"best" single-variable equation is that in eq 13. The "best" two-variable equation is eq 14, which is quite significantly better than eq 13 ($F_{1,10} = 41$). The overall significance of eq 14 is high ($F_{2,10} = 33$; $F_{2,10\ \alpha.005} = 9.4$). It is interesting and logical that apolar forces have no influence on pK_1''. Adding terms in π or P_E to eq 14 does not result in improved correlation. The steric effect of the substituent on pK_1'' is qualitatively the same as for k_3, only much smaller in magnitude. The electronic effect is in the opposite direction.

As with k_3, a different story results from the analysis of molecules 15–18 of Table I. This is summarized in eq 15 and 16. Although a good correlation in terms of

$$pK_1'' = -0.28(\pm 0.29)E_s + 7.33(\pm 0.23) \quad n = 4;\ r = 0.945;\ s = 0.109 \tag{15}$$

$$pK_1'' = -0.45(\pm 0.65)E_s + 0.65(\pm 2.2)\sigma^* + 7.23(\pm 0.41) \quad n = 4;\ r = 0.996;\ s = 0.002 \tag{16}$$

r, eq 15 is not statistically significant ($F_{1,2} = 2.1$; $F_{1,2\ \alpha.1} = 8.5$). However, eq 16 is significant ($F_{2,1} = 69.6$; $F_{2,1\ \alpha.1} = 49.5$). Even though shown to be significant by the F test, very little confidence can be placed in eq 16 because of the few data points. It is simply of interest to note that it is quite different from eq 4.

Compound 14 was not included in deriving any of the above equations. The values predicted by eq 4 and 14 are wide of the mark. This is to be expected, since there are at least seven known examples[6] where a break in the structure–activity relationship of chymotrypsin substrates and inhibitors occurs when π for the side chain is 3.50 or greater. Compound 14 is yet another such example.

The type of derivatives selected by Dupaix, *et al.*,[3] in Table I constitute by far the best set yet studied from the point of view of the physical organic chemist trying to separate substituent effects. Their work, when taken with that of Fife and Milstein, clearly shows that apolar forces are important in the k_3 step.

Acknowledgment.—I wish to thank Professor Neal Cornell for suggesting the present study and for helpful discussions. I also thank Professor T. H. Fife for an enlightening discussion.

Clarification of the Acid-Catalyzed Reaction of Glyoxal with Carbamate Esters

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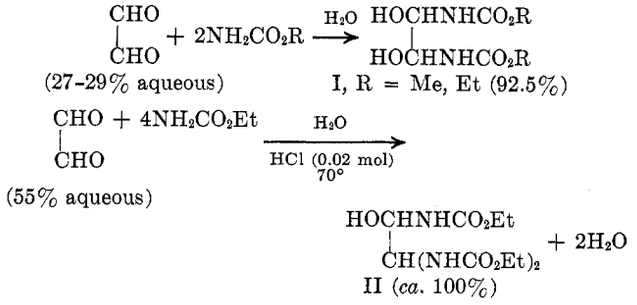
The reaction of glyoxal with ethyl carbamate in the presence of concentrated hydrochloric acid gives 1,1,2,2-tetra(carbethoxyamino)ethane (VI), in contrast with the reports of Pauly and Sauter and Gaylord who claimed that the reaction product was glyoxal bis(carbethoxyimide) (III). The mechanism of formation of the tetracarbamate (VI) is discussed, and it is shown that certain parallels exist between the reactions of glyoxal with carbamate esters and with primary amines.

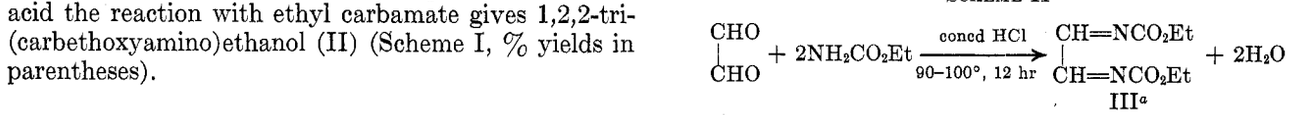
The reaction of glyoxal with carbamate esters yields a variety of products depending on the acidity or basicity of the reaction medium. For example,[1] treatment of neutralized glyoxal with carbamate esters (1:2 molar ratio) is reported to give 1,2-di(carbalkoxyamino)-ethane-1,2-diol (I), whereas in the presence of dilute acid the reaction with ethyl carbamate gives 1,2,2-tri-(carbethoxyamino)ethanol (II) (Scheme I, % yields in parentheses).

SCHEME I



There is some doubt, however, as to the structure of the product formed in stronger acid solution. The reaction of glyoxal with ethyl carbamate in the presence of concentrated hydrochloric acid was investigated first by Pauly and Sauter[2] who reported that the product was an insoluble, microcrystalline powder; the structure assigned was that of glyoxal bis(carbethoxyimide) (III) (Scheme II). No melting point was reported for the

SCHEME II



III[a]

[a] *Anal.* Calcd for $C_8H_{12}N_2O_4$: C, 47.99; H, 6.04; N, 13.99. Found: C, 47.74; H, 6.4; N, 14.07.

product, but the microanalysis was correct for the assigned structure.

A similar result was reported by Gleim[3] who examined the reaction of glyoxal with allyl carbamate in the presence of concentrated hydrochloric acid. The reaction product was claimed to be glyoxal bis(carb-allyloxyimide) (IV); however, the microanalysis was not in good agreement with this structure (Scheme III).

For some obscure reason, the abstract literature[4] subsequently referred to compound III as "carbamic acid, *N,N'* acetylene bis-, diethyl ester," $EtO_2CNHC{\equiv}CNHCO_2Et$ (V), and this prompted Gaylord[5] to re-

(1) British Patent 801,991 (B.A.S.F.); *Chem. Abstr.*, **53**, 7019*a* (1959).

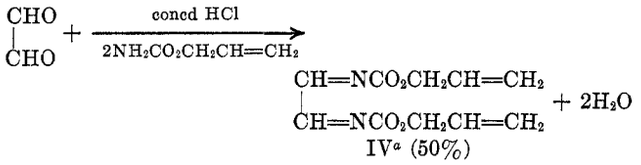
(2) H. Pauly and H. Sauter, *Chem. Ber.*, **63**, 2063 (1930).

(3) C. E. Gleim, *J. Amer. Chem. Soc.*, **76**, 107 (1954).

(4) Subject Index, *Chem. Abstr.*, 3rd Decennial Index, 1927–1936.

(5) N. G. Gaylord, *J. Org. Chem.*, **20**, 547 (1955).

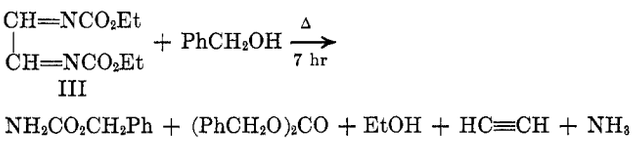
SCHEME III



[a] *Anal.* Calcd for $C_{10}H_{12}N_2O_4$: N, 12.50. Found: N, 10.92.

examine the work of Pauly and Sauter. The reaction of 30% aqueous glyoxal (1 mol), ethyl carbamate (2 mol), and concentrated hydrochloric acid (1.5 mol) at 90–100° for 12 hr was found to give a white solid, mp 286–287°, in 49% yield.[6] The product was insoluble in water, ethanol, ethyl acetate, dioxane, and hexane. The structure of the white solid was concluded to be III, apparently confirming the earlier findings of Pauly and Sauter, on the basis of the ir spectrum which indicated the absence of an acetylenic linkage, the nitrogen analysis (Found: N, 14.26.), and the products obtained on treatment of III with benzyl alcohol (Scheme IV).

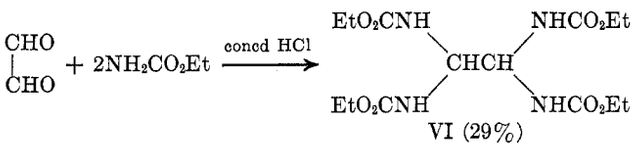
SCHEME IV



$$NH_2CO_2CH_2Ph + (PhCH_2O)_2CO + EtOH + HC{\equiv}CH + NH_3$$

We have repeated the preparation of the white solid according to the method of Gaylord, and we have ascertained that the structure assigned both by Pauly and Sauter and by Gaylord is incorrect. The identity of the white solid, deduced primarily from the mass spectrum, is 1,1,2,2-tetra(carbethoxyamino)ethane (VI) (Scheme V, % yield in parentheses).

SCHEME V



The tetracarbamate VI, mp 286–287° dec (from nitromethane), is insoluble in a wide range of solvents, in accord with Gaylord's observations. The ir spectrum has ν max 3292 (NH stretch) and 1698 cm^{-1} (C=O stretch), which supports the assignment of structure VI but does not uniquely define it. It should be noted that in symmetrical disubstituted acetylenes, the C≡C absorption is often too weak to be detectable[7] and thus the absence of an absorption band in the 2190–2260-cm^{-1} region cannot be cited as evidence against structure V. The nmr spectrum (in DMSO-d_6 at 90°) is in agreement with structure VI, and our microanalysis is in accord also (*Anal.* Calcd for $C_{14}H_{26}N_4O_8$: C, 44.44; H, 6.93; N, 14.80. Found: C, 44.68; H, 6.88; N, 14.94.). Structure III requires N, 13.99%, and it is apparent that the microanalysis reported by Gaylord[5] is inadequate for characterization since a nitrogen analysis of, say, 14.4% could be considered more or less acceptable for either III or VI; clearly a C, H, and N analysis is a minimal requirement in this case.

The key evidence we employed in the elucidation of the structure was derived from the chemical ionization and electron impact mass spectra. The significant features of the mass spectra are shown in Scheme VI (ra = relative abundance; the molecular formula of each fragment was established by exact mass measurement).

The chemical ionization (CI) spectrum with methane shows a quasimolecular ion, QM (M + 1), at *m/e* 379. This is consistent with structure VI and conclusively eliminates structures III and V since the latter two would be expected to show a quasimolecular ion at a much lower *m/e* value. The electron impact spectrum confirms the structure as the tetracarbamate VI; loss of $NHCO_2Et\cdot$ from the molecular ion gives the fragment at *m/e* 290 which then eliminates ethanol affording the ion at *m/e* 244. The major fragmentation pathway is cleavage at the central C–C bond to yield the ion at *m/e* 189 (base peak); the subsequent loss of ethanol and of (CO_2 + C_2H_4) is diagnostic of the carbamate function.[8] The spectrum of the tetracarbamate VI below *m/e* 189 bears a striking resemblance to the spectrum of the structurally related 1,1-di(carbethoxyamino)ethane[9] (VII) (Scheme VII).

The tetracarbamate VI is soluble in hot dimethylformamide and hot DMSO. Attempted tlc, glc, and molecular weight determination (Rast method) were unsuccessful. An independent synthesis of the tetracarbamate VI has been reported by Curtius[10] *via* a rearrangement of ethanetetracarboxylic acid tetrahydrazide (Scheme VIII, % yield in parentheses). However, the product isolated has mp 268° and was soluble in ethanol and in ether, in contrast with our own observations.

The reactions of monoaldehydes with carbamate esters are similar in some respects to the reactions of glyoxal.[11] For example, formaldehyde and ethyl carbamate in the presence of a trace amount of base give ethyl *N*-(hydroxymethyl)carbamate,[12] while in acid solution dicarbamates are formed (Scheme IX, % yields in parentheses).

In contrast, when the aldehyde contains an electron-withdrawing group α to the carbonyl function, the reaction with carbamate esters in the presence of a trace of concentrated sulfuric acid gives *N*-(1-hydroxyalkyl)carbamates[13] (VIII) (Scheme X).

There are two possible pathways which can be envisaged for the acid-catalyzed reaction of aldehydes with carbamate esters (Scheme XI). The first step of the reaction is protonation of the carbonyl group followed by nucleophilic attack of the carbamate ester to give the secondary alcohol VIII; this is the typical acid-catalyzed nucleophilic addition reaction of an aldehyde. In pathway A, protonation of the alcohol followed by loss of water yields the intermediate

(6) The reported yield of 49% was calculated on the basis of the incorrect structure III, although from the figures reported we calculate the yield to be 58%; on the basis of structure VI the yield is 61%.

(7) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Wiley, New York, N. Y., 1966, Chapter 4.

(8) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967.

(9) W. M. Kraft and R. M. Herbst, *J. Org. Chem.*, **10**, 483 (1945).

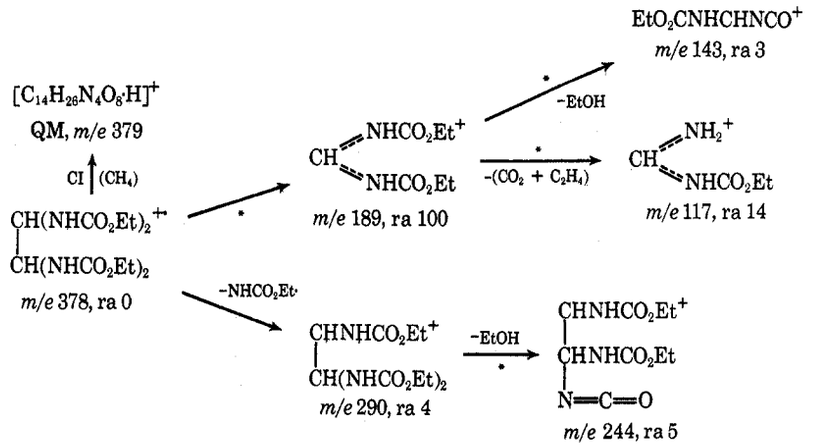
(10) Th. Curtius, *J. Prakt. Chem.*, **94**, 367 (1916).

(11) P. Adams and F. A. Baron, *Chem. Rev.*, **65**, 567 (1967).

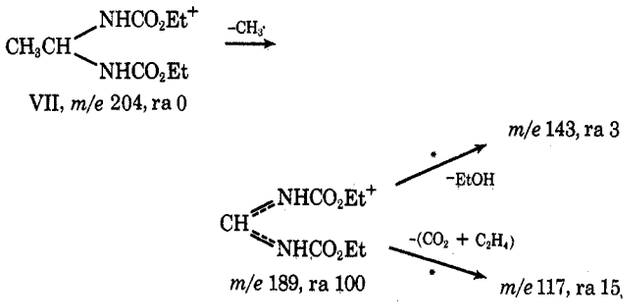
(12) A. Einhorn, *Justus Liebigs Ann. Chem.*, **361**, 113 (1908).

(13) G. Vasilev, *Farmatsiya (Sofia)*, **13**, 40 (1963); *Chem. Abstr.*, **60**, 5378b (1964).

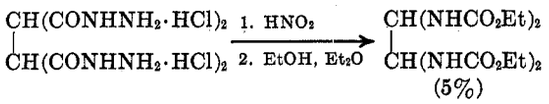
SCHEME VI



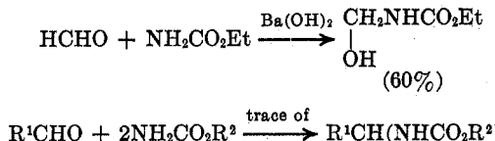
SCHEME VII



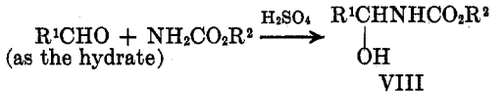
SCHEME VIII



SCHEME IX



SCHEME X



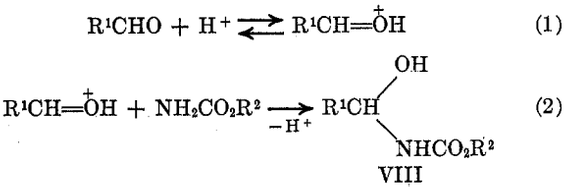
$R^1 = Br_3C$; R^2 = Me, *n*-Pr, *n*-Bu
$R^1 = Cl_3C$; R^2 = *i*-Pr, *n*-Bu, *tert*-Bu
R^1 = MeCHClCCl$_2$; R^2 = Me, *n*-Pr, *n*-Bu

carbonium ion, which undergoes nucleophilic attack by the carbamate ester to give the dicarbamate (SN1 process). In pathway B, loss of water from the secondary alcohol VIII gives the imine, which then participates in a Michael-type addition reaction with the carbamate ester to yield the dicarbamate. The formation of the intermediate imine is analogous to the preparation of hydrazone derivatives of aldehydes.

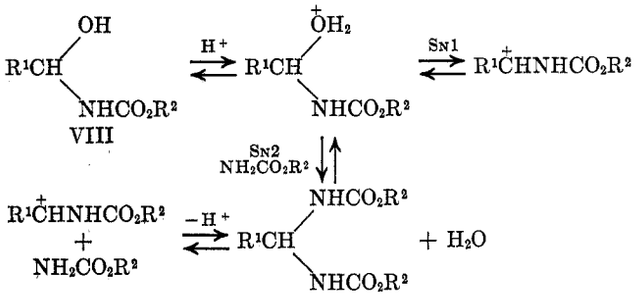
When R^1 contains electron-withdrawing groups, such as Cl_3C– and Br_3C–, the reaction leads to the formation of the secondary alcohol VIII in the presence of trace amounts of acid (Scheme X). It seems likely that further reaction to the dicarbamate is inhibited because the electron-withdrawing effect of the R^1 group destabilizes the transition state leading to the intermediate carbonium ion (Scheme XI, pathway A, SN1 process). However, in the presence of larger amounts of concentrated acid, formation of the dicarbamate could occur *via* an SN2 process directly from protonated VIII.

In the case of glyoxal (Scheme XI, R^1 = CHO), the reaction with carbamate esters in the presence of traces of acid gives the tricarbamate (Scheme I), and, as we have shown, in stronger acid solution the tetracarbamate is formed (Scheme V). It is clear that formation of the tetracarbamate requires more vigorous reaction conditions, and this may be rationalized by considering

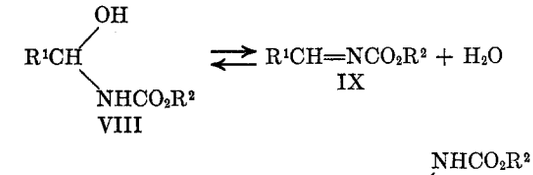
SCHEME XI

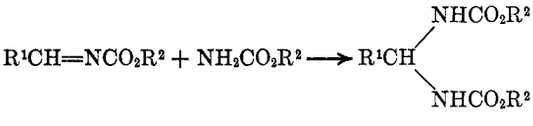


Pathway A



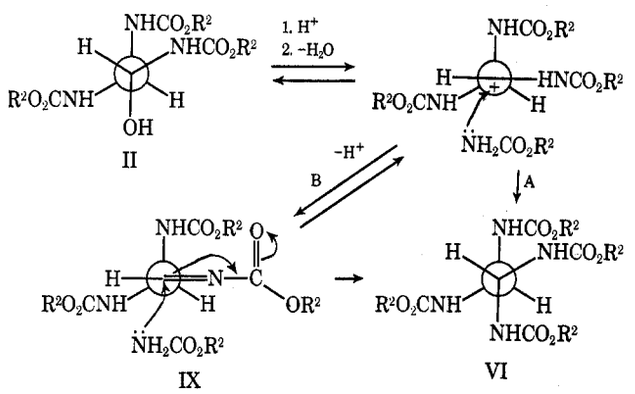
Pathway B,
acid-catalyzed dehydration and Michael-type addition





the intermediates involved in either pathway A or pathway B (Scheme XII). In the case of acid-cata-

SCHEME XII

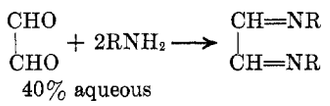


lyzed glyoxal reactions, steric factors appear to be more important than electronic factors in determining the final outcome of the reaction. The tricarbamate II, formed by an analogous sequence of steps to that in Scheme XI has two gauche interactions in its most stable conformation. Protonation of the alcohol function followed by loss of water results in a slight decrease of steric compression in the molecule due to the planarity of the intermediate carbonium ion. If subsequent reaction proceeds *via* pathway B, proton loss affords the intermediate imine IX which then undergoes Michael addition of carbamate ester to give the tetracarbamate VI. If reaction proceeds *via* pathway A, nucleophilic attack of the carbamate ester on the carbonium ion occurs from the less hindered side (as shown) to give VI. VI is a less stable molecule than the starting alcohol II since (a) the steric compression in the tetracarbamate is higher and (b) the stabilization due to intramolecular hydrogen bonding is smaller. Accordingly, the conversion of the tricarbamate II into the tetracarbamate VI *via* pathway A or B will involve a significant energy of activation.

The reaction of glyoxal with aliphatic primary amines in the absence of added acid or base gives conjugated diimines[14] (Scheme XIII, % yields in paren-

SCHEME XIII

REACTION OF GLYOXAL WITH ALIPHATIC PRIMARY AMINES[14]



40% aqueous

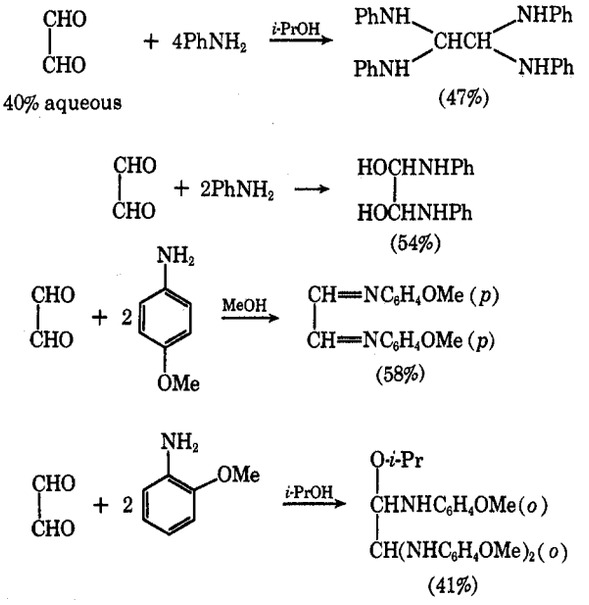
R = cyclohexyl (95%), *i*-Pr (77%), *n*-Bu (18%), *i*-Bu (26%), *tert*-Bu (63%)

theses), while with aromatic primary amines a variety of products are formed[15] (Scheme XIV). In the latter case, the molar ratios and the nature and position of the ring substituents appear to be the main factors in determining the structure of the product. The tentative reaction pathway put forward (Scheme XV) is similar in some respects to the rationalization proposed by us for the acid-catalyzed reactions.

(14) J. M. Kliegman and R. K. Barnes, *Tetrahedron*, **26**, 2555 (1970).
(15) J. M. Kliegman and R. K. Barnes, *J. Org. Chem.*, **35**, 3140 (1970).

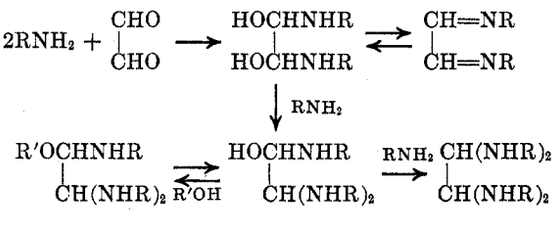
SCHEME XIV

REACTION OF GLYOXAL WITH AROMATIC PRIMARY AMINES[15]



SCHEME XV

TENTATIVE REACTION PATHWAY[15]



Experimental Section

Ir spectra were obtained with a Perkin-Elmer 225 grating infrared spectrophotometer, and nmr spectra were taken using a 100-MHZ JEOL spectrometer. Chemical ionization mass spectra were measured using a quadrupole mass spectrometer, and electron impact spectra were obtained with an AEI MS-902 instrument (source temperature 200°, ionizing voltage 70 eV). Melting points are uncorrected.

The mass spectral data are presented in the following format: *m/e* value (relative abundance), origin of the fragment, molecular formula (difference in parts per million (ppm) between the calculated and observed mass). Metastable peaks, $M_1 \rightarrow M_2$ (observed position of metastable peak).

Preparation of 1,1,2,2-Tetra(carbethoxyamino)ethane (VI).—A mixture of ethyl carbamate (17.8 g, 0.20 mol, mp 48–50°), 30% w/w aqueous glyoxal (19.3 g, 0.10 mol), and concentrated hydrochloric acid (16.1 g, 0.05 mol, sp gr 1.19) was heated on a steam bath for 12 hr. The solid product was collected by filtration, washed with water (six 50-ml portions), triturated with acetone (two 150-ml portions), and dried *in vacuo* to give the crude tetracarbamate (5.62 g, mp 274–276° dec, 30%) a portion of which (0.665 g) was crystallized from hot nitromethane to yield pure VI (0.628 g, mp 286–287° dec, overall yield 29%), a white solid.

The crystallized product was insoluble in water, acetone, hexane, ethanol, ether, chloroform, triethyl phosphate, and hexamethylphosphoramide, slightly soluble in hot nitromethane, and moderately soluble in hot dimethylformamide and hot DMSO.

Variations in Preparative Method.—When 40% aqueous glyoxal was used (molar ratios as above) the yield of VI was significantly higher (crude yield 64%, recrystallized 58%). When the reaction mixture was stirred, considerable frothing and charring was observed, and the yield was considerably lower (crude yield 28%, using 40% aqueous glyoxal).

The spectroscopic characteristics of the recrystallized tetracarbamate are as follows.

Ir spectrum (KBr disk): ν max 3292 (s) (NH stretching vibration due to $RNHCO_2R'$), 2975 (m) (CH stretching vibration), 1698 (s) (C=O stretch in $RNHCO_2R'$), 1549, 1524 (s) (NH bend, amide II band), 1478 (m) (CH asymmetrical deformation), 1370 (m) (CH symmetrical deformation), 1332 (m), 1295 (s) (unassigned), 1241, 1030 (s) (CO stretching vibration), 881 (w), 783 (w) (unassigned), 674 cm^{-1} (m) (NH o.o.p. deformation). The spectrum was identical with that reported[16] for "acetylenedicarbamic acid, diethyl ester."

Nmr spectrum (DMSO-d_6 at 90°): δ 6.64 (d*, 2.8, J = 7 Hz, NH), 5.20 (t*, 1.9, J = 7.5 Hz, $CH(NHCO_2Et)_2$), 3.99 (q, 7.8, J = 7.5 Hz, $NHCO_2CH_2CH_2$), 1.15 (t, 12.0, J = 7.5 Hz, $NHCO_2CH_2CH_3$). (Asterisk indicates broad signals with further splitting present.)

Electron impact mass spectrum (direct insertion at 200°): molecular ion absent; m/e 290 (4), M − $NHCO_2Et$, $C_{11}H_{20}N_3O_6$ (4.6 ppm); 244 (5), m/e 290 − EtOH, $C_9H_{14}N_3O_5$ (3.4 ppm); 202 (0.4), m/e 290 − $NHCO_2Et$, $C_8H_{14}N_2O_4$ (1.9 ppm); 201 (0.9), m/e 244 − NHCO, $C_8H_{13}N_2O_4$ (1.9 ppm); 198 (0.3), m/e 244 − EtOH, $C_7H_8N_3O_4$ (0.4 ppm); 189 (100), M − $CH(NHCO_2Et)_2$, $C_7H_{13}N_2O_4$ (3.6 ppm); 172 (1), m/e 244 − (CO_2 + C_2H_4), $C_6H_{10}N_3O_3$ (2.0 ppm); 161 (1.5), m/e 189 − C_2H_4, $C_5H_9N_2O_4$ (10.9 ppm); 143 (3), m/e 189 − EtOH, $C_5H_7N_2O_3$ (5.3 ppm); 117 (14), m/e 189 − (CO_2 + C_2H_4), $C_4H_9N_2O_2$ (11.6 ppm); 102 (4), m/e 117 − NH, $C_4H_8NO_2$ (5.0 ppm); 90 (1), m/e 117 − HCN, $C_3H_8NO_2$ (11.3 ppm); 89 (9), m/e 117 − C_2H_4, $C_2H_5N_2O_2$ (7.0 ppm); 62 (3), m/e 90 − C_2H_4, CH_4NO_2 (101 ppm). Metastable peaks: 378 → 189 (94.5); 290 → 244 (205.3); 290 → 172 (102.1); 244 → 198 (160.8); 244 → 172 (121.2); 189 → 161 (137.1); 189 → 143 (108.1); 189 → 117 (72.5); 117 → 89 (67.75).

Anal. Calcd for $C_{14}H_{26}N_4O_8$: C, 44.44; H, 6.93; N, 14.80. Found: C, 44.68; H, 6.88; N, 14.94.

1,1-Di(carbethoxyamino)ethane.[9]—The relevant portion of the electron impact mass spectrum is given below (direct insertion at 100°): molecular ion absent; m/e 203 (0.5), M − H, $C_8H_{15}N_2O_4$ (4.9 ppm); 189 (100), M − CH_3, $C_7H_{13}N_2O_4$ (3.8 ppm); 143 (3), m/e 189 − EtOH, $C_5H_7N_2O_3$ (6.5 ppm); 117 (15), m/e 189 − (CO_2 + C_2H_4), $C_4H_9N_2O_2$ (26.5 ppm); 90 (4), m/e 117 − HCN, $C_3H_8NO_2$ (3.0 ppm); 89 (10), m/e 117 − C_2H_4, $C_2H_5N_2O_2$ (1.3 ppm); 62 (13), m/e 90 − C_2H_4, CH_4NO_2 (35.8 ppm).

Registry No.—VI, 17350-57-1; glyoxal, 107-22-2; ethyl carbamate, 51-79-6; 1,1-di(carbethoxyamino)-ethane, 539-71-9.

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(16) "Sadtler Standard Spectra," No. 13888, Sadtler Research Laboratories Inc., Philadelphia, Pa., 1962.

The Chemistry of Sulfonyl Isocyanates. VIII. Kinetics of the Reaction with Hindered Phenols

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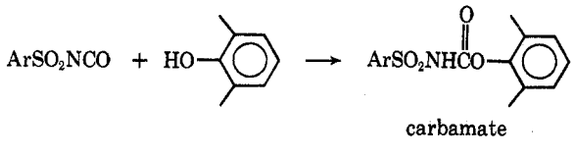
4-Chlorobenzenesulfonyl isocyanate (I) and 4-toluenesulfonyl isocyanate (II) reacted with 2,6-disubstituted and 2,4,6-trisubstituted phenols. The products were highly crystalline carbamates. Kinetic studies showed the reactions to be second order, first order in isocyanate and first order in phenol. The relative rates of reaction of the phenols were 2,6-diisopropyl- > 2,6-dimethyl- > 2,6-dibromo- > 2,4,6-tri-*tert*-butyl- > 2,6-di-*tert*-butyl- > 2,4,6-tribromo-. Isocyanate I was found to be somewhat more reactive than II.

Billeter first showed that benzenesulfonyl isocyanate reacts with phenol and reported the product to be carbamate.[2] It was shown in this laboratory that benzenesulfonyl isocyanate also reacts with 2,6-disubstituted, as well as other substituted, phenols to give crystalline solid derivatives.[3] The products were shown to be carbamates rather than para-substituted amides of phenols.



carbamate

More recently the kinetics of the reactions of hindered triarylcarbinols with sulfonyl isocyanates have been explored.[4-7] These reactions were found to be first order in alcohol and first order in isocyanate. Although the reaction products were in most cases not carbamates such intermediates could not be ruled out.[7]

This paper shows the kinetic results obtained from the reactions of 4-chlorobenzenesulfonyl isocyanate (I) and 4-toluenesulfonyl isocyanate (II) with 2,6-disubstituted phenols.

Experimental Section

Reagents.—4-Chlorobenzenesulfonyl isocyanate (I) and 4-toluenesulfonyl isocyanate (II) were obtained from the Upjohn Co., Carwin Organic Chemicals, and used without further purification. The phenols were commercial products which were redistilled or recrystallized before use. Toluene solvent was reagent grade and dried over sodium metal or molecular sieves. The di-*n*-butylamine was Eastman White Label grade reagent.

Kinetics.—The method used for measuring the concentration of isocyanate in the reaction mixture at various times was that already reported.[7] Second-order kinetics were followed with each of the phenols used from 4:1 to 1:4 isocyanate–phenol ratios. When 1:1 ratios of isocyanate–phenol were employed, plots of $1/(C - C_\infty)$ *vs.* time gave straight lines over at least 2 half-lives. For reactions in which initial isocyanate–phenol ratios were not unity, plots of log $[b(a - x)/a(b - x)]$ *vs.* time were linear.

Isolation of Products.—The products were removed from the reaction mixture (toluene solvent) by cooling to about 25° and adding 1 vol of petroleum ether (bp 60–70°). In most cases this procedure effected quantitative precipitation of the carbamate. When quantitative separation was not realized, the toluene–

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