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Substituent-Induced Chemical Shifts and Coupling Constants in ^{31}P Nuclear Magnetic Resonance Spectra of Ethyl α-Diethylphosphonocinnamates and α-Diethylphosphonocinnamonitriles

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Substituent-induced chemical shifts (SCS) and coupling constants in ^{31}P NMR spectra have been measured for meta- and para-substituted ethyl α-diethylphosphonocinnamates **1** and α-diethylphosphonocinnamonitriles **2**. For both series, reverse correlations, in which electron-withdrawing substituents produce upfield shifts, have been found. ^{31}P chemical shifts correlate well with σ^{13} or σ^+ values in single-substituent parameter treatments. Better correlations are obtained with dual-parameter analyses employing Swain's F and R or Taft's σ_I and σ_R^+ values. SCS values, as well as their field and resonance components, closely parallel those of the corresponding ^{13}C absorptions at other side-chain sites and are interpretable in terms of alternate electron density effects. One-bond coupling constants, $^1J_{PC}$, from series **2** also show excellent correlations. $^1J_{PC}$ values from series **1** give poorer correlations.

Since the early work of Letcher and Van Wazer,[2] who developed a theoretical interpretation of ^{31}P chemical shifts, a number of experimental studies have been reported. Several factors, including the state of hybridization of the phosphorus atom, its bonding angles, and the electronegativities of its ligands, have been identified as being influential in producing the chemical shift. Despite this, relatively few systematic studies have been reported that characterize substituent-induced chemical shifts (SCS) where other factors remain constant within a series. Recent reviews have been given by Gorenstein[3] and Craik.[4]

An interesting finding of the SCS effects is that reverse correlations occur with phenylphosphonic acids,[5] phenylphosphonic dichlorides,[6] phenylphosphonic difluorides,[7] and alkyl phenyl phenylphosphonates.[8] In these correlations, electron-withdrawing substituents lead to increased shielding. On the contrary, a normal effect has been found in (N-phenylimino)triphenylphosphoranes.[9,10] The analogy between these results and those for ^{13}C shifts in substituted styrenes has been noted by Craik.[4]

A large body of evidence now indicates that ^{13}C shifts in substituted styrenes are best correlated by using a dual-substituent-parameter (DSP) approach rather than one involving a single parameter.[11-14] Our previous work[14] suggested that the parameters of Swain, Unger, Rosenquist, and Swain[15] applied in the Swain–Lupton[16] treatment are correlatively superior, on the whole, to parameters used in the Taft DSP analysis[17] when both side-chain carbon atoms are examined. In conjunction with the ^{13}C study, we prepared two series in which the diethylphosphono group is a substituent on the β-carbon atom of the styrene skeleton. We report here the details of the ^{31}P NMR spectra and an analysis of substituent effects based on both single-parameter and dual-parameter approaches.

Experimental Section

Ethyl α-diethylphosphonocinnamates **1** and α-diethylphosphonocinnamonitriles **2** were prepared by condensation of substituted benzaldehydes with ethyl diethylphosphonoacetate and diethylphosphonoacetonitrile, respectively. The synthesis of several examples of **1** has been previously described,[18] as has that of several examples of **2**.[18d,19] Triethyl p-nitro-α-phosphonocinnamate (**1i**) was prepared by the method of Lehnart.[20] Both series utilized the para substituents **a**–**i** and the meta substituents **j**–**p**, in addition to the parent, unsubstituted compounds **1q** and **2q**. The numbers referred to in the text are indicated below the carbon atoms.

A complete spectral characterization was done for each compound. This included ^{1}H, ^{13}C, and ^{31}P NMR spectra, the infrared

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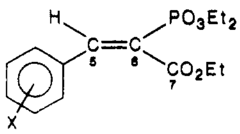

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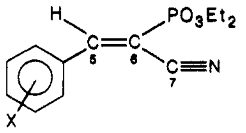

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a, *p*-NMe$_2$
b, *p*-OMe
c, *p*-Me
d, *p*-Ph
e, *p*-F
f, *p*-Cl
g, *p*-Br
h, *p*-CN
i, *p*-NO$_2$
j, *m*-OMe
k, *m*-Me
l, *m*-F
m, *m*-Cl
n, *m*-Br
o, *m*-CN
p, *m*-NO$_2$
q, H

spectrum, and the mass fragmentation pattern. In every case, all data accorded completely with structure. Illustrative data for four representative compounds in each series are tabulated in the supplementary material, Table S-I.

^{13}C NMR spectra were recorded with a Varian CFT-20 spectrometer, Me$_4$Si as an internal standard, and CDCl$_3$ as solvent. Chemical shifts are reported (ppm) downfield from Me$_4$Si. Coupling constants are reported in hertz. ^{31}P spectra were obtained with either a Bruker HFX-90/DIGILAB FTS/NMR-3 spectrometer at 36.43 MHz or a JEOL FX90Q spectrometer at 36.21 MHz. Spectra acquired both with and without proton decoupling were recorded. CDCl$_3$ was used as solvent, and 85% H$_3$PO$_4$ served as an external standard. Shifts are reported (ppm) downfield from H$_3$PO$_4$, and coupling constants are in hertz. Proton NMR spectra were recorded with the JEOL FX90Q spectrometer at 89.55 MHz and Me$_4$Si as internal standard. ^{19}F NMR spectra of the fluoro-substituted compounds were recorded with the JEOL instrument at 84.25 MHz. CDCl$_3$ was used as solvent, and chemical shifts are reported (ppm) downfield from the internal reference CFCl$_3$. All NMR spectra were obtained from solutions containing ~0.5 g of solute in 1.5 mL of CDCl$_3$. Infrared spectra were obtained with a Perkin-Elmer 1330 spectrophotometer. The samples were neat liquids. Mass spectral data for the cinnamates were acquired by means of a Hewlett-Packard Model 5985 GC/MS system and for the cinnamonitriles by means of a Hewlett-Packard 5890 GC/5970A mass selective detector. The molecular ion peak was identified in all cases, and the chloro and bromo compounds gave appropriate M + 2 peaks.

Results and Discussion

Chemical shifts and coupling constants are summarized in Tables I and II. Correlations were determined between the SCS values and various constants by application of the single-parameter (Hammett) equation (1). Correlation

$$\delta_X = \rho\sigma + c \qquad (1)$$

coefficients, *R*, and *F* values for these analyses are presented in Table III. Similarly, correlations were determined between the SCS values and the DSP values of Taft (eq 2) and Swain (eq 3). Multiple correlation coefficients,

$$\delta_X = \alpha\sigma_I + \beta\sigma_R{}^+ + c \qquad (2)$$

$$\delta_X = fF + rR + c \qquad (3)$$

R, and *F* values for these analyses are collected in Table IV. Table V gives further details of the analyses using eq 3, including the parameter estimates and the standard error of the estimates. The contribution of the field parameter can be calculated according to eq 4, and these

$$\%\ F = |f| \times 100/(|f| + |r|) \qquad (4)$$

contributions are also given in Table V. Where the data permit, coupling constants were also analyzed according to eq 3, with the substitution of *J* for δ_X. Multiple correlation coefficients and *F* values for these analyses are compiled in Table VI.

Chemical Shifts. Substituent effects on ^{13}C absorptions of side-chain atoms in the styrene skeleton are interpretable in terms of substituent-induced charge alternation,[14,21] and this model is reinforced by data for the carbon atoms in styrene vinylogues.[21] The reverse substituent effect on ^{31}P in phenylphosphonic acids, phenylphosphonic dichlorides, phenylphosphonic difluorides, and alkyl phenyl phenylphosphonates previously mentioned, along with the normal substituent effect in (*N*-phenylimino)triphenylphosphoranes, suggests that substituent effects on the phosphorus atom in the present styrene systems should also be of the reverse type because of the alternation effect. The chemical shift data from Tables I and II show that, as expected, electron withdrawal by substituents produces an upfield shift. For para substituents, the total range of SCS effects is 4.6–5.2 ppm, while for meta substituents it is only 1.5–1.8 ppm.

Table I. Chemical Shifts and Coupling Constants for Ethyl α-Diethylphosphonocinnamates 1[a]

X	δ_{P31}	δ_{C5}	δ_{C6}	δ_{C7}	J_{PC6}
p-NMe$_2$	16.598	149.31	116.67	167.35	182.6
p-OMe	14.861	147.42	121.81	166.64	180.0
p-Me	14.255	147.87	123.62	166.51	179.8
p-Ph	13.865	147.68	124.26	166.53	179.0
p-F	13.434	146.67	124.89	166.25	179.0
H	13.810	147.91	124.96	166.28	
p-Cl	13.178	146.42	125.77	166.01	178.4
p-Br	13.138	146.30	125.97	165.88	178.0
p-CN	12.182	145.71	128.70	165.51	177.6
p-NO$_2$	11.994	145.49	129.21	165.37	177.8
m-Me	13.623	148.03	124.62	166.41	178.8
m-OMe	13.596	147.62	125.23	166.33	
m-F	12.815	146.39	126.49	165.99	178.0
m-Cl	12.761	146.19	126.72	165.86	177.8
m-Br	12.788	146.03	126.72	165.78	177.9
m-CN	12.142	145.29	128.28	165.48	177.4
m-NO$_2$	12.198	145.14	128.47	165.48	177.8

[a] ^{31}P shifts are reported (ppm) downfield from the external standard H$_3$PO$_4$. ^{13}C shifts are reported (ppm) downfield from the internal standard Me$_4$Si. *J* values are in hertz.

Both single-parameter and DSP approaches have been utilized to analyze SCS effects on phosphorus. Grabiak, Miles, and Schwenzer[6] applied both Hammett σ values and Taft $\sigma°$ values to SCS effects in phenylphosphonic dichlorides. They found rough correlations, with correlation coefficients of 0.90 and 0.91, respectively. Similarly, Szafraniec[7] used standard Hammett values to analyze shifts for phenylphosphonic difluorides and found a correlation coefficient of 0.992. Both Bödeker, Köchritz, Köppel, and Radeglia[9] and Pomerantz et al.[10] have used σ^- values to correlate SCS data for (*N*-phenylimino)triphenylphosphoranes. The former workers found a correlation coefficient of 0.997 for para substituents and 0.951 for meta substituents. The latter group, using 10 compounds in their series, found a correlation coefficient of 0.987.

Analyses of the present data using the single-parameter approach are summarized for comparative purposes in Table III. The previously defined σ^{13} values, based on the chemical shifts at C6 in 17 series of substituted styrenes,[14] give slightly better results than do σ^+ values, although both yield excellent correlations for series **1** and very good correlations for series **2**. Correlations employing σ and σ^- give poorer results. As anticipated, σ^{13} values represent the best constants for the single-parameter treatment. As noted previously, however, they provide a very limited basis for detailed interpretation of electronic effects.[14]

The DSP approach has been explored by Mitsch, Freedman, and Moreland[5] for phenylphosphonic acids and

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Table II. Chemical Shifts and Coupling Constants for α-Diethylphosphonocinnamonitriles 2[a]

X	δ_{P31}	δ_{C5}	δ_{C6}	δ_{C7}	J_{PC5}	J_{PC6}	J_{PC7}
p-NMe_2	14.673	158.34	89.54	117.20	7.7	203.1	10.8
p-OMe	12.9857	158.11	96.20	116.04	7.4	200.1	10.7
p-Me	11.8143	158.67	98.75	115.62	7.0	198.2	9.9
p-Ph	11.8927	158.14	99.71	115.59	7.1	197.8	9.9
p-F	11.4466	157.22	100.15	115.38	7.4	197.7	10.0
H	11.9349	158.56	100.77	115.35	7.0	197.1	10.5
p-Cl	11.2115	157.09	101.11	115.17	7.1	197.2	9.7
p-Br	11.0970	157.14	101.28	115.15	7.1	197.8	9.8
p-CN	9.7167	156.03	105.03	114.68	6.9	195.1	9.6
p-NO_2	9.4756	155.43	105.98	114.62	6.9	194.7	9.3
m-Me	11.6757	158.82	100.18	115.42	7.1	197.3	10.0
m-OMe	11.6033	158.69	100.59	115.45	7.3	197.1	10.5
m-F	10.8439	157.08	102.50	115.04	7.0	196.2	9.8
m-Cl	10.6570	156.85	102.56	114.92	7.0	196.1	9.8
m-Br	10.5244	156.78	102.44	114.83	7.3	196.4	9.7
m-CN	9.8553	155.86	104.20	114.76	7.3	195.3	9.8
m-NO_2	9.8131	155.61	104.80	114.63	7.5	195.1	9.5

[a] ^{31}P shifts are reported (ppm) downfield from the external standard H_3PO_4. ^{13}C shifts are reported (ppm) downfield from the internal standard Me_4Si. J values are in hertz.

Table III. Correlation Coefficients, R, and F Values for Single-Substituent-Parameter Analyses (eq 1)[a]

		treatment							
		σ		σ^+		σ^-		σ^{13}	
series	atom	R	F	R	F	R	F	R	F
1	C5	0.9387	111.1	0.8676	45.7	0.8935	59.4	0.8806	51.7
	C6	0.9796	357.4	0.9958	1764.1	0.9417	117.6	0.9979	3554.5
	C7	0.9854	501.6	0.9541	152.2	0.9566	161.2	0.9637	195.7
	P	0.9816	397.2	0.9903	759.0	0.9370	107.9	0.9910	819.7
2	C5	0.8345	34.4	0.6986	14.3	0.8435	37.0	0.7360	17.7
	C6	0.9729	265.7	0.9956	1716.4	0.9386	110.9	0.9981	4007.6
	C7	0.9636	195.2	0.9908	801.9	0.9077	70.2	0.9841	460.5
	P	0.9852	494.7	0.9808	379.4	0.9556	157.6	0.9885	640.4

[a] Substituent constants were taken from the summary in ref 14.

Table IV. Multiple Correlation Coefficients, R, and F Values for Taft and Swain Treatments

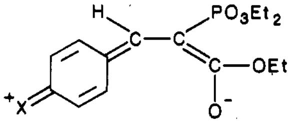
			treatment[a]			
			Taft: $\sigma_I + \sigma_R^+$		Swain: F + R	
series	subst type	atom	R	F	R	F
1	para	C5	0.9826	98.08	0.9784	78.31
		C6	0.9982	987.32	0.9992	2290.01
		C7	0.9896	165.22	0.9888	154.11
		P	0.9973	658.69	0.9978	783.15
	meta	C5	0.9938	200.89	0.9933	186.04
		C6	0.9946	229.30	0.9968	391.69
		C7	0.9897	120.30	0.9904	127.86
		P	0.9865	90.75	0.9806	62.67
2	para	C5	0.9647	46.95	0.9876	138.95
		C6	0.9978	793.72	0.9991	1956.88
		C7	0.9924	226.35	0.9942	299.02
		P	0.9937	277.17	0.9931	252.82
	meta	C5	0.9955	274.06	0.9933	185.89
		C6	0.9962	328.41	0.9971	433.17
		C7	0.9712	41.51	0.9734	45.20
		P	0.9820	67.82	0.9840	76.00

[a] Parameters for the Taft treatment were taken from ref 17 and those for the Swain treatment from ref 15.

by Anttimanninen[8] for alkyl phenyl phenylphosphonates. In the phenylphosphonic acids, meta substituent data correlated with σ_I, whereas para substituents required both σ_I and σ_R. Anttimannien used $\sigma_I + \sigma_R^\circ$ on a fairly restricted data set.

As shown in Table IV, for the present data para substituent effects give excellent correlations with both the Taft DSP analysis of eq 2 and the Swain approach of eq 3. The correlations for meta substituents are somewhat poorer, but are still very good. The parameter estimates for the present series given in Table V permit the separation of total substituent effects into field and resonance contributions, also shown in the table. We note for meta substituents that the field comprises ~74–81% of the total at all sites in the side chain. With para substituents, however, the resonance effect is more important at C6 than at C5, C7, or P, with the exception of C7 in series 2. This overall result is interpretable in terms of the known alternate relay of electron density by ±M substituents attached to an aromatic nucleus, for which simple Hückel calculations show a much greater effect on ortho and para carbon atoms than on meta sites.

It is interesting to compare the contributions to the SCS at phosphorus to those at C7 for para substituents in both series. In each, the ^{31}P shift has a field component of ~54%. At C7, the comparable values are 62.5% and 39.4% for series 1 and 2, respectively. Although it may be possible to advance an argument for the disparity at C7 based on the expected resonance contributions from structures such as 3 and 4, the different anisotropic effects



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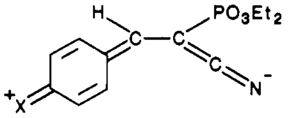

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in the cyano and carbethoxyl groups caution against an over interpretation of these results. This caution is underscored by the apparently unexceptional behavior at C5, C6, and P.

Coupling Constants. In theory, spin–spin couplings depend upon three types of interactions between electron and nuclear spins: a Fermi contact interaction between the electron and nuclear spins, a dipole–dipole interaction between the magnetic dipoles of the spinning electron and

Table V. Parameter Estimates and Standard Errors from Equation 3

			parameter					
			F		*R*			
series	subst type	atom	*f*	S_{est}	*r*	S_{est}	% *F*	% *R*
1	para	C5	−1.786	0.258	−0.667	0.068	72.8	27.2
		C6	2.142	0.147	2.511	0.039	46.0	54.0
		C7	−0.626	0.092	−0.376	0.024	62.5	37.5
		P	−1.073	0.094	−0.917	0.025	53.9	46.1
	meta	C5	−2.351	0.165	−0.538	0.077	81.4	18.6
		C6	2.792	0.144	0.796	0.067	77.8	22.2
		C7	−0.653	0.064	−0.230	0.030	74.0	26.0
		P	−1.276	0.158	−0.318	0.074	80.1	19.9
2	para	C5	−2.440	0.183	−0.424	0.048	85.2	14.8
		C6	2.299	0.206	3.285	0.054	41.2	58.8
		C7	−0.341	0.084	−0.524	0.022	39.4	60.6
		P	−1.223	0.186	−1.021	0.049	54.5	45.5
	meta	C5	−2.366	0.183	−0.740	0.086	76.2	23.8
		C6	3.030	0.159	1.044	0.074	74.4	25.6
		C7	−0.554	0.091	−0.198	0.043	73.7	26.3
		P	−1.596	0.182	−0.414	0.085	79.4	20.6

Table VI. Multiple Correlation Coefficients, *R*, and *F* Values for Correlation of Coupling Constants with Modified Equation 3[a]

			coupling constants, Hz					
			J_{PC5}		J_{PC6}		J_{PC7}	
subst parameters	series	subst type	*R*	*F*	*R*	*F*	*R*	*F*
F + *R*	1	para			0.9697	47.24		
		meta			0.9217	8.47		
	2	para	0.9486	31.20	0.9970	575.51	0.8832	12.41
		meta	0.5800	1.27	0.9890	112.19	0.8089	4.73
F	1	para			0.3404	0.92		
		meta			0.9214	22.49		
	2	para	0.1034	0.09	0.2263	0.43	0.3961	1.49
		meta	0.5585	2.72	0.8746	19.53	0.6989	5.73
R	1	para			0.9572	76.66		
		meta			0.5804	2.03		
	2	para	0.9305	51.66	0.9866	291.33	0.8199	16.41
		meta	0.3483	0.83	0.7471	7.58	0.6328	4.01

[a] *J* was substituted for δ_X in eq 3. *F* and *R* under substituent parameters represent the field and resonance paramater, respectively, in eq 3. *R* and *F* in the column headings represent the multiple correlation coefficient and the *F* value, respectively, for correlations using eq 3.

the nuclear spin, and an orbital–dipole interaction between the magnetic fields due to orbital motion of the electrons and the nuclear magnetic dipole. The contact term between bonded nuclei, according to approximate molecular orbital theory,[22] is measured by the s-overlap populations. Duangthai and Webb have recently shown, using the INDO level of approximation, that the contact term completely dominates the coupling between pentavalent phosphorus and carbon, although this is not true for phosphorus–fluorine coupling.[23]

Empirical correlations between ^{31}P coupling constants and substituent parameters have been explored much less extensively than have correlations of chemical shifts. Albanese, Kreider, Schaeffer, Yoder, and Samples[24] determined coupling constants for a limited substituent set in aryldimethylphosphorane–boranes and found a $^{1}J_{PC}$ dependence on normal Hammett substituent constants. Several correlations were attempted, but the Hammett constants gave the best results, with a correlation coefficient of 0.96. With phenylphosphonic difluorides, Szafraniec[7] found an excellent correlation between $^{1}J_{PF}$ and σ^+ values. She suggested that the coupling interaction is a reflection of p_π–d_π conjugation within the molecule and that the correlation with σ^+ indicates that resonance interactions play a more important role in determining the coupling constant than they do in determining the ^{31}P chemical shift, which correlated better with σ values.

To the contrary, Pomerantz et al.[10] found that in (*N*-phenylimino)triphenylphosphoranes the $^{1}J_{PN}$ values show a linear dependence on σ^-, just as the ^{31}P shifts do. These coupling constants also correlate well with the phosphorus–nitrogen Mullikin overlap populations derived from PRDDO calculations. The correlations were found to hold reasonably well when the calculations were repeated without the inclusion of d orbitals on phosphorus. The authors concluded that π-bonding through σ^* orbitals is at least an energetically reasonable possibility and is likely to be competitive with d-orbital participation.

The coupling constants collected in Tables I and II were analyzed by use of eq 3, in which *J* was substituted for δ_X. The results of these analyses are collected in Table VI. As seen, the one-bond coupling constants, $^{1}J_{PC6}$, for para and meta substituents in series **2** give good to excellent correlations with field and resonance substituent parameters. For series **1**, the correlations are satisfactory. In both series, para substituents give better correlations than do meta substituents. The two-bond coupling constants, $^{2}J_{PC5}$ and $^{2}J_{PC7}$, which were analyzed only for series **2**, give generally poorer correlations.

The analysis of Duangthai and Webb indicates that for $^{1}J_{PF}$ and $^{1}J_{PN}$ the noncontact terms, which are determined by the distribution of the p and d valence electrons around the coupled nuclei, are paramount in determining the coupling constants. Because σ^+ and σ^- values are designed

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[22] Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970; pp 149–158.

[23] Duangthai, S.; Webb, G. A. *Org. Magn. Reson.* **1983**, *21*, 125–129.

[24] Albanese, J. A.; Kreider, D. G.; Schaeffer, C. D., Jr.; Yoder, C. H.; Samples, M. S. *J. Org. Chem.* **1985**, *50*, 2059–2062.

to accommodate such situations, the correlation of Szafraniec between ${}^1J_{PF}$ and σ^+ and that of Pomerantz et al. between ${}^1J_{PN}$ and σ^- values seems reasonable. In contrast, the ${}^1J_{PC}$ coupling is expected to be determined primarily by the contact term. Consequently, it was of interest to see if either resonance or field parameters individually would provide empirical correlations with ${}^1J_{PC}$ coupling constants. The results of such attempts are also contained in Table VI. From these it is apparent that for the one-bond coupling constants correlations for para substituents using the resonance parameter alone are nearly as good as those employing both resonance and field parameters. For meta substituents, there is a definite lack of correlation using the individual parameter sets, except in the case of series 1, for which the correlation with the field parameter is equivalent to that employing both. Thus, in these systems, the resonance parameters alone apparently provide a nearly adequate reflection of trends in the contact term for para-substituted compounds, but not, of course, for the meta series.

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Supplementary Material Available: ^{1}H, ^{13}C, and ^{31}P NMR data, infrared absorptions, and mass spectral fragmentation patterns for four representative compounds from each series (5 pages). Ordering information is given on any current masthead page.

Selective Ring Openings of Isomeric Fused Thiazolium Salts with Nucleophiles[1]

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Different types of reactions have been found with isomeric tricyclic fused thiazolium salts for their interactions with secondary amines. Thus, the angularly fused quinolinium salt **7** gave rise to a stable pseudobase **8**; the related angular isoquinolinium system **9** led to opening of the thiazole ring and enamine **10** was formed; and the linear system **6** underwent opening of the pyridine moiety and gave the aldehyde compound **16**. The reactions were interpreted on FMO theory; the CNDO/2 calculation supported the qualitative picture based on the "annelation effect".

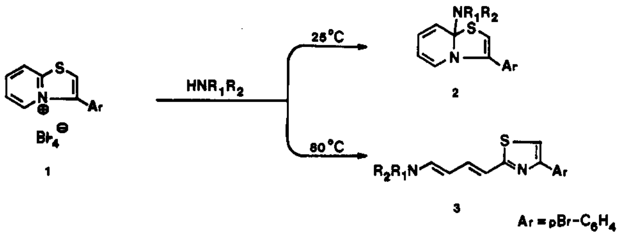
Recently we reported[2] that the reaction of thiazolo[3,2-*a*]pyridinium salt **1** with a secondary amine results in both a pseudobase **2** and thiazolyl dieneamine **3** depending on the reaction conditions (Scheme I). As a consequence of these findings, the question of how the differently annelated benzologues of **1** (i.e., **6**, **7**, and **9**) behave in similar reactions is of interest. In the literature, only a few examples of nucleophilic reactions of tricyclic fused thiazolium salts have been described.[3-5]

Two of the possible benzologue systems, i.e. the angularly fused thiazoloisoquinolinium and quinolinium salts (**7**, **9**), have been reported[5] whereas the linearly fused thiazolo[3,2-*b*]isoquinolinium system has not yet been synthesized.

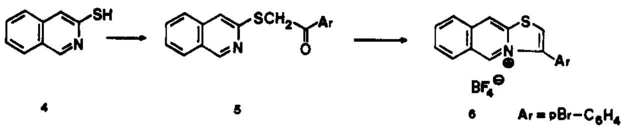
Preparation of this latter linearly fused system (**6**) was accomplished by application of the method described for the angularly fused isomers.[5] Thus, 3-mercaptoisoquinoline (**4**) was treated with *p*-bromophenacyl bromide, and the resulting sulfide (**5**) was cyclized by using concentrated sulfuric acid. The new ring system as well as the earlier known angular ones were transferred to stable fluoborate salts (**6**, **7**, **9**) (Scheme II).

Reaction of 1-(*p*-bromophenyl)thiazolo[3,2-*a*]quinolinium fluoborate (**7**) with morpholine at room temperature gave stable pseudobase **8** that could be converted to the starting thiazolium salt **7** by treatment with acid (Scheme III). Structure **8** is based on ^{1}H NMR data: an alternative structure having a 5-morpholino substituent

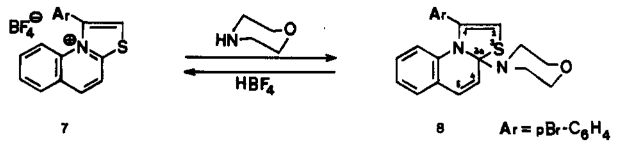
Scheme I



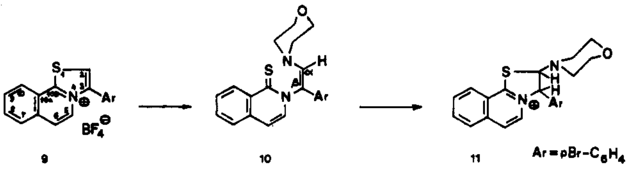
Scheme II



Scheme III



Scheme IV



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[1] Fused Azolium Salts. 10. Part 9: Messmer, A.; Hajós, Gy.; Gelléri, A.; Radics, L. *Tetrahedron* 1986, *42*, 5415.

[2] Hajós, Gy.; Messmer, A. *J. Heterocycl. Chem.* 1984, *21*, 809.

[3] Singh, H.; Lal, K. *J. Chem. Soc., Perkins Trans. 1* 1972, 1799.

[4] Molina, P.; Arques, A.; Cartagena, I.; Noguera, J. A.; Valcarcel, V. *J. Heterocycl. Chem.* 1983, *20*, 983.

[5] Bradsher, C. K.; Lohr, D. F. *J. Heterocycl. Chem.* 1967, *4*, 71.

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