clo[2.2.1]hept-2-ene oxide to **5** by base.[8] The ketone **4** may arise from an oxo carbene that could in turn arise from an oxirene, or the latter could act directly as a carbenoid,[9] by undergoing transannular insertion.

Whatever the actual mechanism of the conversion of **2** to **4**, these results show that, like dehydrohalogenation of halo epoxides,[4] dehalogenation of *vic*-dihalo epoxides leads to the product expected from the generation of an oxo carbene.[10]

Experimental Section

GC was performed on an Antek 461 gas chromatograph equipped with a thermal conductivity detector and fitted with a 1.5 m × 3.2 mm 5% Carbowax 20M on Chromosorb W stainless steel analytical column or a 1 m × 6.4 mm 20% Carbowax 20M on Chromosorb W stainless steel preparative column. The carrier gas was helium at a flow rate of 60 mL/min. IR spectra were taken with a Pye Unicam SP-3-100 spectrometer, and ^{1}H NMR spectra were taken with a JEOL C-60 HL spectrometer in CDCl$_3$ with (CH$_3$)$_4$Si as an internal standard. Zinc dust (J. T. Baker) was used without further treatment. Dioxane (B.D.H.) was refluxed overnight over sodium in a nitrogen atmosphere, distilled, and then stored over type 4-A molecular sieves.

2,4-Dichloro-3-oxatricyclo[3.2.1.$0^{2,4}$]octane (2) was prepared by reacting cyclopentadiene with trichloroethylene and dehydrochlorinating the trichlorobicycloheptenes with KOH in PrOH to give 2,3-dichlorobicyclo[2.2.1]hepta-2,5-diene.[11] The diene was reduced with hydrogen and palladium–charcoal in EtOH to 2,3-dichlorobicyclo[2.2.1]hept-2-ene.[12] The dichloroalkene was epoxidized with 3-chloroperoxybenzoic acid in CH$_2$Cl$_2$ to give **2**.[3b]

Reaction of 2,4-Dichloro-3-oxatricyclo[3.2.1.$0^{2,4}$]octane (2) with Zn. The epoxide **2** (221 mg, 1.23 mmol) and Zn powder (86 mg, 1.31 mmol) in dioxane (5 mL) were stirred under nitrogen at 22 °C for 12 h. Water (15 mL) was added and the mixture was extracted with two 10-mL portions of ether. The ether extracts were dried with anhydrous MgSO$_4$ and evaporated (rotary evaporator, room temperature) to give 132 mg of an oil, the ^{1}H NMR spectrum of which showed it to consist of nortricyclanone (**4**) and nortricyclanol (**5**) in a molar ratio of 9:1, corresponding to 90% and 10%, respectively. **4** and **5** were separated by preparative GC and identified by direct comparison (GC retention times and IR spectra) with authentic samples.[6a,b]

3,3-Dichlorobicyclo[2.2.1]heptan-2-one (6) was made analogously to the method of Shive et al. for the preparation of dibromocamphor.[6c] Bicyclo[2.2.1]heptan-2-one (2.0 g, 18.2 mmol) was placed in a 100-mL round-bottomed flask equipped with a reflux condenser and a dropping funnel. A 2 M solution of Cl$_2$ in AcOH (18 mL, 36 mmol) was added over 15 min, and the mixture was then heated on the steambath for several minutes (until the evolution of HCl ceased). A further 18-mL portion of Cl$_2$ in AcOH was added, and the mixture was heated on the steambath for 24 h. After being cooled to room temperature, the solution was poured over ice and the precipitated product was recrystallized from CH$_2$Cl$_2$–hexane and sublimed to give 2.5 g (77%) of **6**, mp 100–103 °C (lit.[7] mp 101.5–102.5 °C). The IR and ^{1}H NMR spectra corresponded with those reported.[7]

Attempted Reaction of 3,3-Dichlorobicyclo[2.2.1]heptan-2-one (6) with Zn. The dichloro ketone **6** (221 mg, 1.24 mmol) and Zn powder (85 mg, 1.3 mmol) in dioxane (5 mL) were stirred under nitrogen at 22 °C for 12 h. Workup as for the reaction of **2** with Zn gave 214 mg of a liquid that was shown by GC and ^{1}H NMR spectroscopy to be only the starting material **6**.

Reaction of 2-Chloro-3-oxatricyclo[3.2.1.$0^{2,4}$]octane (3) with Zn. The chloro epoxide **3**[7] (221 mg, 1.53 mmol) and Zn powder (100 mg, 1.53 mmol) in dioxane (5 mL) were stirred under nitrogen at 22 °C for 12 h. Workup as for the reaction of **2** with Zn gave 160 mg of a liquid that was shown by GC to consist of nortricyclanol (**5**) and the starting epoxide **3** in the molar ratio ca. 47:53. The identities of **5** and **3** were confirmed by collecting them (preparative GC) and comparing them (GC, IR) with authentic samples.

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Registry No. **2**, 50744-55-3; **3**, 16709-75-4; **4**, 695-05-6; **5**, 695-04-5; **6**, 16720-17-5; Cl$_2$C=CHCl, 79-01-6; cyclopentadiene, 542-92-7; *exo*-5,5,6-trichlorobicyclo[2.2.1]hept-2-ene, 37580-22-6; *endo*-5,5,6-trichlorobicyclo[2.2.1]hept-2-ene, 37580-23-7; 2,3-dichlorobicyclo[2.2.1]hepta-2,5-diene, 18990-07-3; 2,3-dichlorobicyclo[2,2.1]hept-2-ene, 21604-74-0; 3-chloroperbenzoic acid, 937-14-4; bicyclo[2.2.1]heptan-2-one, 497-38-1.

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[10] Besides β-elimination on halo and dihalo epoxides, only these routes to oxo carbenoids have been reported: (a) Diazo ketone decomposition.[1a] (b) Peroxy acid oxidation of alkynes.[1a] (c) Debromination of α,α-dibromo ketones with zinc.[5] (d) Dehydrobromination of α-bromoketones (Kowalski, C. J.; Fields, K. W. *J. Am. Chem. Soc.* **1982**, 104, 321). (e) Extrusion of CO$_2$, etc., from vinylene carbonates or their sulfur analogues (Torres, M.; Clement, A.; Strausz, O. P. *J. Org. Chem.* **1975**, *40*, 1694). Only in diazo ketone decomposition and in the photoexcitation of ketenes has the involvement of oxirenes been rigorously proved.[1]

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Reductive Dephosphorylation of (*Z*)-Bis(diethoxyphosphinyl)stilbene to Diphenylacetylene

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Alkynes represent an exceedingly important and useful class of organic compounds, the chemistry and preparation of which has been reviewed.[1] Only a few synthetic methods are available for the direct conversion of a carbonyl derivative to an alkyne. Structural and regioselective limitations of classical alkyne syntheses by alkylation or elimination procedures make new synthetic methods for the construction of alkynes from carbonyl compounds highly desirable. The most notable syntheses of alkynes from carbonyl compound precursors are (1) oxidation [CuCl/O$_2$[2]; NiO$_2$[3]; AgOCOCF$_3$[4]; HgO[5][of bis hydrazones derived from 1,2-diketones; (2) treatment of 2-substituted [epoxy[6]; OBz[7]; OAc[7,8]; Cl[8]; Br[8]; OMs[8]; SMe[9]] ketones with *p*-toluenesulfonyl hydrazine[6–9] or triphenylphosphine;[10]

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Table I. Reductions of Bis Phosphate Ester 2

			yield, %			
reducing agent/solv	temp, °C	time	diphenylacetylene	stilbene	diphenylethane	recovered[a] starting material
Na(Hg)THF/Me_2SO	0	2 h	80		1	19
Ti/THF	66	24 h	57	3	2	21
$Na(NH_3)$	−78	5 min	40	34		24
$Li(NH_3)$	−78	5 min	39	44	17	
$Na(C_{10}H_8)HMPA$	25	24 h	39	29		32
$Li(C_{10}H_8)/HMPA$	25	24 h	49	24	6	21
Na(DBB)/THF	25	24 h				*b*
Li(DBB)/THF	25/66	24 h				*b*
Al(Hg)/THF/Me_2SO	25	96 h	25	39	12	24
Mg/THF	66	24 h				*b*
Zn/THF	66	24 h				*b*
$H_2(PtO_2)$/EtOH	25	72 h			85	10
$(Bu)_3SnH$/THF	25 + $h\nu$	70 h	14		2	35
$Cr[ClO_4(en)_2]_2$/DMF	25	24 h				*b*
Vitride/Et_2O	25	3 h				*b*
$P(OEt)_3/C_6H_6$	82	24 h				100
$[(CH_3)_2N]_3P$/xylene	106	96 h				*b*

[a] Isolated by chromatography on silica gel 60; 3:4:5 ratios were determined by GLC. [b] Complex mixture of products.

Table II. Reduction of Bis Phosphate Ester 2 with Titanium/Tetrahydrofuran

K[a]	$TiCl_3$[a]	time (h)	bis phosphate	alkyne, %	alkene, %	alkane, %	hydrocarbon yield, %
2	0.67	45	1	90	9	1	47
2.3	0.67	24	1	92	5	3	62
4	0.75	72	1	55	23	23	50
4.1	1.50	48	1	5	4	91	49
6.0	1.67	24	1	8	19	73	40
14.7	5.00	24	1	0	51	49	100

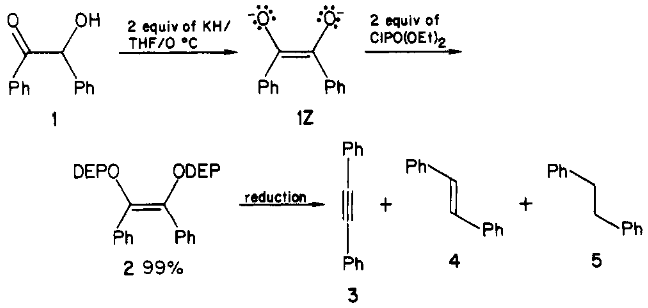
[a] Molar ratio.

and (3) reduction of diethyl enol phosphate esters of β-keto sulfones[11] or the enol triflate esters of vinyl phosphonium salts.[12] The purpose of this note is to report a new synthesis of diphenylacetylene (**3**) from benzoin (**1**).

Diphenylacetylene (**3**) was first prepared by Curtius in 1889.[5a] Several syntheses of diphenylacetylene (**3**) from benzil[13] and benzoin (**1**)[14] have been reported. acyloins (2-hydroxy ketones), such as benzoin (**1**), are readily available by the acyloin[15] or benzoin[16] condensations. The moderate success of Bauer and Macomber[14a] in transforming benzoin (**1**) to diphenylacetylene (35% yield from the bis Me_3Si ether intermediate) via reduction of an intermediate cyclic thiocarbonate ester with triethyl phosphite prompted us to explore the preparation and reduction of bis(diethyl phosphate ester) **2** (Scheme I).

Duhamel and Launay[17] recently reported the formation of enediolate dianion **1*Z*** (≥95% *Z*) from benzoin (**1**) with 2 equiv of potassium hydride in tetrahydrofuran at 0 °C. We found that trapping **1*Z*** with 2 equiv of diethyl chlorophosphate produces (*Z*)-bis(diethoxyphosphinyl)stilbene (**2**) in 99% yield as predominantly a single diastereomer (≥95%). The *Z* stereochemistry was confirmed by examination of the ultraviolet spectrum of **1*Z*** [λ (EtOH) 266 nm (ε 12023)]. Fieser reported the ultraviolet spectra for the corresponding (*Z*)- and (*E*)-stilbenediacetate esters (λ (EtOH) 265 nm (ε 12800); λ (EtOH) 271 nm (ε 23400), respectively].[18] In **2*Z*** the two phenyl groups cannot easily become coplanar. This steric hindrance to coplanarity prevents a overlap of the p orbitals of the two phenyl rings with the central double bond and thus lowers the position of the UV absorption band as well as the extinction coefficient of the *Z* relative to the *E* isomer.

Scheme I[a]



[a] DEP = $PO(OEt)_2$.

Table I shows the various reducing agents explored in this study. In most cases between 2.1 and 4 equiv of reducing agent were used with the exception of reactions 12, 16, and 17. As can be seen from Table I the best conditions for the selective reduction of bis phosphate ester **2** to di-

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phenylacetylene (**3**) are sodium amalgam (4 equiv) in tetrahydrofuran/dimethyl sulfoxide at 0 °C for 2 h.[11] Under these conditions diphenylacetylene (**3**) was produced in 80% yield with a high degree of selectivity.

Our success with the use of freshly prepared, highly activated titanium metal in tetrahydrofuran in the reduction of enol and aryl diethyl phosphate esters[19] together with McMurry and coauthor's[20] observations that these conditions only slowly reduce alkynes prompted us to explore this method as well. Treatment of bis phosphate ester **2** with titanium metal (2.3 equiv of K, 0.67 equiv of $TiCl_3$) in refluxing tetrahydrofuran for 24 h afforded diphenylacetylene (**3**) in 57% yield. Table II shows a series of experiments aimed at optimizing the reaction conditions for the selective reduction of bis phosphate ester **2** with titanium metal in refluxing tetrahydrofuran.

Reduction of bis phosphate ester **2** with alkali metals (Li, Na) in liquid ammonia,[11] in naphthalene/hexamethylphosphoric triamide (HMPA),[21] or in 4,4′-di-*tert*-butylbiphenyl (DBB)/tetrahydrofuran[22] gave reduction products with poor selectivity in the formation of diphenylacetylene (**3**).

Reduction of bis phosphate ester **2** with aluminum amalgam in tetrahydrofuran/dimethyl sulfoxide at 25 °C produced diphenylacetylene (**3**) in 25% yield again with poor selectivity.[23] Treatment of phosphate ester **2** with Rieke[24] magnesium or zinc in refluxing tetrahydrofuran **2** afforded only complex mixtures of products.

Finally, catalytic hydrogenation of bis phosphate ester **2** over platinum oxide in 100% ethanol at 40 psi pressue for 72 h gave 1,2-diphenylethane (**5**) in 85% yield.[25]

Several attempts to prepare the bis(diethyl phosphate ester) **2** [PhPh = $(CH_2)_{10}$] of 2-hydroxycyclododecanone gave only modest and capricious results. Treatment of 2-hydroxycyclododecanone (freshly sublimed) with potassium hydride (4 equiv) in tetrahydrofuran/HMPA (4:1 ratio, respectively) for 24 h followed by quenching the enediolate dianion with diethyl chlorophosphate (4 equiv) produced bis(diethyl phosphate ester) **2** [PhPh = $(CH_2)_{10}$] in 44% yield. All attempts to reduce the latter bis phosphate ester selectively to cyclododecyne under conditions which were successful for diphenylacetylene (**3**) failed to give any useful results.

Experimental Section

Materials and Techniques. Melting points were determined on a Büchi melting point apparatus. All melting points and boiling points are uncorrected and are reported in Celsius degrees. Analytical gas-phase chromatography (GLC) was performed on a Varian Aerograph Model 1400 chromatograph, equipped with a flame ionization detector with helium as the carrier gas, using a 6 ft, stainless steel, $^1/_8$ in. column, packed with 3% SE-30 on Varaport-30, 100/120 mesh (Varian); flow rate 15 mL/min at 190 °C. Silica gel 60, F-254 (E. Merck No. 5765), silica gel 60 (E. Merck No. 7734, 70–230 mesh) and silica gel 60 (E. Merck No. 9485, 230–400 mesh) available from Brinkmann Instruments, were used for thin-layer, column, and medium pressure liquid chromatography (MPLC),[26] respectively. Infrared (IR) spectra were recorded on a Perkin-Elmer grating infrared spectrometer, Model 237B. Samples were taken in spectroquality grade carbon tetrachloride or chloroform as 10% solutions using balanced 0.1-mm sodium chloride cells or were taken as thin films between sodium chloride plates. Nuclear magnetic resonance (NMR) spectra were measured on a Varian Associates Models T-60 and FT-80 spectrometers in the solvent indicated. Mass spectra were recorded on a Hewlett-Packard Model 5933 A spectrometer at 60 eV. Tetrahydrofuran (THF) and ether were freshly distilled under nitrogen from lithium aluminum hydride immediately prior to usage in all reactions. Dimethyl sulfoxide (Me_2SO) and hexamethylphosphoric triamide (HMPA) were freshly vacuum distilled from calcium hydride. Dichloromethane was distilled from phosphorus pentoxide. Anhydrous titanium(III) chloride (Alfa No. 77116) was transferred under nitrogen and utilized directly. All reactions were performed under an atmosphere of dry argon unless otherwise indicated. All equipment was dried in an oven at 120 °C for several hours prior to use and then allowed to cool in a dessicator over Drierite.

Bis(diethoxyphosphinyl)stilbene (2). Potassium hydride (35% in mineral oil, 454 mg, 11.3 mmol) was added to a tared 50-mL round-bottomed flask and washed with freshly distilled Et_2O (3 × 10 mL). Anhydrous THF (30 mL) was added to the KH and the suspension was stirred under Ar at 0 °C while benzoin (948 mg, 4.5 mmol) dissolved in THF (15 mL) was added dropwise over a period of 2 min. The resulting dark red suspension was stirred at 0 °C for 1 h. Diethyl chlorophosphate (1.6 mL, 11.3 mmol) was added dropwise over a period of 5 min, and the resulting light brown mixture was then allowed to warm to 25 °C and stirred for 12 h. The THF was removed in vacuo, and the crude product was triturated with ethyl acetate (20 mL) and injected into a liquid chromatograph (MPLC). The material was purified with a 1.5 × 25 cm silica gel 60 column (300 g), using ethyl acetate as the eluent, at a pressure of 10 psi, collecting 100-mL-sized fractions. Removal of the solvent from the appropriate fractions gave 2.16 g (99%) of bis(diethyl phosphate ester) **2** as a yellow oil: UV (95% EtOH) 266 nm (ϵ 12023), 218 (ϵ 18470); IR (thin film) 1600 (aromatic C=C stretch), 1240 (PO stretch), 1050, 950 cm^{-1} (POC stretch); NMR ($CDCl_3$) δ 7.22 (s, 10 H, Ar H), 4.0 (m, 8 H, $POCH_2$), 1.2 (t, 12 H, CH_3); mass spectrum, *m/e* 484 (theory 484).

Anal. Calcd for $C_{22}H_{30}O_8P_2$: C, 54.38; H, 6.29. Found: C, 54.55; H, 6.24.

Reductions of Bis(diethoxyphosphinyl)stilbene (2). With Sodium Amalgam. Na metal (37 mg, 1.6 mmol) and Hg metal (1.8 g) were combined in a 15-mL round-bottomed flask equipped with a stirring bar, reflux condenser, and Ar inlet. After addition of freshly distilled THF (5 mL) the mixture was heated to reflux and stirred for 1.5 h, at which time it was observed that the metals had combined and then the heat was removed. After cooling to 0 °C, bis(diethoxyphosphinyl)stilbene (202 mg, 0.4 mmol) dissolved in freshly distilled Me_2SO (7 mL) was added dropwise over a period of 10 min, and the mixture was allowed to stir for 2 h at 0 °C. The mixture was filtered, added to H_2O (50 mL), and extracted with Et_2O (3 × 50 mL). The combined ethereal extracts were washed with H_2O (15 mL) and saturated NaCl (15 mL), dried ($MgSO_4$), filtered ($MgSO_4$), and concentrated in vacuo, chromatographed (gravity column, silica gel 60, 10 g, ethyl acetate as the elvent), to give 60 mg (81%) of hydrocarbons. Analysis by GLC: 80% diphenylacetylene; 0% stilbene; 1% 1,2-diphenylethane. Starting material (19%) was recovered.

With Titanium. Anhydrous titanium(III) chloride (290 mg, 1.9 mmol) was stirred in freshly distilled THF (10 mL) under Ar while potassium metal (249 mg, 6.4 mmol, cut in small shiny pieces) was added. The 50-mL round-bottomed flask was then equipped with a reflux condenser and subsequently refluxed under Ar for 1 h until no trace of potassium was visible. Bis(diethoxyphosphinyl)stilbene (1.4 g, 2.8 mmol) dissolved in dry THF (13 mL) was added and the mixture was allowed to stir at reflux for 24 h. The reaction was then cooled to 5 °C and quenched with an excess of methanol, filtered on a short plug of Celite:silica gel (4:1 w/w), concentrated in vacuo, and chromatographed (gravity column, silica gel 60, 50 g, ethyl acetate as the eluent) to give 318

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mg (62%) of hydrocarbons. Analysis by GLC: 57% diphenylacetylene; 3% stilbene; 21% 1,2-diphenylethane. Starting material (21%) was recovered.

With Sodium in Liquid Ammonia. To a three-necked 50-mL round-bottomed flask was added bis(diethoxyphosphinyl)stilbene (402 mg, 0.8 mmol) dissolved in THF (15 mL). The flask was then equipped with a dry ice condenser and stopcock and cooled to −78 °C. Ammonia (15 mL), distilled from Na metal, was admitted to the flask, and Na metal (38 mg, 1.7 mmol) was added in small pieces (under Ar) until the blue color just persisted, at which time the solution was quenched with an excess of *tert*-butyl alcohol. The NH_3 was allowed to evaporate and the material was added to H_2O (50 mL) and extracted with Et_2O (3 × 50 mL). The combined ethereal extracts were dried ($MgSO_4$), filtered ($MgSO_4$), concentrated in vacuo, and chromatographed (gravity column, silica gel 60, 27 g, ethyl acetate as the eluent) to give 110 mg (74%) of hydrocarbons. Analysis by GLC: 40% diphenylacetylene; 34% stilbene; 0% 1,2-diphenylethane. Starting material (24%) was recovered.

With Lithium in Liquid Ammonia. To a three-necked 50-mL round-bottomed flask was added bis(diethoxyphosphinyl)stilbene (312 mg, 0.6 mmol) dissolved in THF (10 mL). The flask was then equipped with a dry ice condenser and stopcock and cooled to −78 °C (dry ice, acetone). Ammonia (15 mL), distilled from Na metal, was admitted to the flask and Li metal (10 mg, 1.4 mmol) was added under vigorous Ar flow, turning the solution a deep blue. The color persisted for approximately 1 min, and additonal small amounts of Li (ca. 1 mg) were added until the color just persisted at which time the solution was quenched with an excess of *tert*-butyl alcohol. The NH_3 was allowed to evaporate and the material was added to H_2O (40 mL) and extracted with Et_2O (3 × 30 mL). The combined ethereal extracts were dried ($MgSO_4$), filtered ($MgSO_4$), and concentrated in vacuo, to give 108 mg (100%) of hydrocarbons. Analysis by GLC: 39% diphenylacetylene; 44% stilbene; 17% 1,2-diphenylethane.

With Sodium Naphthalenide. To a two-necked 50-mL round-bottomed flask was added freshly distilled HMPA (7 mL) and freshly sublimed naphthalene (161 mg, 1.3 mmol) followed by Na metal (26 mg, 1.1 mmol). To this mixture was added bis(diethoxyphosphinyl)stilbene (144 mg, 0.3 mmol) dissolved in THF (4 mL), and the resulting green mixture was stirred under Ar for 12 h. The mixture was added to H_2O (50 mL) and extracted with Et_2O (3 × 30 mL). The combined ethereal extracts were washed with H_2O (3 × 30 mL), dried ($MgSO_4$), filtered ($MgSO_4$), concentrated in vacuo, and chromatographed (gravity column, silica gel 60, 33 g, 100% hexane as the eluent) to give 37 mg (68%) of hydrocarbons by GLC: 39% diphenylacetylene; 29% stilbene; 0% 1,2-diphenylethane. Starting material (32%) was recovered.

With Lithium Naphthalenide. To a two-necked 50-mL round-bottomed flask was added freshly distilled HMPA (7 mL), freshly sublimed naphthalene (5 mg, 0.04 mmol), and Li metal, (5 mg, 0.7 mmol). To this mixture was added bis(diethoxyphosphinyl)stilbene (155 mg, 0.3 mmol) dissolved in THF (2.4 mL), and the resulting green mixture was stirred under Ar for 12 h. The mixture was added to H_2O (50 mL) and extracted with Et_2O (3 × 30 mL). The combined ethereal extracts were washed with H_2O (3 × 3 mL), dried ($MgSO_4$), filtered ($MgSO_4$), concentrated in vacuo, and chromatographed (gravity column, silica gel 60, 33 g, 100% hexane as the eluent) to give 43 mg (79%) of hydrocarbons. Analysis by GLC: 49% diphenylacetylene; 24% stilbene; 6% 1,2-diphenylethane. Starting material (21%) was recovered.

With Hydrogen. To a 250-mL high-pressure Parr flask was added 100% ethanol (20 mL), PtO_2 (29 mg, 0.1 mmol), and bis(diethoxyphosphinyl)stilbene (184 mg, 0.4 mmol). The container was stoppered, flushed with H_2 (4×), charged with H_2 (40 psi), and allowed to stir at this pressure for 72 h. The mixture was filtered, added to saturated $NaHCO_3$ (50 mL), and extracted with Et_2O (3 × 30 mL). The combined ethereal extracts were dried ($MgSO_4$), filtered ($MgSO_4$), concentrated in vacuo to a volume of a few milliliters, and injected directly into a liquid chromatograph (MPLC). The material was purified with a 1.5 × 25 cm silica gel 60 column (300 g), using ethyl acetate as the eluent, at a pressure of 25 psi, collecting 100-mL-sized fractions. Removal of the solvent from the appropriate fractions gave 62 mg (85%) of hydrocarbons. Analysis by GLC: 0% diphenylacetylene; 0% stilbene; 85% 1,2-diphenylethane. Starting material (10%) was recovered.

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Registry No. 2, 93304-54-2; benzoin, 119-53-9; diethyl chlorophosphate, 814-49-3; diphenylacetylene, 501-65-5; 1,2-diphenylethane, 103-29-7; stilbene, 588-59-0.

Studies in Anthracycline Synthesis: Simple Diels–Alder Routes to Pachybasin, ω-Hydroxypachybasin, Aloe-emodin, and Fallacinol

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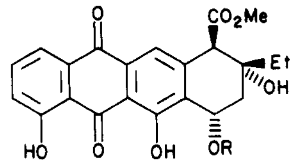
In connection with our interest in developing new synthetic routes to the aglycons of the anticancer anthracycline aclacinomycin A (1) and related structures,[1] we required a simple and practical approach to various 1-hydroxy-3-methylanthraquinones as well as the corresponding ω-hydroxy compounds. The natural products pachybasin (2)[2] and ω-hydroxypachybasin (3)[3] are prototypes of these structures. Using Diels–Alder based methodology, we now report a simple, one-pot synthesis of pachybasin, as well as new syntheses of ω-hydroxypachybasin, aloe-emodin (4), and fallacinol (5).



1, R = rhodosamine, 2-deoxyfucose, and cinerulose A residues

Brassard has shown that the Diels–Alder additions of naphthoquinones to mixed trimethylsilyl vinylketene acetals affords a versatile route to substituted hydroxyanthraquinones.[4] This methodology has been adopted more recently by others in synthetic approaches to anthracyclinone systems.[5]

We felt that pachybasin (2) could be prepared most efficiently by the reaction of 2-bromonaphthoquinone (6)[6] with the readily prepared vinylketene acetal 7 derived from methyl senecioate (8).[7] Indeed, diene 7 reacted rapidly with quinone 5 in methylene chloride at room temperature in the presence of potassium carbonate as HBr scavanger. Heating the reaction mixture with sodium acetate completed the aromatization process, and following acidification pachybasin (2) was isolated cleanly by direct crys-

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