82% yield, characterized by NMR spectroscopy and melting point), cinnamaldehyde (26 mg, 10% yield), and a third unidentified product (16 mg, 5% yield) were obtained. The absence of a possible reaction product, 3-phenylpropanol,[2] was confirmed by a chromatographic comparison of an authentic sample with the reaction mixture (silica gel-$AgNO_3$ plate, elution with hexane–ethyl ether, 80:20).

Reduction of Acyl, Ester, Lactone, and Anhydride Functions. The general technique was the same as described for the reduction of unsaturated ketones. *p*-Nitrobenzoyl chloride (185 mg, 1 mmol) was dissolved in 2 mL of tetrahydrofuran and treated (−18 °C) with 0.33 mmol of BMS under stirring. After 2.5 h, the reaction was stopped and the reaction mixture worked up. By chromatography of the crude mixture on Al_2O_3 (B III, neutral) (6 g) and by elution with hexane–ethyl acetate (95:5), *p*-nitrobenzaldehyde (110 mg, 60% yield) and *p*-nitrobenzyl alcohol (50 mg) were obtained. In other experiments, an increase in temperature (0 °C) led to an increase in yield of the alcohol. Benzyl chloride was unreactive at −18 °C. By raising the temperature to 0 °C, an effective reduction took place, yielding the corresponding alcohol (95%). Likewise, by the same procedure, phenyl methyl ester did not react at −18 °C; by raising the temperature to 15 °C a slow reduction to benzyl alcohol was observed. The phthalic anhydride did not react, even at room temperature. The undecalactone reacted very slowly at room temperature, giving the corresponding diol.

Hydrogenolysis of Electron-Rich Carbonyl Compounds. The following preparative procedures for hydrogenolysis of anthraquinone to anthracene are representative.

Method a (with BMS). This reduction was accomplished, with the general hydroboration procedures previously reported, by dissolving the compound (124 mg, 0.6 mmol) in tetrahydrofuran–benzene (1:1, 6 mL) and by adding, with stirring, BMS (0.08 mmol). The solution was stirred at 30–40 °C for 5 h. At the end of stirring, methanol (0.3 mL) was added and the solvent evaporated in vacuo. The residue was chromatographed on a silica gel column (6 g). By elution with hexane–ethyl ether (80:20), anthracene (72 mg, 70% yield), identical to an authentic sample (R_f value, melting point), and anthraquinone (24 mg, 25% yield) were obtained.

Method b (with Diborane Developed from Sodium Borohydride and Iodine). The compound (124 mg, 0.6 mmol) was dissolved in tetrahydrofuran-benzene (2:1, 12 mL), and the gaseous diborane [generated externally as described[7] using sodium borohydride (840 mg) and iodine (2.8 g)] was bubbled for 1 h in the reaction vessel at 50 °C with stirring. After 2.5 h of additional stirring, the reaction was stopped and the mixture worked up. By chromatography of the crude mixture on a silica gel column (6 g) eluting with hexane–ethyl ether (80:20), anthracene (68 mg, 66% yield) and anthraquinone (31 mg, 30% yield) were obtained. The reduction of aldehydes VIII and IX was accomplished with BMS according to method a using tetrahydrofuran as the only solvent. The crude reaction mixture was chromatographed on a silica gel column eluting with benzene–ethyl ether (90:10), and the reaction products were recognized by NMR spectroscopy and TLC comparison with authentic samples.

Registry No.—VIII, 100-10-7; **IX,** 120-14-9; BMS, 13292-87-0; *p*-nitrobenzoyl chloride, 122-04-3; benzyl chloride, 100-44-7; anthraquinone, 84-65-1; diborane, 19287-45-7.

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(2) A selective reduction to allylic alcohols is otherwise possible by using butane derivatives with a greater steric crowding, such as the 9-BBN.[3]

(3) C. M. L. Gragg, "Organoboranes in Organic Synthesis", Marcel Dekker, New York, N.Y., 1973, p 171; S. Krishnamurthy and H. C. Brown, *J. Org. Chem.*, **40**, 1865 (1975).

(4) J. K. Norymberski and G. F. Woods, *J. Chem. Soc.*, 3426 (1955).

(5) Reference 3, p 331.

(6) We presume, reasonably, that the BMS used would be practically free from BF_3, since we observed a very slow reaction of this reactive with epoxides and lactones, which are both very sensitive to the presence of BF_3,[1a] whereas an effective and fast reaction took place after the addition of a catalytic drop of BF_3.

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(10) A quantity of tetrahydrofuran higher than in method a was used to assure a satisfactory solubility of the gaseous diborane, which is little soluble in benzene.

Correlation of σ^+ and σ^- Substituent Constants with Carbon-13 Shieldings of β Carbons of Para-Substituted β,β-Dichlorostyrenes

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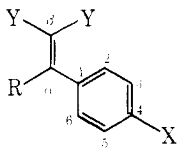
Received August 25, 1977

Carbon-13-NMR spectroscopy is an especially valuable tool for studying the electronic properties of aromatic systems.[1] Of particular interest are four recent reports in which the ^{13}C-NMR spectra for various para-substituted styrene derivatives (**1–5**) were presented.[2–4] For the substituted β,β-dicyanostyrenes (**4a–f**) an excellent linear correlation was found for the chemical shifts of the β carbons and σ^+ substituent constants[5] ($\rho = 5.97$; $r = 0.995$).[3] Likewise a correlation of δ ($^{13}C_\beta$) and the Brown–Okamoto σ^+ values[5] proved to be very successful ($\rho = 3.37$; r = 0.998) for the β-nitrostyrenes **5a–f.**[4] During the course of another study,[6] a number of para-substituted β,β-dichlorostyrenes (**6a–f**) were synthesized and analyzed by ^{13}C-NMR spectroscopy, the interesting results of which are discussed in this report.

Results and Discussion

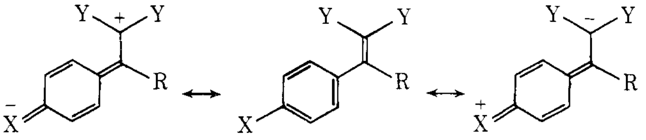
Table I collects the ^{13}C-NMR chemical shifts for compounds **6a–f**; shielding assignments were made on the basis of relative signal intensities and general substituent effects established for substituted benzenes.[7] When the β ^{13}C chemical shifts for the β,β-dichlorostyrenes (**6a–f**) are plotted as a function of σ^+ substituent constants, a straight line is obtained ($r = 0.989$) with a ρ of 4.35. When the data for the styrenes (**1a–f**)[2a] or the α-methylstyrenes (**2a–d,f**)[2b] are subjected to a similar treatment, results ($\rho = 4.55$, $r = 0.983$ and $\rho = 3.47$, $r = 0.974$, respectively) analogous to those found for **6a–f** are obtained. The low correlation coefficients found for **1, 2,** and **6** are in marked contrast to the results found for **4** and **5.** Examination of the plots reveals that the poor correlations observed for **1, 2,** and **6** are attributable to the points for the 4-cyano and 4-nitro substrates.



1, Y = R = H
2, Y = H; R = CH_3
3, Y = H; R = $C(CH_3)_3$
4, Y = CN; R = H
5, Y = NO_2, H; R = H
6, Y = Cl; R = H

a, X = H; b, X = CH_3; c, X = OCH_3; d, X = Cl;
e, X = CN; f, X = NO_2

In order to rationalize the above observations, it is necessary to consider that a para substituent on the aromatic ring of a styrene system can direct via resonance the distribution of the π electrons in either of two ways: (1) the substituent can *donate* the electrons to the ethylenic bond such that the β carbon acquires enhanced electron density (as in A), or (2) the substituent can *accept* electrons from the ethylenic bond with the



B A

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Table I. Carbon-13 NMR Chemical Shifts for Para-Substituted β,β-Dichlorostyrenes 6

Compd	X	Registry no.	C-1	C-2	C-3	C-4	C-5	C-6	C_α	C_β	C_X
6a	H	698-88-4	133.3	128.6	128.4	128.4	128.4	128.6	128.4	120.9	
6b	CH_3	4714-37-8	130.5	128.5	129.1	138.4	129.1	128.5	128.5	119.9	21.2
6c	OCH_3	41448-64-0	125.8	130.1	113.9	159.6	113.9	130.1	128.2	118.5	55.1
6d	Cl	5263-17-2	134.2	129.8	128.6	131.6	128.6	129.8	127.3	121.6	
6e	CN	65085-94-1	137.5	129.1	132.2	111.8	132.2	129.1	127.1	124.4	118.4
6f	NO_2	5281-22-1	139.6	129.4	123.7	147.1	123.7	129.4	126.8	125.2	

Table II. Dual Substituent Parameter Treatment for β Carbons of Para-Substituted β,β-Dichlorostyrenes

σ_R type	$\rho_I{}^p$	$\rho_R{}^p$	SD	f^a
σ_R(BA)	5.0	6.3	0.13	0.05
$\sigma_R{}^0$	4.8	7.8	0.20	0.08
$\sigma_R{}^+$	5.4	3.9	0.24	0.10
$\sigma_R{}^-$(A)	2.9	5.8	0.49	0.19

[a] For a comparison of f with standard correlation coefficients (r), see P. R. Wells, S. Ehrenson, and R. W. Taft, "Progress in Physical Organic Chemistry", A. S. Streitwieser, Jr., and R. W. Taft, Ed., Wiley, New York, N.Y., 1968, p 147. For the β,β-dichlorostyrenes **6**, the plot employing both σ^+ and σ^- values gives f = 0.07, whereas when the standard σ constants are utilized, f = 0.13.[14]

effect that the β carbon assumes partial positive character (as in B). In addition, the electronic properties of the β substituents Y should greatly influence the distribution of the π electrons for styrene derivatives.

For the β,β-dicyanostyrenes **4** the contribution of the resonance hybrid B is very minor since the strongly electronegative cyano groups severely destabilize the adjacent electropositive β carbon; thus only hybrid A is important and hence the excellent correlation for the β ^{13}C-NMR shieldings and σ^+ substituent constants.[3] The same argument holds for the β-nitrostyrenes **5**. For the β,β-dichlorostyrenes **6** the situation should not be so restrictive; the geminal electronegative chlorines attached to the β carbon can stabilize the adjacent carbanionic nature of A via induction, but the chlorines should also be able to stabilize the adjacent carbocationic nature of B via resonance.[8] The latter consideration suggests that σ^- constants be utilized in the Hammett treatment for those substrates bearing substituents capable of accepting electrons via resonance (e.g., cyano and nitro). Indeed, when the β ^{13}C-NMR chemical shifts for **6a–f** are plotted against σ^+ or σ^- (Figure 1) a straight line is obtained (r = 0.998) with a ρ of 3.43.[9] A similar analysis for **1a–f** and **2a–d,f** yields correlation coefficients of 0.995 and 0.996 and ρ values of 3.61 and 2.74, respectively.

Clearly, the combined use of σ^+ and σ^- constants provides a considerable improvement to the use of σ^+ constants alone for evaluating the electronic properties of styrenes **1**, **2**, and **6** by ^{13}C-NMR spectroscopy.[10] The utilization of σ^+ and σ^- constants on the same abscissa is justifiable since σ^- constants are reasonable extensions of σ^+ constants for electron-withdrawing substituents in which the inductive effects are augmented by resonance.[11] Thus, both resonance hybrids A and B are important contributors to the electronic structures of styrenes **1**, **2**, and **6**. Furthermore, the fact that for both the parent styrene system 1 (Y = H) and the β,β-dichlorostyrene system 5 (Y = Cl) the ^{13}C chemical shifts of the β carbons can be satisfactorily correlated jointly with σ^+ and σ^- substituent constants indicates that both hydrogen and chlorine are capable of stabilizing the charge localization of either polarity (negative for A or positive for B) at the β carbons.

In the addition to the combined σ^+, σ^- approach presented above, a dual substituent parameter (DSP) treatment was carried out in order to determine the correlation between the chemical shifts of the β carbons and the combined inductive (I) and resonance (R) effect expression (eq 1):[12]

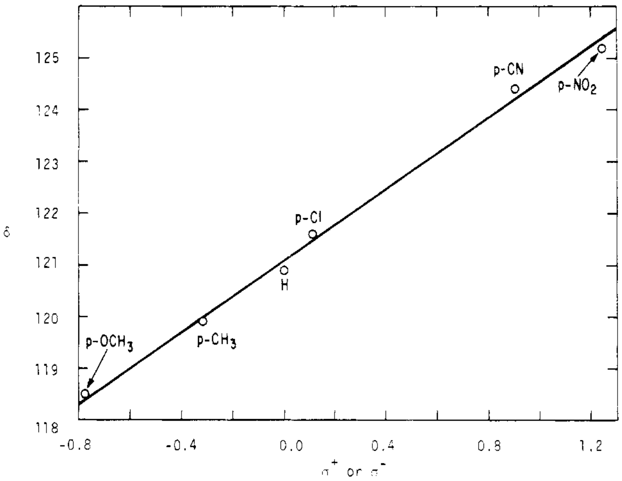

Figure 1. Hammett plot for β carbons of β,β-dichlorostyrenes.

$$P^i = I^i + R^i = \sigma_I\rho_I{}^i + \sigma_R\rho_R{}^i \qquad (1)$$

For eq 1, P is a substituent property (in the present situation, the portion of the chemical shift of the β carbon due to the substituent); i is the index of the position of the substituent (in the present case the substituents are located para to the β,β-dichloroethylene moiety); $\rho_I{}^i$ and $\rho_R{}^i$ are the susceptibility or mixing coefficients and depend on the position of the substituent, the nature of the measurement at the detector center (i.e., the β carbon), and the conditions of solvent and temperature; σ_I and σ_R are the substituent constants. There are four types of σ_R values: σ_R(BA), $\sigma_R{}^0$, $\sigma_R{}^+$, and $\sigma_R{}^-$(A).[12] The substituted benzoic acid based constants, σ_R(BA), gave the best correlation ($f \equiv$ SD/rms = 0.05) with the chemical shifts of the β carbons.[13,14] However, the $\sigma_R{}^0$ and $\sigma_R{}^+$ constants also gave satisfactory correlations (f = 0.08 and 0.10, respectively).[14,15] Complete results of the DSP treatment are summarized in Table II.

The excellent correlation of the ^{13}C chemical shifts with eq 1 using σ_R(BA) suggests that standard σ constants might also give a satisfactory fit for **6a–f.** Such an analysis gives a ρ value of 5.91 with a correlation coefficient of 0.991 which is substantially poorer than that achieved when both σ^+ and σ^- constants are employed.[16]

Experimental Section

The β,β-dichlorostyrenes utilized in the present study were prepared by the decarboxylation of the corresponding β lactones which were synthesized by the cycloaddition of the dichloroketene with the appropriate monosubstituted benzaldehyde.[6] Compounds **6a–d,f** were previously known,[17] while **6e** was recently characterized.[6]

Carbon-13 NMR spectra were measured with a Varian CFT-20 spectrometer utilizing ^{1}H decoupling at 80 MHz and simultaneous ^{13}C observation at 20 MHz; the concentrations were approximately 1 g of substrate per 2 mL of $CDCl_3$ with internal Me_4Si as the reference.

Acknowledgment. The author thanks Dr. E. A. Williams, Mr. J. D. Cargioli, and Mrs. C. W. Joynson for obtaining the ^{13}C-NMR spectra and Professor R. W. Taft and Dr. J. Bromilow for carrying out the DSP analyses.

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(8) For a recent report dealing with the ambident nature of heteroatoms see W. P. Meyer and J. C. Martin, *J. Am. Chem. Soc.*, **98,** 1231 (1976).

(9) Pertinent data for five meta-substituted β,β-dichlorostyrenes have also been obtained;[6] inclusion of these points in the analysis gives $\rho = 3.51$ and $r = 0.996$.

(10) The α-*tert*-butylstyrene system (**3**) gives only poor correlations upon Hammett analysis, presumably on account of severe effects precluding the attainment of coplanarity[2a] of the aryl and the 2-(3,3-dimethyl)butenyl groups.

(11) See also the related discussion in ref 5.

(12) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, "Progress in Physical Organic Chemistry", Vol. 10, A. S. Streitwieser, Jr., and R. W. Taft, Ed., Wiley, New York, N.Y., 1973, Chapter 1.

(13) Ideally, the minimum basis set should also include data for the NR_2 (R = H or CH_3) and F substituents in order to minimize accidental correlatiins between substituent σ_I and σ_R values.[12] However, the absence of these two data points should not be serious since an entire range of substituents (i.e., OCH_3 to NO_2) is utilized.

(14) Correlations of good precision are those for which $f \leq 0.1$.[12]

(15) The fact that satisfactory correlations are achieved with three different sets of substituent constants is not uncommon;[12] see also J. Hine, "Structural Effects in Equilibria in Organic Chemistry", Wiley, New York, N.Y., 1975, pp 79–81.

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Epoxidation of Allenic Phosphonic Acids. Intramolecular Trapping of Allene Oxides[1]

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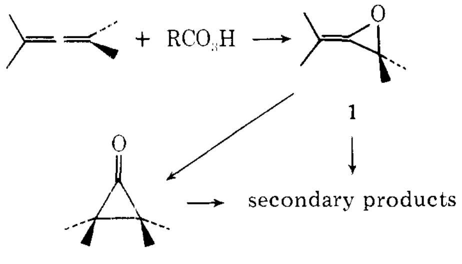
Received December 6, 1977

The epoxidation of allenes has intrigued several groups of investigators over the last decade. Allenes readily react with peracids to give complex mixtures of products which can be rationalized as arising from allene oxides (1) and their cyclopropanone isomers (2).[2] The rearrangement of 1 to 2, as well as some of the subsequent reactions of 1 and 2, have been postulated to involve oxyallyl zwitterion 3[3] (or its conjugate acid), although recent CNDO/2 calculations suggest another lower energy path for the rearrangement.[4] In two cases, the allene oxides themselves have been isolated.[5] For example, the monoepoxide of 1,3-di-*tert*-butylallene can be isolated, and it rearranges cleanly to 2,3-di-*tert*-butylcyclopropanone with a half-life of ca. 5 h at 100 °C.[5a] The gas-phase reaction of allenes with ground state oxygen atoms has also been rationalized in terms of allene oxides, cyclopropanones, and oxallyl radicals.[6]



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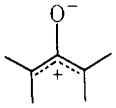

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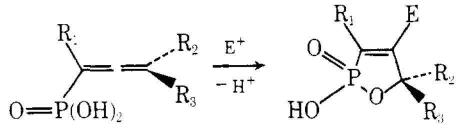
We recently reported that allenic phosphonic acids (4) react with electrophiles such as Brönsted acids, bromine, or mercuric salts to form oxaphospholene.[1,7,8]

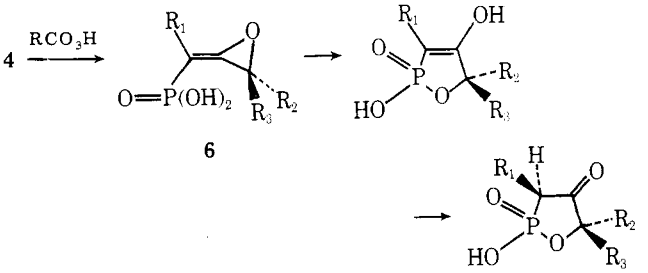


4 5

a, $R_1 = H$; $R_2 = R_3 = CH_3$

b, $R_1 = R_2 =$ *tert*-butyl; $R_3 = H$

From these studies it seemed likely that reaction of 4 with peracids would lead to allene oxide 6, which might rapidly and cleanly isomerize to 4-keto-1,2-oxaphospholane 7.[9]



7

Results and Discussion

When a 20% excess of peracetic acid[10] was added to an aqueous solution of **4a**[7] at 25 °C, ^{1}H NMR indicated 50% consumption of the starting material after 1.8 h. Two major products were formed: acetone (δ 2.21 (s))[11] and A [δ 1.44 (s, 6 H), 2.84 (d, J = 14 Hz, 2 H)[13]] in the ratio 1:3. After 6.3 h, 20% of the starting material remained, and two additional products, B [δ 1.38 (s, 6 H), 3.39 (d, J = 22 Hz, 2 H)[13]] and C [δ 2.98 (d, J = 22 Hz)[13]], had formed such that the four products were present in essentially equal amounts.[14] After 24 h, starting material (10%) remained, along with A (7%), acetone (20%), B (37%), and C (26%).

Reaction of **4a** with a threefold excess of *m*-chloroperbenzoic acid[15] in chloroform[16] resulted in complete conversion to a stable[17] mixture of A and acetone (3:1) after 5.6 h at 25 °C. Extraction with water gave a solution of A, which hydrolyzed quantitatively to B with a half-life of 20 h at 25 °C. Addition of 1.2 equiv of peracetic acid to the solution of B gave C and acetone in essentially equal amounts, with a comparable half-life. Unfortunately, attempts to isolate A, B, and C from these aqueous solutions gave viscous oils whose NMR spectra suggested that polymerization had occurred.

We have previously shown[18] that phosphonic acids can be esterified with diasomethane (8) and under certain conditions carboxylic acids in water may be similarly esterified.[19] The solutions of A, B, and C were separately treated with 8 (large excesses being required for aqueous solutions). Although A and C led to complex mixtures of products, B was esterified

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