Brominations Using Sodium Hypobromite. Preparation of Sodium Hypobromite. A solution of sodium hydroxide (20 g, 0.5 mol) in H_2O (60 mL) was prepared in a 200-mL, three-necked, round-bottomed flask fitted with a thermometer and a dropping funnel. The solution was cooled to 0 °C in an ice–salt bath, and bromine (40 g, 12.81 mL, 0.25 mol) was slowly added with stirring over 25 min at a rate such that the temperature did not exceed 10 °C.

Triethyl Dibromophosphonoacetate (7). Triethyl phosphonoacetate (12 g, 53.5 mmol) was added over 3 min to the freshly prepared, stirred sodium hypobromite solution cooled in an ice–salt bath. The temperature was maintained below 10 °C. When addition was complete, the mixture was immediately extracted with chloroform (4 × 100 mL). The chloroform extracts were washed with water (2 × 20 mL) and dried ($MgSO_4$), and the solvent was removed in vacuo. ^{31}P NMR analysis of the residue showed that triethyl dibromophosphonoaceate (7) (δ = 8.4 ppm) made up 95% of the phosphorus-containing products; the remaining 5% was accounted for by a compound with δ = 10.5 ppm. The identity of this minor side product was not determined.

The residue was partitioned between hexane (400 mL) and H_2O (2 × 5 mL), and the hexane extracts were dried ($MgSO_4$). Removal of the solvent in vacuo left pure triethyl dibromophosphonoacetate (93%) which was vacuum distilled to give a colorless oil, bp 104–106 °C (0.01 mm): ^{31}P NMR ($CDCl_3$) δ = 8.4 ppm (p) (lit.[6] 7.0 ppm). Anal. Calcd for $C_8H_{15}O_5Br_2P$: C, 25.15; H, 3.96. Found: C, 25.20; H, 3.70.

Triethyl 2-Bromophosphonopropionate (14). In a similar reaction, a solution of sodium hypobromite was prepared by mixing NaOH (10 g, 0.25 mol) in H_2O (35 mL) with bromine (20 g, 6.4 mL, 0.125 mol). Triethyl 2-phosphonopropionate (6 g, 25 mmol) was then added over 2 min, and the resulting mixture was immediately extracted with chloroform (3 × 100 mL). The product was isolated in 98% yield; on vacuum distillation it was obtained as a colorless oil, bp 116–118 °C (0.01 mm): ^{31}P NMR ($CDCl_3$) δ = 16.9 ppm (m). Anal. Calcd for $C_9H_{18}O_5BrP$: C, 34.08; H, 5.72. Found: C, 33.83; H, 5.59.

Triethyl Bromochlorophosphonoacetate (10). The sodium hypobromite reagent was prepared by mixing a solution of 4.8 g (0.12 mol) of NaOH in 16 mL H_2O with bromine (9.76 g, 0.06 mol). Triethyl chlorophosphonoacetate (3) (3.18 g, 0.012 mol) was then added over 2 min and the resulting mixture was immediately extracted with chloroform (3 × 75 mL). The product was isolated (96%) by evaporation of the solvent at reduced pressure. It was obtained by vacuum distillation as a colorless oil, bp 103–105 °C (0.01 mm): ^{31}P NMR ($CDCl_3$) δ = 8.4 ppm (p). Anal. Calcd for $C_8H_{15}O_5BrClP$: C, 28.46; H, 4.47. Found: C, 28.14; H, 4.29.

Triethyl Bromofluorophosphonoacetate (9). The sodium hypobromite reagent was prepared as described above from 1.6 g (40 mmol) NaOH, 5.3 mL of H_2O, and 3.2 g (20 mmol) of bromine. Triethyl fluorophosphonoacetate (1 g, 4 mmol) was then added, and the resulting mixture was immediately extracted with chloroform (3 × 25 mL). The combined chloroform extracts were dried ($MgSO_4$) and evaporated at reduced pressure, yielding a residue containing 9 (δ = 5.6 ppm, 92%), starting material (2) and an unidentified minor side product (δ = –0.2 ppm). The crude product was partitioned between hexane (50 mL) and H_2O (3 × 15 mL); the organic phase was then dried ($MgSO_4$) and evaporated at reduced pressure to give 1.1 g (90%) of pure 9. Vacuum distillation provided an analytical sample as a colorless oil, bp 101–102 °C (0.01 mm): ^{31}P NMR ($CDCl_3$) δ = 5.6 ppm (dp). Anal. Calcd for $C_8H_{15}O_5BrFP$: C, 29.92; H, 4.70. Found: C, 30.08; H, 4.70.

Dehalogenation of Dihalophosphonoacetates. Triethyl Chlorophosphonoacetate (3). Triethyl dichlorophosphonoaceate (11.2 g, 38.2 mmol) was dissolved in EtOH (75 mL), and the resulting solution was cooled in an ice bath. A solution of sodium sulfite (9.64 g, 76.5 mmol) in H_2O (300 mL) was added with stirring at a rate such that the temperature could be maintained below 15 °C (15 min). During addition the reaction mixture became turbid; after 20 min of further stirring at room temperature, it was extracted with chloroform (5 × 100 mL). The chloroform extracts were dried ($MgSO_4$), and the solvent was removed in vacuo. ^{31}P NMR of the residue showed that triethyl chlorophosphonoacetate (δ = 13 ppm) made up 97% of the phosphorus-containing products, the remainder being starting material 6 (δ = 8 ppm).

The crude mixture was partitioned between hexane (200 mL) and 0.1 M $NaHCO_3$ (8 × 50 mL). The bicarbonate fractions were combined and reextracted with chloroform (6 × 50 mL). The chloroform extracts were dried ($MgSO_4$), and the solvent was removed in vacuo to give 9.4 g of pure triethyl chlorophosphonoacetate (95%). Vacuum distillation provided the product as a colorless oil, bp 93–95 °C (0.01 mm): ^{31}P NMR ($CDCl_3$) δ = 13.0 ppm (m) (lit.[5] 12.0 ppm). Anal. Calcd for $C_8H_{16}O_5ClP$: C, 37.15; H, 6.23. Found: C, 36.97; H, 6.36.

Triethyl Bromophosphonoacetate (4). To triethyl dibromophosphonoacetate (10 g, 26 mmol) dissolved in EtOH (25 mL) was added with cooling (ice bath) a solution of 5.60 g (25 mmol) of $SnCl_2 \cdot 2H_2O$ in H_2O (50 mL). The temperature was maintained below 10 °C. When addition was complete (20 min), the reaction mixture was stirred for an additional 5 min at room temperature and then extracted with chloroform (4 × 50 mL). The chloroform extracts were dried ($MgSO_4$), and the solvent was removed in vacuo. ^{31}P NMR analysis of the residue showed that triethyl bromophosphonoacetate (δ = 13.2 ppm) made up more than 95% of the phosphorus-containing products. Besides a trace of starting material, two minor side products (δ = 10.5 ppm and δ = 4.5 ppm) were present; these were not further characterized.

The desired product was isolated by partitioning the crude residue between hexane (100 mL) and H_2O (4 × 25 mL). The aqueous fractions were combined and reextracted with chloroform (3 × 50 mL). The chloroform extracts were dried ($MgSO_4$) and evaporated at reduced pressure to provide 6.7 g (85%) of pure triethyl bromophosphonoacetate. Vacuum distillation gave the product as a colorless oil, bp 93–94 °C (0.01 mm): ^{31}P NMR ($CDCl_3$) δ = 13.2 ppm (m). Anal. Calcd for $C_8H_{16}O_5BrP$: C, 31.69; H, 5.31. Found: C, 31.39; H, 5.16.

Acknowledgment. We thank Janet Ng for technical assistar ce in the synthetic work. This research was supported by a grant from the National Institutes of Health (AI21871) and by a Faculty Research and Innovation Fund award from the University of Southern California.

Registry No. 1, 867-13-0; 2, 2356-16-3; 3, 7071-12-7; 4, 23755-73-9; 6, 5823-12-1; 7, 28845-75-2; 8, 101834-88-2; 9, 101834-89-3; 10, 101834-90-6; 11, 3699-66-9; 13, 101834-91-7; 14, 101834-92-8.

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^1H NMR Spectra of (*Z*)- and (*E*)-1,2-Di-9-anthrylethene

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Received August 1, 1986

In connection with our studies on molecular gearing[1] we became interested in (*Z*)-1,2-di-9-anthrylethene (1) as a potential synthetic precursor of (*Z*)-1,2-di-9-triptycylethene.[2] The markedly different splitting patterns in the ^1H NMR spectra of 1 and its *E*-isomer (2) had previously been attributed to hindered rotation around the anthryl–ethylene single bond in 2.[3] However, we find that the room temperature spectra of 1 and 2 are *both* fully con-

(1) Guenzi, A.; Johnson, C. A.; Cozzi, F.; Mislow, K. *J. Am. Chem. Soc.* **1983**, *105*, 1438 and references therein.

(2) Preliminary force-field calculations indicate that (*Z*)-1,2-di-9-triptycylethene behaves as a molecular bevel gear system in which the two 9-triptycyl groups undergo virtually unhindered correlated disrotation. See: McDonald, J. W.; A. B. Thesis, Princeton University, 1986.

(3) Becker, H.-D.; Hansen, L.; Andersson, K. *J. Org. Chem.* **1981**, *46*, 5419.

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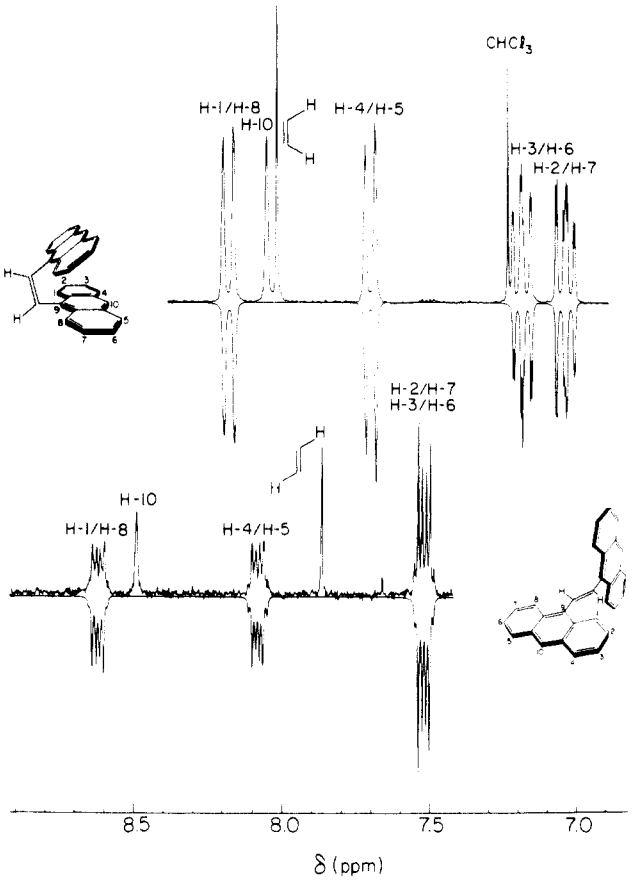

Figure 1. 250-MHz ^{1}H NMR spectra of (*Z*)-1,2-di-9-anthrylethene (**1**, top) and (*E*)-1,2-di-9-anthrylethene (**2**, bottom). Spin-simulated spectra are presented in inverted form for ease of visual matching with the experimentally observed spectra. The simulated spectra do not include the uncoupled 10-anthryl and ethene protons which appear as singlets in the observed spectra.

Table I. Parameters for Simulated ^{1}H NMR Spectra of 1 and 2

δ	1	2	J	1	2
δ_1	8.21	8.63	$J_{1,2}$	8.79	7.91
δ_2	7.07	7.53	$J_{1,3}$	1.35	1.91
δ_3	7.21	7.53	$J_{1,4}$	0.65	0.49
δ_4	8.21	8.09	$J_{2,3}$	6.63	6.32
			$J_{2,4}$	1.00	0.48
			$J_{3,4}$	8.55	8.30

[a] Chemical shifts (δ) relative to tetramethylsilane, in ppm. Coupling constants (J) in hertz. Subscripts refer to numbered positions on the anthracene ring (Figure 1).

sistent with unrestricted rotation on the NMR time scale.[4]

On the assumption of unrestricted rotation, the protons on either side of each anthryl ring in both **1** and **2** are pairwise related by symmetry and are therefore magnetically equivalent (H-1/H-8, H-2/H-7, H-3/H-6, H-4/H-5). The ABCD anthryl spin systems of both compounds are accordingly described by four chemical shifts and six coupling constants (Table I). The simulated spectra closely match the experimentally observed spectra (Figure 1),[5] and the striking difference in the appearance of the spectra of **1** and **2** is thus wholly accounted for by differences in the spectral parameters.[6]

Acknowledgment. We thank Silvio Biali for helpful discussions and the National Science Foundation (CHE-8510067) for support of this work.

Registry No. (*Z*)-1,2-Di-9-anthrylethene, 3162-57-0; (*E*)-1,2-di-9-anthrylethene, 3849-11-4.

(4) An X-ray structure of **2** throws no light on the problem of internal mobility. See: Becker, H.-D.; Engelhardt, L. M.; Hansen, L.; Patrick, V. A.; White, A. H. *Aust. J. Chem.* **1984**, *37*, 1329. However, examination of a CPK model suggests that the anthryl ring flip in **2** should be fairly unrestricted.

(5) Data for the analysis of the ^{1}H NMR spectra were obtained from $CDCl_3$ solutions of **1** and **2** on a Bruker WM 250 spectrometer. Spin simulations were performed by use of the Bruker PANIC simulation program.

(6) The ^{1}H NMR spectrum of **2** at 388 K showed no evidence of coalescence or line broadening. The change in the general shape of the spectrum at that temperature is due to changes in the chemical shifts of the anthryl protons.

Convenient Synthesis of Hex-1-enopyran-3-uloses: Selective Oxidation of Allylic Alcohols Using Pyridinium Dichromate†

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Received February 17, 1986

Hexenuloses have played a major role in carbohydrate chemistry as described in recent reviews.[1-4] Diversely protected hex-1-enopyran-3-uloses are of particular interest, because 1,4 additions allow functionalization and/or chain extension at the anomeric carbon, and their synthetic utility prompted a search for convenient methods of preparation. Earlier reports include the synthesis of a 4,6-benzylidene derivative of enone **1b**[5] and, more recently,[6c] another route to differently protected hex-1-enopyran-3-uloses from D-glucal via acetonation–oxidation or selective protection of primary hydroxyl followed by selective oxidation of the allylic alcohol. In both cases the overall yields were in the range of 20–25%. A more straightforward synthesis of enone **1b** was reported by Tronchet[7] who used Fetizon's reagent[8] to selectively oxidize D-glucal **1a** [After this work was submitted, preparation of compound **1c** from tri-*O*-acetyl-D-glucal (five steps, 35% overall yield) was reported: Fetizon, M.; Duc Do Khac; Nguyen Dinh Tho *Tetrahedron Lett.* **1986**, *27*, 1777.], but with this procedure, which requires a huge excess of reagent,[9] the glucal was not completely oxidized and purification by column chromatography was needed, resulting in low yields.

Because of the drawbacks of these methods, we decided to explore the synthetic utility of our recently developed rapid and high yield pyridinium dichromate (PDC) oxidation procedure[10] for selective oxidation of unprotected glycals. We report herein the results of our study.

D-Glucal **1a** was chosen as the model compound, since it is easily prepared from commercially available tri-*O*-acetyl-D-glucal.

The procedure which had given very good results with saturated carbohydrates, namely PDC in CH_2Cl_2 in the presence of anhydrous acetic acid (AcOH) and molecular

† Dedicated to Professor C. L. Stevens, Wayne State University, Detroit, MI.

0022-3263/86/1951-5472$01.50/0