Hz, CH(CF₃)₂] and complex grouping at 2.5–3.5 for aryl H of approximate area 4; ¹⁹F (external reference) at 84.3 ppm [doublet, J_{HF} = 8.5 Hz, CH(CF₃)₂].

Anal. Calcd for C₁₀H₅F₆NO: C, 44.62; H, 1.87; N, 5.21; F, 42.35. Found: C, 45.01; H, 2.12; N, 5.27; F, 42.31.

A sample of **15** was treated with excess methanol. After the exothermic reaction had subsided, excess methanol was evaporated and the residue of urethan **16** was recrystallized twice from petroleum ether: mp 74–75°; ir 3.08 (NH), 3.27, 3.32, and 3.36 (CH), 5.93 (C=O), 6.29 and 6.70 (aromatic C=C), 6.54 μ (urethan); nmr (saturated CCl₄) H′ at τ 6.38 (singlet, 3, OCH₃),

5.22 [septet, 1, J_{HF} = 8 Hz, CH(CF₃)₂] and complex multiplet at 2.1–2.9 for aryl H and NH (area 5). Addition of CF₃CO₂H moved NH (area 1) to τ 1.81, separate from unsymmetrical aryl H (area 4).

Anal. Calcd for C₁₁H₉F₆NO₂: C, 43.86; H, 3.01; N, 4.65; F, 37.85. Found: C, 44.28; H, 3.40; N, 4.76; F, 37.70.

Structure Assignments in Polysubstituted Ethylenes by Nuclear Magnetic Resonance[1a]

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An nmr technique is described by which structures can be assigned to many di- and trisubstituted ethylenes simply from a knowledge of the vinyl proton resonance positions in the compound under study. The technique depends on the additivity of vinyl substituent shielding effects on the vinyl protons present. Tables of substituent shielding constants (σ values) for several common functional groups are presented, and various methods for obtaining σ values are outlined. Solutions to several structural assignment problems are presented, including cases in which steric and electronic interactions between substituents must be taken into account.

This paper describes a nuclear magnetic resonance technique by which geometric structures can be assigned to a wide variety of di- and trisubstituted ethylenes. The only data required on the compound under study are the resonance positions of its vinyl protons.

The principles underlying this technique were outlined several years ago by Goldstein and coworkers in a series of papers on the origin of nmr shielding effects.[2] The "differential shielding" method of Jackman and Wiley[3] which is also based on these principles provides only the relative vinyl proton chemical shifts in related *cis-trans* isomers. The procedure developed here will predict absolute vinyl proton resonance positions in all mono-, di-, and trisubstituted isomers, and complements existing methods for assigning configurations to *cis* and *trans* isomer pairs based on the magnitude of H–H coupling constants.[4]

The method is based on the independence and additivity of vinyl substituent shielding effects,[1] a concept simultaneously evolved by Pascual, Meier, and Simon.[5] However, the model compound technique described in the latter part of this paper greatly improves the ability of the method to differentiate between

closely related polysubstituted ethylenes in which specific steric and electronic interactions between functional groups occur.

The structure assignment method applies in its simplest form to those ethylenes which can be pictured as being constructed from a relatively open, rigid >C=C< rack and a set of small, symmetrical substituents. The substituents must cause relatively little distortion of the molecular framework when attached to the ethylenic backbone, and be able to assume a geometry relative to the vinyl protons which is unaffected by the introduction of other functional groups. Such substituents will generally be smaller in size than Br, and have threefold (C₃) or greater symmetry with respect to rotation about the bond joining them to the ethylenic backbone.

Goldstein showed[2] that, in several simple ethylenes, introduction of such symmetrical substituents caused characteristic shifts in the nmr positions of nearby vinyl protons. It turns out that in a molecule bearing a number of symmetrical substituents the total shielding experienced by a vinyl proton is simply the sum of the shielding effects exerted by all the substituents present. The resonance position of the vinyl proton in such molecules (**1**) can be accurately calculated from eq 1.

$$
\begin{array}{cc}
X_{cis} & H \\
\diagdown & \diagup \\
& C{=}C \\
\diagup & \diagdown \\
Y_{trans} & Z_{gem}
\end{array}
$$
1
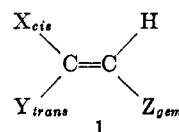
$$\delta_{ppm} = -5.27 + \sigma_{cis-X} + \sigma_{trans-Y} + \sigma_{gem-Z} \qquad (1)$$

In this equation −5.27 ppm represents the resonance position of CH₂=CH₂[6,7] and σ_{cis-X}, $\sigma_{trans-Y}$, and σ_{gem-Z}

(1) (a) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Division of Organic Chemistry, Abstracts of Papers, S24. Taken in part from Chapter VI of the Ph.D. Thesis of S. W. T., University of Wisconsin, Jan 1965. (b) National Institutes of Health Predoctoral Fellow, University of Wisconsin, 1961–1964.

(2) (a) E. B. Whipple, J. H. Goldstein, and L. Mandell, *J. Amer. Chem. Soc.*, **82**, 3010 (1960); (b) E. B. Whipple, J. H. Goldstein, and G. R. McClure, *ibid.*, **82**, 3811 (1960); (c) G. S. Reddy, J. H. Goldstein, and L. Mandell, *ibid.*, **83**, 1300 (1961); (d) G. S. Reddy and J. H. Goldstein, *ibid.*, **83**, 2045 (1961); (e) E. B. Whipple, W. E. Stewart, G. S. Reddy, and J. H. Goldstein, *J. Chem. Phys.*, **34**, 2136 (1963).

(3) (a) L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," The Macmillan Co., New York, N. Y., 1959, pp 119–125; (b) L. M. Jackman and R. H. Wiley, *Proc. Chem. Soc.*, 196 (1958); (c) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881, 2886 (1960); (d) ref 3a, pp 729–741.

(4) (a) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Ltd., London, 1966, pp 711–735; (b) P. Laszlo and P. von R. Schleyer, *Bull. Soc. Chim. Fr.*, 87 (1964); (c) J. Niwa, *Bull. Chem. Soc. Jap.*, **40**, 2192 (1967).

(5) C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966).

(6) Vinyl proton resonances for simple ethylenes occur anywhere between −4.0 and −8.0 ppm (below) tetramethylsilane. A saturated 35° solution of CH₂=CH₂ in CCl₄ containing 5 vol. % TMS internal reference resonates at −5.32₃ ppm. Values obtained under different conditions are tabulated in ref 5.

(7) Ethylene is unique in that it bears no vinyl substituents. From an analysis of nmr data on a large number of substituted ethylenes, ethylene is predicted to resonate at −5.27 ± 0.10 ppm.

TABLE I
NMR σ VALUES (PARTS PER MILLION) FOR Br

Structures (left group):

Br,H / C=C / H,H: -5.75^a, -6.36, -5.83

Br,Br / C=C / Br,H: -7.13

CH$_3$,H / C=C / H,H: -4.95^b, -5.75, -4.87

CH$_3$,H / C=C / CH$_3$,H: -4.59^c

CH$_3$,H / C=C / H,H: -5.97^c; NC,H / C=C / H,H: -5.48, -5.79

Structures (center group) with associated σ values:

Structure			
H,H^h / C=C / H,H (-5.32)	-0.43	-0.51	-1.04
Br,H^i / C=C / Br,H (-6.26)	-0.43^f	-0.51	
			-0.87
H,Br^j / C=C / Br,H (-6.59)	-0.23		-0.84
Br,Br^l / C=C / H,H (-6.98)	-0.15	-0.51 -0.64	-1.15
CH$_3$,H / C=C / H,Br (-5.95^c, -6.08)	-0.31		-1.00
CH$_3$,H -5.46^e / C=C / Br,H -5.28	-0.41	-0.51	
CH$_3$,H -5.78^d / C=C / CH$_3$,Br -6.46^e			-1.19
NC,H / C=C / Br,H -6.16	-0.37	-0.49	

-0.33 ± 0.09^g	-0.53 ± 0.04	-1.02 ± 0.11
$\sigma_{cis\text{-}Br}$	$\sigma_{trans\text{-}Br}$	$\sigma_{gem\text{-}Br}$

^{a} R. E. Mayo and J. H. Goldstein, *J. Mol. Phys.*, **14**, 173 (1964). ^{b} A. A. Bothnerby and C. Naar-Colin, *J. Amer. Chem. Soc.*, **83**, 231 (1961). ^{c} G. S. Reddy and J. H. Goldstein, *ibid.*, **83**, 2045 (1961); 40 MHz. ^{d} L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881 (1960); 40 MHz. ^{e} V. S. Watts and J. H. Goldstein, *J. Chem. Phys.*, **42**, 228 (1965). ^{f} The upper number in these sets is obtained by comparing the resonance position of the disubstituted ethylene with that of the monosubstituted derivative. The lower number is obtained by comparing the resonance position of the disubstituted ethylene with that of the trisubstituted derivative. Chemical shifts without literature references were obtained on a Varian Associates A56/60 spectrometer on 5–10 vol. % solutions in CCl$_4$ or CDCl$_3$ at 35° with 2% tetramethylsilane internal standard and side-band bracketing of resonance positions. ^{g} The indicated uncertainty is the root mean square deviation of the individual σ values from the mean. See H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," 2nd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1956, pp 504–516. Registry numbers are as follows: ^{h} 74-85-1. ^{i} 593-92-0. ^{j} 590-12-5. ^{k} 2597-45-7. ^{l} 590-11-4.

are the shielding constants of X, Y, and Z from the *cis*, *trans*, and *gem* substituent locations.[8-12]

(8) The independence and additivity of nmr shielding effects apply to other open, rigid framework systems. The magnitude of the substituent effects depends, of course, on the nature of the molecular framework. The first study of the additivity principle was carried out on polysubstituted methanes by Shoolery.[9] Additivity has since been demonstrated with varying degrees of success for several other systems.[10-12]

(9) (a) J. N. Shoolery, Technical Information Bulletin, Vol. 2, No. 3, Varian Associates, Palo Alto, Calif., 1959, pp 4-6; (b) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, pp 87-89; (c) H. Primas, R. Arndt, and R. Ernst, *Advan. Mol. Spectrosc.*, 1246 (1962).

(10) R. F. Zurcher, *Helv. Chim. Acta*, **46**, 2054 (1963).

(11) P. L. Corio and B. P. Dailey, *J. Amer. Chem. Soc.*, **78**, 3043 (1956); (b) J. S. Martin and B. P. Dailey, *J. Chem. Phys.*, **39**, 1723 (1963); (c) G. W. Smith, *J. Mol. Spectrosc.*, **12**, 146 (1964).

(12) (a) K. Takahashi, T. Sone, Y. Matsuki, and G. Hasato, *Bull. Chem. Soc. Jap.*, **38**, 1041 (1965); (b) K. Takahashi, I. Ito, and Y. Matsuki, *ibid.*,

Actually, additivity in functional group shielding effects is not altogether surprising. The composition of each substituent on a molecule, its distance and orientation relative to a nearby proton, and the nature of the framework connecting the substituent and the proton are the critical molecular factors which determine the magnitude of the nmr shielding effect produced by each substituent on that proton, *whatever* the shielding mechanism.[13]

40, 605 (1967); (c) S. Gronowitz and R. A. Hoffman, *Ark. Kemi*, **16**, 539 (1960).

(13) Reference 4a, pp 120-151, gives mathematical models of various nmr shielding processes. The additivity principle breaks down when specific steric and electronic interactions between substituents occur. When such interactions are properly taken into account the utility of the additivity principle is preserved (see below).

For each small symmetrical functional group X three vinyl shielding values can be established. These σ values depend on the chemical constitution of X and its location relative to the vinyl proton in question. $\sigma_{cis\text{-}X}$, $\sigma_{trans\text{-}X}$, and $\sigma_{gem\text{-}X}$ are defined as the average parts per million shifts in resonance position of a vinyl proton caused by introducing X *cis*, *trans*, or *gem* to that proton. One set of σ values can be estimated by comparing the totally analyzed ABC spectrum of a monosubstituted ethylene $CH_2\text{=}CHX$[14] with ethylene. Taking vinyl bromide from the first line of Table I, we see that introducing a bromine on the ethylene backbone lowers the resonance position of the *gem* proton -1.04 ppm relative to ethylene. Therefore, $\sigma_{gem\text{-}Br} = -6.36 - (-5.32) = -1.04$ ppm. Similarly, $\sigma_{cis\text{-}Br} = -0.43$ and $\sigma_{trans\text{-}Br} = -0.51$ ppm.

Since the totally analyzed spectra of monosubstituted ethylenes are not always available, and because steric and electronic interactions do occur, even between symmetrical substituents, values obtained solely by this method are not always reliable. σ values are best obtained, as shown in Table I, by averaging the apparent shielding effects of a given functional group in a series of compounds bearing substituents of varying size and electron-donating or -withdrawing ability. Note that from all three positions on the ethylenic backbone Br moves the proton resonance downfield, that this effect is greatest from the *gem* position, and that $\sigma_{trans\text{-}Br}$ is significantly greater than $\sigma_{cis\text{-}Br}$.[15] Note also that an average uncertainty of ± 0.1 ppm (6 Hz) for each σ_{Br} value does exist.[16]

Tables II, III, and IV derive the σ values for Cl, CH_3, and CN, three other common small symmetrical substituents. Although the value of $\sigma_{gem\text{-}Cl}$ from Table II is essentially the same as $\sigma_{gem\text{-}Br}$, $\sigma_{cis\text{-}Cl}$, and $\sigma_{trans\text{-}Cl}$ are much smaller in magnitude than the values for Br, and are *not* significantly different.[15] Table III shows that, whereas the *gem* methyl group causes a large downfield shift in vinyl proton resonance,[17a] *cis* and *trans* methyl groups cause equal upfield displacements. The data in Table IV show that the CN group causes a significantly different downfield displacement in the vinyl proton resonance position from each location. Unlike Br and Cl this effect is *smallest* from the *gem* position.[17b]

Taken altogether, the data in Tables I–IV show clearly that irrespective of the sign or magnitude of σ, the effective shielding values of all small symmetrical groups show uncertainties of ± 0.1 ppm depending on the substituent environment. However, within these limits σ values can be treated as constants, readily transferable from one ethylenic compound to another. That this is so is shown in Figure 1. Insertion of the 12 σ values from Tables I–IV into eq 1 faithfully repro-
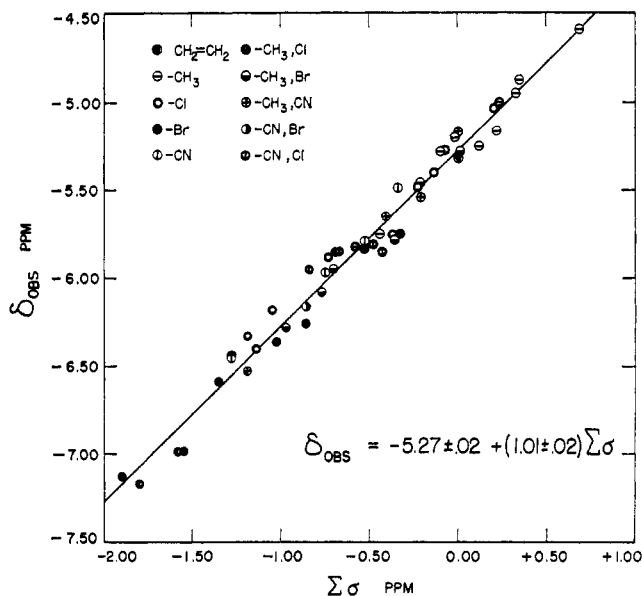

Figure 1.—Plot of the 50 values of δ_{obsd} vs. $\Sigma\sigma$ for the 39 substituted ethylenes in Tables I–IV. The substituents present on the various ethylenes are indicated by the key.

duces the 50 nmr positions of the 39 compounds in the tables.

If the additivity relationship were perfect, the calculated points would all fall on a line of slope 1.00 and pass through -5.32 ppm (ethylene) at $\Sigma\sigma = 0.0$. The best least-squares line through the data actually has slope 1.00 ± 0.02, the mean deviation of the points from this line is ± 0.09 ppm, and, at $\Sigma\sigma = 0.0$, $\sigma = -5.27$ ppm.[6,7] This shows that at least for the compounds used in constructing the tables the additivity approximation is valid. Furthermore, the plot shows that uncertainties in σ values *tend to compensate rather than propagate* when used additively.

The most meaningful assessment of the σ additivity principle simply involves finding out how well compounds having the same substituents and similar resonance positions can be differentiated. For example, *cis*- and *trans*-dichloroethylene resonate at -6.40 and -6.33 ppm. Using the average σ values for Cl in eq 1, *cis*-dichloroethylene is predicted to resonate at -6.39 ± 0.16 ppm, and the *trans* isomer at -6.43 ± 0.14 ppm. Although both the observed resonances lie well within the uncertainty limits set on the predicted values, thus easily fulfilling the *correlation* requirement outlined by Pascual, Meier, and Simon,[5] *differentiation* between the two compounds using σ values alone is not possible.[18] This is due simply to the fact that $\sigma_{cis\text{-}Cl}$ and $\sigma_{trans\text{-}Cl}$ are not significantly different. Actually, the predicted resonance positions are in inverted order from the observed values.

As a general rule, geometric isomers of related polysubstituted ethylenes having resonance positions within 0.2 ppm (12 Hz) cannot be differentiated using σ values alone, owing to the σ uncertainty of ± 0.1 ppm. Outside this limit, the σ additivity principle provides a rapid and reliable method for establishing the proton resonance positions and/or geometric structures of many polysubstituted olefins.

(14) See E. W. Garbisch, Jr., *J. Chem. Educ.*, **45**, 402 (1968), for an excellent discussion of the analysis of three-spin systems.

(15) For a discussion of vinyl halogen shielding effects and nmr data on a few vinyl iodides, see (a) F. Hruska, H. M. Hutton, and T. Schaefer, *Can. J. Chem.*, **43**, 2392 (1965); (b) F. Hruska, D. W. McBride, and T. Schaefer, *ibid.*, **45**, 1081 (1967); (c) R. C. Neuman, Jr., and D. N. Roark, *J. Mol. Spectrosc.*, **19**, 421 (1966).

(16) To minimize uncertainties due to taking literature data from many different sources, data were chosen from recent results obtained at 60 MHz on 5–20 vol. % solutions in CCl₄, CDCl₃, or cyclohexane at 30–35° with internal TMS standard. Some 40-MHz data were necessarily used, and are so indicated.

(17) (a) Possible origins of this remarkable *gem*-CH₃ effect have been investigated by Bothnerby and Naar-Colin. See ref *b*, Table I. (b) See ref 2c for a discussion of the CN group effect.

(18) *cis*- and *trans*-dichloroethylene can be readily differentiated by their H–H coupling constants, obtained from analysis of the ¹³C side-band spectra. See R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.* (London), **A269**, 385 (1962).
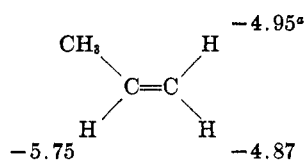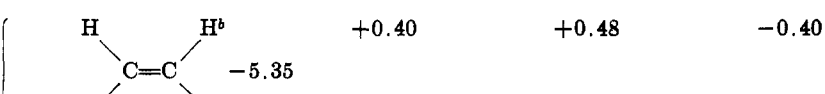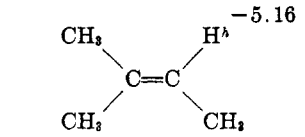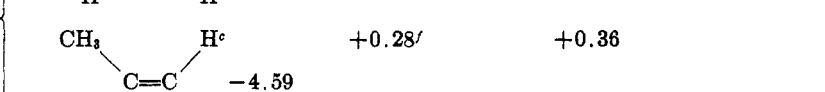
TABLE II
NMR σ VALUES (PARTS PER MILLION) FOR Cl

Reference compounds (left column):

- Vinyl chloride: Cl and H on one carbon (−6.18, H); C=C; H (−5.40^a), H (−5.27)
- Trichloroethylene: Cl, Cl^l on carbons; Cl, H (−6.45)
- Propene (CH₃CH=CH₂): CH₃ (−5.75), H; C=C; H (−4.95^b), H (−4.87)
- Isobutylene: CH₃, CH₃; C=C; H (−4.59^c), H
- Acrylonitrile (NC–CH=CH₂): NC (−5.48), H; C=C; H (−5.97^c), H (−5.79)

Right portion — structures with σ values in three columns ($\sigma_{cis\text{-}Cl}$, $\sigma_{trans\text{-}Cl}$, $\sigma_{gem\text{-}Cl}$):

Structure	$\sigma_{cis\text{-}Cl}$	$\sigma_{trans\text{-}Cl}$	$\sigma_{gem\text{-}Cl}$
H,H C=C H,H (−5.32)	−0.08	+0.05	−0.86
Cl, H^k C=C Cl, H (−5.48, −0.21^i)	−0.21^i	−0.08	−0.97
H, Cl C=C Cl, H (−6.33^d)	−0.15		−0.93
Cl, Cl C=C H, H (−6.40^d, −5.00^c)		−0.12 / −0.22	−1.13
H,H (−5.00^c)	−0.05		
CH₃, H C=C Cl, H (−5.03)	−0.16	−0.05	
CH₃, H C=C H, Cl (−5.88^c, −5.82)	−0.07		−0.93
CH₃, Cl^{e,m} C=C H, Cl (−5.85)		+0.03	
CH₃, H C=C CH₃, Cl (−5.77^d)			−1.18
NC, H^n C=C H, Cl (−7.17^f, −5.81)	−0.33		−1.20
NC, Cl^{g,o} C=C H, H (−5.85, −6.99)		−0.37	−1.20
NC, H C=C Cl, H (−5.95^h, −5.85)	−0.06	+0.02	

	-0.14 ± 0.08^j	-0.09 ± 0.11	-1.05 ± 0.13
	$\sigma_{cis\text{-}Cl}$	$\sigma_{trans\text{-}Cl}$	$\sigma_{gem\text{-}Cl}$

^{a} See Table I, footnote a. ^{b} See Table I, footnote b. ^{c} See Table I, footnote c. ^{d} N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962. ^{e} J_{CH_3-H} = 6.9 Hz. ^{f} J_{H-H} = 14.0 Hz. See F. Scotti and E. J. Frazza, *J. Org. Chem.*, **29**, 1800 (1964). ^{g} J_{H-H} = 7.6 Hz. ^{h} V. S. Watts, G. S. Reddy, and J. H. Goldstein, *J. Mol. Spectrosc.*, **11**, 325 (1963). ^{i} See Table I, footnote f. ^{j} See Table I, footnote g. Registry numbers are as follows. ^{k} 75-35-4. ^{l} 79-01-6. ^{m} 563-58-6. ^{n} 37213-8-8. ^{o} 3721-37-7.

TABLE III

NMR σ VALUES (PARTS PER MILLION) FOR –CH₃

Structures	$\sigma_{cis\text{-}CH_3}$	$\sigma_{trans\text{-}CH_3}$	$\sigma_{gem\text{-}CH_3}$
	+0.40	+0.48	−0.40
	+0.28[f]	+0.36	
			−0.60
	+0.50		−0.30
		+0.09	
		+0.47	−0.41
	+0.12		
	+0.36		−0.48
	+0.27	+0.37	
			−0.37
	+0.37	+0.47	
	+0.41		−0.33
		+0.17	
		+0.31	−0.49
	+0.26		−0.56
	+0.25	+0.32	
	+0.32 ± 0.09[g]	**+0.34 ± 0.10**	**−0.44 ± 0.09**

(Left column structures and chemical shift values:)

CH₃ / H −4.95[a]; C=C; H / H −5.75, −4.87

CH₃ / H[h] −5.16; C=C; CH₃ / CH₃

Cl / H −5.40[b]; C=C; H / H −6.18, −5.27

Cl / H; C=C −5.48; Cl / H

Br / H −5.75[b]; C=C; H / H −6.36, −5.83

Br / CH₃[d]; C=C; H / CH₃ −5.78

NC / H −5.97[c]; C=C; H / H −5.48, −5.79

(Middle column structures and chemical shift values:)

H / H[b] −5.35; C=C; H / H

CH₃ / H[c] −4.59; C=C; CH₃ / H

H / CH₃[c,d] −5.25; C=C; CH₃ / H

CH₃ / CH₃[c,d] −5.28; C=C; H / H −5.88[c]

Cl / H; C=C; H / CH₃ −5.82

Cl / H −5.03[c]; C=C; CH₃ / H −5.00 −5.85[c]

Cl / H; C=C; Cl / CH₃ −5.28[c]

Br / H; C=C; CH₃ / H −5.46 −6.08[c]

Br / H; C=C; H / CH₃ −5.95

NC / CH₃[c]; C=C; H / H −5.17 −6.28

NC / H −6.53[c]; C=C; H / CH₃ −5.22

NC / H −5.65[c]; C=C; CH₃ / H −5.54

[a] See Table I, footnote b. [b] See Table I, footnote a. [c] See Table I, footnote c. [d] See Table I, footnote d. [e] See Table II, footnote e. [f] See Table I, footnote f. [g] See Table I, footnote g. [h] Registry number: 513-35-9.

TABLE IV
NMR σ VALUES (PARTS PER MILLION) FOR -CN

		$\sigma_{cis\text{-}CN}$	$\sigma_{trans\text{-}CN}$	$\sigma_{gem\text{-}CN}$

Left reference structures:

-5.97 H,CN[a] / H,H (C=C) -5.79, -5.48

CH$_3$,H / H,H (C=C) -4.95[b], -5.75, -4.87

Cl,H / H,H (C=C) -5.40[c], -6.18, -5.27

Br,H / H,H (C=C) -5.75[c], -5.83

Structure (shifts)	$\sigma_{cis\text{-}CN}$	$\sigma_{trans\text{-}CN}$	$\sigma_{gem\text{-}CN}$
H,H / H,H -5.32	-0.65	-0.47	-0.16
CH$_3$,H / H,CN -5.22[a], -6.53	-0.78		-0.27
CH$_3$,CN[a] / H,H -6.28, -5.17		-0.43	-0.30
CH$_3$,H / NC,H -5.54[a], -6.53... -5.65	-0.78	-0.59	
Cl,H / H,CN -5.81[d], -7.17	-0.99		-0.41
Cl,CN[e] / H,H -6.99, -5.85		-0.81	-0.58
Cl,H / NC,H -5.85[f], -5.95	-0.68	-0.45	
Br,H / NC,H -6.16[g], -6.46	-0.63	-0.41	
	-0.75 ± 0.10[h]	-0.53 ± 0.12	-0.30 ± 0.12

[a] See Table I, footnote c. [b] See Table I, footnote b. [c] See Table I, footnote a. [d] See Table II, footnote f. [e] See Table II, footnote g.
[f] See Table II, footnote h. [g] See Table I, footnote e. [h] See Table I, footnote g.

Table V illustrates one such case. Even though the methyl group shields both protons equally, $\sigma_{cis\text{-}Br}$ is sufficiently different from $\sigma_{trans\text{-}Br}$ to indicate that the vinyl proton resonance assignments for 2-bromopropene (2) should be the reverse of those indicated in the Varian catalog, spectrum 23.[19]

Table VI illustrates a second case. Hydrolysis of tetrachlorocyclopropene in aqueous ammonia produces a single dichloroacrylonitrile (3) in 25% yield.[20]

(19) (a) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962. (b) N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "NMR Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963.

(20) (a) S. W. Tobey and R. West, *Tetrahedron Lett.*, 1179 (1963); (b) S. W. Tobey and R. West, *J. Amer. Chem. Soc.*, **86**, 56 (1964); (c) S. W. Tobey and R. West, *ibid.*, **86**, 4215 (1964); (d) S. W. Tobey and R. West, *ibid.*, **88**, 2478, 2481 (1966).

This product shows vinyl proton resonance at -7.23 ppm. The β,β-dichloro structure can be eliminated, and 3 can confidently be assigned the *cis*-dichloro structure in preference to the *trans*.

The structure assignment method can also be applied in a straightforward way to ethylenes bearing symmetrical planar substituents such as the phenyl group. The distribution of nuclei and electrons in all planar substituents is markedly different in the plane of the group from that above or below the plane, and the magnetic and electronic properties of all such substituents are inherently anisotropic. Irrespective of the mechanism by which any planar substituent shields nearby protons, this shielding will depend not only on the location of the substituent relative to the vinyl pro-

ASSIGNMENT OF VINYL PROTON RESONANCE
POSITIONS IN 2-BROMOPROPENE (2)

Predicted δ's using
σ values

Literature assignment[e]

$$\delta_{H_A}{}^a = -5.48 \pm 0.10 \text{ ppm}^b$$

$$\delta_{H_B}{}^c = -5.26 \pm 0.14 \text{ ppm}^d$$

[a] $\delta_{H_A} = -5.27 + \sigma_{cis\text{-}CH_3} + \sigma_{trans\text{-}Br} = -5.27 + (+0.32 \pm 0.09) + (-0.53 \pm 0.04) = -5.48 \pm 0.10$. [b] This uncertainty is the square root of the sum of the squares of the uncertainties in the δ values used in calculating δ. See Table I, ref g, p 515. [c] $\delta_{H_B} = -5.27 + \sigma_{trans\text{-}CH_3} = \sigma_{cis\text{-}Br} = -5.27 + (+0.34 \pm 0.10) + (-0.33 \pm 0.09) = -5.26 \pm 0.14$. [d] The correct assignment for 2-bromopropene has previously been deduced from the 1.4- and 0.8-cps cis and trans H–CH₃ coupling constants. See ref 2a. [e] See ref 19.

TABLE VI

ASSIGNMENT OF STRUCTURE TO THE DICHLOROACRYLONITRILE
(3) OBTAINED IN THE AMMONOLYSIS OF
TETRACHLOROCYCLOPROPENE HAVING δ = −7.23

| Structure	Predicted δ, ppm	Observed δ, ppm[a]
	−5.84 ±0.18	
	−6.99 ±0.18	−7.02
	−7.16 ±0.18	−7.23

[a] J. E. Lancaster, American Cyanamid Co., Stamford, Conn., private communication. Registry numbers are as follows. [b] 7436-85-3. [c] 19647-20-2. [d] 3533-66-2.

tons, but also on the time-averaged *angular orientation* of the group relative to the plane of the ethylenic backbone. Since an unsubstituted or *para*-substituted phenyl group has twofold (C₂) symmetry with respect to the bond joining it to the ethylenic backbone, the orientation of such phenyl groups is adequately specified by the dihedral angle between the substituent and ethylenic planes. This angle can have values between 0 and 90° and depends on the steric environment of the phenyl group.

Table VII shows data used to determine the three σ values for a phenyl group in an *uncrowded* environment. Theory and experiment both indicate[21] that protons near the plane of a phenyl group experience a downfield shift in resonance position which decreases quite rapidly with increasing distance of the proton from the ring center, but which is relatively insensitive to the angular location of the proton relative to the ring plane as long as this angle is less than about 20°. The observed σ_PH values in Table VII are consistent with these conclusions. A phenyl group free to lie approximately coplanar with the ethylenic backbone causes a very large

(−1.42 ppm) downfield shift in resonance position of a vinyl proton from the *gem* position, a modest (−0.38 ppm) downfield shift from the *cis* position, but very little shift (∼0.0 ppm) from the *trans* position. Note that in *all* of the polyphenylated ethylenes each phenyl substituent exerts a shielding effect which is indistinguishable from that which a single phenyl group exerts in styrene. This clearly implies that in polyphenylated ethylenes each phenyl group is capable of assuming a time-averaged orientation which is within 20° of the coplanar orientation of the phenyl group in styrene. This conclusion is quite different from that reached by Jackman.[3a]

Superimposed on the magnetic shielding of nearby protons by the phenyl ring is shielding arising from electronic interaction between the ring and C=C π systems. The data on *para*-substituted styrenes in Table VIII show clearly that electron-withdrawing groups (*e.g.*, *p*-NO₂ and *p*-Cl) on the benzene ring lead to enhanced deshielding of all the vinylic protons, and that electron-donating groups (*e.g.*, *p*-OCH₃) cause net shielding. Interestingly, the effect of a *para* substituent is much smaller on the *gem* proton than on the more distant *cis* and *trans* proton, while the effect on these two latter protons is essentially *equal*. These facts suggest
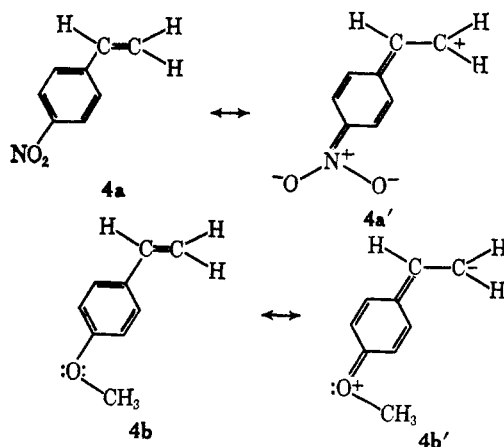
gest that the resonance forms 4' contribute heavily to the interaction between the ring and ethylenic π systems. These interactions alter the electron density only at the β carbon. Protons attached to this center should be affected more than at the α carbon. Because the β protons are symmetrically placed relative to the β carbon, changes in electron density at this center should affect them equally.[22]

Twisting the phenyl group more than about 20° out of the ethylenic plane causes dramatic changes in the shielding effects of this group on nearby protons.[21] This distortion is most easily accomplished by introduction of a bulky substituent *cis* to the phenyl group.[23] As Table IX shows, σ_gem-Ph for the phenyl group in *cis*-β-bromostyrene (5) falls from its normal −1.42 value to −1.09 ppm. Although enforced loss of phenyl coplanarity necessarily decreases resonance interaction of the type 4–4', this is not the major reason for the di-

(21) (a) D. G. Farnum and C. F. Wilcox, *J. Amer. Chem. Soc.*, **89**, 5379 (1967); (b) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958); (c) J. S. Waugh and R. W. Fessenden, *J. Amer. Chem. Soc.*, **79**, 846 (1957), and correction in **80**, 6697 (1958).

(22) See Gurudata, J. B. Stothers, and J. D. Talman, *Can. J. Chem.*, **45**, 731 (1967), and T. A. Wittstruck and E. N. Trachtenberg, *J. Amer. Chem. Soc.*, **89**, 3803 (1967), for additional discussion.
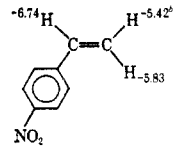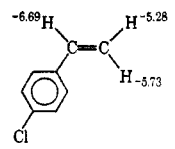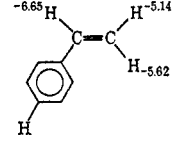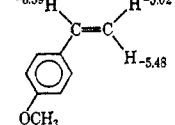
(23) *ortho* substitution on the phenyl ring can also prevent coplanarity. See ref b, Table VIII, and ref f, Table VII.

TABLE VII

NMR σ VALUES (PARTS PER MILLION) FOR A STERICALLY UNCROWDED PHENYL GROUP

Ph—C=C—H[k] (−5.62), −6.65, −5.14

H—C=C—H (−5.32) −0.30 +0.18 −1.33

Ph—C=C—H[l] (−6.94), Ph, Ph

Ph—C=C—Ph[a] +0.10[i] −1.41 ; −0.39 ; −6.55

Ph—C=C—H[a] (−7.10) −0.45 +0.16 −1.48

Ph—C=C—H[m] (−5.40) −0.26 +0.22 ; −1.54

CH₃—C=C—H (−5.05[a]), Ph, H, −5.36

CH₃—C=C—Ph[b] ; Ph, H (−6.78)

CH₃—C=C—H (−4.95[e]) −0.49 −0.10 ; −0.41 ; −5.75, −4.87 ; −1.29

CH₃—C=C—H (−6.24[b]), Ph, H, −6.16

CH₃—C=C—Ph[f] +0.08 ; −6.08

CH₃—C=C—H (−5.49[c]), CH₃, H

CH₃—C=C—H (−6.21[b]), CH₃, Ph ; −1.62

Ph—C=C—Ph[n], H, Cl, −6.85, −6.63[g], −0.07

Ph—C=C—H (−6.63[g]), H, Cl −0.45 −0.07 −1.38

H—C=C—H (−6.18[d]), −5.27, H, Cl, −5.40

H—C=C—H (−6.25[g]), Ph, Cl, −6.78, −6.88, −0.07 −1.61

Cl—C=C—H (−5.48), Cl, H

Cl—C=C—H[o] (−6.75), Cl, Ph ; −1.27

Br—C=C—H (−5.75[d]), H, H, −6.36, −5.83

Br—C=C—H (−7.10[h]), H, Ph, −6.75 ; −0.39 −1.35

	$\sigma_{cis\text{-Ph}}$	$\sigma_{trans\text{-Ph}}$	$\sigma_{gem\text{-Ph}}$
	−0.39 ± 0.08[i]	+0.06 ± 0.12	−1.43 ± 0.12

[a] See Table II, footnote d. [b] H. Rottendorf, S. Sternhell, and J. R. Wilmhurst, *Aust. J. Chem.*, **18**, 1759 (1965). [c] See Table I, footnote c. [d] See Table I, footnote a. [e] See Table I, footnote b. [f] R. van der Linde, O. Korver, P. K. Korver, P. J. van der Haak, J. Veenland, and Th. deBoer, *Spectrochem. Acta*, **21**, 1893 (1965). [g] L. J. Dolby, C. Wilkins, and T. G. Frey, *J. Org. Chem.*, **31**, 1110 (1966). [h] The data reported here are from ref d, Table II. See also ref g, Table VII, and D. T. Witiak and B. P. Chaudhari, *J. Org. Chem.*, **30**, 1467 (1964). [i] See Table I, footnote f. [j] See Table I, footnote g. Registry numbers are as follows. [k] 100-42-5. [l] 58-72-0. [m] 530-48-3. [n] 948-98-1. [o] 698-88-4.

TABLE VIII
EFFECT OF *para* SUBSTITUENTS ON THE NMR
SHIELDING PROPERTIES OF THE PHENYL GROUP

	$\Delta\sigma_{cis\text{-Ph}}{}^a$	$\Delta\sigma_{trans\text{-Ph}}$	$\Delta\sigma_{gem\text{-Ph}}$
NO₂	−0.21	−0.28	−0.09
Cl	−0.11	−0.14	−0.04
H	0.00	0.00	0.00
OCH₃	+0.14	+0.12	+0.06

a $\Delta\sigma$ is the difference in resonance position (ppm) between a vinyl proton in the *para*-substituted styrene and the corresponding vinyl proton in styrene itself. *b* Data for this table taken from R. H. Wiley and T. H. Crawford, *J. Polym. Sci., Part A*, **3**, 829 (1965).
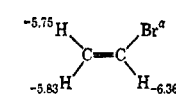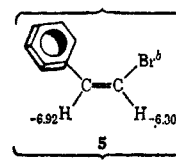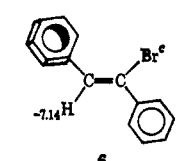
TABLE IX
THE EFFECT OF Br ON σ VALUES FOR
NEIGHBORING PHENYL GROUPS

$\sigma_{gem\text{-Ph}} = -1.09$

$\sigma_{trans\text{-Ph}} = +0.06$

$\sigma_{cis\text{-Ph}} = -0.22$

a See Table I, footnote *a*. *b* See Table VII, footnotes *g* and *h*, and also D. Seyferth, L. G. Vaughan, and R. Suzuki, *J. Organometal. Chem.*, **1**, 437 (1964). The data of L. A. Singer and N. P. Kong [*J. Amer. Chem. Soc.*, **89**, 5251 (1967)] appear to be in error. *c* H. H. Freedman and G. A. Doorakian, The Dow Chemical Co., Eastern Research Laboratory, private communication.

minished $\sigma_{gem\text{-Ph}}$ effect in **5**. A 30° dihedral angle between the phenyl group and ethylenic backbone should decrease resonance interaction between the π systems by only about 15%,[24] and the effects of this perturbation should show up primarily as an altered $\sigma_{trans\text{-Ph}}$ value. No such effect is observed. On the other hand, a 30° dihedral angle should, according to theory,[21] move the *gem*-vinyl proton into a region near the phenyl ring where it will experience essentially *no* magnetic deshielding. We can therefore estimate that the phenyl group *cis* to Br in **5** lies somewhere near 25° out of plane.

Table IX also shows that phenyl *gem* to Br is *not* forced appreciably out of coplanarity. Comparing bromo-*trans*-stilbene (**6**) with **5**, a $\sigma_{cis\text{-Ph}}$ value of −0.22 ppm is obtained. Although this value falls among the lowest entries for $\sigma_{cis\text{-Ph}}$ in Table VII (uncrowded phenyls), it is not significantly different from them. Therefore the conformation of **6** can adequately be pictured as shown in Table IX. The following calculations support this view.

The resonance position of the vinyl proton in bromo-*trans*-stilbene calculated assuming normal σ values for both phenyls is −7.60 ppm. If the phenyl *cis* to Br in **6** is assumed to have the same crowded environment as the phenyl group in **5**, and is assigned a $\sigma_{gem\text{-Ph}}$ value of −1.09, while the phenyl *gem* to Br is presumed to be sterically uncrowded and have a normal −0.38-ppm $\sigma_{cis\text{-Ph}}$ value, **6** is predicted to show vinyl proton resonance at −7.27 ± 0.16 ppm, in satisfying agreement with the −7.14-ppm observed value. In other ethylenes bearing sterically crowded phenyl groups similar perturbation of $\sigma_{gem\text{-Ph}}$ values should be anticipated.

The data and principles outlined above permit rapid confirmation of a number of rather arduously assigned

(24) M. J. S. Dewar, *J. Amer. Chem. Soc.*, **74**, 3345 (1952).

styrene structures. Davis and Roberts have synthesized both isomers of α-methyl-β-bromostyrene, shown in Table X.[25] As pointed out by the original authors the relative magnitudes of $J_{\text{H--CH}_3}$ in the two isomers are *not* a reliable indicator of structure, and the *cis–trans* structure assignments were made on the bases of relative chemical reactivity, mechanism of synthesis, and relative boiling point and uv absorption characteristics. The excellent agreement between the calculated and observed vinyl proton resonance positions provides unambiguous proof of these structures. In this case both the relative and absolute vinyl proton resonance positions help in assigning the structures. In cases where only one isomer is reported the absolute value of the predicted resonance position alone often suffices.

Reed has reported[26] that halogenation of α-methylstyrene with N-chlorosuccinimide provides, in addition to α-chloromethylstyrene, a single α-methyl-β-chlorostyrene (**8**) with the nmr spectrum summarized in Table XI. From the predicted resonance positions **8** can confidently be assigned the *trans* structure. It is instructive to note that $J_{\text{CH}_3\text{--H}}$ in this *trans* compound happens to be the same as $J_{\text{CH}_3\text{--H}}$ in the *cis* Br isomer of **7**![27]

It is, of course, possible to tabulate functional group shielding parameters for an almost endless variety of vinyl substituents. Pascual, Meier, and Simon[5] list 30 vinyl substituents and their σ values, calculated from the spectra of 1070 compounds! It should be noted that the independent compilations of σ values for the substituents Br, Cl, CH₃, CN, and Ph agree very well. Pascual, Meier, and Simon's results are summarized here for convenience in Table XII.

Pascual, Meier, and Simon recognize that specific interactions between vinyl substituents can profoundly alter their effective group σ values. They have con-
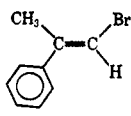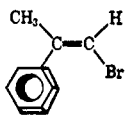
(25) D. R. Davis and J. D. Roberts, *ibid.*, **84**, 2252 (1962).
(26) S. F. Reed, Jr., *J. Org. Chem.*, **30**, 3258 (1965).
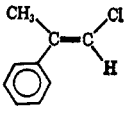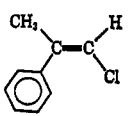(27) See W. A. Nasutavicus, S. W. Tobey, and F. Johnson, *ibid.*, **32**, 3325 (1967), for assignment of structures to several phenyl alkylacrylonitriles using the technique outlined here.

TABLE X
NMR DATA FOR *cis*- AND *trans*-α-METHYL-β-BROMOSTYRENE 7[a]

α-Methyl-β-bromostyrene	δ_{CH_3}, ppm	J_{CH_3-H}, Hz	$\delta_{H_{obsd}}$, ppm	$\delta_{H_{calcd}}$, ppm
7 (trans)	−2.12	1.25 ± 0.04	−6.30	−6.33 ± 0.17
7 (cis)	−1.97	1.50 ± 0.04	−6.03	−5.92 ± 0.19

[a] See ref 25.

TABLE XI
ASSIGNMENT OF STRUCTURE TO THE α-METHYL-β-CHLOROSTYRENE (8) OBTAINED IN NCS CHLORINATION OF α-METHYLSTYRENE

| α-Methyl-β-chlorostyrene 8[b]	$\delta_{H_{calcd}}$, ppm	$\delta_{H_{obsd}}$,[a] ppm
trans	−6.36 ± 0.18	−6.34
cis	−5.94 ± 0.20	

[a] δ_{CH_3} = −2.15, J_{CH_3-H} = 1.51 ± 0.02 Hz. [b] See ref 26.

jugation are present together (conj). The resonance positions for vinyl protons in all compounds containing such substituents are still calculated using eq 1.

We feel this approach is oversimplified. The co-operative shielding properties of two functional groups capable of conjugative interaction can easily be shown to depend *heavily* on the relative geometries of the two substituents. The data in Table XIII illustrate this point for −OCH₃[28] and −CO₂CH₃.[29] Five of the six σ values show variations of more than 0.5 ppm. It seems clear that strong dipole–dipole and steric interactions (in addition to conjugative interactions) must be operating between these highly polar, anisotropic substituents.

TABLE XII
VINYL SUBSTITUENT SHIELDING PARAMETERS AS OBTAINED BY PASCUAL, MEIER, AND SIMON
(δ_H −5.27 + ΣσPPM)

Substituent	σ_{cis}, ppm	σ_{trans}, ppm	σ_{gem}, ppm	Substituent	σ_{cis}, ppm	σ_{trans}, ppm	σ_{gem}, ppm
−H				>C=C< solo[b]	+0.04	+0.21	−0.98
H	0.00	0.00	0.00	conj	−0.08	+0.01	−1.26
CH₃−, C₂H₅−, etc.	+0.26	+0.29	−0.44				
Alkyl ring[a]	+0.33	+0.30	−0.71	−C(=O)− solo	−1.13	−0.81	−1.10
				conj	−1.01	−0.95	−1.06
−Cl	−0.19	−0.03	−1.00				
−Br	−0.40	−0.55	−1.04	−C(=O)OH solo	−1.35	−0.74	−1.00
−CN	−0.78	−0.58	−0.23	conj	−0.97	−0.39	−0.69
−C≡C−	−0.35	−0.10	−0.50	−C(=O)OR solo	−1.15	−0.56	−0.84
−Ph	−0.37	+0.10	−1.35	conj	−1.02	−0.33	−0.68
−CH₂O−, CH₂I	+0.02	+0.07	−0.67	−C(=O)H	−0.97	−1.21	−1.03
−CH₂S−	+0.15	+0.15	+0.53				
−CH₂Cl, −CH₂Br	−0.12	−0.07	−0.72	−C(=O)Cl	−1.41	−0.99	−1.10
−O−alkyl	+1.06	+1.28	−1.18				
−OAr, −O−conj	+0.65	+1.05	−1.14	−C(=O)N<	−0.93	−0.35	−1.37
−OCOR	+0.40	+0.67	−2.09				
−N(alkyl)₂	+1.19	+1.31	−0.69				
−N(Ar)₂, −N(conj)₂	+0.73	+0.81	−2.30				
−SR	+0.24	+0.04	−1.00				
−SO₂R	−1.15	−0.95	−1.58				

[a] The "alkyl ring" increment is used when the C=C bond being studied forms part of a ring. [b] The increment for "R conj" is used instead of the "R solo" value when either the R substituent *or* the double bond being studied is further conjugated with other substituents.

cluded that these perturbations are primarily due to conjugative interaction between substituents.[5] They have attempted to take this into account by listing two sets of σ values for carbonyl and other unsaturated substituents. One set is to be used when such substituents are present alone on the double bond (solo). The other is to be used when two or more groups capable of con-

In general, when two asymmetric (C_s or lower symmetry) substituents are present together on an ethylenic

(28) (a) C. N. Banwell and N. Sheppard [*Mol. Phys.*, **3**, 351 (1960)]; (b) J. Feeney, A. Ledwith, and L. H. Sutcliffe [*J. Chem. Soc.*, 2023 (1962)], and (c) W. Brügell, Th. Ankel, and F. Krückeberg [*Z. Elektrochem.*, **64**, 1121 (1960)] discuss the origin of −OCH₃ shielding effects.

(29) See ref 3a, pp 121–125, and G. J. Karabatsos, G. C. Sonnichsen, N. Hsi, and D. J. Fenoglio, *J. Amer. Chem. Soc.*, **89**, 5067 (1967), for discussion of carbonyl shielding effects.

TABLE XIII

EFFECT OF RELATIVE GEOMETRY AND SUBSTITUENT ENVIRONMENT ON THE APPARENT σ VALUES FOR —CO_2CH_3 AND —OCH_3

Structure (chemical shifts)	OCH_3, ppm cis	OCH_3, ppm trans	OCH_3, ppm gem	CO_2CH_3, ppm cis	CO_2CH_3, ppm trans	CO_2CH_3, ppm gem
CO_2CH_3, H / CH_3O, CO_2CH_3 (−6.10[b])		+0.77[a]		−1.40		−0.49 / −0.82
CO_2CH_3, H•, H, CO_2CH_3 / CH_3O, CO_2CH_3 (−6.87, −6.40, −4.70[b])		+1.50	−0.68	−0.67	+0.03	
H, H / CO_2CH_3[c], H, H (−5.82, −6.20, −5.23, −6.38); H, H / OCH_3[d] (−3.88, −6.43, −4.02)	+1.30 (+1.06)	+1.44 (+1.28)	−1.11 (−1.18)	(−1.15), −1.06, (−1.02)[e]	(−0.56), −0.50, (−0.33)[e]	(−0.84), −0.88, (−0.68)[e]
H, OCH_3 / OCH_3, CO_2CH_3[f] (−6.20, −5.15)	+1.05		−1.17	−1.12	±0.00	−0.88
CH_3O, H / CO_2CH_3, CO_2CH_3[b] (−5.15, −7.55)	+1.05		−1.13		±0.00	

[a] σ values in *italics* denote gross departure from "normal" behavior. Data in parentheses are σ values listed by Pascual, Meier, and Simon[5] for these groups in solo, and conjugative (c) situations. [b] E. Winterfeldt and H. Preuss, *Chem. Ber.*, **99**, 450 (1966). [c] See Table II, footnote d. [d] R. T. Hobgood, Jr., G. S. Reddy, and J. H. Goldstein, *J. Phys. Chem.*, **67**, 110 (1963). [e] Registry number: 624-49-7. [f] Registry number: 624-48-6.

SCHEME I

12a, $\delta_{calcd} = -5.64 \pm 0.09$

12b, $\delta_{calcd} = -6.98 \pm 0.09$

backbone, neither one retains the angular orientation it assumes if present alone. Also, the average orientation and effective σ values of each asymmetric group *vary*, depending on the exact nature and relative location of the other asymmetric group with which it is paired. Therefore, attempts to tabulate σ "constants" for asymmetric substituents that will be of any great use in differentiating between closely related ethylenes are ordinarily fruitless.

In predicting the resonance positions of vinyl protons in trisubstituted ethylenes bearing two asymmetric substituents most of the problems just discussed are avoided by use of a "model compound" approach. A compound is chosen from the literature which bears the asymmetric substituents in the appropriate geometry and environment, and in which the vinyl proton resonance positions can be unambiguously assigned. This model compound is then "transformed" into the desired trisubstituted ethylene by applying the σ value for one of the small, highly symmetric groups listed in Tables I–IV. This procedure automatically takes into account most of the major interactions between asymmetric groups.

The remainder of this paper describes several structural assignment problems which cannot be unambiguously solved using the simple additivity principle, but which can be simply solved using the model compound technique. Where relevant, the chemical implications of the assignments are discussed.

Bromouliginosin-B.—Uliginosin-B (9), an antibiotic isolated from a Central American herb, has been under investigation by a group in this laboratory.[30] The structure of 9 was initially deduced from a painstaking study of its nmr, ir, uv, and mass spectra.[30a] However, it was desired to confirm structure 9 by a single crystal X-ray diffraction study on a heavy atom derivative.[30b] To this end the carbon–carbon double bond in a sample of 9 was brominated in CCl_4 to dibromide 11 and dehydrobrominated in pyridine without purification to provide a single bromouliginosin-B (12) which showed singlet vinyl proton resonance at -7.04 ppm. The nmr spectrum of uliginosin-B includes two doublet resonances ($J_{HH} = 9.9$ Hz) in the vinyl region at -6.65 and -5.31 ppm[30a] which can be unambiguously assigned

to the protons shown in structure 9 by their similarity to those in eriostoic acid (10).[31]

9

10
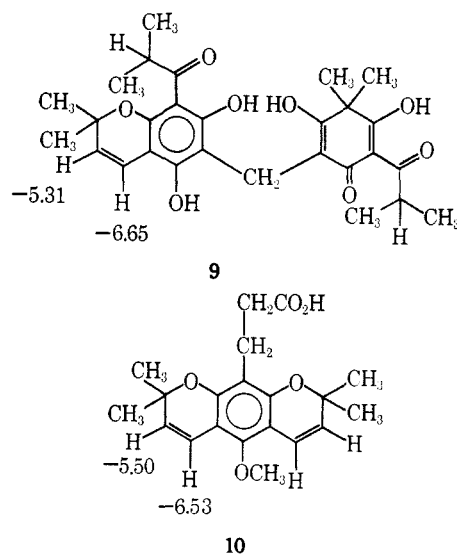
The question arose as to whether the bromine in 12 was α or β to the phenyl ring (12a) or (12b). Mechanisms leading to both derivatives from the intermediate dibromide seemed plausible. E2 abstraction of the acidic α proton by pyridine would lead to 12a *via* a bromobenzylic anion, whereas E1 ionization of α bromine, would lead to 12b *via* a benzylic cation.[32] This problem was quickly laid to rest using the σ additivity principle. (See Scheme I.)

Application of $\sigma_{cis\text{-}Br}$ from Table I (-0.33 ± 0.09 ppm) to the two resonance positions in 9 shows that the vinyl proton in 12a should resonate at -5.64 ± 0.09 ppm, whereas the vinyl proton in 12b should resonate at -6.98 ± 0.09 ppm. This latter value is in excellent agreement with the observed -7.04-ppm value for 12, and the β-Br structure was subsequently confirmed in the X-ray study.

(30) (a) W. L. Parker and F. Johnson, *J. Amer. Chem. Soc.*, **90**, 4716 (1968); (b) W. L. Parker, J. J. Flynn, and F. P. Boer, *ibid.*, **90**, 4723 (1968).

(31) Reference 19, spectrum 344.

(32) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1959, Chapter 12, pp 472–485.

TABLE XIV
ASSIGNMENT OF THE VINYL PROTON RESONANCES IN ATROPIC ACID (13)

$$CH_2=C\begin{smallmatrix}Ph\\\\CO_2H\end{smallmatrix}$$

$$\delta_{H_A\ obsd} = -5.95\ ppm$$
$$\delta_{H_B\ obsd} = -6.52\ ppm$$
$$J_{HH} = 1.5\ Hz$$

A. Using the Differential Shielding Method of Jackman and Wiley[a]

$$\Delta Ph_{cis-trans} = -0.39$$

$$\Delta CO_2H_{cis-trans} = -0.66$$

$$\Delta_{(H_B-H_A)} = -0.66 - (-0.39) = -0.27\ ppm,\ therefore\ H_B\ downfield$$

B. Using Eq 1 and σ Data from Table XII[d]

$$\delta_{H_A\ calcd} = -6.03 \qquad \delta_{H_A\ calcd} = -6.38$$
$$\delta_{H_B\ calcd} = -6.14 \qquad \delta_{H_B\ calcd} = -6.52$$

C. Using β-Methylatropic Acids as Models[f] and σ_{gem-CH_3} Data from Table III

$$\delta_{H_A\ calcd} = -5.96 \pm 0.09 \qquad \delta_{H_B\ calcd} = -6.6 \pm 0.2$$

[a] See ref 3. [b] See Table II, footnote d. [c] See Table I, footnote b. [d] See ref 5. [e] The model compound used in the calculation is shown at the center of each block, along with the resonance position of its key vinyl proton. The vinyl substitutions required to "transform" the model compound into the desired compound are shown by arrows, and the shifts in resonance position of the key vinyl proton caused by such substitution are shown along the arrows. [f] See ref 34.

Atropic Acid.—Atropic acid (13)[33,34a] shows doublet vinyl proton resonances at −5.95 and −6.52 ppm, as shown at the top of Table XIV. Part A of the table illustrates the assignment of these resonances to the appropriate vinyl protons by the "differential shielding" method of Jackman and Wiley.[3] Comparing α-methylstyrene with propene (the standard reference compound used in this method) the phenyl group causes a −0.49-ppm downfield shift in the resonance position of the proton *cis* to phenyl, whereas the resonance position of the proton *trans* to phenyl is only moved downfield

−0.10 ppm. Therefore, according to Jackman and Wiley, the phenyl group exerts a differential (*cis vs. trans*) shielding of −0.39 ppm. By a similar comparison of methacrylic acid with propene, the carboxyl group "differential shielding" is −0.66 ppm. In atropic acid, the β-vinyl protons experience *both* these differential shieldings but in *opposition* to one another. Therefore, one predicts that the proton *cis* to carboxyl in atropic acid will resonate −0.27 ppm (downfield) from the proton *cis* to phenyl. This prediction is qualitatively correct (see below) and serves as the basis for the assignment of the vinyl proton resonances in atropic acid given by Nilsson and Sternhell.[34]

Despite its success in this case the differential shielding method has two drawbacks. First, the differential shielding exerted by a group is always calculated using a model compound in which the group under considera-

(33) Prepared from atrolactic acid following the explicit directions of W. A. Bonner and R. T. Rewick, *J. Amer. Chem. Soc.*, **84**, 2334 (1962), mp 107–108°. The vinyl proton resonances in atropic acid are doublets, J_{HH} = 1.5 Hz. See ref 34a also.
(34) (a) K. Nilsson and S. Sternhell, *Acta Chem. Scand.*, **19**, 2441 (1961); (b) K. Nilsson, *ibid.*, **19**, 612 (1965).

TABLE XV
PREDICTIONS OF THE RESONANCE POSITION FOR THE ETHYL CHLOROALKOXYACRYLATE ESTER **15**
OBTAINED IN THE ETHANOLYSIS OF TETRACHLOROCYCLOPROPENE[a,b]

A. Using Eq 1 and σ Data from Table XIII

B. Using the Model Compound Approach and σ_{Cl} Data from Table II
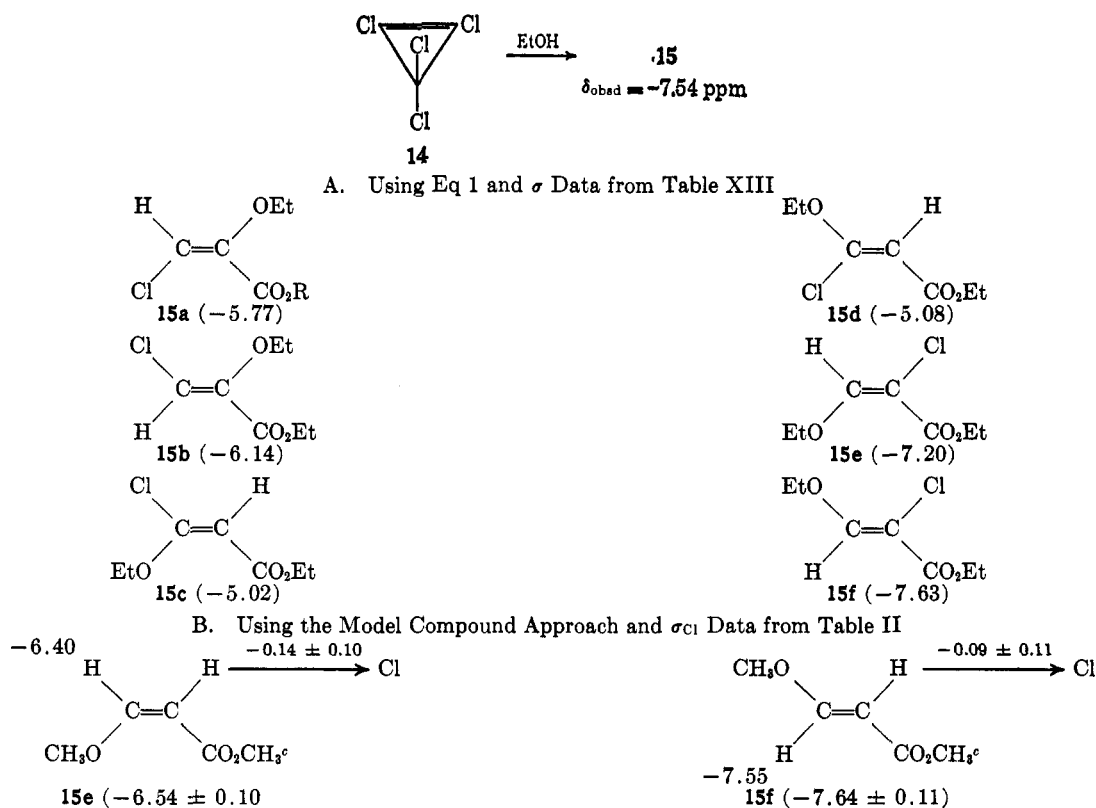
[a] See ref 20. [b] δ_{obsd} values are given in parentheses. [c] See Table XIII, footnote b.

tion is *gem* to $-CH_3$. Since the shielding properties of a group *are* affected by its environment (both steric and electronic), sole reliance on the propenes as model compounds gives a false sense of consistency in group shielding behavior. This deficiency manifests itself in this instance as a grossly underestimated value of the differential shielding (-0.27 ppm calculated *vs.* -0.57 ppm observed). A second and more serious shortcoming of the technique is simply that it fails to make full use of the data at hand. No information on the *absolute* locations of the resonance positions is obtained, despite the fact that all the data required to make such a prediction must be obtained in order to make the differential shielding calculation.

Part B of Table XV shows the vinyl proton resonance positions for **9** predicted using the σ additivity data of Pascual, Meier, and Simon from Table XII.[5] The results of calculations assuming both "solo" and "conjugated" σ values for the $-CO_2H$ group are shown. Definitionally,[5] only the σ_{conj} values should have been employed, since the ethylenic system "stands in conjugation"[5] with the phenyl group. However, the reason for using σ_{conj} values is presumably to take into account conjugative interactions between the $-CO_2H$ and $-Ph$ groups. In atropic acid these groups are *cross*-conjugated rather than conjugated. The fact is that neither set of calculations satisfactorily fits the observed data. One set skews both resonances upfield, the other set downfield.
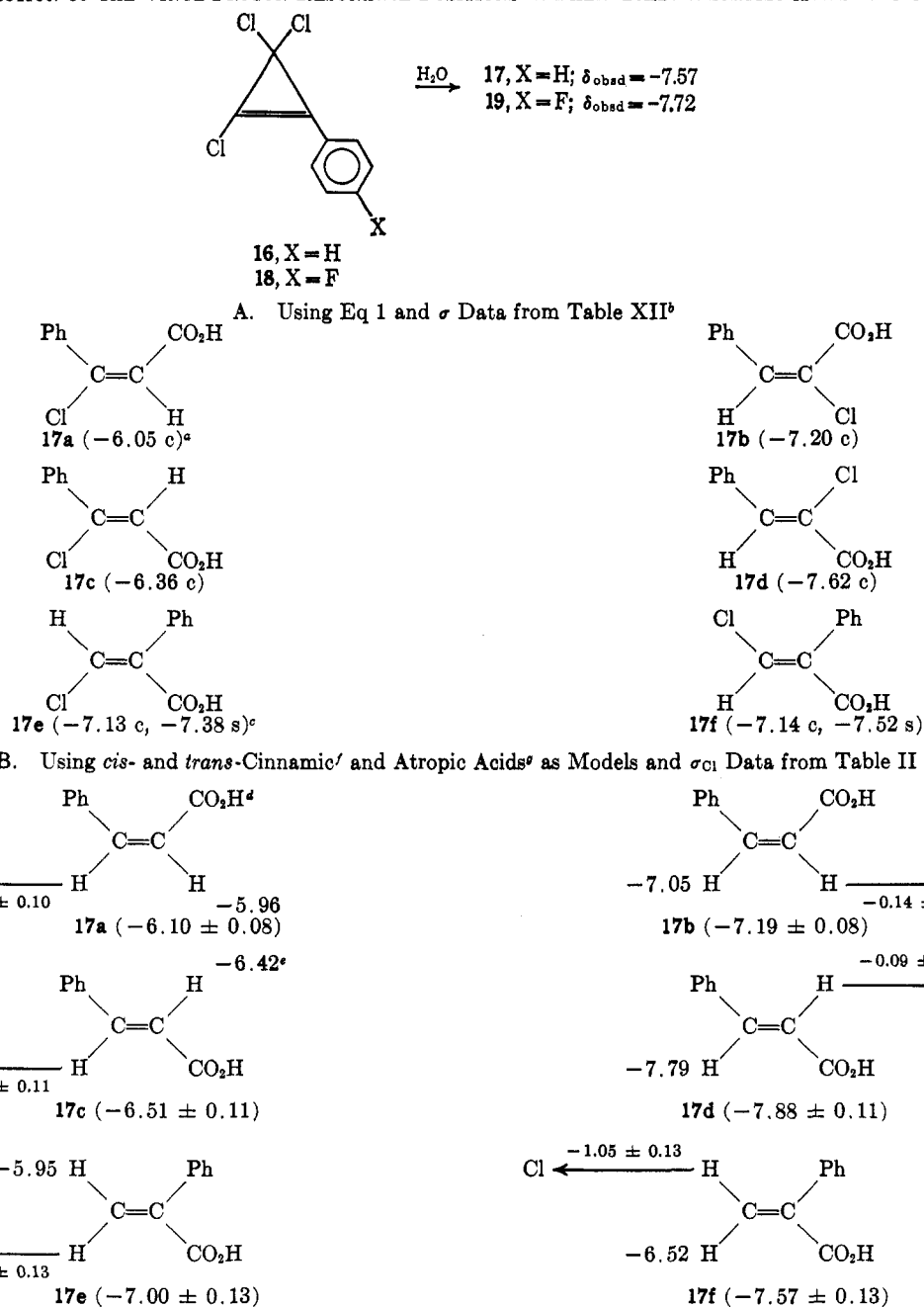
Since the differential between the calculated δ values in each set is sufficiently small, and so far within the (overlapping) uncertainty limits which must reasonably be assigned to each δ, assignment of the observed resonances to the appropriate vinyl protons in atropic acid

using Pascual, Meier, and Simon's method is simply not possible.

The failure of the simple σ additivity calculation derives primarily from its inability to evaluate properly the highly specific interactions which undoubtedly occur between geminal $-CO_2H$ and $-Ph$ groups. For the purposes of the model compound nmr structural assignment technique, illustrated in part C of Table XV, it is not essential to understand in detail either the origin or exact nature of these interactions, but only to appreciate that they exist. Nilsson[34] has unambiguously assigned structures to the *cis* and *trans* β-methylatropic acids used as the models in part C from detailed consideration of their uv, ir (and nmr) spectra. Simply by applying the -0.44 ± 0.09 ppm σ_{gem-CH_3} correction from Table III to the nmr data on the β-methylatropic acids, the proton *cis* to $-Ph$ in atropic acid is predicted to resonate at -5.96 ± 0.09 ppm, in excellent agreement with the -5.95-ppm observed value. Similarly the proton *cis* to $-CO_2H$ is predicted to resonate at -6.6 ± 0.2 ppm in excellent agreement with an observed -6.52-ppm value. The larger uncertainty in this latter prediction arises from the fact that the vinyl proton resonance in the model compound is buried in a broad phenyl resonance region.

Tetrachlorocyclopropene Solvolysis Products.—When tetrachlorocyclopropene (**14**) is solvolyzed in ethanol, one of the minor reaction products is a chloroalkoxyacrylate ester **15** which shows vinyl proton resonance at -7.54 ppm.[20] Given the extent of molecular rearrangement and substitution required to convert **14** into **15**, none of the six possible geometric isomers of **15** can be disregarded as being impossible. Part A of Table XV shows predicted resonance positions for the six

TABLE XVI

PREDICTION OF THE VINYL PROTON RESONANCE POSITIONS IN PHENYLCHLOROACRYLIC ACIDS 17 AND 19[a]

$\xrightarrow{\text{H}_2\text{O}}$ 17, X = H; $\delta_{obsd} = -7.57$
19, X = F; $\delta_{obsd} = -7.72$

16, X = H
18, X = F

A. Using Eq 1 and σ Data from Table XII[b]

17a (−6.05 c)[a]

17b (−7.20 c)

17c (−6.36 c)

17d (−7.62 c)

17e (−7.13 c, −7.38 s)[c]

17f (−7.14 c, −7.52 s)

B. Using *cis-* and *trans*-Cinnamic[f] and Atropic Acids[g] as Models and σ_{Cl} Data from Table II

17a (−6.10 ± 0.08)

17b (−7.19 ± 0.08)

17c (−6.51 ± 0.11)

17d (−7.88 ± 0.11)

17e (−7.00 ± 0.13)

17f (−7.57 ± 0.13)

[a] δ_{calcd} values are given in parentheses.   [b] See ref 5.   [c] c denotes δ_{calcd} using $\sigma_{conj\ CO_2H}$; s denotes δ_{calcd} using $\sigma_{solo\ CO_2H}$.   [d] J_{HH} = 12.9 Hz.   [e] J_{HH} = 16.1 Hz.   See ref 19, spectrum 230 also.   [f] See ref 37.   [g] See ref 33.

possible isomers of 15 using eq 1 and σ_{solo} values from Table XII. The first four structures can be eliminated immediately since the predicted δ values deviate so greatly from the observed resonance position. Bearing in mind the uncertainties in σ values which occur when –OR and –CO$_2$R are present together, 15f (δ_{calcd} = −7.63) would be judged the more likely structure, though 15e (δ_{calcd} = −7.20) could not be excluded.

That structure 15f is indeed correct is demonstrated by model compound calculations shown in part B of the table. Using the Winterfeldt and Preuss data[35] for *cis-* and *trans*-methyl 2-methoxyacrylate and applying corrections for *cis* and *trans* Cl, 15f is predicted to resonate at −7.64 ± 0.11 ppm. On the other hand, 15e is predicted to resonate at −6.54 ± 0.10 ppm, *consider-*

(35) See footnote *b*, Table XIII.

ably removed from both the observed resonance, and the −7.20-ppm resonance position calculated assuming simple σ additivity.

Phenyltrichlorocyclopropene Hydrolysis Products.— Hydrolysis of 1-phenyl-2,3,3-trichlorocyclopropene (16) provides a phenylchloroacrylic acid (17) which shows vinyl proton resonance at −7.57 ppm.[36] Hydrolysis of 1-*p*-fluorophenyl-2,3,3-trichlorocyclopropene (18) produces a *p*-fluorophenylchloroacrylic acid (19) showing vinyl proton resonance at −7.72 ppm.[20] Table XVI, part A, shows the vinyl proton resonances predicted for the six possible isomers of 17 using simple σ additivity.[5] Structures 17a and c can be quickly discarded. However, *no* choice from among the remaining four isomers

(36) D. C. Zecher and R. West, University of Wisconsin, private communication.

can be made, especially if it is (reasonably) assumed that in the chlorocinnamic derivatives (**17a–d**) $\sigma_{conj\ CO_2H}$ values should be used, whereas in the chloroatropic acids (**17e** and **f**) $\sigma_{solo\ CO_2H}$ values should be employed.

Part B of Table XVI shows the contrasting results of predicting the vinyl proton resonances for **17a–f** using *cis*-[37,38] and *trans*-cinnamic and atropic acids[33] as model compounds. Structure **17f** is uniquely indicated.

16, X = H
18, X = F

17f, X = H
19f, X = F
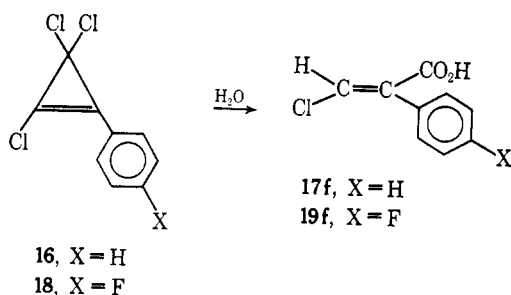
Comparison of **17** and **19** shows that introduction of *p*-fluorine has caused a −0.15-ppm downfield shift in the vinyl resonance. This observation corroborates assignment of structure **17f** to the hydrolysis product and decisively excludes structures **17b** and **d**, the only two which have predicted resonances anywhere near **17f**. **17b** and **d** have hydrogen α to the phenyl, whereas **17f** has hydrogen β to the ring. From the data in Table VIII, introduction of *p* fluorine should have negligible effect on the resonance position of α hydrogen[39]—a prediction contrary to the fact presuming either structure **17b** or **d** but should cause an approximately −0.10 ± 0.05 ppm downfield shift in resonance position of β hydrogen—clearly in agreement with fact assuming structure **17f**.

α-Cyanocinnamic Ester Geometry.—In their paper,[5] Pascual, Meier, and Simon list several compounds for which the difference between the observed vinyl proton resonance position and that calculated assuming σ additivity exceeds 0.5 ppm. Among them is one taken from the Varian catalog, spectrum 290:[19] ethyl α-cyanocinnamate, **20**. This compound shows vinyl proton resonance at −8.22 ppm and is assigned a *cis* geometry. As shown in part A of Table XVII, *cis* **20** is actually predicted to resonate at −7.74 using Pascual, Meier, and Simon's data, while the *trans* isomer is predicted to resonate at −8.22 ppm. That the compound listed in the Varian catalog should be reassigned the *trans* **20** structure seems clear, particularly since the analogous methyl ester, spectrum 576, showing vinyl proton resonance at −8.27 ppm, is assigned *trans*.

A recent paper by Hayashi,[40] in which both *cis* and *trans* **20** are discussed, supports this conclusion; the vinyl proton resonance for *trans* **20** is given as −8.22 ppm. However, the paper makes the disconcerting assertion that *cis* **20** resonates at −7.26 ppm, 0.5 ppm *up*field from the location predicted using σ additivities!

Because the applicability of simple σ additivities to compounds of type **20** is open to question (particularly for the *cis* isomer in which space-filling models suggest that neither the −CO₂Et nor −Ph groups can achieve normal coplanarity with the ethylenic backbone), it seemed worthwhile to prepare model compounds of *trans* and *cis* **20**. Methyl *trans*-cinnamate (**21**) was therefore photoisomerized for 3 hr in CDCl₃ to an approximately 2:1 mixture of *trans*:*cis* **21** and the nmr data shown in part B of Table XVII were recorded.[41]

TABLE XVII
PREDICTION OF THE VINYL PROTON RESONANCE POSITIONS IN
ETHYL α-CYANO-*cis*- AND -*trans*-CINNAMATES[a]

A. Using Eq 1 and σ Data from Table XII

20 *cis* (−7.73)

20 *trans* (−8.22)
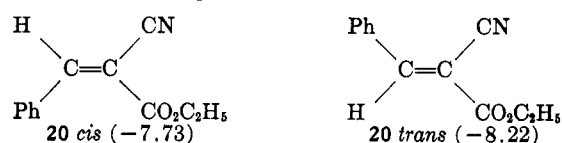
B. Using *cis*- and *trans*-Methyl Cinnamate (**21**) as Models and σ_{CN} Data from Table IV

cis **20** (−7.67 ± 0.10)

$\delta_{obsd} = -7.64$

trans **20** (−8.21 ± 0.12)

$\delta_{obsd} = -8.22$
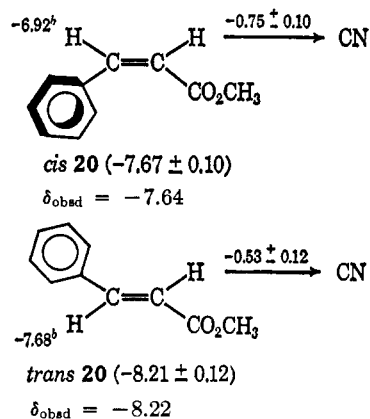
[a] δ_{calcd} values (parts per million) are given in parentheses. [b] The proton *gem* to −CO₂CH₃ in *cis*-methyl cinnamate resonates at −5.92 ppm and J_{HH} = 12.5 Hz. The methyl group resonates at −3.79 ppm. In the *trans* compound the vinyl proton *gem* to −CO₂CH₃ resonates at −6.41 ppm and J_{HH} = 16.2 Hz. The methyl group resonates at −3.68 ppm. The difference in σ values for −CO₂CH₃ and −CO₂C₂H₅ is negligible.

Application of the σ constants for −CN to these data leads to vinyl proton resonance positions for *cis* and *trans* **20** of −7.67 ± 0.10 and −8.21 ± 0.12 ppm, respectively. Two conclusions seemed inescapable: *trans* **20** should indeed be assigned the −8.22-ppm resonance position, and Hayashi's data for *cis* **20** must be in error.

Hayashi's nmr spectrum[40] of the photoequilibrated mixture of methyl α-cyanocinnamates is reproduced below in Figure 2. The −8.22- and −7.26-ppm "vinyl proton" resonances are of comparable intensity, whereas the methyl resonances (which should be of the same relative intensities) are *not*. The spectrum in Figure 2 was obtained on a CDCl₃ solution of the ester mixture isolated from the benzene solution in which it was prepared by photoisomerization. We concluded that the −7.26-ppm resonance assigned to *cis* **20** was in reality due to the small amount of CHCl₃ ($\delta = -7.27$ ppm)[19]

(37) *cis*-Cinnamic acid was obtained as a 1:2 mixture with the *trans* isomer by photoisomerization for 2 hr.[38]

(38) Photoisomerizations were carried out on 5–10% w/v solutions in clear Pyrex nmr tubes (uv cutoff 3000 Å) centrally suspended in a Southern New England Ultraviolet Co. Rayonet RPR-100 photochemical reactor fit with RPR 3000-Å lamps.

(39) The combined inductive and resonance effects of *p*-fluorine are comparable with those with Cl. See (a) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709, 3146 (1963); and (b) ref 32, Chapter 7, especially p 221.

(40) T. Hayashi, *J. Org. Chem.*, **31**, 3253 (1966).

(41) The data of A. J. Speziale and C. C. Tung [*ibid.*, **28**, 1353 (1963)] would have been very useful but for the fact that the nmr data were taken on the neat liquids in which horrendous solvent shifts occur.
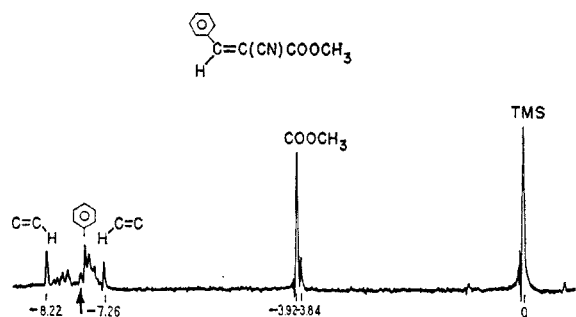
Figure 2.—The CDCl₃ nmr spectrum of *cis*- and *trans*-methyl α-cyanocinnamates photoequilibrated in benzene. Reprinted from T. Hayashi, *J. Org. Chem.*, **31**, 3253 (1966). Copyright 1966 by the American Chemical Society. Reprinted by permission of the copyright owner. Note the relative sizes of the −7.26 and −8.22 resonances assigned by Hayashi to the vinyl protons in the *cis* and *trans* isomers *vs.* the relative sizes of the methyl resonances at −3.84 and −3.92 ppm. Note also the resonance at −7.64 ppm indicated by the arrow.

normally present in CDCl₃, and the small, unassigned blip at −7.64 ppm was due to *cis* **20**.

To prove this point **20** was synthesized from benzaldehyde and ethyl cyanoacetate,[42] and photoisomerized for 24 hr in deuteriobenzene.[43] Figure 3A shows the CDCl₃ nmr spectrum of the resulting product mixture. In addition to the vinyl proton resonance for *trans* **20** at −8.22 ppm the spectrum shows a strong singlet at −7.64 ppm in the position predicted for *cis* **20** using model compounds. That this resonance is indeed due to the vinyl proton in *cis* **20** (and not to a phenyl resonance) is demonstrated by the spectrum shown in Figure 3B. This latter spectrum was taken on a photoisomerized sample of **20** prepared from benzaldehyde containing 50% aldehydic deuterium.[44-46] The peaks at −8.22 and −7.64 ppm are reduced to half-intensity while all other bands in Figures 3A and B are of comparable size. It is thus clear that *trans* and *cis* **20** *do* resonate in the positions accurately predicted by the model compound calculations.

It is worthwhile noting here that the original photoisomerized solution of *cis* and *trans* **20** in C₆D₆ showed *no* peak at −7.64 ppm. The −8.22 peak for *trans* **20** was observed at −7.99, shifted upfield +0.23 ppm. The −7.64 peak for *cis* **20** was subsequently shown by the deuterium labeling experiment to fall at −7.07 ppm in C₆D₆, shifted upfield +0.57 ppm into the complex phenyl region (which also moves upfield in C₆D₆).

Figure 3.—(A) The CDCl₃ spectrum of *cis*- and *trans*-methyl α-cyanocinnamate after 24-hr photoequilibration at 300 mμ in C₆D₆. The vinyl and ethyl group resonances characteristic of the initial *trans* isomer are indicated at the base of the spectrum. Note the −8.22- and (photogenerated) −7.64-ppm resonance lines. (B) An analogous spectrum of photoequilibrated ester containing 50% vinyl deuterium. Note the essentially identical sizes of the ethyl group resonances in spectra A and B and the much smaller (due to deuteration) sizes of the −8.22- and −7.64-ppm resonances in spectrum B.

This differential shielding of the vinyl protons in *cis* and *trans* **20** in C₆D₆ *vs.* CDCl₃ is only one example of a very general effect produced by such strongly anisotropic solvents as pyridine and benzene.[47] The important point to keep in mind is that the σ parameters and additivity calculations used in this paper are *only* applicable to dilute solutions in isotropic solvents. Vinyl proton nmr positions predicted from data obtained on neat,[41] concentrated, or anisotropic solvent solutions[5] may be in considerable error.

The examples given in this paper illustrate the ease with which structures can be assigned to a wide variety of simple polysubstituted ethylenes using the σ additivity principle,[48] and demonstrate the distinct advantages of the model compound approach to solving trisubstituted ethylene structure assignment problems in which specific polar, steric, and resonance interactions between substituents must be taken into account.

Registry No.—**2**, 557-93-7; **5**, 588-73-8; **6**, 15022-93-2; **7** (*trans*), 16917-35-4; **7** (*cis*), 19647-26-8; **8** (*trans*), 16917-32-1; **8** (*cis*), 16917-31-0; **12a**, 19713-69-0; **12b**, 19647-29-1; **13**, 492-38-6; **15a**, 19647-31-5; **15b**, 19647-45-1; **15c**, 19647-46-2; **15d**, 19647-47-3;

(42) Benzaldehyde and cyanoacetic ester (0.1 mol each) were refluxed in 50 ml of benzene containing 1 ml of piperidine and 20 g of Linde Molecular Sieve 4A for 3 hr.

(43) Photoisomerization of **20** in CDCl₃ and cyclohexane does not occur to any measurable extent in 3 hr.

(44) Benzaldehyde-*d* has been synthesized by a variety of routes.[45] The material used in this work was made[45] by stirring 0.1 mol (10.6 g) of benzaldehyde with 100 ml of D₂O, 1 g of NaCN, and 350 ml of tetrahydrofuran at room temperature for 48 hr. The resulting solution was saturated with K₂CO₃; the upper THF layer was drawn off and dried over additional K₂CO₃. Filtration, followed by removal of solvent under vacuum, left a white crystalline powder (presumably benzoin) moist with benzaldehyde. Trituration of this material with 25 ml of petroleum ether, filtration, and removal of solvent under vacuum provided 3.2 g of high-purity benzaldehyde showing 50 ± 5% deuterium incorporation in the carbonyl position by nmr analysis.

(45) (a) R. A. Olofson and D. M. Zimmerman, *J. Amer. Chem. Soc.*, **89**, 5057 (1967); (b) J. C. Craig and L. R. Kray, *J. Org. Chem.*, **33**, 871 (1968); (c) D. Seebach, B. W. Erickson, and G. Singh, *ibid.*, **31**, 4303 (1966).

(46) The synthesis suggests itself immediately from a consideration of the probable mechanism of the benzoin condensation. See ref 32, pp 394–397, and references cited there.
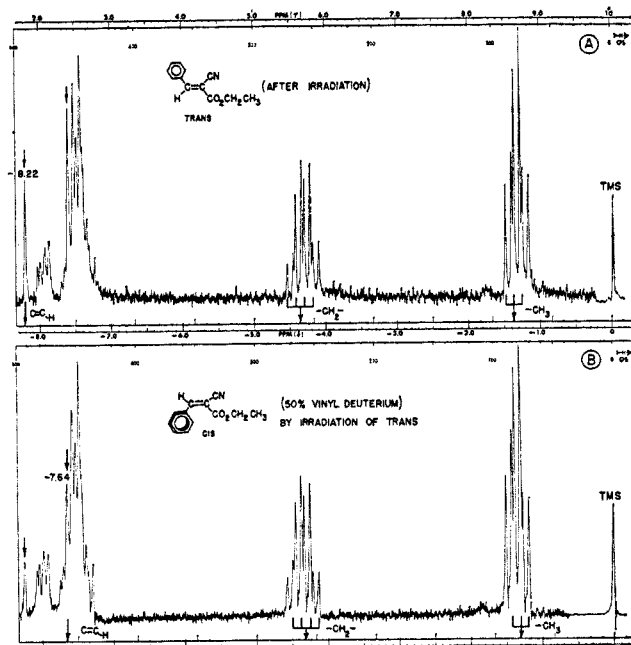
(47) For an excellent explanation of this effect and leading references to numerous specific examples, see T. Ladaal, *Tetrahedron Lett.*, 1683 (1968).

(48) A number of other papers in which the σ additivity principle has or can be used in assigning structures to trisubstituted ethylenes are (a) A. N. Kurtz, W. E. Billups, R. B. Greenlee, H. F. Hamil, and W. T. Pace, *J. Org. Chem.*, **30**, 3141 (1965); (b) M. Barbieux, N. Defay, J. Pecher, and R. H. Martin, *Bull. Soc. Chim. Belges*, **73**, 716 (1964); (c) C. Rappe, T. Nilsson, G. B. Carlsson, and K. Anderson, *Ark. Kemi*, **24**, 95 (1965); (d) C. Rappe, *Acta. Chem. Scand.*, **19**, 31 (1965); (e) C. Rappe and K. Anderson, *ibid.*, **21**, 1741 (1967); (f) A. W. Douglas and J. H. Goldstein, *J. Mol. Spectrosc.*, **16**, 1 (1965).

Photolyses of Trienes.   III.   Photoreactions of 2,3,7,7-Tetramethylcycloheptatriene

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Irradiation of a benzene solution of 2,3,7,7-tetramethylcycloheptatriene (7) in a Pyrex tube with a Hanovia medium-pressure mercury arc lamp yields a complex mixture. The major reaction products were identified as 2,2,6,7-tetramethylbicyclo[3.2.0]hepta-3,6-diene (9) and 1,2,6,7-tetramethylcycloheptatriene (13). Secondary photoproducts (10 and 11) were also produced. These reaction products are the result of a selective (1,7) sigmatropic methyl migration and electrocyclization reaction.
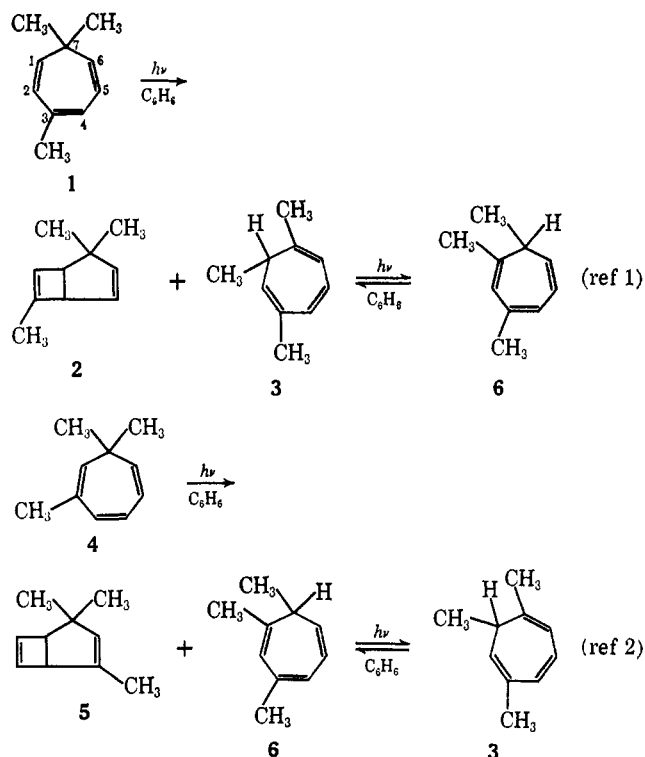
Previous studies[1,2] have indicated that methyl substituents attached to vinyl carbon atoms in various cycloheptatrienes exert a strong directive influence on the course of photochemical cyclization and methyl and hydrogen migration reactions. Specifically, irradiation of 3,7,7-trimethylcycloheptatriene[1] (1) induces an electrocyclization reaction across C_1 and C_4 to give 2 and promotes methyl migration from C_7 to C_1 to give the new cycloheptatriene 3. On the other hand, when 2,7,7-trimethylcycloheptatriene (4) is irradiated,[2] a methyl shift from C_7 to C_6 is observed to give 6, and cyclization occurs across C_3 and C_6 to give 5. Secondary photoproducts were observed in each reaction arising from selective hydrogen migration in the new triene photoproducts to give 6 in the case of 1, and 3 in the case of 4. These reactions are summarized in Chart I. The selectivity noted in the methyl and hydrogen migration reactions was rationalized on the basis of a series of molecular orbital calculations, and the selectivity of the cyclization reactions was accounted for primarily on the basis of steric considerations.[1,2]

Based on our observations that the direction of these photochemical cyclization and migration reactions is dependent upon whether the methyl group is located at C_2 or C_3, it was of interest to prepare a cycloheptatriene with methyl substituents located both at positions 2 and 3 to determine which substituent exerts the stronger effect. It was anticipated that the photochemistry of 2,3,7,7-tetramethylcycloheptatriene (7) would be more complex and that the selectivity would be less than that observed during photolysis of either 1 or 4. With this in mind, we have studied the photolysis of 7 in benzene solution with a 450-W Hanovia medium-pressure mercury arc lamp.

2,3,7,7-Tetramethylcycloheptatriene (7) was prepared by the addition of methylmagnesium bromide to eucarvone, followed by acid-catalyzed dehydration.[3,4]

CHART I

As observed by Conrow,[4] this procedure gives rise to a mixture of 7 (the predominant component) and 2-methylene-3,7,7-trimethyl-3,5-cycloheptadiene (8). These materials are readily separable by vapor phase chromatography (vpc).

As anticipated, the photoisomerization reactions of 7 proved to be extremely complex. Irradiation of a benzene solution of 7 to 40% reaction gave a mixture which upon vpc[5] was shown to consist of 1% a group of minor bicyclic products, 11% a group of major bicyclic

(1) L. B. Jones and V. K. Jones, *J. Amer. Chem. Soc.*, **89**, 1880 (1967).
(2) L. B. Jones and V. K. Jones, *ibid.*, **90**, 1540 (1968).
(3) E. J. Corey, H. J. Burke, and W. A. Remers, *ibid.*, **78**, 180 (1956).
(4) K. Conrow, *ibid.*, **83**, 2958 (1961).

(5) A column packed with SE-30 suspended on base-washed Chromosorb P was employed.