243 (M − 15, 7), 149 (8), 95 (37), 93 (100), 79 (22), 73 (56). Anal. Calcd for $C_{14}H_{27}ClSi$: C, 64.95; H, 10.51. Found: C, 65.04; H, 10.44.

1,4(*E*)-Undecadiene. A solution of 4-trimethylsilyl-1,4(*Z*)-undecadiene (III, R = $CH_2CH{=}CH_2$, 0.27 g, 1.2 mmol) in 1.2 ml of benzene was treated with constant boiling hydriodic acid (51 μl, 0.60 mmol) at room temperature for 1 h as previously reported procedure.[1d] The reaction mixture was diluted with 20 ml of pentane and quenched with 2 ml of saturated aqueous solution of $NaHCO_3$. The combined pentane extracts were washed (10% $Na_2S_2O_3$), dried (Na_2SO_4), and distilled (Kugelrohr) to afford 183 mg of 1,4(*E*)-undecadiene (quantitative), bp (bath temperature) 120–125 °C (120 mm).

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Registry No.—I, 15719-55-8; III (R = CH_3), 58801-94-8; III (R = CH_3) *E* isomer, 58801-95-9; III (R = $CH_2CH{=}CH_2$), 58801-96-0; III [R = $CH_2C(CH_3){=}CH_2$], 58801-97-1; III (R = $CH_2CCl{=}CH_2$), 58801-98-2; IV, 18408-64-5; VI, 58801-99-3; VI *Z* isomer, 58802-00-9; 1-octyne, 629-05-0; trimethylchlorosilane, 75-77-4; triethylchlorosilane, 994-30-9; methyl iodide, 74-88-4; allyl chloride, 107-05-1; methallyl chloride, 563-47-3; 2,3-dichloropropene, 78-88-6; 1,4(*E*)-undecadiene, 55976-13-1.

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(2) Analogous reaction has been studied by J. J. Eisch and G. A. Damasevitz, *J. Org. Chem.*, preceding paper in this issue. We thank Professor Eisch for communicating his results to us in advance of publication.

(3) The aluminum compound was neither isolated nor identified by spectrometry. The reaction mixture was quenched by deuterium oxide affording 1-deuterio-1-trimethylsilyl-1-octene. The regioselectivity is in harmony with the analogous reported case[4] and with the consideration of electronic characteristic of silicon atom.

(4) Hydralumination of trimethylsilylphenylacetylene was studied: (a) J. J. Eisch and M. W. Fixton, *J. Org. Chem.* **36**, 3520 (1971); (b) J. J. Eisch and S.-G. Rhee, *J. Am. Chem. Soc.*, **97**, 4673 (1975), and references cited therein

(5) Quenched with water gave 1-triethylsilyl-1(*E*)-octene (purity 94%).

(6) Hydralumination and isomerization have reviewed: J. J. Eisch, *Ind. Eng. Chem., Prod. Res. Dev.*, **14**, 11 (1975).

(7) The hydralumination product of trimethylsilylphenylacetylene was subjected first to treatment with methyllithium and then with methyl iodide affording (*E*)-1-phenyl-2-trimethylsilylpropene (isolated yield 98%, purity >99%) and analogous reaction with allyl chloride gave 1-phenyl-2-trimethylsilyl-1(*E*),4-pentadiene (isolated yield 98%, purity >99%). These results also suggested the retention of configuration during alkylation.

(8) Lewis bases such as tertiary amines and ethers coordinate to aluminum and prohibit *Z*–*E* isomerization; see also ref 6.

(9) Hydralumination and successive allylation of acetylenes via organocopper compounds were reported.[10]

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(13) Several attempts at obtaining a pure sample was fruitless. A sample obtained by preparative GLC was sufficiently pure for spectral analyses, but not for elemental analyses.

Steric Effects. 7. Additional υ Constants

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We have previously defined[1] and successfully applied[2–7] the υ steric parameters to a number of different reactions and substrates. Thus, it seems to us that the utility of the υ parameters has been established. It therefore seemed useful to determine as many additional υ values as possible. To this end, we have correlated 11 sets of rate constants for esterification and acid-catalyzed ester hydrolysis with the modified Taft equation.

$$\log k_X = \psi \upsilon_X + h \qquad (1)$$

Table I. Data Used in Correlations

29. k, $XCO_2H + EtOH$ in EtOH at 25 °C, catalyzed by HCl[a]
i-Pr, 0.156; *sec*-Bu, 0.038; Et_2CH, 0.0031; c-C_6H_{11}, 0.081
30. k, $XCO_2H + EtOH$ in EtOH at 25 °C catalyzed by HCl[b]
Bu, 0.268; $BuCH_2$, 0.267; $C_2H_3CH_2CH_2$, 0.274; $PhCH_2CH_2$, 0.321; *i*-Bu, 0.0518; *i*-$BuCH_2$, 0.247; Pr_2CH, 0.00285; c-$C_6H_{11}CH_2$, 0.0809; c-$C_6H_{11}CH_2CH_2$, 0.141; Et, 0.550; *i*-Pr, 0.156; Pr, 0.270
31. k, $XCO_2H + MeOH$ in equimolar $MeOH–H_2O$ at 15 °C catalyzed by HCl[c]
H, 0.128; Me, 0.00955; Et, 0.00965; Pr, 0.00531; Bu, 0.00567; $BuCH_2$, 0.00532; $BuCH_2CH_2$, 0.00544; CH_2OH, 0.00723
32. k, $XCO_2H + MeOH$ in equimolar $MeOH + H_2O$ at 25 °C, catalyzed by HCl[c]
H, 0.273; Me, 0.0221; Et, 0.0221; Pr, 0.0122; Bu, 0.0133; $BuCH_2$, 0.0134; $BuCH_2CH_2$, 0.0125; CH_2OH, 0.0181; $EtOCH_2$, 0.00954; $EtSCH_2$, 0.00872; $ClCH_2$, 0.0101
33. k, $XCO_2H + MeOH$ in equimolar $MeOH–H_2O$ at 35 °C catalyzed by HCl[c]
H, 0.603; Me, 0.0484; Et, 0.0493; Pr, 0.0274; Bu, 0.0294; $BuCH_2$, 0.0295; $BuCH_2CH_2$, 0.0272; CH_2OH, 0.0409
34. k, $XCO_2Me + H_2O$ in equimolar $MeOH–H_2O$ at 15 °C catalyzed by HCl[c]
H, 0.0347; Me, 0.00169; Et, 0.00167; Pr, 0.00094; Bu, 0.00106; $BuCH_2$, 0.00100; $BuCH_2CH_2$, 0.00087; CH_2OH, 0.00205
35. k, $XCO_2Me + H_2O$ in equimolar $MeOH–H_2O$ at 25 °C catalyzed by HCl[c]
H, 0.0810; Me, 0.00445; Et, 0.00423; Pr, 0.00239; Bu, 0.00254; $BuCH_2$, 0.00249; $BuCH_2CH_2$, 0.00225; CH_2OH, 0.0056; $EtOCH_2$, 0.00302; $EtSCH_2$, 0.00228; $ClCH_2$, 0.00356
36. k, $XCO_2Me + H_2O$ in equimolar $MeOH–H_2O$ at 35 °C catalyzed by HCl[c]
H, 0.193; Me, 0.0102; Et, 0.00985; Pr, 0.00563; Bu, 0.00617; $BuCH_2$, 0.00595; $BuCH_2CH_2$, 0.00541; CH_2OH, 0.0133
37. k, $XCO_2Me + H_2O$ in H_2O at 25 °C catalyzed by HCl[d]
Pr, 0.00423; Bu, 0.00441; $BuCH_2$, 0.00410; $BuCH_2CH_2$, 0.00412; *i*-Bu, 0.00151; *sec*-Bu, 0.00138; *t*-Bu, 0.000709
38. k, $XCO_2H + MeOH$ in MeOH at 60.0 °C catalyzed by TsOH[e]
Me, 22.1; $PhCH_2$, 9.43; Ph_2CH, 0.825
39. k, $XCO_2Et + H_3O^+$ in 70% $MeAc–H_2O$ (v/v) at 25 °C[f]
Me, 4.30; CH_2Cl, 2.65; $PhCH_2$, 1.50

[a] G. D. Advani and J. J. Sudborough, *J. Indian Inst. Sci.*, **6**, 41 (1923). [b] B. V. Bhide and J. J. Sudborough, *J. Indian Inst. Sci. Sect. A*, **8**, 89 (1925). [c] M. H. Palomaa and T. A. Siitonen, *Ber.*, **69B**, 1338 (1936); M. H. Palomaa and K. R. Tukkimaki, *ibid.*, **68**, 887 (1935); M. H. Palomaa and T. Kaski, *Suom. Kemistil., B*, **19**, 85 (1946); M. H. Palomaa, *ibid.*, **19**, 53 (1946). [d] E. J. Salmi, *Ann. Acad. Sci. Fenn., Ser. A*, **48**, No. 4 (1937). [e] K. Bowden, N. B. Chapman, and J. Shorter, *J. Chem. Soc.*, 5239 (1963). [f] I. Minimida, Y. Ikada, K. Uneyama, W. Taguki, and S. Oae, *Tetrahedron*, **24**, 5293 (1968).

The data used in the correlations are set forth in Table I. Results of the correlations are reported in Table II. The υ constants required for correlation with eq 1 are taken from the first paper in this series[1] or from this work.

Of the 11 sets correlated with eq 1, nine gave excellent, one gave very good, and one gave good results. The two sets which did not give excellent correlations (as determined by the confidence level of the *F* test) had only three points. We believe that these sets are useful for the calculation of new υ values. Of the six sets, 31–36, the best results were obtained with set 35, which was therefore chosen for the calculation of new υ values. In Table III new υ values are presented, with the set from which they were calculated. Set numbers less than 29 refer to the first paper of this series.[1]

It is now possible to draw certain conclusions regarding structural effects upon υ values.

A comparison of υRCHOH with υRCHMe shows (Table IV) that when R is alkyl there is a considerable decrease in υ for the oxygen containing groups. In the case of the substitution of OMe for Et, a comparison of υRCHOMe with υRCHEt

Table II. Results of Correlations with Equation 1

Set	ψ	h	r^a	F^b	$s_{est}{}^c$	$s_\psi{}^c$	$s_h{}^c$	n^d
29	−2.25	0.883	0.9998	$4177.^c$	0.0200	0.0348^e	0.0375^f	4
30	−2.27	0.977	0.985	329.7^e	0.108	0.125^e	0.105^e	12
31	−1.96	−0.945	0.985	199.1^e	0.0862	0.139^e	0.0818^e	8
32	−1.97	−0.623	0.961	108.3^e	0.122	0.189^e	0.114^e	11
33	−1.90	−0.264	0.990	290.7^e	0.0692	0.111^e	0.0656^f	8
34	−2.23	−1.50	0.994	530.6^e	0.0603	0.0969^e	0.0572^e	8
35	−2.19	−1.12	0.995	818.4^e	0.0491	0.0764^e	0.0462^e	11
36	−2.19	−0.746	0.994	517.8^e	0.0597	0.0960^e	0.0567^e	8
37	−1.43	−1.39	0.996	704.2^e	0.0295	0.0540^e	0.0477^e	7
38	−1.95	2.35	0.99991	$5653.^f$	0.0139	0.0259^f	0.0228^f	3
39	−2.45	1.95	0.9998	$3273.^g$	0.00566	0.0444^h	0.0271^f	3

[a] Correlation coefficient. [b] F test for significance of correlation. Superscript indicates confidence level. [c] Standard errors of the estimate, ψ, and h. Superscripts indicate confidence levels of regression coefficients ψ and h. [d] Number of points in set. [e] 99.9% confidence level (CL) [f] 99.0% CL. [g] 97.5% CL. [h] 98.0% CL.

Table III. New Values of υ

X	υ	Set[a]
c-C_3H_5	1.06	29
c-C_4H_7	0.51	29
c-C_5H_9	0.71	29
EtPrCH	1.51	29
n-C_9H_{19}	0.68	30
n-$C_{11}H_{22}$	0.68	30
n-$C_{13}H_{27}$	0.68	30
n-$C_{15}H_{31}$	0.68	30
n-$C_{17}H_{35}$	0.68	30
cis-$H(CH_2)_8CH{=}CH(CH_2)_{11}$	0.67	30
trans-$H(CH_2)_8CH{=}CH(CH_2)_{11}$	0.68	30
i-$Pr(CH_2)_3$	0.68	30
MePrCH	1.05	30
$Me(C_2H_3CH)CH$	1.04	30
MeBuCH	1.07	30
$Me(PhCH_2)CH$	0.98	30
Me-i-PrCH	1.29	30
Me-i-BuCH	1.09	30
EtBuCH	1.55	30
c-C_7H_{13}	1.00	30
$MeOCH_2$	0.63	35
$PrOCH_2$	0.65	35
i-$PrOCH_2$	0.67	35
$BuOCH_2$	0.66	35
i-$BuOCH_2$	0.62	35
$MeOCH_2CH_2$	0.89	35
$EtOCH_2CH_2$	0.89	35
$PrOCH_2CH_2$	0.89	35
i-$PrOCH_2CH_2$	0.87	35
$BuOCH_2CH_2$	0.89	35
i-$BuOCH_2CH_2$	0.89	35
$MeO(CH_2)_3$	0.69	35
$EtO(CH_2)_3$	0.69	35
$PrO(CH_2)_3$	0.70	35
$BuO(CH_2)_3$	0.71	35
9-Ethyl-9-fluorenyl	1.53	38
9-Isopropyl-9-fluorenyl	2.21	38
9-*tert*-Butyl-9-fluorenyl	2.63	38
9-Phenyl-9-fluorenyl	2.10	38
9-Butyl-9-fluorenyl	1.59	38^b
9-Benzyl-9-fluorenyl	1.63	38^b
9-OH-9-fluorenyl	0.98	38^b
9-Anthracenyl	1.18	38
10-Xanthyl	1.18	38^b
10-Thioxanthyl	1.42	38^b
$C_2H_3Ph_2CCH_2$	2.74	38^b
$PhOCH_2$	0.74	39
$EtOCH_2$	0.61	39
$MeO(CH_2)_4$	0.68	35
$EtO(CH_2)_4$	0.67	35
$HOCH_2CH_2$	0.77	35
$MeSCH_2$	0.70	35
$MeSCH_2CH_2$	0.78	35
$EtSCH_2CH_2$	0.79	35
ICH_2CH_2	0.93	35
$ClCH_2CH_2$	0.97	35
$MeOCH_2CH_2OCH_2$	0.57	35
$EtOCH_2CH_2OCH_2$	0.56	35
$PrOCH_2CH_2OCH_2$	0.56	35
$BuOCH_2CH_2OCH_2$	0.55	35
$MeO(CH_2)_3OCH_2$	0.62	35
$MeOCH_2CH_2OCHMe$	0.67	35
$MeOCH_2CH_2OCH_2CH_2OCH_2$	0.56	35
CH_2OH	0.53	37
MeCHOH	0.50	37
EtCHOH	0.71	37
PrCHOH	0.71	37
BuCHOH	0.70	37
$BuCH_2CHOH$	0.71	37
$EtC{=}O$	0.79	37
$PrC{=}O$	0.80	37
EtCHOMe	1.22	37
PrCHOMe	1.22	37
BuCHOMe	1.20	37
C_2H_3	1.51	37
$C_2H_3CH_2$	0.69	37
$C_2H_3CH_2CH_2$	0.75	37
$C_2H_3CH_2CH_2CH_2$	0.75	37
Ph_2CMe	2.34	38
Ph_2CEt	2.75	38
Ph_3C	2.92	38
9-Fluorenyl	1.08	38
9-Methyl-9-fluorenyl	1.41	38
$EtSCH_2$	0.71	39
$PhSCH_2$	0.82	39
$(EtS)_2CH$	1.39	39
EtSCHMe	1.10	39
2,5-Dithiacyclopentyl	0.89	39
2,6-Dithiacyclohexyl	1.16	39
t-$BuOOCMe_2$	1.49	5^c
t-$BuOCH_2CMe_2$	1.30	5^c
t-$BuCH_2OCMe_2$	1.23	5^c
C_2H_3	1.31^d	$7,8,9^e$
$CMe{=}CH_2$	1.56	$7,8,9^e$
$C_2H_3CH_2CH_2$	0.74	$7,8,9^e$

[a] Rate constants used to calculate υ values are from the same reference as the set from which the υ values were calculated unless otherwise indicated. [b] K. Bowden and R. C. Young, *Can. J. Chem.*, **47**, 2775 (1969). [c] W. H. Richardson, R. S. Smith, G. Snyder, B. Anderson, and G. L. Kranz, *J. Org. Chem.*, **37**, 3915 (1972). [d] Average value. [e] C. G. Evans and J. D. R. Thomas, *J. Chem. Soc. B*, 1502 (1971).

Table IV

Comparison of υ Constants of RCHOH with RCHMe

R	H	Me	Et	Pr	Bu
υRCHOH	0.53	0.50	0.71	0.71	0.70
υRCHMe	0.56	0.76	1.02	1.05	1.07
Δ[a]	0.03	0.26	0.31	0.34	0.37

Comparison of υ Constants of RCHOMe with RCHEt

R	H	Et	Pr	Bu
υRCHOMe	0.63	1.22	1.22	1.20
υRCHEt	0.68	1.51	1.51	1.55
Δ	0.05	0.29	0.29	0.35

Comparison of υ Constants of $ROCH_2$ with RCH_2CH_2

R	H	Me	Et	Pr	*i*-Pr	Bu	*i*-Bu
$\upsilon ROCH_2$	0.53	0.63	0.61	0.65	0.67	0.66	0.62
υRCH_2CH_2	0.56	0.68	0.68	0.68	0.68	0.73	0.68
Δ	0.03	0.05	0.07	0.03	0.01	0.07	0.06

Comparison of υ Constants of $ROCH_2CH_2$ with $RCH_2CH_2CH_2$

R	H	Me	Et	Pr	*i*-Pr	Bu
$\upsilon ROCH_2CH_2$	0.77	0.89	0.89	0.89	0.87	0.89
$\upsilon RCH_2CH_2CH_2$	0.68	0.68	0.68	0.73	0.68	0.73
Δ	−0.09	−0.21	−0.21	−0.16	−0.19	−0.16

Comparison of υ Constants of $RO(CH_2)_3$ with $R(CH_2)_4$

R	Me	Et	Br	Bu
$\upsilon RO(CH_2)_3$	0.69	0.69	0.70	0.71
$\upsilon R(CH_2)_4$	0.68	0.73	0.73	0.68
Δ	−0.01	0.04	0.03	−0.03

Comparison of υ Constants for XCH_2CH_2 with Corresponding Alkyl Groups

X	MeS	EtS	I	Cl	C_2H_3
υXCH_2CH_2	0.78	0.79	0.93	0.97	0.75
υalkyl	0.68	0.68	0.68	0.68	0.68
Δ	−0.10	−0.11	−0.25	−0.29	−0.07

Comparison of υ Constants for XCH_2 with Corresponding Alkyl Groups

X	F	Cl	Br	I	MeS	EtS	C_2H_3
υXCH_2	0.62	0.60	0.64	0.67	0.70	0.71	0.69
υalkyl	0.56	0.56	0.56	0.56	0.68	0.68	0.68
Δ	−0.06	−0.04	−0.08	−0.11	−0.02	−0.03	−0.01

Comparison of υ Constants for Groups Containing S in Place of CH_2 with Corresponding Groups Containing CH_2

X(S)	$MeSCH_2$	$EtSCH_2$	$MeSCH_2CH_2$	$EtSCH_2CH_2$	$PhSCH_2$	EtSCHMe	$(EtS)_2CH$
υX(S)	0.70	0.71	0.78	0.79	0.82	1.10	1.39
$\upsilon X(CH_2)$	0.68	0.68	0.68	0.68	0.70	1.05	1.54
Δ	−0.02	−0.03	−0.10	−0.11	−0.12	−0.05	0.15

Comparison of υ Values for Groups Capable of Resonance, X, with Values of Model Groups, X^1

X	Ph	C_2H_3	c-C_3H_5	EtC=O	PrC=O
X^1	c-C_6H_{11}	Et	c-C_4H_7	EtCHOH	PrCHOH
υX	1.66	1.31[b]	1.06	0.79	0.80
υX^1	0.87	0.56	0.51	0.71	0.71
Δ	−0.79	−0.75	−0.55	−0.08	−0.09

Effect of Chain Length on υ for Alkyl Groups $H(CH_2)_n$

n	1	2	3	4	5	6	7	8	9	11	13	15	17
	0.52	0.56	0.68	0.68	0.68	0.73	0.73	0.68	0.68	0.68	0.68	0.68	0.68

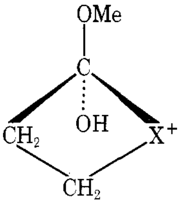
Effect of Ring Formation on υ for Alkyl Groups

Ring	c-C_4H_7	c-C_5H_9	c-C_6H_{11}	c-C_7H_{13}
Alkyl group	CHMeEt	$CHEt_2$	CHEtPr	$CHPr_2$
υ ring	0.51	0.71	0.87	1.00
υ alkyl	1.02	1.51	1.51	1.54
	0.51	0.80	0.74	0.54

[a] Δ = the lower υ value − the upper υ value. [b] This value was chosen as more reliable since it is the average of three determinations.

(Table IV) again shows that when R is alkyl there is a considerable decrease in υ for the oxygen containing groups. Replacement of CH_2 by O in a chain gives interesting results. A comparison of $\upsilon ROCH_2$ with υRCH_2CH_2 (Table IV) results in a small decrease in υ for the oxygen containing groups. This decrease is probably significant as it is shown for all R groups. A comparison of $RO(CH_2)_2$ with $R(CH_2)_3$ by contrast shows a large increase in υ for oxygen containing groups when R is alkyl (Table IV). A comparison of υ constants for XCH_2CH_2 with those of the alkyl groups of the same size shows large increases in υ when X is Cl or I, and smaller increases when X is MeS or EtS (Table IV). A comparison of υ for XCH_2 groups with υ for alkyl groups of the same size shows generally a small increase in υ (Table IV). Furthermore, a comparison of υ for

$RO(CH_2)_3$ with $R(CH_2)_4$ suggests no significant difference in υ. The question arises, then, as to how to account for the behavior of groups of the type XCH_2CH_2 where X = RO, Cl, I, RS. Such groups appear to have unexpectedly large υ values. A possible explanation is that the protonated ester is stabilized as shown in I and therefore is less reactive to the water molecule.



I

A comparison of υ values for groups in which CH_2 is replaced by S (Table IV) shows little effect when the group is of the type RSCHR.[1]

Taft[8] has suggested that the E_S values of α,β-unsaturated substituents such as Ph and C_2H_3 include an appreciable resonance effect. If we choose appropriate alkyl groups as models of the steric effect of α,β-unsaturated substituents and compare their respective υ values (Table IV) we can arrive at an estimate of the magnitude of the resonance effect. The cyclopropyl group shows a somewhat smaller but still considerable resonance effect, as might be expected.[9] The propanoyl and butanoyl groups show a small increase in υ which may not be significant. Thus, the resonance contribution to υ for these groups is at best small.

Let us consider the effect of chain length on the υ values for normal alkyl groups. Inspection of the values shown in Table IV shows that once the chain has reached a length of three carbon atoms the value of υ remains essentially constant. Finally, we may examine the behavior of cycloalkyl groups as compared with the corresponding alkyl groups (Table IV). Excluding the cyclopropyl group because for this substituent υ undoubtedly includes a resonance contribution, the cycloalkyl groups all show υ values very much smaller than those of the corresponding alkyl groups.

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Nucleophilicity of Aromatic Sulfenamides and the "α Effect"

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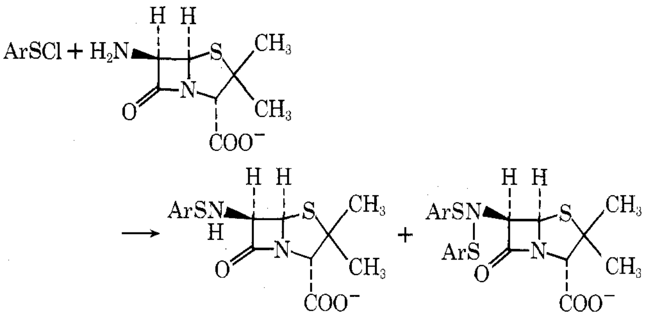
Sulfenamides, the sulfenic acid isosteres of carboxylic acid amides, resemble such amides generally in being water insoluble, crystalline compounds of greatly reduced basicity. The greater nucleophilicity of sulfenamide nitrogen has been noted, however, in that sulfenamides of ammonia or primary amines may be condensed with carbonyl compounds to yield sulfenimines or acylated with activated carboxylic acids under relatively mild conditions to yield *N*-acylsulfenamides. The ready cleavage of the S–N linkage by dilute mineral acid has also been noted.[1-3] The literature concerning mechanistic aspects of the chemistry of the sulfur–nitrogen bond in sulfenamides has been reviewed.[4] In this paper we report further observations on the nature of the nucleophilic character of nitrogen in primary aromatic sulfenamides derived from 6-aminopenicillanic acid (6-APA) which suggest that in certain instances, this nucleophilicity obeys the rules of the "α effect" postulated by Klopman et al.[5] and is sensitive to and regulated by substitution on the aromatic ring.

The desirability of readily available, stable, crystalline sulfenamide derivatives of 6-APA which could be subsequently acylated and converted into useful semisynthetic penicillin derivatives provided the impetus for our initial efforts in this area. The ready availability and suitable reactivity of aromatic sulfenyl halides[6] led to the use of phenylsulfenyl chloride in initial experiments. The sulfenylation of 6-APA under aqueous conditions was achieved by means of a modified Schotten–Baumann procedure. From the outset it was readily apparent that the major product from this reaction was not the desired 6-APA phenylsulfenamide (1) but was instead the dibenzenesulfenimide (2). The structure of 2, produced in about 90% yield (based on sulfenyl chloride), was determined through its spectral characteristics and it was separated from approximately 10% of the minor product (1) by conversion of the mixture to their respective methyl esters with diazomethane and column chromatography. Differences thus determined between the NMR shifts of the β-lactam protons were found to be characteristic of the series and were used to assign product ratios in subsequent experiments (see below).



1 2

Whereas dibenzenesulfenimides of ammonia,[7] amidines,[8] and other amines[9] have been known for some time, the conditions for their formation have generally been more vigorous and the formation of dibenzenesulfenimides under weak base catalysis has been reported to proceed in poor yield.[10] Since 2 was formed preferentially over a wide range of reaction conditions, other factors affecting the course of this reaction were investigated. To this end, the reaction conditions were held constant while the aromatic substitution pattern of the phenylsulfenyl chloride was varied. As the electron-withdrawing power of the aromatic ring substituents increased, an orderly *decrease* in the proportion of 6-APA diarylsulfenimide formed occurred together with a corresponding increase in the proportion of 6-APA arylsulfenamide, culminating in the isolation of quantitative yields of *o*-nitro- and *p*-nitrophenyl-6-APA sulfenamides (Table I). This observation strongly suggests that the initial product forming step in the sulfenylation of 6-APA is the formation of the desired sulfenamide (1) but, with appropriate aryl substitution present, this sulfenamide may itself react with 6-APA competitively, thus generating a mixture of sulfenamide 1 and