

It is obvious that interesting differences exist between the reactivity and selectivity of electrophilic reagents towards benzenes and thiophenes. We are studying this problem further.

Experimental. Nitration of 3-iodothiophene. A mixture of 5.0 g (0.024 mole) of 3-iodothiophene⁶ and 10 g acetic anhydride was cooled to -10° , and a mixture of 3.0 g fuming nitric acid in 6.0 g of acetic anhydride was added dropwise with stirring. The mixture was stirred for another 10 min and then poured onto crushed ice. The yellow crystalline product (5.4 g, 89%) was filtered off. No additional product was obtained by extracting the aqueous filtrate with chloroform. NMR-analyses showed the product to contain 64% 3-iodo-2-nitrothiophene and 36% of 3-iodo-5-nitrothiophene. Recrystallisation from acetic acid gave pure 3-iodo-2-nitrothiophene, m.p. $140-141^{\circ}$ (Lit. value,⁷ m.p. $140-141^{\circ}$). NMR-spectrum (acetone) of 3-iodo-2-nitrothiophene: $\tau_5 = 2.08$ ppm, $\tau_4 = 2.61$ ppm, $J_{45} = 5.6$ c/s. NMR-spectrum (acetone) of 3-iodo-5-nitrothiophene $\tau_{\text{ringhydrogen}} = 1.92$ ppm, 1.97 ppm. $J_{24} = 1.7$ c/s.

Acetylation of 3-iodothiophene. 10.0 g (0.048 mole) of 3-iodothiophene, and 4.0 g (0.051 mole) of acetyl chloride were dissolved in 75 ml of dry benzene and 6.0 ml of SnCl_4 was added dropwise and the mixture stirred for 2 h at $50-60^{\circ}$. The reaction mixture was then cooled in ice and decomposed by adding dilute hydrochloric acid. The benzene layer was separated, dried, and the solvent removed *in vacuo* leaving 10.0 g (82%) of a half-crystalline product. NMR-spectral analysis gave 83% of 3-iodo-2-acetylthiophene and 17% of 3-iodo-5-acetylthiophene. Recrystallization from cyclohexane yielded pure 3-iodo-2-acetylthiophene, m.p. $64-66^{\circ}$. NMR-spectrum (dimethyl sulphoxide): $\tau_5 = 2.44$ ppm, $\tau_4 = 2.95$ ppm, $J_{45} = 5.0$ c/s. (Found: C 28.96; H 2.11; S 12.69. Calc. for $\text{C}_6\text{H}_5\text{IOS}$ ((252.1): C 28.59; H 2.00; S 12.69).

NMR-spectrum (dimethyl sulphoxide) of 3-iodo-5-acetylthiophene $\tau_{\text{ring-hydrogen}} = 2.16$, ppm, 2.34 ppm, $J_{24} = 1.2$ c/s.

The iodination and mercuration of 3-iodothiophene has already been described.⁶

The NMR-spectra were recorded on a Varian A-60 high resolution spectrometer. The chemical shifts are given as τ -values.⁸

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On the Mechanism of the Michaelis-Arbuzov Rearrangement in Acetonitrile

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Buck and Yoke¹ recently reported that in the two-stage Michaelis-Arbuzov reaction of trialkyl phosphites with alkyl halides in acetonitrile the second step appears to be rate determining. The authors studied the system tri-butyl phosphite and ethyl iodide in acetonitrile at 31°C by a conductometric method. We have studied the same system under the same conditions by measuring the infrared absorption of reactants and products. The acetonitrile was distilled over phosphorus pentoxide before use. After 20.5 h, the infrared spectrum of the reaction mixture showed that the amount of dibutyl ethanephosphonate ($\text{P}=\text{O}$ band as a doublet at 1227 and 1248 cm^{-1}) was nearly zero; whereas, according to Buck and Yoke approximately 80% of the tributyl phosphite should have been transformed to phosphonate. When the acetonitrile contained small amounts of water (less than 0.2%) we found that under the experimental conditions specified by Buck and Yoke a rapid autocatalytic transformation

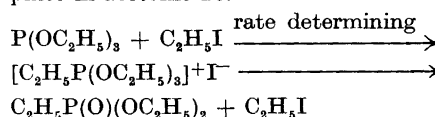
Table 1. Data for the reaction between triethyl phosphite and ethyl iodide in acetonitrile.

Run No.	Temp. °C	Conc. (mole/l)		Added NaI (mole/l)	Pseudo 1st order rate const. $h^{-1} \times 10^2$	2nd order rate const. $l \text{ mole}^{-1} h^{-1} \times 10^1$
		Triethyl phosphite at 25.5°C	Ethyl iodide at reaction temp.			
1	69.9	0.1996	0.2134	0	3.70	1.73
2	69.9	0.1735	0.1961	0.01378	3.24	1.65
3	65.0	0.4409	0.4506	0	4.55	1.01
4	65.0	0.2003	0.2133	0	2.37	1.11
5	60.1	0.2039	0.2223	0	1.64	0.74

of tributyl phosphite to dibutyl hydrogenphosphite took place. Since the authors report that their reaction mixture showed infrared absorption in the region 7.8–8 μ (1265–1250 cm^{-1}), dibutyl hydrogenphosphite ($P=O$ band at 1260 cm^{-1}) may well have been their major product. Their drying procedure of acetonitrile with barium oxide also seems doubtful, and no special precaution to remove dibutyl hydrogenphosphite by distillation of the phosphite over sodium is mentioned.

In the following, some results from a study of the Michaelis-Arbuzov rearrangement of triethyl phosphite with ethyl iodide in dry acetonitrile are reported. The measurements were performed on a Unicam spectrophotometer, Model SP 100. The rate of formation of the rearrangement product, diethyl ethanephosphonate, was

followed by measuring the intensity of the phosphoryl band which appeared as a doublet with peaks at 1223 and 1246 cm^{-1} . The estimated error in the measured concentrations is $\pm 5\%$. Typical runs are shown in Fig. 1. It is seen that the reaction follows pseudo first order kinetics. This result can be interpreted as due to a *rate determining first step* in the Michaelis-Arbuzov rearrangement of triethyl phosphite in acetonitrile:



This mechanism demands that the concentration of ethyl iodide remains constant during the reaction. The constancy of the ethyl iodide concentration determined from the absorption band of ethyl iodide at 1204 cm^{-1} during the reaction showed this to be the case. Determination of the pseudo first order rate constant at different ethyl iodide concentrations showed that the rate constant was directly proportional to the ethyl iodide concentration (Table 1). A separate indication of a rate determining first step was the non-influence of added sodium iodide upon the rate of the rearrangement (Table 1).

A full account of the kinetic studies of the Michaelis-Arbuzov rearrangement of phosphites, phosphonites and phosphinites in acetonitrile as well as without added solvent will be given later.

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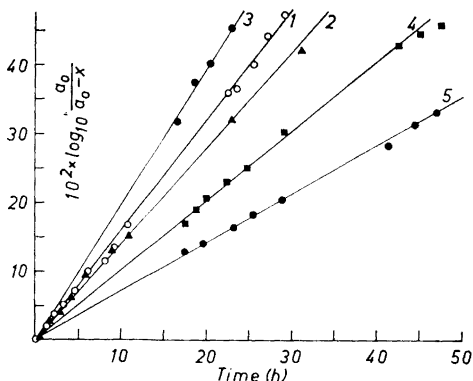


Fig. 1. Pseudo first order plot of the reaction between triethyl phosphite and ethyl iodide. The numbers on the curves refer to the run numbers specified in Table 1.