of cyclohexene[17] which is reported to yield mainly vicinal diacetates.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 457 instrument while nuclear magnetic resonance spectra were obtained on a Varian HA 100 spectrometer. Qualitative and quantitative gas chromatographic analyses were performed on Porapak Q, PEG 20M and SE-30 columns fitted on a Carlo Erba Model GT 200 gas chromatograph.

Reagents and Solvents. Cyclohexene (Fluka, high purity) was fractionally distilled over Drierite several times: bp 83 °C (760 mm); n^{20}_{D} 1.4451 [lit.[18] bp 82.8 °C (759 mm); $n^{20.05}_{D}$ 1.446 37]. Oxygen and nitrogen (chromatographic purity) were supplied by Sapio. Sulfur dioxide (SiO) was purified[19] by passage of gaseous SO_2 through concentrated sulfuric acid and P_2O_5; after it was condensed over P_2O_5 at −78 °C, it was degassed by evacuation for 1 h, refluxed over P_2O_5 for 1 h, and distilled. Acetic acid (Carlo Erba) was always fractionally distilled immediately before use; the acid used had a freezing point of 16.6 °C which agrees with the value reported[20] for acetic acid of minimum conductivity. Potassium acetate (Carlo Erba) was reagent grade and was not further purified.

Cyclohexene–SO_2 Adduct. Alkaline Hydrolysis. At −30 °C dry nitrogen was used to sweep sulfur dioxide (2.50 g, 39.02 mmol) into 3.32 g of cyclohexene (40.41 mmol); a blue-green color instantly developed while a white precipitate was formed. The gas stream was reverted to nitrogen while the solution was allowed to warm to room temperature; 20 mL of diethyl ether was added to the solution and the white precipitate, removed by quick filtration, was carefully dried. Unreacted cyclohexene (2.40 g, 29.21 mmol) was recovered by fractionating the filtrate while the white precipitate was immediately neutralized with sodium hydroxide in ethanol. The isolated sodium salt, which is stable at room temperature, was recrystallized (1.09 g, 6.48 mmol) from water–ethanol. The infrared spectrum (solid in KBr) contained a weak band at 1640 cm^{-1} (C=C),[21] a strong band at 1016 cm^{-1}, and a band of medium intensity at 962 cm^{-1} which may be assigned to the SO asymmetric and symmetric vibrations, respectively.[22] The ^1H NMR spectrum (in D_2O; sodium 3-(trimethylsilyl)propanesulfonate as internal standard) showed signals at δ 1.63 (CCH_2C, m, 4 H), 2.01 (CH_2C=, m, 2 H), 3.60 ($CHSO_2Na$, m, 1 H; relative to the value reported for the free acid, the observed shift to higher fields is consistent with previous data reported for some alkylsulfinic acids, e.g., 1-hydroxyethanesulfinic acid[23]), and 6.10 (=CH, m, 2 H).

Anal. Calcd for $C_6H_9O_2SNa$: C, 42.84; H, 5.39; S, 19.06. Found: C, 43.34; H, 5.69; S, 18.71.

SO_2-Induced Oxidation of Cyclohexene. General Procedure. Oxidations were carried out in a mechanically stirred stainless-steel autoclave (475 mL). In a typical run, 100 mL of an 0.8 M solution of potassium acetate in acetic acid and 13.14 g of cyclohexene (160 mmol) were charged in the autoclave which was subsequently closed and cooled to −30 °C while deaerating under vacuum. After the required liquified amount of sulfur dioxide (2.60 g, 40.58 mmol) was injected the autoclave was brought to room temperature and pressurized with oxygen (10 atm) and nitrogen (100 atm) while stirring. On reaching (1 h) the reaction temperature (110 °C) a periodic repressurizing with nitrogen was necessary to maintain the pressure for the designated period of time (1 h); during that time, in some runs samples were periodically withdrawn through a sampling valve in order to monitor the reaction. After that time, the autoclave was rapidly cooled to room temperature; gas samples were analyzed by carefully venting known portions of the noncondensible gases into an evacuated stoppered flask. Only traces of CO_2 were found.

After the noncondensible gases were vented, the recovered reaction mixture was quenched with water and immediately extracted with chloroform; in the aqueous phase, free sulfate ions were determined (37.90 mmol).

The organic layer was repeatedly washed with aqueous sodium hydroxide to completely remove acetic acid. The aqueous layers were acidified and extracted with diethyl ether to determine if other carboxylic acids were present; the extracts were dried (Na_2SO_4), concentrated, and treated with BF_3–MeOH reagent,[24] without finding new carboxylic acids by this procedure.

After the neutralized organic solution was dried over anhydrous sodium sulfate, the solvent and unreacted cyclohexene (4.92 g, 59.89 mmol) were removed under vacuum, leaving a residue which was fractionated by vacuum distillation. The fraction boiling at 60–70 °C (12 mm) gave 6.19 g (67%) of 2-cyclohexen-1-one (4.14 g, 43.15 mmol); it was spectrally and chromatographically identical with an authentic sample prepared by lithium aluminum hydride reduction of 3-ethoxy-2-cyclohexen-1-one and subsequent acid hydrolysis.[25] A second fraction boiling at 115–125 °C (12 mm) yielded 0.72 g of 1,2-cyclohexanediol diacetate (3.59 mmol) as a mixture of cis (44%) and trans (56%) isomers. The identification of the diacetoxy derivatives was performed by comparison with independently prepared samples obtained by selenium dioxide[17] and thallic acetate[26] oxidation of cyclohexene.

Registry No. Sulfur dioxide, 7446-09-5; cyclohexene, 110-83-8; cyclohex-2-enesulfinic acid Na, 74465-45-5; 2-cyclohexen-1-one, 930-68-7; *cis*-1,2-cyclohexanediol diacetate, 2396-76-1; *trans*-1,2-cyclohexanediol diacetate, 1759-71-3; oxygen, 7782-44-7.

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Oxidation of Diphenylacetylene by I^{7+} and I^{5+} Compounds

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The oxidation of diphenylacetylene with H_5IO_6 in acetic acid affords benzil. In methanol the principal products are the monoketal and the diketal of benzil, depending upon water content. Similar products are formed in methanol when I_2O_5 is the oxidizing agent. The latter and the alkyne in ethylene glycol afford benzil and the corresponding diketal. Both systems appear to require the presence of iodine for effective action.

The extensive use of paraperiodic acid for the cleavage of vicinal glycols has overshadowed this reagent's potential for other preparative procedures, most of which have been reviewed by Fatiadi.[1] We have been examining its utility

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Table I. Oxidation of Diphenylacetylene[a] with Paraperiodic Acid in Acetic Acid[b]

mmol of H_5IO_6	temp, °C	% yield of benzil	mmol of H_5IO_6	temp, °C	% yield of benzil
10	25	38	10	55	67[c]
10	55	95	20	55	62
10	95	93			

[a] The amount used in every case was 10 mmol. [b] Volume 150 mL, reaction time 20 h. [c] Reaction solvent 10% (v/v) water in acetic acid (150 mL).

and that of related oxidants with arylacetylenes. An interesting one-step conversion of diphenylacetylene to ketals of benzil by means of periodate or iodates is the subject of this article.

Results and Discussion

When equimolar amounts of diphenylacetylene (**1**) and paraperiodic acid were stirred at room temperature in acetic acid overnight, only one product, benzil (**2**), was detected and isolated (eq 1). The yield of **2**, 38%, was

$$\underset{\mathbf{1}}{C_6H_5C{\equiv}CC_6H_5} \xrightarrow[CH_3COOH]{H_5IO_6} \underset{\mathbf{2}}{C_6H_5COCOC_6H_5} \quad (1)$$

increased to greater than 90% by elevating the reaction temperature to 55 °C and higher. There was a decrease in the yield of benzil to 62% when the molar quantity of oxidant was doubled, due to the cleavage of the benzil itself to benzoic acid.[2] A decrease of the same magnitude occurred when the volume percent of water in acetic acid was 10% for equimolar conditions at 55 °C. These results are summarized in Table I.

The oxidation of 1 with H_5IO_6 in methanol was carried out at the temperature of reflux under nitrogen because there was no reaction at room temperature. In this case, benzil was neither the sole nor the principal product. In a reaction with equimolar ratios of reactants, **2** was formed in 5% yield (eq 2). The principal product was the monoketal of benzil (**3**), 2,2-dimethoxy-2-phenylacetophenone, isolated in 71% yield and shown to be identical with material prepared by the reaction of barium oxide, methyl iodide, and **2**.[3] Two other identified products were methyl benzoate (**4**, 5%) and the diketal of benzil, 1,1′-(1,1,2,2-tetramethoxy-1,2-ethanediyl)bis(benzene) (**5**). The latter was formed in less than 1% yield and was identified by comparison with the product of the electrochemical treatment of α,α'-dimethoxystilbene.[4] The two ketals were not artifacts of **2**, methanol, and acid, since **2** did not form these products upon treatment with refluxing methanol containing *p*-toluenesulfonic acid. Under the oxidation conditions **2** was converted to methyl benzoate in 38% yield.

$$\mathbf{1} \xrightarrow[CH_3OH]{H_5IO_6} \mathbf{2} + \underset{\mathbf{3}}{C_6H_5COC(OCH_3)_2C_6H_5}$$
$$\underset{\mathbf{4}}{C_6H_5COOCH_3} + \underset{\mathbf{5}}{C_6H_5C(OCH_3)_2C(OCH_3)_2C_6H_5} \quad (2)$$

Several experiments with different conditions of reaction were carried out and data are given in Table II. Distinct differences are brought about by the use of water or acid. Most striking is the effect of a small amount of zinc wherein the monoketal **3** is practically the sole product.

Table II. Oxidation of Diphenylacetylene (10 mmol) with Paraperiodic Acid (10 mmol) in Refluxing Methanol (75 mL)

conditions	% yield of products 2	3	4	5
under N_2, overnight	5	71	5	1
under N_2, overnight, 10 mmol of H_2SO_4	25	8	60	3
under N_2, overnight, 6% (v/v) H_2O	74	8	15	1
under N_2, overnight, 0.1 mmol of Zn	1	80		

Table III. Oxidation of Diphenylacetylene (10 mmol) with I_2O_5 in Refluxing Methanol (75 mL) under Nitrogen

molar ratio of oxidant/alkyne	product yields, % 3	5	2
0.25	75	24	1
0.50	53	46	1
1.0	60	24	10
1.0[a]	30	65	2
2.0	90	5	
4.0	63	6	26

[a] Reaction solvent was freshly distilled methanol stored over molecular sieves (4A).

When the periodic acid was refluxed overnight in methanol without **1**, iodine was formed. The addition of **1** to such a solution and a subsequent refluxing was carried out. There was no oxidation. This observation coupled with the need for heat or zinc in the above reactions of paraperiodic acid suggested that a species not at the +7 oxidation level was responsible for the oxidation.

We then examined the behavior of I^{5+} compounds under similar conditions and noted that iodic acid in refluxing methanol oxidized **1** to the dimethyl ketal of benzil (**2**) in 81% yield. Such oxidations of organic compounds with iodates or iodic acid are less common than those with periodates. Adler and co-workers have used iodates for the oxidations of phenols.[5] Fatiadi reported their use in oxidations of certain 1,3-diketones.[1]

For minimization of the amount of water in the reagent so as to increase the amount of the diketal **5**, iodine pentaoxide was used instead of iodic acid. After an equimolar reaction mixture of **1** and I_2O_5 in methanol was stirred overnight at room temperature, no products of oxidation were detected. A similar reaction carried out at refluxing temperature afforded **2** (10%), its monoketal (60%), and its diketal (25%). Other results of reactions between these two reactants as they relate to product distribution are given in Table III. Noteworthy is the increase in diketal formation with a decrease in water content of the methanol. When the oxidant to alkyne ratios were 2 or 4, a fourth product was formed in yields of 5% or less. A singlet in the ^1H NMR spectra at 3.7 ppm suggested an ester other than methyl benzoate (3.9 ppm). The substantial amounts of **5** in this system contrast with the minor amounts of it formed in the periodic acid oxidation.

This novel one-step oxidation of an alkyne to a diketal prompted an extension to ethylene glycol. In a similar reaction of **1** and iodine pentaoxide in ethylene glycol, **2** and its bidioxalane (**6**) were formed in yields of 20% and

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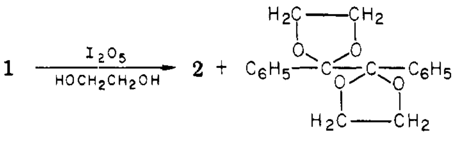
75%, respectively (eq 3). The latter compound was identical with material prepared from the acid-catalyzed ketalization of **2** with ethylene glycol.[6]



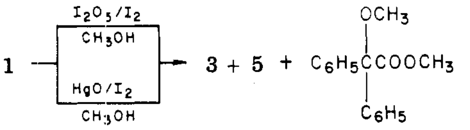
6

(3)

As in the paraperiodic acid case, no oxidation of **1** took place after I_2O_5/methanol had been refluxed overnight. Only a small amount of diiodostilbene was isolated. It would seem that I^{5+} also is not the direct oxidant in these oxidations. The general similarity of products in the oxidations of **1** in methanol by both H_5IO_6 and I_2O_5 indicates that the reactive species is neither an oxide of I^{7+} nor an oxide of I^{5+}. The intermediacy of nonoxygenated and electrophilic species such as I^+ might be postulated. This species could arise by an interaction of iodine and one of several oxides in a higher oxidation state. The source of iodine in these systems would be the slow oxidation of the solvent or decomposition of the oxidants with heating or light. Several observations are consonant with the formation of an iodine cation. Anisole in refluxing methanol containing I_2O_5 was converted to a mixture of iodoanisoles and diiodoanisoles. More to the point was the finding that an equimolar mixture of I_2, I_2O_5, and **1** in methanol *at room temperature* overnight under nitrogen afforded **3** and **5** in a ratio of 2:1 with complete conversion of **1**.

An additional product, **7**, was detected but could not be separated from **5**. It was identified by ^{1}H NMR comparison with the known methyl ester of the methyl ether of benzilic acid.[7] Such a product suggests a carbenium ion rearrangement induced by an electrophilic attack on an intermediate alkene.

If a function of these oxidizing systems is the generation of an iodine cation, then oxidants other than I_2O_5 or H_5IO_6 might be used to generate that cation from iodine. This seems to be so. When iodine, HgO, and **1** (molar ratio 4:1:1, respectively) were reacted in hot methanol overnight, the products were the same as for the I_2/I_2O_5 reaction (eq 4). Previously used for the oxidation of alkenes in CCl_4, the HgO/I_2 system has been studied by Goosen and coworkers, who postulated iodonium attack following the intermediacy of I_2O.[8]



7

(4)

For all these oxidations of **1** a mechanistic picture of electrophilic attack by I^+ emerges as a distinct possibility for the initial step in contrast to a direct attack by electrophilic oxygens of paraperiodic acid or iodine pentaoxide such as in the permanganate oxidation of alkynes.[9] The so-formed vinyl cation could be captured by solvent to afford an enol ether with methanol or an enol with water. Subsequent attacks on the olefins by I^+ and then solvent lead to intermediates which are hydrolyzed to the final products upon workup. There is ample precedent for such halonium ion attack followed by solvent attack. For alkynes it has been demonstrated by Reed[10] who used *N*-chlorosuccimide in methanol, and by Ogata, who used iodine and peracetic acid in acetic acid.[11] For alkenes it has been shown by the works of the Mangoni group for iodine/iodate or *N*-iodosuccinimide in acetic acid[12,13] and by Woodgate for ozone and iodine in acetic anhydride.[14]

Experimental Section

Oxidation of 1 with H_5IO_6 in Acetic Acid. Diphenylacetylene (1.78 g, 10 mmol) was dissolved in acetic acid (150 mL), and H_5IO_6 (2.27 g, 10 mmol) was added. After being stirred at 55 °C for 20 h, the solution was diluted with water (100 mL) and extracted with chloroform. The organic layer was washed with water and 5% sodium bicarbonate, dried with $MgSO_4$, and concentrated to give a yellow solid: 1.99 g; mp 90–92 °C. A mixture melting point with benzil was undepressed. The infrared spectra were superimposable.

Benzil (2.10 g, 10 mmol) was oxidized with H_5IO_6 (2.27 g, 10 mmol) as above. After the workup, benzil (1.0 g) was recovered, and benzoic acid (0.8 g) was obtained by acidifying the bicarbonate wash.

Oxidation of 1 with H_5IO_6 in Methanol. Diphenylacetylene (1.78 g, 10 mmol) was dissolved in methanol (75 mL). H_5IO_6 (2.27 g, 10 mmol) was added, and the mixture was heated to reflux with stirring under nitrogen overnight. The mixture was poured into water (200 mL) and extracted with CH_2Cl_2 (200 mL). The latter layer was washed with water and 10% sodium thiosulfate, dried over $MgSO_4$, and evaporated to a yellow oil: 1.7 g; IR (neat) 2970, 2920, 1720, 1690, 1600, 1450, 1240, 1120, 1020, 1050, 1030, 870, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.15 (s, 25 H) 3.4 (s, 1 H), 3.6 (s, 2 H), 3.8 (s, 2 H), 7.2–8.1 (m, 57 H).

A portion (1.2 g) was applied to a column of silica gel and eluted with hexane. Fraction 1: 50 mg; ^{1}H NMR ($CDCl_3$) δ 3.9 (s, 3 H), 7.5 (m, 3 H), 8.0 (m, 2 H); IR (neat) 2970, 1710, 1430, 1270, 1100 cm^{-1}. Fraction 2: 0.10 g; ^{1}H NMR ($CDCl_3$) δ 3.2 (s, 6 H), 3.7 (s, 6 H), 3.9 (s, 1 H), 7.3–8.1 (m, 76 H); IR (neat) 2970, 2920, 1690, 1680, 1450, 1240, 1120, 1060, 1050, 1030, 870 cm^{-1}; TLC (silica, ethyl acetate–hexane, 1:4) R_f 0.53 and 0.49. Fraction 3: 0.80 g; ^{1}H NMR ($CDCl_3$) δ 3.15 (s, 6 H), 7.2–8.1 (m, 10 H); IR (neat) 3020, 2950, 2910, 1690, 1660, 1440, 1230, 1180, 1050, 1040, 1010, 860, 750 cm^{-1}; TLC (silica, ethyl acetate–hexane, 1:4) R_f 0.49. This fraction was identical with a sample of 2,2-dimethoxy-2-phenylacetophenone purchased from Aldrich Chemical Co. and a sample prepared by the reaction of benzil and methyl iodide in the presence of barium oxide.[3]

Oxidation of 1 with I_2O_5 in Methanol. Diphenylacetylene (1.78 g, 10 mmol) was dissolved in methanol (70 mL). I_2O_5 (3.34 g, 10 mmol) was added and the mixture stirred at room temperature overnight under nitrogen. No new material was detected on TLC. The mixture was refluxed for 24 h. The mixture was diluted with CH_2Cl_2 (100 mL) and washed with water (3 × 100 mL). The organic layer was washed with 10% sodium thiosulfate (100 mL), dried over $MgSO_4$, and evaporated to a red liquid: 2.0 g; IR ($CHCl_3$) 3025, 1700, 1450, 1240, 1180, 1150, 1100, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.2 (s, 9 H), 3.4 (s, 6 H), 7.1 (s, 5 H), 7.2–8.2 (m, 16 H). A portion (1.0 g) was subjected to silica column chromatography with hexane as eluant. First fraction: 0.6 g; ^{1}H NMR ($CDCl_3$) δ 3.2 (s, 6 H), 7.2–8.2 (m, 10 H). Second fraction: 0.29 g; mp 138–140; IR ($CHCl_3$) 3025, 1180, 1150, 1100, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.4 (s, 12 H), 7.15 (s, 10 H); mass spectrum, *m/e* (relative intensity) 225, 197, 151 (100), 105. Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.37; H, 7.20.

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Oxidation of 1 with I_2O_5 in Ethylene Glycol. Diphenylacetylene (1.78 g, 10 mmol) and I_2O_5 (3.34 g, 10 mmol) were heated in ethylene glycol (70 mL) at 70 °C overnight. After the workup procedure used for the methanol cases, a yellow solid was obtained: 2.05 g; IR ($CHCl_3$) 2950, 1700, 1230, 1110, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.7 (s, 10 H), 7.2-7.5 (m, 20 H). A portion (1.0 g) was crystallized twice from $CHCl_3$ to give white needles: 0.6 g; mp 175-178 °C; IR ($CHCl_3$) 2950, 1230, 1110, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.7 (s, 8 H), 7.2-7.5 (m, 10 H); mass spectrum, *m/e* (relative intensity) 258, 227, 210, 182, 165 149 (100), 105. Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08. Found: C 72.43; H, 6.01. The remainder of the material was subjected to silica gel column chromatography with chloroform as eluant. First fraction: 0.2 g; mp 91-92 °C (benzil). Second fraction: 0.75 g; mp 175-178 °C (diketal). The second fraction had the same IR, NMR, and mass spectral characteristics as those of the material prepared by the reaction of benzil (21 g, 0.1 mol), ethylene glycol (8 mL), and *p*-toluenesulfonic acid (0.5 g) in benzene (150 mL).

Oxidation of Anisole with I_2O_5 in Methanol. Anisole (1.08 g, 10 mmol) was dissolved in methanol (75 mL) and the solution was refluxed overnight under nitrogen with I_2O_5 (3.34 g, 10 mmol). After the aforementioned workup, a red liquid was obtained: 1.3 g; ^1H NMR ($CDCl_3$) δ 3.7 (s, 7 H), 3.8 (s, 8 H), 6.65-7.5 (m, 19 H); IR (neat) 1600, 1490, 1470, 1280, 1250, 1030, 820 cm^{-1}; mass spectrum, *m/e* (relative intensity) 360 (100), 345 (30), 234 (30), 219 (70), 191 (30), 107 (20), 91 (70).

Oxidation of 1 with I_2/I_2O_5 in Methanol.[15] Diphenylacetylene (1.78 g, 10 mmol), iodine (10.2 g, 40 mmol), and I_2O_5 (1.67 g, 5 mmol) were stirred in methanol (100 mL) for 14 h at room temperature under nitrogen. After the usual workup the residue from evaporation of the CH_2Cl_2 was treated with CCl_4. Insoluble white crystals of diiodostilbene (125 mg) were collected. The CCl_4 was evporated. A portion (1.35 g) of the CCl_4-soluble products was chromatographed on silica gel. First fraction: 36 mg; ^1H NMR (CD_2Cl_2) δ 3.3 (s, 9 H), 7.0 (s, 7 H), 7.3 (s, 9 H). Second fraction: 637 mg; ^1H NMR δ 3.3 (s, 19 H), 7.0 (s, 14 H); compound **5**. Third fraction: 193 mg; ^1H NMR δ 3.1 (s, 9 H), 3.35 (s, 18 H), 3.65 (s, 6 H), 7.0-8.0 (m, 35 H). Fourth fraction: 401 mg; ^1H NMR δ 3.1 (s, 23 H), 7.1-8.1 (m, 34 H); compound **3**.

Oxidation of 1 with I_2-HgO in Methanol. Diphenylacetylene (1.78 g, 10 mmol) was treated with iodine (10.16 g, 40 mmol) and mercuric oxide (2.16 g, 10 mmol) in methanol under nitrogen for 24 h. After the usual workup, a red oil was obtained: 1.6 g; ^1H NMR ($CDCl_3$) δ 3.2 (s, 7 H), 3.4 (s, 1 H), 3.7 (s, 1 H), 7.1-8.2 (m, 20 H); IR (neat) 1735, 1700, 1450, 1230, 1110, 1060 cm^{-1}.

Registry No. 1, 501-65-5; 2, 134-81-6; 3, 24650-42-8; 4, 93-58-3; 5, 39787-30-9; 6, 25062-95-7; 7, 51552-62-6; H_5IO_6, 10450-60-9; I_2O_5, 12029-98-0; I_2, 7553-56-2; ethylene glycol, 107-21-1; anisole, 100-66-3.

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[15] This experiment was performed by M. Cohen, New York University.

Improved Synthesis of the Perhydroindenone Precursor of Dendrobine

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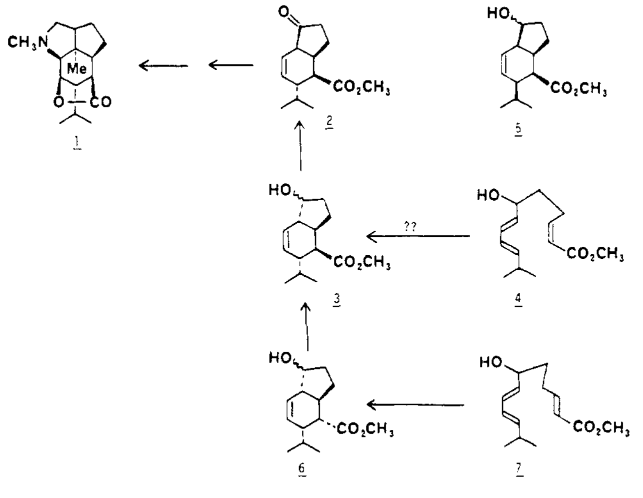
An improved synthesis of the perhydroindenone precursor (**2**) of dendrobine is described. The route requires only eight steps from 4-pentynoyl chloride (**8**) and proceeds in greater than 20% overall yield. The key step of this synthesis is the exo intramolecular Diels-Alder cyclization of (*Z,E,E*)-triene **14**.

We recently described a total synthesis of (±)-dendrobine (**1**) which proceeded via perhydroindenone **2** and alcohol **3**.[1] In considering routes to these intermediates, we recognized that each of the stereocenters in **3** could *formally* be introduced from **4** by an intramolecular Diels-Alder reaction. However, this approach was not pursued because it was assumed that the cyclization **4** → **3**, an exo Diels-Alder reaction, would be disfavored relative to the endo pathway leading to **5**, a useless stereoisomer of **3**. Rather, intermediates **2** and **3** were synthesized from **7** as indicated in Scheme I. During the course of these studies we discovered that the assumption regarding **4** was incorrect,[2] since alcohols **3** are, in fact, the major products of the Diels-Alder reaction of **4**. Subsequently, we have found that the unexpected behavior of **4** is general for trienes of this type.[3] We report herein on an improved synthesis of **2** by a route which utilizes the exo cycloaddition reaction of **14** as the key step.

Scheme I



The new route to **2** is outlined in Scheme II. The known acid chloride **8**[4] was transformed via the imidazolide **9**[5] (2.0 equiv of imidazole, THF, 98%; mp 85-87 °C)[6] into phosphorane **10** (mp 141-144 °C; 2.0 equiv of $(C_6H_5)P{=}CH_2$, C_6H_6)[7] by standard procedures in 80% overall yield. Condensation of **10** with 4-methylpent-2(*E*)-enal[8] in re-

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