g of 2,5-diphenyloxazole (PPO), and 0.25 g of 1,4-bis-2-(4 methyl-5-phenyloxazole)benzene (Me_2POPOP), and one part of Triton X-100 (v/v). Ultraviolet spectra were obtained using a Coleman Model 124 recording double beam spectrophotometer. Thin-layer chromatography was performed using silica gel HF support with chloroform-methanol (95:5) as the eluent. Spots were visualized by uv light or by spraying with 10% ethanolic sulfuric acid followed by heating at 110° for 10 min. Paper chromatography was performed by the descending method using ethyl acetate-formic acid-acetic acid-water (18:1:3:4, v/v) as irrigant followed by visualization with aniline hydrogen phthalate spray reagent.[13] D-Glucose-*2-^{3}H* was prepared enzymatically as described in previous reports[6,7] and was diluted to a suitable level, as needed, with inert D-glucose, followed by recrystallization from water-ethanol.

Preparation of D-Xylose-*2-^{3}H*. D-Glucose-*2-H* (100 g, specific activity = 1.0 μCi/mmol) was converted to 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose[14] (mp, mmp 108°) in 54% yield and then to 1,2-*O*-isopropylidene-D-glucofuranose,[14] which after recrystallization from ethyl acetate gave 25 g of material (mp, mmp 160°). This material was converted to syrupy 1,2-*O*-isopropylidene-D-xylo-1,5-dialdose-*2-^{3}H* by periodate oxidation,[15] and then reduced to 1,2-*O*-isopropylidene-D-xylofuranose with sodium borohydride.[15] The resulting syrupy material was dissolved in 100 ml of 0.1 *N* sulfuric acid and refluxed for 1 hr. After neutralization with barium carbonate, the resulting filtered solution was evaporated to dryness at reduced pressure to give a syrup which contained only D-xylose as evidenced by paper chromatography. To this syrup was added .5 g of inert D-xylose and sufficient water to produce a thick syrup, which slowly crystallized. The resulting crystalline D-xylose-*2-^{3}H*, which was isolated on a filter, washed with methanol, and dried *in vacuo*, had a specific activity of 2.42 × 10^{-2} μCi/mmol.

Conversion of D-Glucose-*2-^{3}H* to II. D-Glucose-*2-^{3}H* (200 g, specific activity = 0.916 μCi/mmol) was added to 2400 ml of 2 *N* sulfuric acid, and the solution was refluxed for 3.5 hr. The solution was extracted three times with chloroform and the extract was dried over anhydrous sodium sulfate and evaporated to dryness. The II contained by the residue was isolated by preparative thin-layer chromatography and identified by its chromatographic flow rate, which was identical with a standard sample, and from its uv spectrum (λ_{max} 278 mμ), which was identical with that of a standard sample. The overall yield of II was approximately 15 mg as determined from spectral measurements. Approximately half of this sample was converted to the oxybis(5-methylene-2-furaldehyde)[12] by heating at 100° for 2 hr. The resulting material (mp 113°) had a chromatographic flow rate and exhibited a uv spectrum identical with those of an authentic sample. This material, amounting to 5.7 mg, was counted and found to have a specific activity of 0.154 μCi/mmol. A further sample of II was converted to 5-(hydroxymethyl)-2-furoic acid,[8] which was purified by preparative thin-layer chromatography and had a thin-layer chromatographic flow rate and a uv spectrum identical with those of an authentic sample, amounted to 1.9 mg and had a specific activity of 8 × 10^{-3} μCi/mmol.

Conversion of D-Xylose-*2-^{3}H* to I. This conversion was made in 6 *N* sulfuric acid starting with 2.0 g of sugar (specific activity of 2.42 × 10^{-2} μCi/mmol) as described previously.[5] The 2-furaldehyde-*^{3}H* contained in 250 ml of distillate was identified by its ultraviolet spectrum which showed maxima at 227 and 278 mμ. Assuming a molar absorptivity of 16,000,[16] the absorbance at 278 mμ indicated a yield of 33%. The I in a 100-ml aliquot of the distillate was converted to 2-furaldehyde phenylhydrazone-*^{3}H* (mp, mmp 95°) which had a specific activity of 3.25 × 10^{-3} μCi/mmol. The I in a further 100 ml aliquot was converted to 2-furoic acid (mp, mmp 131°) which after purification by sublimation at 110° and 0.3 mm was found to be radiochemically inert.

Registry No.—I, 98-01-1; II, 67-47-0; D-xylose, 58-86-6; D-glucose, 50-99-7; 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose, 582-52-5; 1,2-*O*-isopropylidene-D-glucofuranose, 18549-40-1; oxybis(5-methylene-2-furaldehyde), 7389-38-0; 2-furaldehyde phenylhydrazone, 2216-75-3; 2-furoic acid, 88-14-2.

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Preparation and Characterization of Propiolyl Chloride

Walter J. Balfour,* Colin C. Greig, and Somyong Visaisouk

Department of Chemistry, University of Victoria,
Victoria, British Columbia, Canada

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Propiolyl chloride is the simplest of the acetylenic acid chlorides. We became interested in the compound, from the spectroscopic point of view, as part of a program to study the influence of conjugation and halogen substitution on the energies and stabilities of (π^*, n) electronic states. While unsuccessful attempts to prepare propiolyl chloride have been reported,[1] brief mention is made in the chemical patent literature of its use in dye and plastics manufacture.[2]

The present communication describes a straightforward synthesis from propiolic acid and phosphorus pentachloride. The major product of the reaction is identified as

$$HC{\equiv}CCOOH + PCl_5 \longrightarrow HC{\equiv}CCOCl + POCl_3 + HCl$$

propiolyl chloride from spectroscopic and chemical evidence. The boiling point of the propiolyl chloride prepared in this way does not correspond to that of a compound prepared by pyrolysis of α,β-dichloropropionyl chloride, and claimed by Schaefer[2b] to be propiolyl chloride. Our product boils at 58–60° while Schaefer reports a boiling point in the range 72–75°.

Experimental Section

Preparation. Propiolic acid (5 g, 0.07 mol) was added dropwise to a small excess of PCl_5 (16 g, 0.075 mol) at room temperature over 3-4 hr. In early experiments the resulting clear, pale yellow liquid was fractionally distilled at atmospheric pressure through a 10-cm packed glass column, when a lachrymatory liquid, subsequently characterized as propiolyl chloride, distilled at 58-60°. However, on several occasions the sample so obtained ignited spontaneously on exposure to air. On the assumption that this behavior was due to trace amounts of monochloroacetylene,[3] formed by thermal decomposition during distillation, purification was subsequently effected without heating. The reaction mixture, cooled to liquid nitrogen temperature, was allowed to warm up. On warming, the volatile components were pumped off through two cold traps, the first at *ca.* $-78°$, the second at *ca.* $-135°$. The trap at *ca.* $-78°$ effectively removed all the $POCl_3$ produced and propiolyl chloride was collected in the second trap in yields ranging from 45 to 60%.

Propiolyl chloride is a clear, colorless liquid which fumes slightly in air and slowly turns yellow on standing at room temperature. It can be stored in the dark at Dry Ice temperature without appreciable decomposition.

Characterization. A. Spectroscopic Evidence. Ir spectra were recorded on a Beckman IR-20 grating spectrophotometer and the Raman spectrum on a Cary 81 He/Ne laser spectrophotometer. The pmr spectrum was obtained on a Perkin-Elmer R12A spectrometer with tetramethylsilane as the internal standard. The mass spectrum was run on a Hitachi Perkin-Elmer RMU-7 double-focusing instrument. The elemental analysis was carried out on a Perkin-Elmer Model 240 C, H, N analyzer.

The gas-phase infrared spectrum of propiolyl chloride shows the expected relatively simple spectrum. Five strong peaks are found above 300 cm^{-1}: 3332, 2120, 1771, 1000, and 659 cm^{-1}, which can readily be assigned to the HC≡, C≡C, C=O, C-C, and C-Cl stretching modes, respectively. The corresponding (liquid) Raman displacements are found at ~3300 (vw), 2118 (s), 1747 (ms), 1005 (w), and 653 cm^{-1} (s). The pmr spectrum in $CDCl_3$ shows one sharp singlet at τ 6.29.[4] The parent ion is very weak in the mass spectrum. The most prominent peaks occur for *m/e* 53.006 (${}^{12}C_3{}^1H^{16}O$ = 53.003, 100%, $M^+ - Cl$), 59.979 (${}^{12}C_2{}^1H^{35}Cl$ = 59.977, 15%, $M^+ - CO$), 28 (27%, CO), and 25 (25%, $M^+ - COCl$).

B. Chemical Evidence. 1. Propiolamide was prepared by reaction of a solution of propiolyl chloride in methylene chloride at $-30°$ with ammonia. Insoluble ammonium chloride was removed by filtration and recrystallization of the propiolamide from chloroform gave white crystals: mp 58-58.5° (lit.[1] mp 60.5-61°); pmr ($CDCl_3$) τ 7.15 (s, 1, C≡CH) [lit.[5] pmr (CCl_4) τ 7.10]; mass spectrum (70 eV) *m/e* 69.021 (${}^{12}C_3{}^1H_3{}^{14}N_1{}^{16}O$ = 69.022, 94%, M^+), 53 (100%, $M^+ - NH_2$), 44 (24%, $M^+ - C_2H$), 41 (52%, $M^+ - CO$).

2. 4.-Nitrophenyl propiolate was prepared by reaction of 4-nitrophenol with propiolyl chloride under similar conditions to those of Miller.[2c] Recrystallization from CCl_4 gave a white, crystalline solid, mp 135-135.5° (lit.[2c] mp 132-133°).

Anal. Calcd for $C_9H_5NO_4$: C, 56.54; H, 2.64; N, 7.33. Found (extended combustion): C, 55.93; H, 2.62; N, 7.23.

Ir ($CHCl_3$ solution) 3300 (≡CH), 3030 (ArH), 2130 (C≡C), 1755 (C=O), 1630, 1605, 1500 (aromatic C-C), 1540, 1360, ($C-NO_2$), 1185, 1020 cm^{-1} (ArO-); pmr ($CDCl_3$) τ 1.73 (m, 2) and 2.64 (m, 2) (ArH), 6.82 (s, 1, C≡CH); mass spectrum (70 eV) *m/e* 191.020 (${}^{12}C_9{}^1H_5{}^{14}N^{16}O_4$ = 191.022, 9%, M^+), 174 (7%, $M^+ - OH$), 163 (11%, $M^+ - CO$), 53 (100%, $M^+ - C_6H_4NO_3$).

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Registry No.—Propiolic acid, 471-25-0; phosphorus pentachloride, 10026-13-8; propiolyl chloride, 50277-65-1; 4-nitrophenyl propiolate, 35665-87-3.

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Nuclear Magnetic Resonance and Stereochemical Assignments of a Double Diels-Alder Adduct.[1] A Demonstration of Steric Compression

John Mantzaris and Edward Weissberger*

Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457

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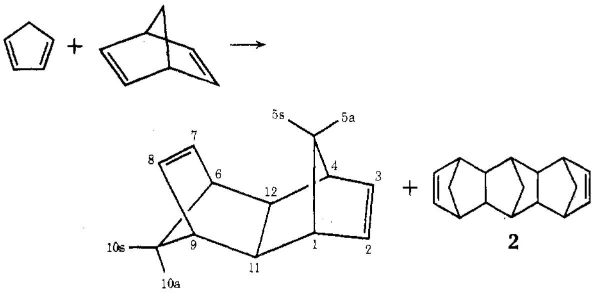
During the course of our studies[2,3] of metal carbonyl induced coupling of olefins to carbon monoxide, we have considered the nmr and stereochemical assignments[3] of several polycyclic norbornyl systems. Difficulties encountered in assigning proton resonances only slightly downfield from an internal tetramethylsilane standard has caused us to consider the stereochemistry of a double Diels-Alder adduct.

Two products are obtained from the Diels-Alder reaction between cyclopentadiene and norbornadiene[4] (eq 1). Compound **2**, an adduct formed from two molecules of cyclopentadiene and one molecule of norbornadiene, is produced in addition to diene **1**. Marchand and Rose[5] first reported the nmr assignments of diene **1**. Their assignment was later elaborated upon by Wege,[6] who pointed out that the high-field doublet at δ 0.95 was due to the 5a proton. Proton 5s, which one might expect to be shielded by the Δ^7 bond, is in fact sterically deshielded.[6,7] By considering the stereochemistry of adduct **2**, we have confirmed this assignment. In Table I we report additional assignments for strained olefin **1**.



(1)

1

2

The nmr spectra of **2** are shown in Figure 1 with assignments tabulated in Table II. Diene **2** shows but one olefinic resonance (δ 5.87), implying that **2** has a high degree of symmetry. Only two compounds, **2a** and **2b**, meet this requirement and have both external rings exo to the central ring. This latter requirement is discussed shortly.

The distinction between **2a** and **2b** is unequivocal and is based upon both spectral and reactivity data. First, the expected olefinic resonance for isomer **2b** is δ 6.17, corresponding to the appropriate resonance found for diene **1** and the corresponding monoene,[2] **3a**. The observed olefinic resonance at δ 5.87 corresponds to the 7,8 protons of **1** and the observed resonance for the monoene[2] **3b**.