brought to reflux, and TLC analysis indicated complete disappearance of 16 after 30 min. The solution was cooled to room temperature, water (25 mL) was added, and the product was extracted into chloroform $(3 \times 10 \text{ mL})$. The combined organic layers were washed with brine, dried, and evaporated to leave a light yellow oil. Heating of this material in a sublimation apparatus at 70 °C (0.02 torr) afforded 49 mg (68%) of 20 as a colorless solid: mp 90.5-92.0 °C (from petroleum ether); IR (CCl₄) 2965, 2865, 1492, 1363, 1318, 1249, 1233, 1177, 968, 849 cm⁻¹; ${}^{1}H$ NMR (CDCl₃) δ 5.94 (dd, J = 6, 3 Hz, 1 H), 5.67 (br s, 1 H), 5.30–5.07 (m, 2 H), 2.99 (6 lines, J = 3, 2 Hz, 1 H), 2.78 (t, J =5 Hz, 1 H), 1.11 (s, 9 H), 1.08 (s, 9 H). Anal. Calcd for $\rm C_{16}H_{24}N_2O:$ C, 73.81; H, 9.29. Found: C, 73.94; H, 9.36.

Determination of Electrocyclic Ring-Opening Rates for 12. Bicyclooctatriene 12 was generated in C_6D_6 by photolysis of α -diketone 11 (~10 mg) in an NMR tube at ~5 °C in the predescribed manner. The tube was then placed in the probe of a Bruker HX-90 NMR spectrometer preset to the desired temperature and allowed to equilibrate for 5 min. The disappearance

of 12 was then monitored as a function of time by integration of the δ 3.72 absorption relative to the residual proton peak of the solvent. Plots of the natural logarithm of the relative concentration of 12 as a function of time gave straight lines over the entire time period examined which generally exceeded 2 half-lives. The rate constants as a function of temperature obtained by this method are given in Table I along with the activation parameters calculated from these data.

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Registry No. 4, 76794-05-3; 6, 732-26-3; 7, 1988-75-6; 8, 20778-61-4; 9, 20784-84-3; 10, 34105-76-5; 11, 85067-22-7; 12, 85067-23-8; 13, 85067-24-9; 16, 85067-25-0; 17, 85067-26-1; 20, 85096-89-5; (cyclobutadiene)iron tricarbonyl, 12078-17-0; ceric ammonium nitrate, 16774-21-3; cyclobutadiene, 1120-53-2; Nmethyltriazolinedione, 13274-43-6.

Infrared Spectra and Transmission of Electronic Effects in Substituted Phenyl N.N.Dimethylcarbamates and S.Phenyl N.N-Dimethylthiocarbamates

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Carbonyl stretching frequencies in CCl₄ and CHCl₃ and hydroxyl stretching frequency shifts of phenol as a proton donor in CCl4 were measured for series of substituted phenyl N,N-dimethylcarbamates (I) and S-phenyl N,N-dimethylthiocarbamates (II). The data were correlated with Hammett σ substituent constants and with ν (C=O) and $\Delta \nu$ (OH) values of N,N-dimethylbenzamides (III). The results were compared with similar correlations for series of substituted N,N-dimethyl-N'-phenylureas (IV) and N,N-dimethylcinnamamides (V). The transmission of electronic effects through O, S, NH, and CH=CH moieties and the conformations of compounds I, II, and IV are discussed. The σ_p^+ substituent constants of OCONMe₂ and SCONMe₂ groups have been estimated to be approximately -0.08 and 0.13, respectively, by using carbonyl stretching frequencies and linear correlations.

Spaargaren et al.¹ reported the carbonyl stretching frequencies and hydroxyl stretching frequency shifts of phenol as a proton donor in CCl₄ for a series of substituted N,N-dimethylbenzamides and -cinnamamides and correlated them with Swain-Lupton substituent constants, amide rotation barriers, and results of Hückel molecular orbital calculations. Laurence and Berthelot² showed that statistically most significant results are obtained by correlating the carbonyl stretching frequencies of substituted N,N-dimethylbenzamides with Hammett σ substituent constants. Jones and Wilkins³ have found reasonably good linear correlations for ¹³C NMR chemical shifts of N,Ndimethylbenzamides with the Swain-Lupton and Dewar equations.

Several papers⁴⁻⁸ have been devoted to the investigation

of transmission of polar effects through systems containing an oxygen or sulfur atom. It has been observed⁹ that the transmission through moieties with lone-pair electrons is markedly influenced by the solvent. Marcus et al.¹⁰ compared the transmissive ability of oxygen and sulfur atoms in various series and concluded that it is strongly dependent on the electronic structure of the whole system under consideration. In a number of cases, anomalously enhanced transmissibility has been observed^{11,12} for systems containing O, S, and NH groups and was called by Litvinenko¹² "the positive bridge effect". The explanation of this phenomenon was suggested¹³ to be a result of

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Substituted Phenyl N,N-Dimethylcarbamates

complicated superposition of inductive and resonance effects of the substituted aromatic ring, the bridge group, and the reaction site.

In connection with our previous investigations⁴⁻⁸ and in the interest of further elaborating the topic of transmission of electronic effects through oxygen and sulfur atoms, we investigated the carbonyl stretching frequencies and hydroxyl stretching frequency shifts of phenol as a proton donor for series of substituted phenyl N,N-dimethylcarbamates (I) and S-phenyl N,N-dimethylthiocarbamates



(II) and compared the values with the analogous data for N,N-dimethylbenzamides (III),¹ N,N-dimethyl-N'phenylureas (IV),¹⁴ and N,N-dimethylcinnamamides (V).¹ For series III additional data were determined by using a set of 11 available derivatives.

Results and Discussion

Carbonyl Stretching Frequencies. The carbonyl stretching frequencies of series I-III are given in Table I. The values measured for benzamides III are in good agreement with those reported previously.¹

The carbonyl stretching frequencies of compounds II, IV, and I are higher by approximately 31, 42, and 87 cm^{-1} respectively, than those of comparable benzamides III. This order is in qualitative agreement with increasing electron-withdrawing effects of the phenylthio, phenylamino, and phenyloxy groups. The C=O stretching frequencies of carbamates I are larger than those of thiocarbamates II and ureas IV, probably because of a larger -I effect for the phenyloxy group than for the phenylthio and phenylamino groups. The frequency difference between the ν (C=O) of carbamates I and thiocarbamates II is similar to that observed for analogous esters and thioesters of carboxylic acids.^{15,16}

The carbonyl absorption bands of all compounds I, II, and IV¹⁴ have a simple and symmetrical shape, indicating a great preponderance of only one of the two possible nearly planar conformations.

 \ddot{O} ki and Nakanishi¹⁷ observed that methyl N,N-dialkylcarbamates exhibit bifurcated ν (C=O) bands and assigned the maxima to the s-trans and s-cis conformations. In the spectra of ethyl carbamates¹⁷ only the lower frequency band was found and ascribed to the s-trans conformation.

A plot of the ν (C=O) value of phenyl N,N-dimethylcarbamate (Ih, measured by us in CCl₄) together with the carbonyl stretching frequencies¹⁷ of *s*-trans-methyl N,Ndimethylcarbamate (1711 cm⁻¹) and s-trans-ethyl N,Ndimethylcarbamate (1706 cm⁻¹) against Taft's σ^* values of Ph, Me, and Et groups reveals a linear relationship.

Table I. Carbonyl Stretching Frequencies (ν (C=O)) and Hydroxyl Frequency Shifts ($\Delta \nu$ (OH)) of Substituted Phenyl N,N-Dimethylcarbamates (I), S-Phenyl N,N-Dimethylthiocarbamates (II), and

N, N-Dimethylbenzamides (III)

	$\frac{\nu(C=0) \text{ cm}^{-1}}{\nu(C=0) \text{ cm}^{-1}}$						
	V		$\Delta \nu$ (OH),				
compa	X		CHCI ₃	cm ·			
Ia	4-OBu	1729.5	1715.5	220			
Ib	4-OMe	1729.5	1716.5	219			
Ic	4-OEt	1730.0	1715.0	220			
Id	4-t-Bu	1730.0	1715.5	218			
Ie	4-Me	1730.5	1716.0	217			
If	4-Et	1730.5	1716.0	215			
Ig	4 -P h	1731.0	1717.0	212			
Ih	Н	1732.0	1718.0	212			
Ii	4-SMe	1732.0	1718.5	211			
Ij	4 -F	1733.0	1720.5	207			
Ik	4-I	1735.0	1721.0	203			
Il	4-Cl	1734.5	1721.5	204			
Im	4-Br	1734.5	1721.5	203			
In	4-COOMe ^a	1736.0	1722.5	190			
Io	4-COOEt °	1735.5	1722.5	192			
Ip	4-COMe ^c	1736.0	1723.5	203 <i>a</i>			
Ir	4-CN	1739.0	1727.5	179			
Is	$4-NO_2$	1739.5	1729.5	186			
IIa	4-OBu	1674.5	1659.5	234			
IIb	4-OMe	1674.5	1660.0	234			
IIc	4-OEt	1674.5	1660.0	234			
IId	4-t-Bu	1675.5	1660.0	229			
IIe	4-Me	1675.5	1660.5	232			
\mathbf{IIf}	4-Et	1675.5	1660.5	227			
IIg	Н	1677.0	1663.0	224			
IIh	4-SMe	1676.0	1662.0	225			
IIi	4-F	1677.5	1664.0	223			
IIj	4-I	1678.5	1665.5	219			
IIk	4-Cl	1678.0	1665.5	218			
III	4-Br	1677.5	1664.0	217			
IIm	4-COOMe ^e	1679.5	1666.0	198			
IIn	4-COMe ⁷	1680.5	1666.0	213^{a}			
IIo	4-CN	1682.0	1670.5	185			
IIp	$4 - NO_2$	1682.5	1672.0	200			
IIIa	4-OBu	1642.5	1619.0	322			
IIIb	4-OMe	1643.0	1619.5	311			
IIIc	4-Me	1644.5	1622.5	308			
IIId	3-Me	1645.3 ^g	_	300 ^g			
IIIe	H	1646.0	1627.5	299			
\mathbf{IIIf}	4-SMe	1645.5	1627.0	303			
IIIg	4-F	1647.0	1628.5	294			
IIIh	3-OMe	1646.5^{s}		300 ^g			
IIIi	4-I	1646.5	1628.0	285			
IIIj	4-Cl	1647.0	1629.5	287			
IIIk	4-Br	1647.5	1630.0	288			
IIII	3-F	1648.2^{g}		280 ^g			
IIIm	3-CI	1648.5^{s}		279 ⁸			
IIIn	3-Br	1648.5^{g}		281 ^g			
IIIo	3-CN	1651.5^{g}		268 ^g			
IIIp	4-CN	1652.0	1636.5	266			
IIIr	3-NO ₂	1652.1^{g}		265 ^g			
IIIs	$4-NO_2$	1652.5	1639.5	268			

^a For COOMe: $\nu(C=0) = 1732.5 (CCl_4), 1716.5 \text{ cm}^{-1}$ (CHCl₃). ^b For COOEt: $\nu(C=0) = 1727.0 (CCl_4), 1719.5 \text{ cm}^{-1}$ (CHCl₃). ^c For COMe: $\nu(C=0) = 1690.5 (CCl_4), 1684.0 \text{ cm}^{-1}$ (CHCl₃). ^d Hydrogen bonding of type CH₃--C=O···H--O-. ^e For COOMe: $\nu(C=0) = 1730.0 (CCl_4), 1723.5 \text{ cm}^{-1} (CHCl_3).$ ^f For COMe: $\nu(C=0) = 1692.5 (CCl_4), 1684.5 \text{ cm}^{-1} (CHCl_3).$ ^g Data taken from ref 1.

This suggests that the $\nu(C==0)$ absorption of Ih can be assigned to the nearly planar s-trans conformation, which is probably favored for all carbamates of series I. It is reasonable to suppose that the same is true also for the thiocarbamates II. The preference of the s-trans conformation in the compounds of series I could result from a larger steric repulsion between the lone-pair electrons of ether-oxygen and nitrogen atoms (the so-called "rabbit

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ear"; cf. Hutchins and Eliel^{18,19}) as a result of a strong -I effect of the phenyl group, which causes a destabilization of the s-cis conformation. For N,N-dimethyl-N'-phenyl-ureas (IV) the s-trans conformation has been proposed.¹⁴ Kruk and Spaargaren²⁰ have shown that in the favored conformation of the N,N-dimethylcinnamamides (V), the C=O group is s-cis with respect to the C=C bond. This s-cis conformation in series V is analogous to the s-trans conformation illustrated below.



The comparison of data measured in CCl₄ and CHCl₃ shows that the carbonyl stretching frequencies of compounds I and II exhibit a smaller solvent effect than benzamides III. When the $\nu(C=0)$ values in CHCl₃ are plotted against those in CCl₄, practically equal slopes are obtained for series I and II while in the case of series III the slope is much greater. This indicates that not only the electrons of the C=O group oxygen atom but also the lone-pair electrons of the bridge atoms (Y = O or S) take part in the hydrogen bonding interaction with chloroform. On the other hand, the solvent effect on the carbonyl stretching frequencies of dimethylphenylureas IV¹⁴ is comparable to that of the ν (C=O) values of benzamides III. This demonstrates that the lone-pair electrons of the NH group form practically no hydrogen bonds with chloroform. This probably results from significantly greater steric hindrance in series IV than in carbamates I and thiocarbamates II.

Hydrogen Bonding with Phenol. Compounds of series I and II interact with phenol to form hydrogen bonds to the oxygen atom of their C=O groups as do those of the benzamides III, cinnamamides V,¹ and ureas IV.¹⁴ The hydroxyl stretching frequency shifts of phenol $[\Delta\nu(OH) = \nu(OH)_{\text{free}} - \nu(OH)_{\text{bonded}}]$ can be considered as a measure of the relative strength of both the hydrogen bond and the C=O group²¹ basicity.

To obtain for series I and II $\Delta\nu(OH)$ values comparable to those reported for benzamides III, we attempted to reproduce the measurements under the conditions reported.¹ This resulted in excessively weak absorptions for the stretching vibration of bonded OH groups, however, and caused relatively large errors in determination of $\Delta\nu(OH)$ values. Consequently, the previously²² examined conditions and concentrations of substrate, compound, and phenol were chosen for the present study in order to improve the accuracy of the determinations.

The $\Delta\nu(OH)$ values for series I–III are listed in Table I. In the case of benzamides III most of the data are in satisfactory agreement with those published before,¹ except for the 4-nitro compound (IIIs) for which the $\Delta\nu(OH)$ was 14 cm⁻¹ higher than reported.¹

According to the empirical equation (eq 1),²³ the energy

$$-\Delta H = 0.067 \Delta \nu (\text{OH}) + 2.64 \text{ (kJ/mol)}$$
(1)

(18) R. O. Hutchins, L. D. Kopp, and E. L. Eliel, J. Am. Chem. Soc., 90, 7174 (1968).

of hydrogen bonding with phenol can be estimated. For carbamates I and thiocarbamates II, eq 1 gives $-\Delta H = 15-18 \text{ kJ/mol}$, and for benzamides III, ureas IV, and cinnamamides V, it gives $-\Delta H = 20-24 \text{ kJ/mol}$.

The $\Delta \nu$ (OH) values of compounds I and II are 87-75 cm⁻¹ lower than those of benzamides III. In contrast, the hydroxyl frequency shifts of ureas IV and cinnamamides V are only 18 and 26 cm⁻¹ lower and higher, respectively, than those of benzamides III. This arrangement is in reasonably good accordance with the idea that in both series I and II the lone-pair electrons of group Y participate in the hydrogen bonding interaction with phenol. Consequently, the hydrogen bonding between the C=O and hydroxyl groups becomes much weaker than in the case of benzamides III and ureas IV. The relatively strong hydrogen bonding in ureas IV is attributable to increased conjugation of the carbonyl group with the lone-pair electrons of the adjacent nitrogen over that possible with the oxygen and sulfur electrons in series I and II. In a similar manner, conjugation between the C=O group and π electrons of the ethylenic C=C group causes the hydrogen bonds formed by the cinnamamides V to be stronger than those of the benzamides I.

Linear Free-Energy Relationships. The results of correlation analysis for $\nu(C=0)$ and $\Delta\nu(OH)$ values of series I-III and V are given in Table II. It is evident that for all series the carbonyl stretching frequencies measured in CCl_4 and $CHCl_3$ give reasonably good correlations with Hammett σ substituent constants. The statistical results of correlations become much less satisfactory when Brown–Okamoto σ^+ values²⁵ are used. The application of carbonyl stretching frequencies of substituted acetophenones proposed instead of substituent constants² leads also to less significant results. As has already been explained,² the better quality Hammett correlation of carbonyl stretching frequencies of benzamides III with σ than with σ^+ is due to a competition between +M effects of the dimethylamino and phenyl groups. This competition causes a strong deconjugation between the benzene ring and the C=O group. Analogous conditions exist also in series I, II, IV, and V.

Good linear correlations are obtained also when the $\nu(C=0)$ values of series I, II, and V are plotted against the corresponding carbonyl stretching frequencies of benzamides III as a reference series in accordance with of the Laurence-Berthelot approach.² Analogously, the $\Delta\nu(OH)$ values of above series correlate well with hydroxyl frequency shift of phenol for benzamides III. The plots of $\Delta\nu(OH)$ values in series I-III and V against the corresponding carbonyl stretching frequencies also show a linear course.

In all correlations the $\Delta\nu(OH)$ values of 4-COMe derivatives were omitted because of preferred hydrogen bonding of acetyl groups with phenol. In other cases some data were not included in the correlations on account of their larger deviations from the straight lines compared to the majority of experimental points.

Substituent Effects of OCONMe₂ and SCONMe₂ Groups. In the case of compounds Ip, IIn, and IIm the $\nu(C=0)$ bands of 4-COMe and 4-COOMe substituents are significantly separated from the carbonyl absorptions of the CONMe₂ group (see footnotes *e* and *f* of Table I). The frequencies of these absorption bands can be utilized to estimate quantitatively the values of substituent effects for 4-OCONMe₂ and 4-SCONMe₂ groups. Statistically

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Table II. Correlations of Carbonyl Stretching Frequencies and Hydroxyl Frequency Shifts of Series I-III and V

series	correlation ^{<i>a</i>}	solvent	r ^b	ρ ^c	id	s ^e	n ^f	g
I	ν (C=O) vs. σ	CCl	0.986	9.35 ± 0.40	1732.1	0.6	18	
I	$\nu(C=O)$ vs. σ	CHĊl,	0.973	12.25 ± 0.73	1718.4	1.0	18	
I	$\Delta \nu$ (OH) vs. σ	CCl	0.986	-40.95 ± 1.83	209.9	2.1	16	Ip, Is
I	$\Delta \nu (OH)$ vs. $\nu (C=O)$	CCl	0.983	-4.28 ± 0.22	7620.9	2.4	15	Ik, Ip, Is
Ι	$\nu(C=O)$ vs. $\nu(C=O)^{III}$	CCl	0.983	1.06 ± 0.07	-16.0	0.7	10	Ik
I	ν (C=O) vs. ν (C=O) ^{III}	CHCl ₃	0,963	0.69 ± 0.06	595.3	1.3	11	
I	$\Delta \nu(OH)$ vs. $\Delta \nu(OH)^{III}$	CCl ₄	0.969	0.63 ± 0.06	20.2	2.6	10	Ir
II	ν (C=O) vs. σ	CCl₄	0.987	7.45 ± 0.33	1676.6	0.4	16	
II	ν (C=O) vs. σ	CHCl ₃	0.973	10.71 ± 0.68	1662.5	0.9	16	
II	$\Delta \nu$ (OH) vs. σ	CCl₄	0.991	-31.51 ± 1.27	224.6	1.3	13	IIm, IIn, IIo
II	$\Delta \nu$ (OH) vs. ν (C=O)	CCl_4	0.972	-6.49 ± 0.48	11109.2	3.6	13	IIj, IIn, IIp
II	ν (C=O) vs. ν (C=O)III	CCl₄	0.988	0.84 ± 0.05	299.8	0.5	10	IIj
II	ν (C=O) vs. ν (C=O) ^{III}	CHCl ₃	0.966	0.62 ± 0.06	652.8	1.0	11	
II	$\Delta \nu$ (OH) vs. $\Delta \nu$ (OH) ^{III}	CCl ₄	0.959	0.63 ± 0.07	35.6	3.1	10	IIo
III	ν (C=O) vs. σ	CCl₄	0.987	9.02 ± 0.37	1645.6	0.5	18	
III	ν (C=O) vs. σ	CHCl ₃	0.984	17.74 ± 1.08	1625.7	1.2	11	
III	$\Delta \nu$ (OH) vs. σ	CCl ₄	0.986	-52.35 ± 2.35	299.2	2.9	16	IIIh, IIIs
III	$\Delta \nu(OH)$ vs. $\nu(C=O)$	CCl	0.977	-5.46 ± 0.31	9281.9	3.8	17	IIIi
\mathbf{V}^{h}	ν (C=O) vs. σ	CCl	0.949	4.99 ± 0.48	1657.8	0.6	14	4- F
V^h	$\Delta \nu$ (OH) vs. σ	CCl	0.962	-29.86 ± 2.57	329.4	2.6	13	$3-CN$, $4-NO_2$
\mathbf{V}^{h}	$\Delta \nu$ (OH) vs. ν (C=O)	CCl	0.974	-5.76 ± 0.43	9883.3	2.2	12	4-F, 3-CN, 4 -NO ₂
\mathbf{V}^{h}	ν (C=O) vs. ν (C=O) ^{III}	CCl	0.980	0.66 ± 0.04	576.4	0.3	13	$4-CN, 4-NO_{2}$
V^h	$\Delta \nu$ (OH) vs. $\Delta \nu$ (OH) ^{III}	CCl_4	0.955	0.60 ± 0.06	149.5	2.8	13	$3-CN, 4-NO_2$

^a Well characterized σ constants taken from ref 24. ^b Correlation coefficient. ^c Slope. ^d Intercept. ^e Standard deviation. ^f Number of compounds used in correlation. ^g Excluded from correlation. ^h Data for correlations taken from ref 1.

Table III. Transmissive Factors of Electronic Effects for O, S, NH, and CH=CH Moieties

moiety (Y)	series	correlation	solvent	$\pi'(\mathbf{Y})$	$\overline{\pi'(\mathbf{Y})^a}$
0	I	ν (C=O) vs. σ	CCl4	1.04 ± 0.09	
0	Ι	$\nu(C=O)$ vs. $\nu(C=O)^{III}$	CCl	1.06 ± 0.07	1.05 ± 0.08
0	Ι	$\nu(C=O)$ vs. σ	CHCl,	0.69 ± 0.08	
0	I	$\nu(C=O)$ vs. $\nu(C=O)^{III}$	CHCl,	0.69 ± 0.06	0.69 ± 0.07
0	I	$\Delta \nu$ (OH) vs. σ	CCl	0.78 ± 0.07	
0	I	$\Delta \nu (OH)$ vs. $\Delta \nu (OH)^{III}$	CCl_4	0.63 ± 0.06	0.70 ± 0.06
S	II	ν (C-O) vs. σ	CCl_4	0.83 ± 0.07	
S	II	$\nu(C=O)$ vs. $\nu(C=O)^{III}$	CCl_4	0.84 ± 0.05	0.83 ± 0.06
S	II	ν (C=O) vs. σ	$CHCl_3$	0.60 ± 0.08	
S	II	ν (C=O) vs. ν (C=O) ^{III}	CHCl ₃	0.62 ± 0.06	0.61 ± 0.07
S	II	$\Delta \nu$ (OH) vs. σ	CCl_4	0.60 ± 0.05	
S	II .	$\Delta v(OH)$ vs. $\Delta v(OH)^{111}$	CCl_4	0.63 ± 0.07	0.61 ± 0.06
NH	IV b	ν (C=O) vs. σ	CCl_4	1.19 ± 0.12	
NH	IV ^b	$\nu(C-O)$ vs. $\nu(C=O)^{III}$	CCl_4	1.08 ± 0.08	1.13 ± 0.10
NH	IV b	ν (C=O) vs. σ	CHCl ₃	0.99 ± 0.12	
NH	IV ^b	$\Delta \nu$ (OH) vs. σ	CCl ₄	0.92 ± 0.19	0.96 ± 0.15
CH=CH	v	ν (C=O) vs. σ	CCl_4	0.55 ± 0.08	
CH=CH	V	ν (C=O) vs. ν (C=O) ^{III}	CCl_4	0.66 ± 0.04	0.60 ± 0.06
CH=CH	v	$\Delta \nu$ (OH) vs. σ	CCl ₄	0.57 ± 0.07	
CH=CH	V	$\Delta \nu$ (OH) vs. $\Delta \nu$ (OH) ^{III}	CCl_4	0.60 ± 0.07	0.58 ± 0.07

^{*a*} Average values. ^{*b*} Taken from ref 14.

significant correlations between the ν (C=O) values² of substituted acetophenones or methyl benzoates and C=O stretching frequencies of 4-OCONMe₂ and 4-SCONMe₂ groups of compounds Ip, IIn, and IIm from Table I were employed for this purpose.

The σ^+ constants were estimated as average values obtained from two or four determinations by using two types of correlation equations and two series of compounds:

$$\sigma_{\rm p}^+ ({\rm OCONMe}_2) \simeq 0.08$$

 $\sigma_{\rm p}^+ ({\rm SCONMe}_2) \simeq 0.13$

The substituent effects of the 4-OCONMe₂ and 4-F groups are thus seen to be quite similar, and the influence of the 4-SCONMe₂ group is practically equal to that of a 4-I substituent.

Transmission of Electronic Effects. The results of linear correlations (Table II) can be applied to determine the transmissive factors of polar effects $\pi'(Y)$ for bridge

groups Y according to the definition of Jaffé.²⁶ The $\pi'(Y)$ values were calculated as follows

$$\pi'(O) = \rho(I) / \rho(III) \qquad \pi'(S) = \rho(II) / \rho(III)$$

$$\pi'(NH) = \rho(IV) / \rho(III) \qquad \pi'(CH=CH) = \rho(V) / \rho(III)$$

where $\rho(I)$ through $\rho(V)$ are the slopes of linear correlations of $\nu(C=0)$ vs. σ and $\Delta\nu(OH)$ vs. σ for series I–V, respectively. The values for $\pi'(Y)$ were also taken to be equal to the slope of the line resulting from direct correlation²⁷ of $\nu(C=0)$ vs. $\nu(C=0)^{III}$. The accuracy of transmissive factors determined in this way is somewhat higher than when they are calculated as the ratios of two slopes. The transmissive factors obtained by using both methods are given in Table III.

The transmissive ability of oxygen and sulfur atoms expressively decreases when chloroform is used as the

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solvent. This effect has been explained for other series^{6,9} as resulting from hydrogen bonding between the bridge atoms (Y = O or S) and chloroform molecules. On the other hand, the NH group, which does not as easily form hydrogen bonds with chloroform, appears to exhibit more nearly the same transmissibility in CHCl₃ and CCl₄.

When the $\pi'(Y)$ values for O and S atoms determined in CCl₄ are compared with those obtained previously for other series^{9,28} [$\pi'(O) = 0.86$ and $\pi'(S) = 0.63$], it can be concluded that the transmission of polar effects is strongly enhanced in series I and II. The same is true for the series of N,N-dimethyl-N'-phenylureas IV in both CCl₄ and CHCl₃ solutions. The transmissive factors of O and NH groups approach or even exceed unity. This indicates that the substituent effects in series I and IV are transmitted as readily or more so than they are in benzamides III. This is similar to the so-called "positive bridge effect" reported previously.^{11,12}

The transmissive factors of oxygen and sulfur atoms obtained from data measured in CHCl₃ are in reasonable agreement with those determined earlier.^{9,28} Similar results were obtained by using $\Delta\nu(OH)$ vs. σ and $\Delta\nu(OH)$ vs. $\Delta\nu$ -(OH)^{III} correlations for determination of $\pi'(O)$ and $\pi'(S)$ values. The lower transmissibility of oxygen and sulfur atoms under conditions of hydrogen bonding with phenol can be explained in a similar manner as in the case of chloroform solutions.

The enhanced efficiency of transmission of electronic effects through O, S, and NH groups in series I, II, and IV is in good harmony with the suggestion that in these compounds the s-trans conformation is favored. It was shown by investigation of monochloroacetates²⁹ that the transmissive ability of the s-trans conformation is higher than that of the s-cis form. A similar conclusion follows from the comparison of carbonyl stretching frequencies of alkyl carbamates.¹⁷ The above results are consistent with the assumption that in the s-trans conformation of I, II, and IV, due to the close proximity of the carbonyl group and the substituted phenyl ring, electronic effects of substituents are transmitted not only through the chemical bonds but also by a through-space mechanism.

Experimental Section

Preparation of the Compounds. The compounds used herein were prepared according to the general methods described below. Unless specifically included below, purified specimens exhibited melting points and/or boiling points and refractive indecies in agreement with available values from the literature.

Phenyl N,N-Dimethylcarbamates (I). To a cold $(0-5 \,^{\circ}\text{C})$ slurry of 2.7 g (66 mmol) of NaH (previously washed free of dispersing oil with petroleum ether or hexane) in 15 mL of anhydrous (activated molecular sieves) dimethylformamide (DMF) in a nitrogen atmosphere was added dropwise and with stirring over 10 min a solution of 60 mmol of the appropriately substituted phenol in 30 mL of DMF. After hydrogen evolution ceased, the solution was cooled to 10 °C in an ice bath, and 80 mmol of N,N-dimethylcarbamoyl chloride in 15 mL of DMF was added all at once.

The resulting solution was heated slowly (ca. 1 h) to 75 °C and maintained there for an additional hour. The mixture was cooled and then poured into 200 mL of 1% aqueous KOH. Sufficient NaCl was added to saturate the solution, which was then decanted and extracted (3×70 mL) with a mixture (4:1) of benzene-petroleum ether (bp 60-70 °C). The organic extract was washed successively with 100 mL of 1% HCl and water (3×100 mL), dried over anhydrous Na₂SO₄, filtered, and evaporated with a rotary evaporator. The crude carbamate ester was recrystallized from ethanol, hexane, cyclohexane, or acetonitrile or vacuum distilled. The following physical constants and analytical data were observed for previously unreported compounds. Compound Ie (4-OBu), mp 44-46 °C (hexane). Anal. Calcd for $C_{13}H_{19}NO_3$: C, 65.80; H, 8.07. Found: C, 65.93; H, 8.11. Compound Ic (4-OEt), mp 64.5-67.5 °C (hexane). Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23. Found: C, 63.34; H, 7.41. Compound If (4-Et): bp (110 °C (1 mm)]; $n^{21.5}_{D}$ 1.5135. Anal. Calcd for C₁₁H₁₅NO₂: C, 68.37; H, 7.82. Found: C, 68.15; H, 7.87. Compound Ig (4-Ph), mp 138.5-140 °C (ethanol). Anal. Calcd for C₁₅H₁₅NO₂: C, 74.66; H, 6.27. Found: C, 74.73; H, 6.36. Compound Ij (4-F): previously reported without physical constants; bp 62 °C (0.16 mm); $n^{21.5}$ 1.4989. Anal. Calcd for C₉H₁₀FNO₂: C, 59.00; H, 5.50. Found: C, 59.25; H, 5.66. Compound Ik (4-I), mp 49-52 °C (hexane). Anal. Calcd for C₉H₁₀INO₂: C, 37.14; H, 3.46. Found: C, 37.26; H, 3.52. Compound In (4-CO₂Me), mp 96-97.5 °C (ethanol). Anal. Calcd for C₁₁H₁₃NO₄: C, 59.18; H, 5.87. Found: C, 59.30; H, 5.88. Compound Io (4-CO₂Et), mp 63-65 °C (hexane). Anal. Calcd for C₁₂H₁₅NO₄: C, 60.75; H, 6.37. Found: C, 60.89; H, 6.33.

S-Phenyl N,N-Dimethylthiocarbamates (II). When the corresponding thiophenols were commercially available, compounds of this series were prepared from reaction of the thiophenol in a nitrogen atmosphere with NaH and N,N-dimethylcarbamoyl chloride in a manner analogous to that described above for the preparation of compounds of series I.

When the corresponding thiophenol was unavailable, compounds of this series were obtained from pyrolytic rearrangement of the corresponding O-phenyl N,N-dimethylthiocarbamates by a published procedure³⁰⁻³² [compounds IIb (4-OMe), IIi (4-F), and IIp (4-NO₂) were prepared by both methods].

The pyrolytic isomerizations involved heating the neat starting materials at the appropriate temperature for various periods of time. Progress of the rearrangements was followed by changes in the ¹H NMR spectrum reflecting conversion of the well-resolved doublet of the dimethylamino moiety of the O-phenyl thiocarbamate into a sharp singlet shifted upfield for the corresponding moiety of the S-phenyl thiocarbamate. In those cases with electron-accepting substituents in the phenyl group, the conversion was thus observed to be essentially complete within 0.5-2 h. The isomerization required extended time, was usually less complete, and sometimes resulted in decomposition in those compounds which contained electron-releasing phenyl substituents. The temperatures, periods of pyrolysis, and estimated percentages of conversion (¹H NMR) varied respectively from 180 °C, 0.5 h, and 100% for compound IIp (4-NO₂) to 250 °C, 10.25 h, and 66% for compound IIc (4-OEt). The S-phenyl thiocarbamates were purified by recrystallization from methanol, acetonitrile, or cyclohexane, by vacuum distillation, by vacuum sublimation, or by chromatographic elution from alumina with a solvent gradient ranging from petroleum ether to benzene to diethyl ether.

The following pyrolytic conditions, conversion percentages, physical constants, and analytical data were observed for previously unreported compounds. Compound IIa (4-OBu) on pyrolysis at 256 °C for 4 h gave 66% conversion; mp 60-61.5 °C (eluted from alumina by ca. 80% benzene-20% diethyl ether). Anal. Calcd for C₁₃H₁₉NO₂S: C, 61.66; H, 7.51. Found: C, 61.55; H, 7.55. Compound IIc (4-OEt) on pyrolysis at 250 °C for 10.25 h gave 66% conversion; mp 85-87 °C (eluted from alumina by ca. 80% benzene-20% diethyl ether). Anal. Calcd for $C_{11}H_{15}NO_2S$: C, 58.67; H, 6.67. Found: C, 58.69; H, 6.70. Compound IIf (4-Et) on pyrolysis at 240 °C for 6 h gave 80% conversion; bp 165–168 °C (3 mm) (vacuum distilled before and after elution from alumina over the solvent range of 40% benzene-60% petroleum ether to 90% benzene-10% petroleum ether). Anal. Calcd for C₁₁H₁₅NOS: C, 63.16; H, 7.18. Found: C, 63.13; H, 7.22. Compound IIh (4-SCH₃) on pyrolysis at 240 °C for 3 h gave 100% conversion; mp 111.8-112.8 °C [from methanol followed by vacuum sublimation at 74-106 °C (0.3 mm)]. Anal. Calcd for C₁₀H₁₃NOS₂: C, 52.83; H, 5.76. Found: C, 52.95; H,

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5.87. Compound IIi (4-F) on pyrolysis at 248 °C for 6.5 h gave 87.5% conversion; bp 122–124 °C (3 mm). Anal. Calcd for $C_9H_{10}FNOS$: C, 54.25; H, 5.06. Found: C, 54.25; H, 5.10. Compound IIj (4-I) on pyrolysis at 220–235 °C for 1.5 h gave 95% conversion; mp 87.5–88.8 °C [vacuum sublimed at 106 °C (0.7 mm)]. Anal. Calcd for $C_9H_{10}INOS$: C, 35.19; H, 3.28. Found: C, 35.22; H, 3.33.

O-Phenyl N,N-Dimethylthiocarbamates. Compounds of this class required for pyrolytic conversion to compounds of series II above were prepared by reaction of the corresponding phenol in a nitrogen atmosphere with NaH and N,N-dimethylthiocarbamoyl chloride in a manner analogous to that described for these compounds by Newman and Karnes.³⁰ The following physical constants and analytical data were observed for previously unreported compounds. O-p-n-Butoxyphenyl N,N-dimethyl-thiocarbamate, mp 69-70.5 °C (ethanol). Anal. Calcd for C₁₃H₁₉NO₂S: C, 61.63; H, 7.56. Found: C, 61.78; H, 7.60. O-p-Ethoxyphenyl N,N-dimethylthiocarbamate, mp 85.5-86.5 °C (ethanol). Anal. Calcd for C₁₁H₁₅NO₂S: C, 58.64; H, 6.71. Found: C, 58.51; H, 6.83. O-p-Ethylphenyl N,N-dimethylthiocarbamate, mp 59-62.5 °C (ethanol). Anal. Calcd for C₁₁H₁₅NOS: C, 63.12; H, 7.22. Found: C, 62.97; H, 7.37. O-p-Fluorophenyl N,N-dimethylthiocarbamate, mp 77-78.2 °C (ethanol). Anal. Calcd for C₉H₁₀FNOS: C, 54.25; H, 5.06. Found: C, 54.32; H, 5.15. O-p-Iodophenyl N,N-dimethylthiocarbamate, mp 109.5-110.5 °C (ethanol). Anal. Calcd for C₉H₁₀INOS: C, 35.19; H, 3.28. Found: C, 35.15; H, 3.36.

N,N-Dimethylbenzamides (III). The compounds of this series were the same as those employed in an earlier investigation.³

Infrared Spectra. The spectra were taken on Perkin-Elmer Model 567 and 180 grating spectrometers. The carbonyl stretching frequencies were measured at 25 °C in NaCl cells of 0.1-, 1.0-, and 5.0-mm thickness by using CCl_4 and $CHCl_3$ as solvents. Concentrations were chosen to give absorption between 70% and 75%. The instrument calibrations were verified by using water vapor and indene standard spectra. Peak positions were determined by averaging the results of three measurements and are believed to be accurate to ± 0.5 cm⁻¹.

The hydroxyl frequency shifts of phenol by the compounds were measured in solutions of CCl₄ contained in NaCl cells of 5.0-mm path length, the concentrations of compounds of series I–III and phenol being 1.6×10^{-2} and 2.0×10^{-2} mol/L, respectively. Peak positions were determined with an accuracy of ±3 cm⁻¹.

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Registry No. Ia, 84694-98-4; Ib, 7305-10-4; Ic, 73986-55-7; Id, 5461-74-5; Ie, 7305-08-0; If, 84694-99-5; Ig, 84695-00-1; Ih, 6969-90-0; Ii, 3983-30-0; Ij, 7541-20-0; Ik, 84695-01-2; Il, 7305-03-5; Im, 7308-55-6; In, 38491-27-9; Io, 84695-02-3; Ip, 52916-82-2; Ir, 14100-44-8; Is, 7244-70-4; IIa, 84695-03-4; IIb, 13511-98-3; IIc, 84695-04-5; IId, 13511-96-1; IIe, 7322-85-2; IIf, 84695-05-6; IIg, 7304-68-9; IIh, 69734-16-3; IIi, 84695-06-7; IIj, 84695-07-8; IIk, 7304-69-0; III, 7305-13-7; IIm, 13511-93-8; IIn, 13511-90-5; IIo, 19290-43-8; IIp, 7305-12-6; IIIq, 67024-50-4; IIIb, 7291-00-1; IIIc, 14062-78-3; IIId, 011-74-5; IIIf, 25771-25-9; IIIg, 24167-56-4; IIIi, 24167-53-1; IIIj, 14062-80-7; IIIk, 18469-37-9; IIIp, 24167-50-8; IIIs, 7291-01-2; phenol, 108-95-2; N,N-dimethylcarbamoyl chloride, 79-44-7; O-(p-n-butoxyphenyl) N,N-dimethylthiocarbamate, 84695-08-9; O-(p-ethoxyphenyl) N,N-dimethylcarbamate, 84695-09-0; O-(p-ethylphenyl) N,N-dimethylcarbamate, 84695-10-3; O-(p-fluorophenyl) N,N-dimethylcarbamate, 84695-11-4; O-(p-iodophenyl) N,N-dimethylcarbamate, 84695-12-5.

Synthesis of Certain 5,6-Diamino-*as*-triazines: Precursors for Fused Heterocyclic Systems¹

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An improved synthesis of 6-amino-as-triazine-3,5-dione (1) and selective thiation of this heterocycle provides two key intermediates, 6-amino-3-oxo-as-triazine-5-thione (2) and 6-amino-as-triazine-3,5-dithione (3). Methylation of 2 and 3 under basic conditions leads to their methylmercapto derivatives, which on treatment with methanolic ammonia furnish 5,6-diamino-as-triazine-3-one (6a) and 5,6-diamino-3-(methylthio)-as-triazine (7a), respectively, in good overall yield.

o-Diamino heterocycles have attracted considerable attention as synthons to fused heterocyclic systems. Of interest to us are the 5,6-diamino-as-triazines, which are potential precursors to novel 5:6 and 6:6 fused heterocycles. Recently, several investigators described and used such intermediates to synthesize the imidazo[4,5-e]-as-triazine^{2,3} and v-triazolo[4,5-e]-as-triazine⁴ ring systems. Without exception, the as-triazines used in these studies were alkylated at either the N2 or C3 positions, and all but one contained alkylated exocyclic amino groups. We now report the preparation of the diamines 5,6-diamino-as-triazine-3-one (**6a**) and 5,6-diamino-3-(methylthio)-as-triazine (**7a**, Scheme I). The advantages offered by **6a** and **7a** are that ring closure and simple chemical modification can lead to the parent imidazo- and v-triazolo[4,5-e]-as-triazine and pyrazino[2,3-e]-as-triazine ring systems.

6-Amino-*as*-triazine-3,5-dione (1) was chosen as the starting material for this project. The reported synthetic procedure for 1^5 gave low yields especially on scale-up and at times did not work. Faced with this dilemma, we explored more effective routes for the preparation of this heterocycle. It was found that when 6-bromo-*as*-triazine-3,5-dione⁵ was heated at 80 °C in a steel reaction vessel with liquid ammonia and a catalytic amount of fine copper powder, 1 was obtained in 98% yield.

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