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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(4) On prolonged standing, samples developed a weak AB quartet at τ 2.90 (Δ_{AB} = τ 1.20, J_{AB} = 13.6 Hz) in the pmr spectrum. These peaks can be assigned to *trans*-3-chloroacryloyl chloride, the product of the electrophilic addition of HCl to propiolyl chloride.
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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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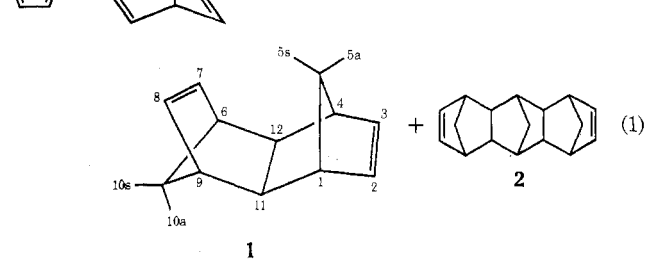
During the course of our studies[2,3] of metal carbonyl induced coupling of olefins to carbon monoxide, we have considered the nmr and stereochemical assignments[3] of several polycyclic norbornyl systems. Difficulties encountered in assigning proton resonances only slightly downfield from an internal 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**.



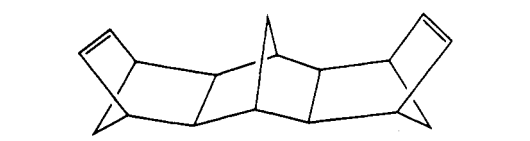
1 **2** (1)

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.

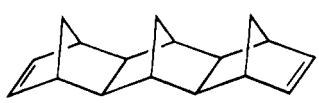
The distinction between **2a** and **2b** is unequivocal and is based upon both spectral and reactivity data. First, the expected olefinic resonance for isomer **2b** is δ 6.17, corresponding to the appropriate resonance found for diene **1** and the corresponding monoene,[2] **3a**. The observed olefinic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

Table I
Chemical Shift and Coupling Constant Assignments for Diene 1

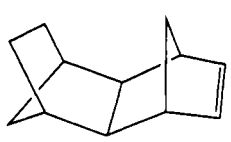
Proton	Chemical shift, δ ppm	Coupling constant	Hz
1, 4	2.47	$J_{1,5s}$	1.8
2, 3	6.17	$J_{1,5a}$	1.1
5a	0.95	$J_{1,2}$	1.6
5s	2.60	$J_{5a,5s}$	8.5
6, 9	2.64	$J_{5a,11}$	0.6
7, 8	5.99	$J_{5s,2}$	0.3
10a	1.19	$J_{6,7}$	2.0
10s	1.33	$J_{6,10}$	1.7
11, 12	2.19	$J_{6,12}$	0.8
		$J_{7,10a}$	0.5
		$J_{10a,10s}$	7.7



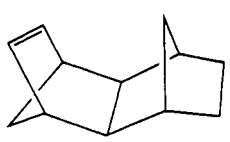
2a



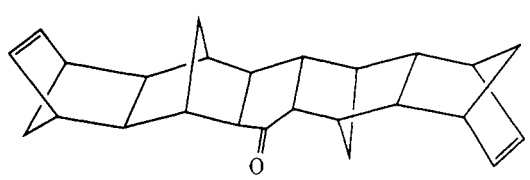
2b



3a



3b



1a

Of equal importance is the reactivity of **2** toward coupling by $Fe(CO)_5$. When diene **1** is treated with $Fe(CO)_5$, it couples[2,3] to form ketone **1a**. Monoene **3a** is also reactive in that it couples to the corresponding ketone, while **3b** is unreactive. On the basis of these data, we would expect **2a** to be unreactive while **2b** would easily couple to a series of ketonic products. Diels–Alder adduct **2** is unreactive, leading us to conclude that **2a** depicts the correct stereochemistry of the double Diels–Alder adduct.

Spin-decoupling studies have been particularly helpful in analyzing the nmr spectrum of **2a**. Irradiation at δ 2.80 (6, 9 protons decoupled) markedly changes the spectrum. The triplet at δ 5.87 collapses to a sharp singlet ($J_{6,7}$ = 2.0 Hz) while the triplet assigned to the 2,3 protons at δ 1.82 reduces to a moderately sharp singlet ($J_{3,6}$ = 2.0 Hz). Further, the AB pattern of the doublet of triplets assigned to the 10s,10a protons centered at δ 1.23 is converted to a simple AB pattern of singlets with a 10a,10s geminal coupling constant of 8.0 Hz. The poorly resolved triplet centered at δ 1.92, assigned to the bridgehead (1,4) protons, sharpens to a well-resolved triplet (J = 2.0 Hz). This sharpening is due to the removal of long-range coupling ("W" rule) between protons 1 and 9. The triplet could be due to proton 1 coupled to the two equivalent number 2 protons, or to the equivalent (5) bridge protons. Decoupling the 2,3 protons at δ 1.82 does not change the 1,4 triplet, suggesting that the 1,4 protons are coupled to the bridge (5) protons. This is not unusual for coupling between bridge and bridgehead protons in norbornyl systems.[8] Further, the fact that $J_{1,2}$ is unobserved implies[9] that the 2,3 protons are endo to the central norbornyl ring. Long-range coupling between protons 2,3 with 5′ is observed when the 2,3 protons are irradiated.

Table II
Chemical Shift and Coupling Constant Assignments for Olefin 2

Proton	Chemical shift, δ ppm	Coupling constant	Hz
1, 4	1.92	$J_{1,5}$	2.0
2, 3	1.82	$J_{2,8}$	1.0
5, 5′	1.53	$J_{3,6}$	2.0
6, 9	2.80	$J_{6,7}$	2.0
7, 8	5.87	$J_{9,10}$	1.5
10a	1.17	$J_{10a,10s}$	8.0
10s	1.28		

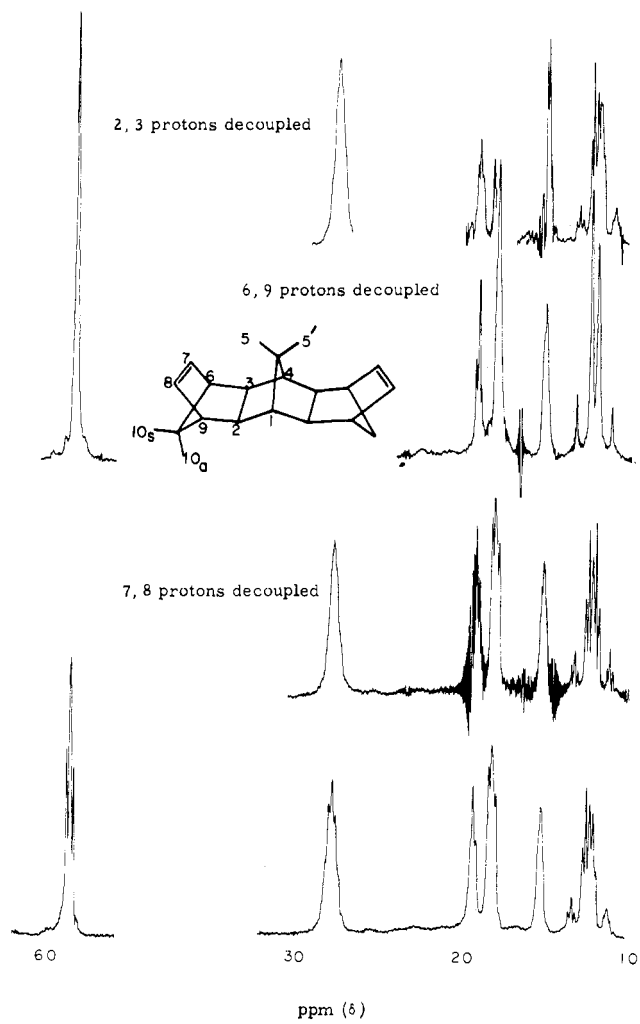


Figure 1. 90-MHz spectrum of Diels–Alder adduct **2**.

Additional decoupling studies provide data which allow chemical shifts to be assigned to the 10s and 10a protons. Irradiation at δ 5.87 decouples the olefinic protons and sharpens the high-field portion of the AB pattern corresponding to the 10s,10a protons. This is due to the loss of stereospecific coupling between the 7(8) and 10a protons. Therefore, the high-field absorption centered at δ 1.17 is assigned to proton 10a while the absorption centered at δ 1.28 is assigned to the 10s proton. Similar conclusions are reported in the literature.[5,10] The triplet assigned to the 2,3 protons also sharpens, since long-range coupling between protons 2 and 8 is removed.

In view of the assignment of 2 to stereochemistry **2a** and the observation that the bridge protons (5) absorb at δ 1.53, there being no high-field resonance, we conclude that steric deshielding of the 5s protons in compounds such as **1** is operative.

Experimental Section

Proton magnetic resonance spectra were obtained in $CDCl_3$ on a Bruker 90-MHz spectrometer and are reported downfield from an internal tetramethylsilane (TMS) standard. Diels–Alder adducts were prepared according to literature procedures.[4] We did find that the Diels–Alder reaction could be efficiently carried out in an annealed glass pressure bottle (Fisher and Porter) fitted with a pressure gauge, gas inlet, and pressure-release valve. Standard chromatographic and liquid–liquid extraction procedures were applied where appropriate.

Acknowledgment. Financial support from Wesleyan University and a fellowship to one of us (J. M.) are gratefully acknowledged. We especially wish to thank Dr. T. H. Regan of the Eastman Kodak Co. for obtaining the 90-MHz spectra for us.

Registry No.—**1**, 15914-94-0; **2a**, 50415-43-5.

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Nucleophilic Reactions of α-Bromoacetophenone Oxime. Preparation of *anti*-Acetophenone Oxime

Jerry H. Smith

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233

E. T. Kaiser*

Searle Chemistry Laboratory, University of Chicago, Chicago, Illinois 60637

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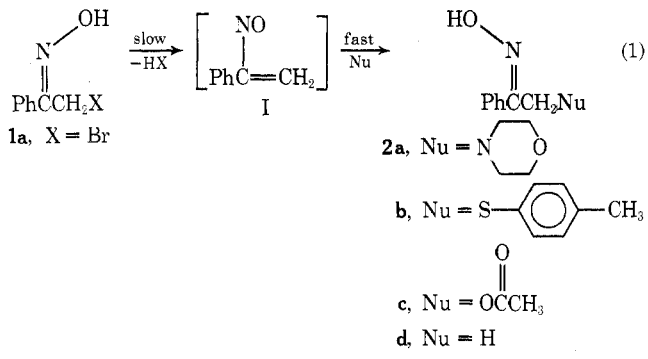
We have recently described the reaction of α-halo oximes with nucleophiles which involves the stereoselective trapping of a reactive intermediate.[1] This reaction can be summarized by eq 1, where X is halogen and Nu is a nucleophile. As shown, it was suggested that the intermediate might be α-nitrosostyrene (I), which reacts more rapidly in the s-trans conformation than in the s-cis, giving the thermally unstable anti alkyl aryl ketoxime isomer.[2] The preparation of the previously unknown *anti*-α-bromoacetophenone oxime from **2a** which had been obtained by the route of eq 1 was also reported.[1b] To explore the general synthetic utility of this reaction and to gain further insight into its mechanism, we have varied the nature of the nucleophile Nu in eq 1. In the present communication we report the results of this investigation, including the facile, one-step conversion of **1a** to *anti*-acetophenone oxime (**2d**), a previously unisolated material.



(1)

When **1a** dissolved in acetonitrile is added to an aqueous acetonitrile solution of $NaBH_4$, rapid evolution of a gas takes place. After 5 min at room temperature, extraction of the reaction mixture gives in high yield *anti*-acetophenone oxime (**2d**). In the nmr spectrum ($CDCl_3$), absorption due to the methyl group of **2d** occurs at δ 2.20 ppm while the corresponding resonance in the syn isomer is detected at 2.28 ppm.[3] The uv spectrum for **2d** in ethanol has λ_{max} 235 nm (log ϵ 3.86) compared to λ_{max} 245 nm (log ϵ 4.10) for the syn isomer. This difference is in agreement with previously reported spectra for isomeric alkyl aryl oximes.[1a,4] When **2d** was refluxed in chlorobenzene solution, there was a gradual decrease in intensity of the methyl resonance at 2.20 ppm and a corresponding increase in intensity of a peak at 2.28 ppm, resulting in a final mixture composed of 5% **2d** and 95% of the thermally generated product. This material was isolated and identified as *syn*-acetophenone oxime. A sample of **2d** was subjected to Beckmann rearrangement conditions and the major product obtained was *N*-methylbenzamide, confirming the stereochemical assignment.[5]

The borohydride reduction of **1a** to give **2d** takes place in ethanol and 1,2-dimethoxyethane as well as in aqueous acetonitrile. In each of these solvents, 1 mol of $NaBH_4$ is required for each mole of **1a** reduced. When 0.5 mol of $NaBH_4$ is used, 50% of **1a** is converted to **2d** while the remaining 50% is recovered. The reaction was complete within 5 min at room temperature and longer reaction times did not affect the yields or isomeric composition of the product. In a control experiment, *syn*-acetophenone oxime was recovered unreacted from an aqueous acetonitrile solution of $NaBH_4$. This finding agrees with results of previous workers.[6]

The conversion of **1a** to **2d** is thought to proceed *via* intermediate I of eq 1. The HBr produced would be expected to react with $NaBH_4$ to release hydrogen gas. If intermediate I is in fact α-nitrosostyrene, as has been proposed,[1b] then the postulated $NaBH_4$ reduction of I would be reasonable. It is known that the carbon–carbon double bond of 1-nitro alkenes[7] and α,β-unsaturated aldehydes and ketones[8] can be reduced by $NaBH_4$ to give the corresponding 1-nitro alkanes and saturated alcohols. Conjugate addition of borohydride to the proposed α-nitrosostyrene would result in an oxime product which is inert to further reduction. The anti stereochemistry of the product is in agreement with the previous results obtained with displacement by morpholine.[1]

We have also investigated the reaction of **1a** with sulfur and oxygen nucleophiles. When *p*-tolyl thiolate is added to **1a** in aqueous solution, the product isolated is *anti*-α-(*p*-tolylthio)acetophenone oxime (**2b**). The nmr spectrum ($CDCl_3$) of **2b** is similar to that of the syn isomer **1b**, prepared by an independent route (eq 2), except that the methylene resonance is shifted upfield by 0.27 ppm (δ 4.17 for the syn isomer and δ 3.90 for the anti isomer).[3] Thermal isomerization of **2b** in $CDCl_3$ resulted in a mixture of