TABLE IV

SPECTROPHOTOMETRIC DATA FOR RATE MEASUREMENTS. OPTICAL DENSITY OF BENZALDEHYDES AND CINNAMIC ACIDS IN ACIDIC METHANOL (5 ML. OF CONCD. SULFURIC ACID IN 1 L. OF METHANOL)[a]

Materials	Concentration, (M) × 10^5	Optical Density at Various Wave Lengths		
		(245 mμ)	(251 mμ)	(273 mμ)
C_6H_5CHO	384	0.802	0.805	0.080
$C_6H_5CH{:}CHCO_2H$	3.84	0.112	0.175	0.410
		(240 mμ)	(245 mμ)	(278 mμ)
p-$Cl.C_6H_4CHO$	213	1.074	0.972	0.058
p-$Cl.C_6H_4CH{:}CHCO_2H$	7.10	0.101	0.162	0.876
		(250 mμ)	(265 mμ)	(297.5 mμ)
p-$O_2N.C_6H_4CHO$	19.2	0.608	0.872	0.210
p-$O_2N.C_6H_4CH{:}CHCO_2H$	9.60	0.144	0.271	0.746
		(255 mμ)	(260 mμ)	(285 mμ)
p-$H_3C.C_6H_4CHO$	250	1.100	1.053	0.140
p-$H_3C.C_6H_4CH{:}CHCO_2H$	8.33	0.349	0.481	1.002

[a] It was shown that Beer's law was obeyed in these solutions, and that these optical densities were unaltered with the modest variation of the acidity of the solvent.

of trialkylamines used was conveniently eliminated by the addition of a small amount of sulfuric acid as noted previously. Moreover, the addition of sulfuric acid is advantageous, because the absorption of benzaldehydes is markedly reduced, while that of cinnamic acids is almost unchanged; thus it is possible to estimate accurately a small change in the composition of any reaction mixture.

Complementary experiments. Since most of the kinetic runs were followed only up to 2% conversion, some complementary tests seemed necessary in order to ensure the reaction path. It was confirmed in preliminary tests that the reaction followed spectrophotometrically was truly the Perkin reaction and no appreciable side reaction occurred and also that the sulfuric acid in methanol did not cause any oxidation of benzaldehydes. A typical run carried out with the same reaction mixture as in the kinetic experiments up to 30% conversion at 160° shows a satisfactory agreement of the observed reaction course with the calculated one (Fig. 5).

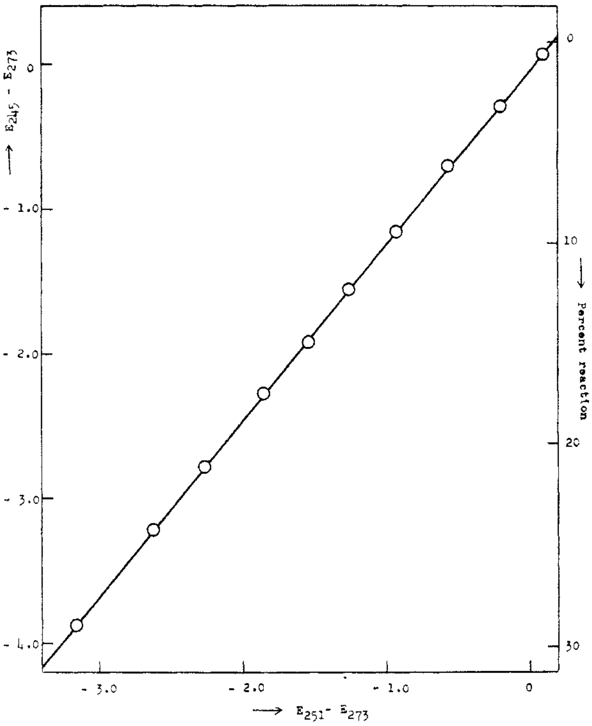

Fig. 5. Agreement of the observed reaction course (circles) with the calculated one (a line). E's are optical densities at the subscripted wave lengths

It was confirmed that no appreciable quantity of acetic acid was produced from the acetic anhydride used, since no kinetic deviation was observed with the same typical runs carried out after three weeks. It is sure also that acetic and cinnamic acids produced during the reaction will have little catalytic effect, since an addition of benzoic acid to the reaction mixture did not change the rate, especially with p-nitrobenzaldehyde, where no effect was observed until separation of the solution into two layers occurred (*ca.* 20% conversion). A report[26] that the effect of the added acid was very small in the base-catalyzed Knoevenagel condensation of cyanoacetic acid with aldehydes at high temperature is consistent with the above observation.

YOSHIDA, KYOTO, JAPAN

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(26) M. J. Astle and W. C. Gergel, *J. Org. Chem.*, **21**, 493 (1956).

[CONTRIBUTION NO. 75 FROM E. I. DU PONT DE NEMOURS & COMPANY, INC., ELASTOMER CHEMICALS DEPARTMENT]

Chemistry of Aryl Isocyanates: Rate and Equilibrium Constants for the Formation of Ethyl α,γ-Diarylallophanate

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By means of the near infrared spectrum the equilibrium and rate constants for the formation of ethyl α,γ-diarylallophanates from aryl isocyanates and ethyl substituted carbanilates at elevated temperatures have been measured.

In the near infrared region between 14,000 and 4,000 cm.$^{-1}$ are found the absorption bands arising from N—H, C—H and O—H stretching vibrations. In particular, the first overtone of the NH stretching vibration is found near 6750 cm.$^{-1}$ Recently, we have shown that the NH group of ethyl, ethyl-p-methyl and ethyl o-methylcarbanilate exhibit absorption in the region of 6750 cm.$^{-1}$ However, the

NH group of ethyl α,γ-diphenylallophanate does not exhibit this absorption.[1] This absence of absorption is characteristic for this type of structure. This suggests that near infrared spectroscopy can be used to obtain equilibrium and rate data for the formation of ethyl α,γ-diarylallophanate by following the rate of disappearance of carbanilate NH absorption.

Aryl isocyanates react with ethyl carbanilates at 125–140° to give the ethyl α,γ-diarylallophanate.[2] In the presence of a small quantity of a tertiary amine such as *N*-methylmorpholine, the sole product of the reaction is triarylisocyanurate[2] in excellent yield. Evidence that the formation of triarylisocyanurate proceeds through ethyl α,γ-diarylallophanate and aryl isocyanate dimer was presented. Additional evidence for ethyl α,γ-diarylallophanate as one of the intermediates in the reaction is presented in this paper.

EXPERIMENTAL

Materials. Eastman Kodak phenyl isocyanate, *o*- and *p*-tolyl isocyanate were carefully redistilled immediately prior to use. Ethyl alcohol was purified by the method of Fieser.[3]

Ethyl carbanilate and ethyl *o*- and *p*-methylcarbanilate were prepared by a known procedure.[4]

Measurements in 10 cm. cylindrical quartz cells were made with a Cary Model 14 spectrophotometer using a scan speed of 5 mμ per second. The cell holder was thermostatically controlled at 26 ± 0.5°. Redistilled carbon tetrachloride was used as the solvent.

Procedure. The reactants were carefully weighed into a 125 ml. Erlenmeyer flask equipped with a drying tube. The Erlenmeyer and its contents were placed in a constant temperature bath and shaker for 2.5 to 3 min., depending upon the temperature at which the reaction was run. This procedure allowed for the expansion of the reaction mixture. Zero time of reaction was taken immediately after this expansion period. The error involved in this heating period due to reaction between the carbanilate and isocyanate is negligible since the over-all reaction is very slow. At various intervals a 5 ml. aliquot of the solution was quickly removed and dropped into a tared 50 ml. volumetric flask containing 25 ml. of cold carbon tetrachloride (T = 5°). The weight of the 5 ml. aliquot was noted. The solution was allowed to reach room temperature, the volume increased to 50 ml. with additional carbon tetrachloride and the spectrum taken. At room temperature there is no measurable reaction between an aryl isocyanate and ethyl carbanilate. In the concentration range used, the absorbance of radiation at 6750 cm.$^{-1}$ follows the Beer-Lambert law. Aryl isocyanate and ethyl α,γ-diarylallophanate were found to exert no effect on the absorbance of the carbanilates.

The spectra obtained throughout a typical run with ethyl carbanilate and phenyl isocyanate are shown in Fig. 1. Ethyl carbanilate, which exhibits a major band characteristic of the NH group at 6750 cm.$^{-1}$, decreases with time until the equilibrium point is reached.

The calculations for the equilibrium and rate constants are based upon equation (I). The expression for the rate constants was derived on the basis that the forward reaction is pseudo-first order, with the concentration of isocyanate constant.

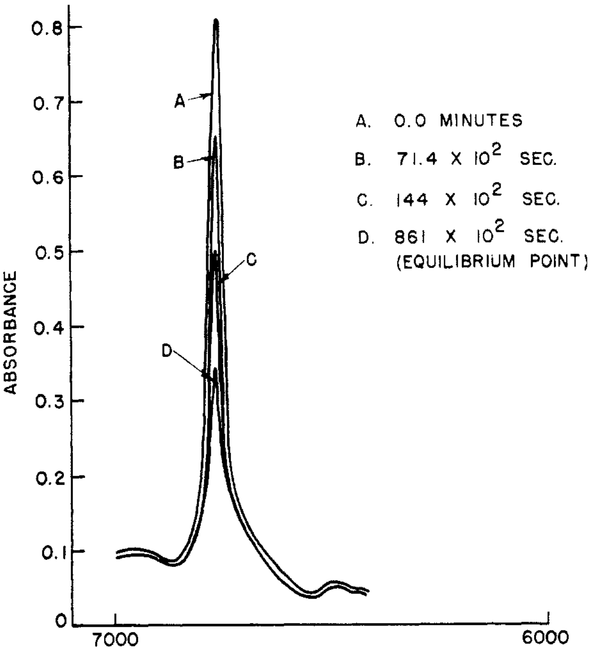
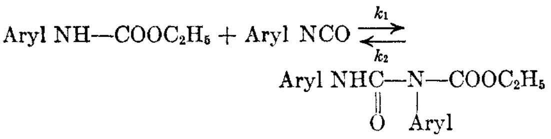


Fig. 1. Near infrared absorption spectra of the reaction of ethyl carbanilate with phenyl isocyanate in the mole ratio of 12:1. Temperature, 128°.



$$\text{Aryl NH—COOC}_2\text{H}_5 + \text{Aryl NCO} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{Aryl NH}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—}\underset{\underset{\text{Aryl}}{|}}{\text{N}}\text{—COOC}_2\text{H}_5 \quad \text{(I)}$$

In order to simplify our calculations, the trace quantity of aryl isocyanate dimer formed as a by-product of the reaction[2] was assumed to be too small to appreciably affect the calculations of the rate and equilibrium constants. Thus,

$$K_{\text{eq}} = \frac{k_1}{k_2} = \frac{X_e}{(u - X)\,(i - X)}$$

$$k_1 = \frac{2.303}{t(i + 1/K_{\text{eq}})} \log \frac{iu}{iu - X(i + 1/K_{\text{eq}})}$$

where X = no. of moles of allophanate formed at time t, X_e = no. of moles of allophanate formed at equilibrium, $u - X$ = no. of moles of carbanilate remaining at time t, i = no. of moles of isocyanate initially. The values for the heat and entropy of reaction and the energy of activation were calculated from the equilibrium and rate constants in the usual manner.

Second order rate plots were obtained by plotting log $\frac{iu}{iu - X(i + 1/K_{\text{eq}})}$ against time. A typical plot shows the straight line obtained for the phenyl isocyanate/ethyl carbanilate reaction of Fig. 2.

RESULTS AND DISCUSSION

Inspection of the experimental data in Table I, Nos. 3, 5 and 7, shows that the equilibrium constant for the phenyl isocyanate/ethyl carbanilate reaction remains constant at 128° over a concentration range of phenyl isocyanate/ethyl carbanilate of 9.1 to 18.0. An increase in reaction temperature

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(1) I. C. Kogon, *J. Am. Chem. Soc.*, **79**, 2253 (1957).

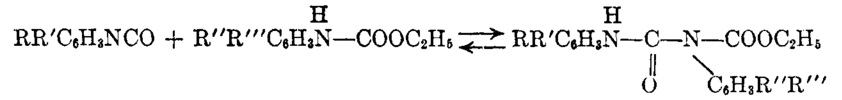
(2) I. C. Kogon, *J. Am. Chem. Soc.*, **78**, 4911 (1956).

(3) L. Fieser, *Experiments in Organic Chemistry*, D. C. Heath and Co., New York, 1941, p. 358.

(4) H. Vittenet, *Bull. soc. chim. France*, [9] **21**, 952 (1899).

TABLE I

RATE AND EQUILIBRIUM CONSTANTS FOR THE REACTION OF ETHYL SUBSTITUTED CARBANILATE WITH ARYL ISOCYANATE



$$RR'C_6H_3NCO + R''R'''C_6H_3\overset{H}{N}{-}COOC_2H_5 \rightleftarrows RR'C_6H_3\overset{H}{N}{-}\underset{\underset{O}{\|}}{C}{-}\underset{\diagdown C_6H_3R''R'''}{N}{-}COOC_2H_5$$

No.	R	R′	R″	R‴	Temp., °C.	NCO/NH	$K_{equil.}$ Liters/Mole	k × 10^4 Liters/Mole/Sec.	ΔE[a] $K_{calcd.}$	ΔH[b] $K_{calcd.}$	ΔS[c] Calcd./deg.
1	H	H	H	H	137	12.6	0.203	0.065			−13.2
2	H	H	H	H	137	12.6[d]	...	0.072			
3	H	H	H	H	128	12.6	0.242	0.042	15.9	−6.7	−13.8
4	H	H	H	H	128	12.6[d]	...	0.050			
5	H	H	H	H	128	9.1	0.243	0.050			−13.8
6	H	H	H	H	106	12.6	0.397	0.1017	16.5	−6.8	−15.9
7	H	H	H	H	128	18.0	0.248	0.036			−14.0
8	H	H	H	*p*-CH_3	128	12.6	0.349	0.036			
9	H	H	H	*o*-CH_3	128	12.6	0.568	0.127			
10	H	*o*-CH_3	H	*o*-CH_3	143	12.6	0.146	0.070			
11	H	*p*-CH_3	H	*p*-CH_3	143	12.6	0.094	0.043			

[a] Energy of activation. [b] Heat of reaction. [c] Entropy of reaction. [d] Catalyzed by *N*-methyl morpholine.

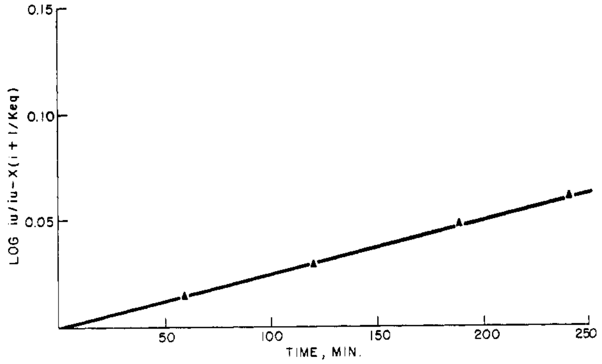


Fig. 2. 2nd Order plot of phenyl isocyanate + ethyl carbanilate. Temp. 137°.

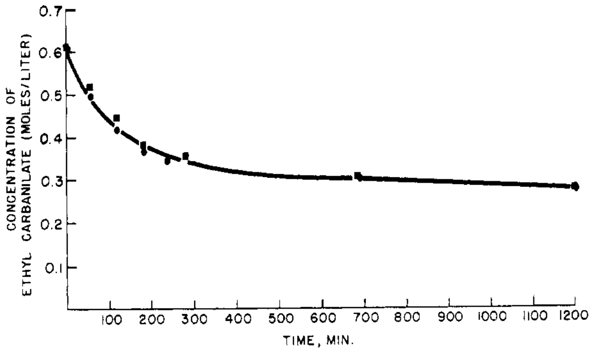


Fig. 3. The rate of disappearance of ethyl carbanilate as followed by the near infrared spectra

■ Uncatalyzed

● Catalyzed with 0.5% *n*-methylmorpholine

from 106° to 137° results in a decrease of the value for K_{eq}. Thus the quantity of ethyl α,γ-diphenylallophanate at *equilibrium* decreases as the temperature increases, (Table I, Nos, 1, 3, 6). This indicates that at the equilibrium point of the reaction a higher yield of ethyl α,γ-diphenylallophanate should be obtained as the temperature is decreased.[5]

The results of the rate measurements given in Table I, (Nos. 3, 8, 9) show that substitution in the *p*-position of the aromatic ring by a methyl group decreases the rate of reaction compared to the unsubstituted and *o*-methyl substituted carbanilate. This is contrary to what we had expected. The mechanism previously proposed for this reaction involved the nucleophilic attack of the carbanilate NH group on the carbon of the isocyanate group followed by a proton shift to give the allophanate.[2] On the basis of this mechanism one would predict that even a weak electron-repelling group such as methyl in the *p*-position of the aromatic ring of the carbanilate should enhance the rate of the forward reaction. However, as Mukaiyanai and Iwanami[6] showed in their thermal decomposition studies of carbanilates at elevated temperatures, benzyl *o*-methylcarbanilate and benzyl carbanilate in the presence of a primary amine, dissociate faster to benzyl alcohol and aryl isocyanate than benzyl *p*-methylcarbanilate. Their mechanism postulates an initial ionization of the carbanilate to the enol anion of the carbanilate followed by dissociation to the substituted benzyl alcohol and aryl isocyanate. Thus, assuming ionization of the carbanilate occurs at elevated temperature the decreased rate of reaction of ethyl *p*-methylcarbanilate with phenyl isocyanate (Table I, No. 8) compared to ethyl carbanilate with phenyl isocyanate (Table I, No. 3) is probably due to retardation of the ionization of the carbanilate to the enol anion by the *p*-methyl group. The greater rate constant for the formation of ethyl α,*o*-tolyl, γ-phenylallophanate (Table I, No. 8) is probably due to steric strain between the *o*-methyl and carbanilate groups of ethyl *o*-methyl-

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(5) This has been verified by us and is the subject of another paper.

(6) T. Mukaiyanai and M. Iwanami, *J. Am. Chem. Soc.*, **79**, 73 (1957).

carbanilate which results in an increased tendency toward ionization to the enol anion. The enolic form can then react with phenyl isocyanate to give allophanate containing a stable pseudo six-membered ring containing an intramolecular hydrogen bond.[1]

When the aromatic ring of the aryl isocyanate and the ethyl carbanilate both contain a methyl group (Table I, Nos, 10, 11) the rate of reaction of *o*-tolyl isocyanate with ethyl *o*-methylcarbanilate is slightly greater than the rate of reaction of *p*-toly isocyanate with ethyl *p*-methylcarbanilate. Two factors are taken into consideration to account for this enhanced reactivity of the *o*-methyl system; (*a*) effect of the methyl substituent on the aromatic ring of the isocyanate and (*b*) effect of the methyl substituent on the aromatic ring of the carbanilate. It was previously shown that at room temperature *p*-tolyl isocyanate reacts approximately 4 times faster than *o*-tolyl isocyanate toward alcohol or water at 25°.[7] However, as the temperature of the reaction is increased to 100° the relative rates of reaction of the *o*- and *p*-methyl groups begin to approach each other and are different by a factor of approximately 2. On the other hand, as shown above, an *o*-methyl group activates the carbanilate group approximately 3.5 times greater than a *p*-methyl group. Therefore, a larger rate constant should be observed for the formation of allophanate from *o*-tolyl isocyanate with ethyl *o*-methylcarbanilate than from *p*-tolyl isocyanate with ethyl *p*-methylcarbanilate.

The results of the rate measurements for the *N*-methylmorpholine catalyzed reaction of phenyl isocyanate with ethyl carbanilate show that the amine does not have any appreciable catalytic effect on allophanate formation (Table I, Nos, 2 and 4). The spectral data show that carbanilate concentration decreases with time at the same rate as the uncatalyzed reaction (Fig. 3). As the reaction approaches equilibrium a large exotherm occurs followed by solidification of the solution to a mixture of triphenylisocyanurate and ethyl carbanilate. Thus the disappearance of the carbanilate NH absorption band with time indicates that ethyl α,γ-diphenylallophanate is being formed and is an intermediate reaction product in the formation of triphenylisocyanurate from phenyl isocyanate and ethyl carbanilate.

Acknowledgment. The writer wishes to thank Dr. Karl Frensdorff for his aid in deriving the rate equation used in this paper.

WILMINGTON, DEL.

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(7) (a) J. Burkus and C. F. Eckert, presented before the Division of Paints and Plastics at the 132nd National Meeting of the American Chemical Society, New York, New York, September 1957. (b) K. C. Smeltz, E. J. Goldberg, I. C. Kogon, W. C. Woodland, Reaction of Water with Isocyanate," submitted for publication.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

A New Synthesis of 9-Phenanthrol; Absorption Spectra of the Quinhydrone-Type Molecular Compound between 9-Phenanthrol and Phenanthrenequinone

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A new synthesis of 9-phenanthrol from phenanthrene is described in which the novel step is a quantitative pinacol rearrangement of *cis*- or *trans*-9,10-dihydro-9,10-phenanthrenediol. The infrared spectra of 9-phenanthrol shows it to be completely enolized in both the solid state and in solution. Infrared and ultraviolet absorption spectra, combustion analysis, and chromatographic separation support the conclusion that 9-phenanthrol forms a quinhydrone-type molecular compound with phenanthrenequinone in a 1:1 molar ratio.

9-Phenanthrol. 9-Phenanthrol (III), first prepared by Lachowitz[1] *via* 9,10-phenanthrenequinone (I) and 10,10-dichloro-9,10-dihydro-9-phenanthrone, has been of interest because of its conversion in high yields to 9-phenanthrylamine and *N*-alkyl-9-phenanthrylamines (Bucherer reaction) which are structurally related, in at least one important respect, to morphine.[2] III also has marked analgesic properties[3a] and fungi toxicity.[3b]

Improvements in Lachowitz' procedure,[4,5] or alternatively, reduction of I with hydriodic acid and phosphorus,[6,7a] with hydrazine in absolute ethanol[8]

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(1) B. Lachowitz, *J. prakt. Chem.*, **28**, 172 (1883); *Ber.*, **17**, 1161 (1883).

(2) L. F. Fieser, R. P. Jacobsen, and C. C. Price, *J. Am. Chem. Soc.*, **58**, 2163 (1936).

(3) (a) N. B. Eddy, *J. Pharmacol. Exptl. Therap.*, **48**, 183 (1933); **51**, 75 (1934). (b) S. Rich and J. G. Horsfall, *Proc. Natl. Acad. Sci. U. S.*, **40**, 139 (1954); *Chem. Abstr.*, **48**, 8831 (1954).

(4) J. Schmitt and H. Lumpp, *Ber.*, **41**, 4215 (1908).

(5) S. Goldschmidt and M. A. Bredig, *Ann.*, **445**, 135 (1925).

(6) F. R. Japp and F. Klingemann, *J. Chem. Soc.*, **63**, 770 (1893).

(7) (a) E. Fourneau and J. Matti, *Bull. soc. chim.*, **7**, 615 (1940). (b) E. Fourneau and J. Matti, *Bull. soc. chim.*, **9**, 633 (1942).