two interacting chromophores. They interpreted these results as being due to the reciprocal influence of two oscillators. This is another way of looking at the phenomenon, and it leads to the same conclusions as derived from the molecular orbital approach.

Experimental Section

The molecular orbital calculations were carried out on an IBM 360-65 computer for molecules requiring over a 41 × 41 matrix or when vectors were required; otherwise, a program written by the author for the IBM-1130 was used. The standard convention was adopted for heteroatoms (x) in which h_x and k_{cx} were related, respectively, to the Coulomb integral (α_x) and the resonance integral (β_{cx}) by the relationships $\alpha_x = \alpha_0 + h_x\beta_0$ and $\beta_{cx} = k_{cx}\beta_0$.[8] An auxiliary inductive parameter, AIP $= 0.1\ \Sigma_x\ h_x$, was used for all carbon atoms adjacent to heteroatoms.

Heteroatom Parameter Optimization.—Dr. D. M. Sturmer, of the Kodak Research Laboratories, supplied the heteroatom parameters used in this work, which he optimized as follows. A special program was used to calculate transition energies (in units of β_0) for a large number of compounds using an initial set of values (h_x and k_{cx}) for the heteroatom. The calculations for all the compounds were then repeated with another set of values for h_x and k_{cx}. The procedure was repeated continuously while varying h_x and k_{cx} systematically. After each set of calculations a linear correlation was made between the observed transition energies and those calculated with that particular set of values. A contour surface was generated when both h_x and k_{cx} were plotted against the standard deviations of the linear correlations. This produced the best set of values for the heteroatom in those compounds.

The values for sulfur were optimized for a large number of cyanine dyes using for ring nitrogen $h_x = 1.5$ and $k_{cx} = 1.0$. The values used for the chain nitrogen in the R_2 groups were optimized for a limited number of 8-azacarbocyanines and 8-azadicarbocyanines. The oxygen parameters were chosen to correlate with the spectra of the 1,6-diethoxy-, 1,4-diethoxy-, and 1,4,7-triethoxyphenalenium ions. The values are summarized below in the order $h_x(k_{cx})$.

S = 0.75 (0.6)
ring alkyl N = 1.5 (1.0)
O = 1.0 (0.7)
chain N = 0.7 (1.0)
CH_3C = −0.1 (inductive model)

Registry No.—**3**, 40083-03-2; **4**, 40083-04-3; **5**, 40083-05-4; **6**, 40083-06-5; **7**, 40036-99-5; **8**, 40083-07-6; **9**, 40083-08-7; **10**, 40083-09-8; **11**, 40083-10-1; **12**, 40083-11-2; **13**, 40083-12-3; **14**, 40083-13-4; **15**, 40083-14-5; **16**, 40083-15-6; **17**, 40083-16-7; **18**, 40083-17-8; **20**, 40037-00-1; **21**, 40083-18-9; **22**, 40083-19-0; **23**, 40083-20-3; **24**, 40083-21-4.

Acknowledgment.—The author is greatly indebted to Dr. D. M. Sturmer for supplying the optimized parameters and for those calculations requiring the use of the IBM 360-65 computer.

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Transmission of Substituent Effects in Heterocyclic Systems. Evidence for Coplanarity in 2-Phenylthiazole, and a Determination of $\sigma_p{}^+$ for the Coplanar Phenyl Substituent[1]

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The rate of solvolysis of 1-(2-phenyl-5-thiazolyl)ethyl chloride has been studied and compared with other solvolysis data in the thiazole system. The rate of solvolysis is 20 times that expected for a substituent having a $\sigma_p{}^+$ value of −0.179. This rate is, however, consistent with a $\sigma_p{}^+$ value of −0.34. These results are explained in terms of a coplanar thiazole–phenyl system.

In conjunction with studies from these laboratories of the transmission of substituent effects in heterocyclic systems[2-4] we have had occasion to observe the same substituent in several different electronic and geometric environments. Data on the phenyl substituent in the thiazole system are unique and can be used to understand more fully this versatile substituent. In earlier studies of electrophilic substitution reactions it has been observed that the effect of the *p*-phenyl substituent is variable and inconsistent.[5-7] Stock and Brown have pointed out that the σ^+ substituent constant for phenyl is variable[7,8] and shows much more scatter as evaluated from a variety of reactions than do most electrophilic substituent constants, and that this is probably the result of noncoplanarity.

Berliner and Shieh[9] studied the constrained system 1-(2-fluorenyl)ethyl chloride and found its rate of solvolysis to be 700 times that of 1-phenylethyl chloride. In evaluating the large rate acceleration in this system and in 2-(2-fluorenyl)-2-chloropropane, Brown and Inukai[10] pointed out that a phenyl moiety constrained to coplanarity is much more effective in electron release than a typical biphenyl system. They calculated a replacement constant, $\sigma_{Ar}{}^+$, for the fluorenyl moiety of −0.49. It may be concluded that a *p*-phenyl substituent held to a planar geometry should result in a $\sigma_p{}^+$ value of approximately −0.37 (correcting for *m*-CH_2 and *o'*-CH_2).

In our studies of the transmission of substituent effects in thiazoles, we have analyzed the 1-(2-x-5-thiazolyl)ethanol system where x = H, CH_3, Cl, SCH_3, and OCH_3. These data gave excellent correla-

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[1] Supported in part by a grant from the National Science Foundation, GP-6133X.

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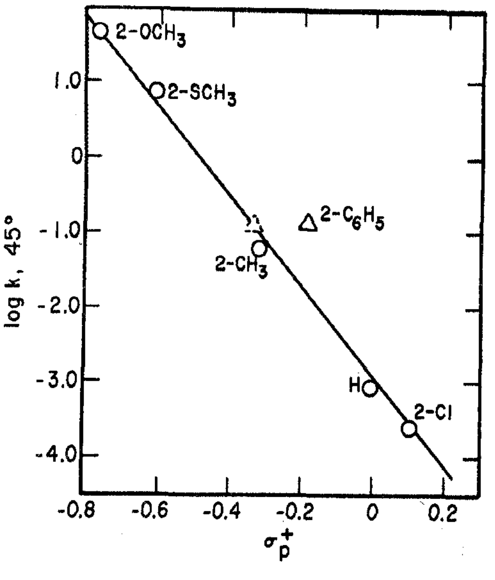

Figure 1.—Correlation of solvolysis rates of substituted 1-(5-thiazolyl)ethyl chlorides in 80% ethanol with $\sigma_p{}^+$.

tion with $\sigma_p{}^+$.[11] However, the additional data shown in Table I for the phenyl substituent do not fit the same correlation as is apparent from Figure 1. Although the original $\sigma_p{}^+$ constant for phenyl, −0.179,[12] is substantially less negative than the $\sigma_p{}^+$ constant for methyl, −0.311, in the present instance phenyl is more activating than methyl.

Table I

Rate Constants for the Solvolysis of 1-(2-Phenyl-5-thiazolyl)ethanol Derivatives in 80% Ethanol

Compound solvolyzed	T, °C	Method[a]	k_1, sec^{-1}
1-(2-Phenyl-5-thiazolyl)ethyl p-nitrobenzoate	25.0		1.73×10^{-8} [b]
	75.0	A	1.17×10^{-5}
	110.0	A	4.06×10^{-4}
1-(2-Phenyl-5-thiazolyl)ethyl chloride	25.0	B	8.24×10^{-3}
1-(5-Thiazolyl)ethyl chloride[c]	25.0	B	8.55×10^{-5}

[a] A, using sealed ampoules; B, at constant pH. [b] Extrapolated from data at higher temperatures. [c] From ref 11.

Recent molecular orbital calculations of Bodor, Farkas, and Trinajstic[13] agree with these data. Their studies suggest that the planar configuration of 2-phenylthiazole is the most stable form. In contrast, their calculations for the 2-phenylthiazolium cation suggest that it is not planar and that there is an appreciable angle of twist between the two rings. Thus the complete absence of ortho hydrogens apparently allows coplanarity, but the presence of one ortho hydrogen apparently leads to a system with an appreciable angle of twist between the two rings. Concordant with this suggestion is our previous observation[4] that the solvolysis rate of 1-(5-phenyl-2-thienyl)ethyl p-nitrobenzoate is in line with the usual constant for phenyl.

Our rate data may therefore be used as an independent basis for calculating an electrophilic substituent constant $\sigma_p{}^+$, for a coplanar phenyl moiety. Using a reaction constant, ρ, of −6.14,[11a] the $\sigma_p{}^+$ constant is −0.34, which is in very satisfying agreement with that calculated above from the fluorenyl moiety.

Experimental Section[14]

2-Phenylthiazole (1).—The procedure of Hantzsch[15] for the synthesis of 2-methylthiazole was modified for the preparation of **1**. A solution of oxalic acid (13.5 g, 0.15 mol) in chloroacetaldehyde dimethyl acetal (18.7 g, 0.15 mol) was heated to reflux for 0.5 hr producing a clear, light tan solution. The oil bath was removed for 10 min and thiobenzamide (20.5 g, 0.15 mol) was added as a solid. The solution was slowly heated and maintained at reflux for 2 hr. After cooling, 70 ml of 30% hydrochloric acid was added with stirring. After refluxing for 5 min, the solution was filtered and extracted with 3 × 50 ml of ether. The combined ether layers were dried ($MgSO_4$) and concentrated to give a light yellow oil which was distilled to yield 14.25 g (59%) of pure 2-phenylthiazole: bp 144–146° (38 mm) [lit.[16] 135–138° (18 mm)]; ir (neat) 3110, 1675, 1475, 1440, 1415, 1310 cm^{-1}; nmr ($CDCl_3$) δ 7.87 (m, 3, 4-H and o-phenyl H) and 7.33 (m, 4, 5-H and m- and p-phenyl H).

Anal. Calcd for C_9H_7NS: C, 67.05; H, 4.38; N, 8.69; S, 19.88. Found: C, 67.31; H, 4.61; N, 8.56; S, 19.65.

1-(2-Phenyl-5-thiazolyl)ethanol (2).—Ether (500 ml) was stirred at −80° under a nitrogen atmosphere while 2-phenylthiazole (10.0 g, 0.062 mol) in 50 ml of ether was added dropwise from a dropping funnel. Simultaneously, n-butyllithium (0.07 mol, 43.4 ml in hexane) was added from a second dropping funnel. The thiazole was kept in slight excess during the 30-min addition period. After the addition was complete, the solution was stirred for 75 min before rapidly adding acetaldehyde (11.7 ml, 0.2 mol). After stirring for 1 hr, the colorless solution was quenched with 100 ml of water. The layers were separated and the aqueous layer was extracted with 2 × 100 ml of ether. The combined organic layers were dried ($MgSO_4$) and concentrated, and impurities were distilled away to give the crystalline alcohol **2** in 76% yield: mp 84.5–85° (lit.[17] mp 87–88°); nmr ($CDCl_3$) δ 7.80 (m, 2, o-phenyl H), 7.50 (s, 1, 4-H), 7.33 (m, 3, m- and p-phenyl H), 5.10 (q, 1, J_{CH,CH_3} = 6.2 Hz, $CHCH_3$), 3.17 (s, 1, OH), 1.58 (d, 3, J_{CH-CH_3}) = 6.2 Hz, $CHCH_3$).

Anal. Calcd for $C_{11}H_{11}NOS$: C, 64.32; H, 5.41; N, 6.84; S, 15.63. Found: C, 64.11; H, 5.24; N, 6.62; S, 15.49.

1-(2-Phenyl-5-thiazolyl)ethyl Chloride (3).—Alcohol **2** was converted into the chloride **3** in 75% yield using phosphorus pentachloride. Crystallization from hexane afforded a pure sample of **3**: mp 35.5–37.0°; nmr ($CDCl_3$) δ 1.87 (d, 3, J = 6.7 Hz, $CHCH_3$), 5.31 (q, 1, J = 6.7 Hz, $CHCH_3$), 7.37 (m, 3, m- and p-phenyl H), 7.68 (s, 1, 4-H), 7.87 (m, 2, o-phenyl H).

Anal. Calcd for $C_{11}H_{10}ClNS$: C, 59.06; H, 4.51; Cl, 15.84; N, 6.26. Found: C, 59.20; H, 4.38; Cl, 15.72; N, 6.44.

1-(2-Phenyl-5-thiazolyl)ethyl p-Nitrobenzoate (4).—The alcohol **2** was converted into the lithium salt using butyllithium and treated with p-nitrobenzoyl chloride. Work-up in the usual manner afforded the ester **4** in 85% yield. Crystallization from hexane gave the pure ester **4**: mp 89.5–90.5°; nmr ($CDCl_3$) δ 1.85 (d, 3, J = 6.1 Hz, $CHCH_3$), 6.52 (q, 1, J = 6.1 Hz, $CHCH_3$), 7.43 (m, 3, m- and p-phenyl H), 7.50 (s, 1, 4-H), 7.90 (m, 2, o-phenyl H), 8.30 (s, 4, p-nitrophenyl H).

Anal. Calcd for $C_{18}H_{14}N_2O_4S$: C, 61.01; H, 3.98; N, 7.90; S, 9.05. Found: C, 61.17; H, 4.14; N, 8.09; S, 9.13.

Kinetic Procedures. Kinetic procedures have been reported previously.[3]

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Registry No.—**1**, 1826-11-5; **2**, 10045-48-4; **3**, 40187-13-1; **4**, 40187-14-2; oxalic acid, 144-62-7; chloroacetaldehyde dimethyl acetal, 97-97-2; thiobenzamide, 2227-79-4; acetaldehyde, 75-07-0; phosphorus pentachloride, 10026-13-8; *p*-nitrobenzoyl chloride, 122-04-3.

The Formation of Allenes on Alkaline Treatment of 3-Nitroso-4,5,5-trialkyl-2-oxazolidones[1]

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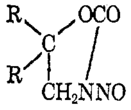
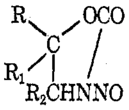
On treatment of 3-nitroso-4-methyl-5,5-pentamethylene-2-oxazolidone (**3**) with sodium 2-methoxyethoxide in 2-methoxyethanol, or with sodium methoxide in methanol, ~15–20% yields of 1,1-pentamethyleneallene (**4**) are obtained, together with several other compounds. Similarly, 3-nitroso-4,5,5-trimethyl-2-oxazolidone (**11**) yields 6–7% 1,1-dimethylallene (**13**), and 3-nitroso-4,5-dimethyl-5-*tert*-butyl-2-oxazolidone (**12**) yields 1-methyl-1-*tert*-butylallene (**14**) in 15% yield. The reaction of pinacolone with zinc and methyl α-bromopropionate yields the expected mixture of diastereoisomers of methyl 3-hydroxy-2,3,4,4-tetramethylpentanoate (**15**), if carried out under mild conditions. Long refluxing, however, results in the formation of α,β,β,γ-tetramethylvalerolactone (**16**).

Studies of the reactions which occur when 3-nitroso-5,5-dialkyl-2-oxazolidones (**1**) are treated with bases have proved of interest not only because of the wide variety of products produced but also because of the multiplicity of mechanistic interpretations used to account for the results.[3] The present study on the reactions of 3-nitroso-4,5,5-trialkyl-2-oxazolidones (**2**) was undertaken for three main reasons: (1) to find out the synthetic utility of such reactions, (2) to learn more about the behavior of unsaturated cations, and (3) to compare the products formed from diastereoisomers of type **2**.

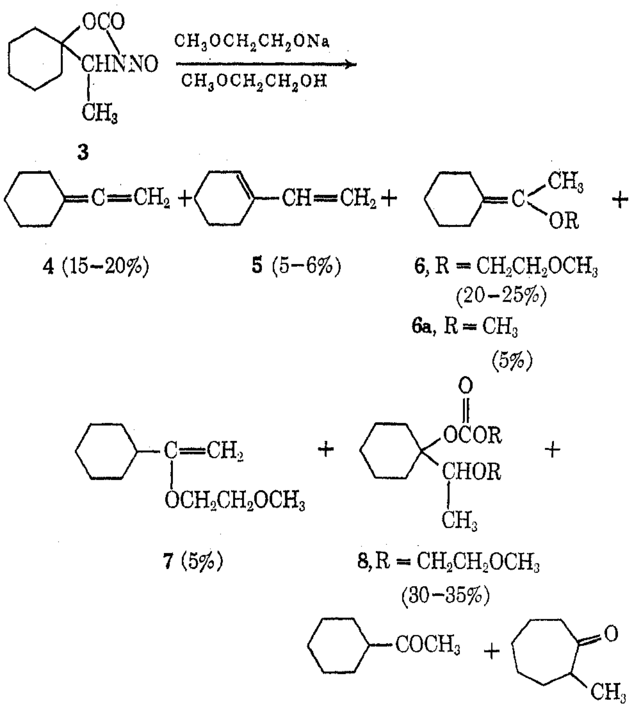


1



2

The most detailed study of reaction products was carried out with 3-nitroso-4-methyl-5,5-pentamethylene-2-oxazolidone (**3**) when treated with sodium 2-methoxyethoxide in 2-methoxyethanol. The main products were 1,1-pentamethyleneallene[4] (**4**), 1-(2-methoxyethoxy)ethylidenecyclohexane (**6**), and 1-[1-(2-methoxyethoxy)ethyl]cyclohexyl 2-methoxyethyl carbonate (**8**). Smaller amounts of 1-vinylcyclohexene[5] (**5**), 1-methoxyethylidenecyclohexane (**6a**), 1-(2-methoxyethoxy)vinylcyclohexane (**7**), methyl cyclohexyl ketone (**9**), and 2-methylcycloheptanone (**10**) were present. Because of the large number of products formed and the fact that none is formed in a large yield, the utility of such reactions will probably be minimal. Probably the most interesting result is that a new allene synthesis has been discovered.



3

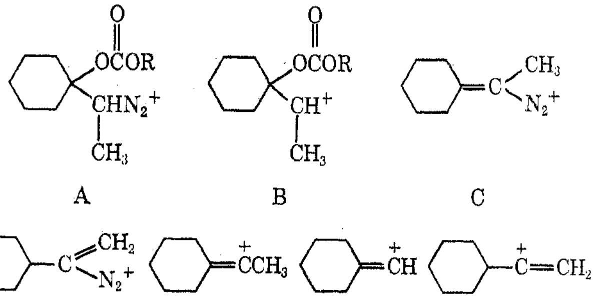
4 (15–20%) **5** (5–6%) **6**, R = $CH_2CH_2OCH_3$ (20–25%)

6a, R = CH_3 (5%)

7 (5%) **8**, R = $CH_2CH_2OCH_3$ (30–35%)

9 (5%) **10** (5%)

The formation of these compounds may be explained by assuming attack of the alkoxide ion at the carbonyl group of **3** followed by changes outlined previously[3c,d] to yield the intermediate (A). Loss of nitrogen from A yields cation B, which can react with solvent to produce **8**.[6] Base-catalyzedel imination of alkylcar-



A B C

D E F G

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[1] This work was supported in part by Grant 12445X of the National Science Foundation.

[2] This work was done in an undergraduate research program by Mr. Ving Lee during 1970–1971.

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