

NH); 1485, 1433, and 1378 (CH); 1240 (P → O); 1164, 1024, 975 (P—O—C).

Anal. Calcd. for  $C_6H_{14}NO_4P$ : N, 7.18. Found: N, 7.30.

Attempted selective hydrolysis of this compound to (carbamoylmethyl)phosphonic acid resulted in complete hydrolysis to phosphonic acid.

*Diisopropyl (methoxycarbonylmethyl)phosphonate*. Methyl bromoacetate (153 g., 1 mole) was added dropwise to hot triisopropyl phosphite (200 g., 1 mole) at a rate which maintained boiling. Distillation of the resulting solution gave a fraction boiling between 88° and 94° at 0.08–0.4 mm. This colorless liquid was redistilled, and the fraction boiling at 93–96°/0.09 mm. was collected and analyzed; yield, 172 g. (72%).

*Spectral data*.  $\nu$  in  $cm^{-1}$  (film): 2980 (aliphatic CH); 1740 (ester C=O); 1445, 1395, 1385 (CH); 1280 (P → O); 1180, 1110, 985 (P—O—C).

Anal. Calcd. for  $C_9H_{16}O_5P$ : C, 45.38; H, 8.04; P, 13.01. Found: C, 45.78; H, 8.75; P, 12.58.

*Phosphonic acid*. Diisopropyl (methoxycarbonylmethyl)phosphonate (72 g., 0.3 mole) was heated with concentrated hydrochloric acid (300 ml.) on a water bath for 4 hr. A portion of the hydrochloric acid (150 ml.) was removed by distillation at atmospheric pressure, and the remainder was removed under reduced pressure. Distillation with benzene removed the last traces of water azeotropically. Evaporation of the benzene gave an oil which crystallized on standing overnight in a desiccator over phosphorus pentoxide and potassium hydroxide. Recrystallization from acetic acid gave 33.2 g. (79%) of the free acid, m.p. 143° (lit.<sup>8</sup> m.p. 142–143°).

*Spectral data*.  $\nu$  in  $cm^{-1}$  (KBr): 2900 (acidic hydrogen); 2300 (shoulder, P—OH); 1705 (acid C=O); 1410 (CH); 1125 (P → O, hydrogen bonded).

Anal. Calcd. for  $C_9H_{16}O_5P$ : C, 17.16; H, 3.60; P, 22.13. Found: C, 17.43; H, 3.43; P, 21.78.

*Dibenzyl (carbamoylmethyl)phosphonate (IIc)*. Molten sodium (2.3 g., 0.1 mole) was shaken with a Vibro-mixer in boiling toluene (50 ml.), and the fine dispersion was allowed to cool with shaking to give powdered sodium. The toluene was decanted and replaced with ether (200 ml.). Absolute ethanol (4.6 g., 0.1 mole) was added and the suspension was refluxed until all the sodium had disappeared (8 hr.). A solution of dibenzyl phosphite (26.3 g., 0.1 mole) in 50 ml. of ether was added dropwise in an atmosphere of nitrogen to give a clear solution of sodium dibenzyl phosphite. This solution was added dropwise to a suspension of 2-chloroacetamide (9.3 g., 0.1 mole) in ether with stirring and cooling. After the addition was completed, the mixture was heated under reflux for 1 hr. The ether was decanted from the gummy precipitate which had formed, and was washed with water (3 × 100 ml.), dried over magnesium sulfate, and evaporated under reduced pressure. The residue (3.6 g.) from the ether evaporation crystallized when the walls of the vessel containing it were scratched. Recrystallization of a sample of this material from water gave long, colorless needles, m.p. 93°.

The gummy residue from the ether decantation was dissolved in benzene and washed with water (3 × 100 ml.) to remove sodium chloride. Evaporation of the benzene solution, which had been dried over magnesium sulfate, gave a residue (5.8 g.) which crystallized when scratched. After recrystallization from water, the product melted at 93–94°; total yield, 9.4 g. (29%).

*Spectral data*.  $\nu$  in  $cm^{-1}$  (KBr): 3360, 3180 (NH); 3050 (aromatic CH); 2980, 2905 (aliphatic CH); 1665 (amide C=O); 1645 (amide); 1505 (phenyl); 1430, 1410, 1390 (CH); 1240 (P → O); 1005, 980 (P—O—C); 750, 700 (mono-substituted benzene).

Anal. Calcd. for  $C_{16}H_{18}NO_4P$ : C, 60.19; H, 5.68; N, 4.39; P, 9.70. Found: C, 60.67; H, 5.46; N, 4.32; P, 9.75.

*(Carbamoylmethyl)phosphonic acid (IIa) (A)*. Free acid. A solution of dibenzyl (carbamoylmethyl)phosphonate (1 g., 3 mmoles) in 25 ml. of absolute ethanol was hydrogenated in

the presence of 5% palladium-on-charcoal catalyst (0.5 g.). Hydrogen uptake stopped after 165 ml. had been consumed (calculated 155 ml.). The catalyst was removed by filtration and washed with ethanol. The residue from the evaporation of the combined filtrate and washings was recrystallized from methanol; yield of white needles, 0.3 g. (68%); m.p. 171°.

*Spectral data*.  $\nu$  in  $cm^{-1}$  (KBr): 3375, 3220 (NH); 2400–2300 (P—OH); 1675 (amide C=O); 1605 (amide NH); 1460, 1405 (CH); 1170 (P → O, hydrogen bonded).

Anal. Calcd. for  $C_9H_8NO_4P$ : C, 17.27; H, 4.35; N, 10.08; P, 22.28. Found: C, 17.58; H, 4.42; N, 10.22; P, 22.41.

*B. Dilithium salt (IIc)*. Phosphonic acid (14 g., 0.1 mole) and 70 g. of thionyl chloride were mixed. Immediate evolution of hydrogen chloride occurred. When the evolution began to slow down, heat was applied. After completion of the reaction, excess thionyl chloride was removed under reduced pressure with the addition of several portions of benzene. The residue, a reddish yellow oil free of thionyl chloride odor, was dissolved in dry dioxane (180 ml.), and gaseous ammonia was bubbled through the solution for 1 hr. The yellow precipitate that formed was filtered off rapidly and extracted with hot glacial acetic acid. Most of the ammonium chloride remained undissolved, but a small amount crystallized from the acetic acid on cooling. It was removed by filtration, and the acetic acid was evaporated under reduced pressure. The remaining orange-colored oil was dissolved in 200 ml. of 5% hydrochloric acid. Neutralization with a saturated solution of lithium hydroxide, followed by the addition of an equal volume of ethanol, gave an almost white precipitate, which was collected by filtration and dried *in vacuo* over phosphorus pentoxide at 110°.

*Spectral data*.  $\nu$  in  $cm^{-1}$  (KBr): 3200 (NH); 1660 (amide C=O); 1610 (amide NH); 1440, 1390 (CH); 1105, 1085 (ionic phosphonate); 1005 (P—C).

Anal. Calcd. for  $C_9H_4Li_2NO_4P$ : C, 15.92; H, 2.67; N, 9.29; P, 20.53. Found: C, 16.24; H, 3.02; N, 9.39; P, 20.36.

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## An Extension of the Woodward Rules Concerning Alkyl Substituents in Conjugated Aliphatic Systems

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It is known<sup>1a,b</sup> that alkyl substitution in  $\alpha,\beta$ -unsaturated aldehydes and ketones affords ap-

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TABLE I  
RELATIONSHIPS BETWEEN WAVE LENGTH OF MAXIMAL ABSORPTION AND SUBSTITUTION  
IN  $\alpha,\beta$ -UNSATURATED ALDEHYDES AND KETONES

Compound	In Ethanol		In Cyclohexane	
	$\lambda_{\max}$ , m $\mu$	Displacement on replacement of $\beta$ -hydrogen atom by methyl, m $\mu$	$\lambda_{\max}$ , m $\mu$	Displacement on replacement of $\beta$ -hydrogen atom by methyl, m $\mu$
$\text{CH}_2=\text{CH}\cdot\text{CHO}$	207		203	
$\text{CH}_3\cdot\text{CH}=\text{CH}\cdot\text{CHO}$	218	11	213	10
$(\text{CH}_3)_2\text{C}=\text{CH}\cdot\text{CHO}$	235.5	17.5	228	15
$\text{CH}_2=\text{C}(\text{CH}_3)\cdot\text{CHO}$	216		213	
$\text{CH}_3\cdot\text{CH}=\text{C}(\text{CH}_3)\cdot\text{CHO}$ (Tiglaldehyde)	226	10	222.5	9.5
$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)\cdot\text{CHO}$	245	19	240	17.5
$\text{CH}_2=\text{CH}\cdot\text{CO}\cdot\text{CH}_3$	208.5		205	
$\text{CH}_3\cdot\text{CH}=\text{CH}\cdot\text{CO}\cdot\text{CH}_3$	220	11.5	215	10
$(\text{CH}_3)_2\text{C}=\text{CH}\cdot\text{CO}\cdot\text{CH}_3$	236	16	231	16
$\text{CH}_2=\text{C}(\text{CH}_3)\cdot\text{CO}\cdot\text{CH}_3$	217.5		214.5	
$\text{CH}_3\cdot\text{CH}=\text{C}(\text{CH}_3)\cdot\text{CO}\cdot\text{CH}_3$	228	10.5	223	8.5
$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)\cdot\text{CO}\cdot\text{CH}_3$	245.5	17.5	238.5	15.5

TABLE II  
EFFECT OF TERMINAL METHYL GROUPS ON WAVE LENGTH OF MAXIMAL ABSORPTION IN CONJUGATED DIENES

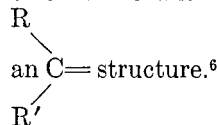
Compound	In Ethanol		In Cyclohexane	
	$\lambda_{\max}$ , m $\mu$	Displacement on replacement of hydrogen atom by methyl, m $\mu$	$\lambda_{\max}$ , m $\mu$	Displacement on replacement of hydrogen atom by methyl, m $\mu$
$\text{CH}_2=\text{CH}\cdot\text{CH}=\text{CH}_2$	217.5		218.5	
$\text{CH}_3\cdot\text{CH}=\text{CH}\cdot\text{CH}=\text{CH}_2$	223	5.5	224	5.5
$(\text{CH}_3)_2\text{C}=\text{CH}\cdot\text{CH}=\text{CH}_2$	232.5	9.5	234	10
$\text{CH}_3\cdot\text{CH}=\text{CH}\cdot\text{CH}=\text{CH}\cdot\text{CH}_3$	226	8 5/2	226.5	8/2
$(\text{CH}_3)_2\text{C}=\text{CH}\cdot\text{CH}=\text{C}(\text{CH}_3)_2$	241	15/2	242	15.5/2

proximately constant, additive, displacements in the wave length of maximal absorption. A  $\beta$ -alkyl group gives a larger displacement than an  $\alpha$ -alkyl group<sup>1b</sup> and for  $\alpha,\beta$ -unsaturated ketones average figures of 12 and 10 m $\mu$ , respectively, have been quoted.<sup>2</sup>

We have recently examined the spectra of methyl substituted derivatives of acrolein and methylvinyl ketone and have observed that a second  $\beta$ -methyl substituent gives rise to a considerably larger displacement than the first (see Table I). Similar figures appear to be found for a number of cyclic  $\alpha,\beta$ -unsaturated ketones. In alcohol, 1-acetylcyclopentene has  $\lambda_{\max}$  239 m $\mu$ , 1-acetyl-2-methylcyclopentene has  $\lambda_{\max}$  253 m $\mu$ ,<sup>3</sup> a displacement of 14 m $\mu$ ; 1-acetylcyclohexene has  $\lambda_{\max}$  232–233 m $\mu$ , 2-methyl-1-acetylcyclohexene has  $\lambda_{\max}$  249 m $\mu$ ,<sup>3</sup> a displacement of 16–17 m $\mu$ . A related phenomenon is shown by the infrared carbonyl bands of the aldehydes. In carbon tetrachloride, acrolein shows

a carbonyl band at 1704 cm.<sup>-1</sup>, crotonaldehyde at 1696 cm.<sup>-1</sup>,<sup>4</sup> and  $\beta$ -methylcrotonaldehyde at 1683 cm.<sup>-1</sup><sup>5</sup>

Table II shows an analogous effect for conjugated dienes. It is of interest that an empirical correlation of maximal wave length for conjugated dienes with structure suggested the use of a parameter 0.13 for R and 0.17 for R' in compounds with R



The point arises whether the effect of the second group is caused by its occurrence as part of a gem-dimethyl group, or whether it is caused by the second group usually taking up a position *cis* to the carbonyl or second vinyl group. This question is being investigated. Frequently the *cis*-isomer would be anticipated to absorb at shorter wave length because of steric interactions.<sup>7</sup> However,

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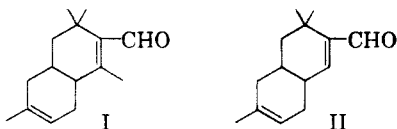
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there is evidence that sometimes the *cis*-isomer absorbs at longer wave length in spite of steric interactions. For example, in ethanol, angelic acid has  $\lambda_{\max}$  215.5  $\mu$ , whereas tiglic acid has  $\lambda_{\max}$  212.5  $\mu$ .<sup>8</sup> In *n*-heptane, *cis*-piperylene has  $\lambda_{\max}$  226  $\mu$ , whereas *trans*-piperylene has  $\lambda_{\max}$  223  $\mu$ , and the same order is found in the vapor phase.<sup>9</sup>

In contrast to our observations, the wave length displacement between compounds I and II is only



5  $\mu$ ,<sup>10</sup> and the displacement between 1-vinylcyclohexene ( $\lambda_{\max}$  230  $\mu$ ) and 2-methyl-1-vinylcyclohexene ( $\lambda_{\max}$  233  $\mu$ ) is only 3  $\mu$ .<sup>11</sup> In the former set of data, the structures have, however, been assigned only tentatively, and both sets of data are not recent. We, therefore, consider it probable that some of these spectral data are in error.

#### EXPERIMENTAL

Spectra were determined by standard methods on a Unicam SP 500 or Beckman DU spectrophotometer. The purification of the compounds, the absorption intensity values, and the spectral curves will be described separately in a fuller discussion of the relevant compounds.

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### Near Infrared Studies. Rate Constants for the Alcohol/Aryl Isocyanate Reaction

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In the near infrared spectrum (14,300–4000  $\text{cm}^{-1}$ ) are found the overtone and combination frequencies of the OH, NH, CH, and SH fundamental stretching vibration. In a recent paper, we have shown that this region can be used to reveal the presence of an intramolecular hydrogen bond in aryl allophanates and biurets.<sup>1</sup> Similarly, the ki-

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

netics of the alcohol/isocyanate reaction can be studied by using the near infrared spectrum to follow the course of the reaction.

Davis and McC. Farnum<sup>2</sup> were the first to study the relative reactivity of phenyl isocyanate with lower aliphatic alcohols. The kinetics of the tertiary amine catalyzed reaction of aromatic mono-isocyanates with methanol were studied by Baker and Holdsworth.<sup>3</sup> They showed that the reaction of an alcohol with phenyl isocyanate follows second order kinetics. Baker and Gaunt<sup>4</sup> studied both the base-catalyzed and uncatalyzed reactions of phenyl isocyanate with lower alcohols in di-*n*-butyl ether and in benzene and have obtained kinetic evidence for the mechanism of this reaction.

#### EXPERIMENTAL

*Materials.* Every effort was made to exclude water from the solvent and reactants in order to keep hydrolysis to a minimum. Ethyl alcohol was dried by the method of Fieser.<sup>5</sup> Eastman Kodak phenyl, *p*-tolyl, and *o*-tolyl isocyanate and Du Pont toluene-2,4-diisocyanate and toluene-2,6-diisocyanate were carefully redistilled into preflamed 10-ml. glass ampoules and sealed under dry nitrogen. A reagent grade of carbon tetrachloride was used without further purification. Triethylamine was purified by distillation over lithium aluminum hydride into ampoules and sealed under dry nitrogen.

*Spectrophotometric method.* The intense absorption of near infrared radiation at a wave length of approximately 6750  $\text{cm}^{-1}$  caused by the NH group of a carbanilate provides an excellent method for following the rate of reaction between ethyl alcohol and an aryl isocyanate. The rate of increase of carbanilate formed from the alcohol/isocyanate reaction was noted by the increase in absorption at 6750  $\text{cm}^{-1}$  at regularly timed intervals. Measurements were made in a 10.0-cm. quartz cell using the Cary Spectrophotometer model No. 14. The instrument was provided with a thermostatically controlled cell holder and was held at  $28 \pm 0.2^\circ$ .

The concentration of carbanilate at time  $t$  was determined from the absorption  $\log I_0/I$  by the Beer-Lambert formula where  $\log I_0/I$  is the intensity of absorption,  $L$  is the length of the cell in centimeters,  $c$  is the concentration of carbanilate in moles per liter, and  $e$  is the molar absorptivity.

$$\log I_0/I = eLc \quad (1)$$

The molar absorptivity for ethyl carbanilate (I), ethyl-4-methylcarbanilate (II), ethyl-2-methylcarbanilate (III), ethyl-3-isocyanato-4-methylcarbanilate (IV), and ethyl-3-isocyanato-2-methylcarbanilate (V) was obtained from the slope of the straight line by plotting  $\log I_0/I$  against concentration of carbanilate. A typical plot is shown in Fig. 1. The strong polar effect of ethyl alcohol upon the absorption of radiation by the NH group and, therefore, upon the molar absorptivity for the carbanilates was taken into consideration in the following manner. A sufficient quantity of ethyl alcohol was present in each solution of carbon tetrachloride and carbanilate (representing a point on the straight

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