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There is no information in the literature on the phosphorylation of ketones with a pyrimidine ring or other group containing a basic element. We have found that pyrimidines with a keto group having a labile α -hydrogen atom [1] are readily phosphorylated by phosphorus chlorides at oxygen in the presence of organic bases. For example, substituted phenylpyrimidine (I) reacts with diethyl chlorophosphite in the presence of triethylamine (B:) and is completely converted (as indicated by NMR spectroscopy) to substituted vinyl phosphite (II), which is unstable to hydrolysis and thus is converted without isolation to the product of thionylation (III) and oxidation (IV).



The structures of the reaction products were indicated from their spectra. The reaction mixtures and reaction products after separation do not have characteristic IR bands for the C=O group but do have a band at 1645 cm⁻¹ (C=C). The ¹H and ³¹P NMR spectra of product (II) correspond to 0,0-dialkyl-0-vinyl phosphites, while these spectra for products (III) and (IV) correspond to phosphates with Z-configuration [2, 3]. The PMR spectra of these compounds have doublets in the olefinic proton region with a characteristic phosphorus coupling constant [3]. This phosphorylation reaction is extremely stereoselective. NMR spectroscopy indicates that the Z stereoisomer is formed to an extent greater than 95%.

<u>2-Phenacyl-5-phenylpyrimidine (I)</u> was obtained according to our previous method [1] in 60% yield, mp 139-142°C (from benzene-ethanol). Found: C 78.8; H 4.98; N 10.3%. Calculated for $C_{18}H_{14}N_{2}O$: C 78.8; H 5.14; N 10.2%.

<u>0,0-Diethyl-0-(1-phenyl-2-(5-phenyl)pyrimidin-2-yl)vinyl thiophosphate (III).</u> Diethyl chlorophosphite was added to a solution of ketone (I) and triethylamine in CHCl₃. An equimolar amount of triethylamine and diethyl chlorophosphite was added over 24 h in an excess such that the PMR spectrum of the reaction solution showed the absence of ketone (I). The product phosphite (II) had δP + 139.2 ppm and a PMR doublet at 6.59 ppm, ⁴J_{HP} = 1.9 Hz. An excess of freshly prepared sulfur powder was added to the reaction mixture until the ³¹P NMR signal of phosphite (II) disappeared. The reaction mixture was washed two or three times with water and dried over magnesium sulfate. Chloroform was replaced as the solvent by ether and the mixture was left stand in dry ice. The precipitate was recrystallized from hexane to give a yield of ~30%, mp 106.5-107°C. Found: N 6.90; P 7.24; S 7.56%. Calculated for $C_{22}H_{23}N_2O_3PS$: N 6.57; P 7.26; S 7.52%. PMR spectrum (δ , ppm, Hz): -CH= , 1H, 6.84, ⁴J_{HP} = 2.4. δP = +62.34 ppm.

0,0-Diethyl-0-(1-phenyl-2-(5-phenyl)pyrimidin-2-yl)vinyl phosphate (IV). Dry 0₂ was passed through a solution of vinyl phosphite (II) in CHCl₃ to give complete oxidation of the phosphite to phosphate (IV). The product was separated by analogy with the procedure for thio-

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phosphate (III). The yield was ~35%, mp 80-81°C (from hexane). Found: C 7.12; P 7.55%, Calculated for $C_{22}H_{23}N_2O_4P$: N 6.82; P 7.54%. PMR spectrum: 6.83 (1H, CH=), ⁴J_{HP} = 1.9 Hz, $\delta P = -7.49$ ppm.

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CATALYTIC ACTIVITY OF DEPOSITED CLUSTER COBALT CARBONYL COMPLEXES IN THE SYNTHESIS OF HYDROCARBONS FROM CO AND H_2

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Deposited cluster cobalt carbonyl complexes are well known as catalysts in the synthesis of hydrocarbons from CO and H_2 [1-4]. The aim of the present work was to study the influence of the geometry and multinuclearity of the initial carbonyl complex on the activity of the catalyst obtained.

We were therefore the first to study the catalytic activity of the cluster carbonyl complexes $Ph_2C_4Co_4(CO)_{12}$, $Ph_2C_2Co_2(CO)_6$, $Ph_2Ge(C_2H)_2[Co_2(CO)_6]_2$, $Ph_2Si(C_2H)_2[Co_2(CO)_6]_2$, $C_6H_4 (C_2H)_2Co_4(CO)_{12}$, $Co_3(CO)_9CC1$, deposited on the surface of thermally activated γ -Al_2O_3. The complexes were deposited in an amount of 2% (calculated with respect to the metal) from a solution in n-pentane at ~20°C, and then the samples were heated in a current of deoxygenated inert gas to 473°K. The reaction was carried out in a flow type apparatus at atmospheric pressure, in the temperature range of 468-503°K, for 5 h. The CO:H₂ ratio was 1:2, and the time of contact 30 sec. On all the catalysts studied the conversion of CO into the C₁-C₃ hydrocarbons varied from 5 to 30%. The main products in the reaction were saturated hydrocarbons.

It was found that the conversion of CO is dependent on the geometry of the complex. In particular, $Ph_2C_4Co_4(CO)_{12}$ has the highest activity, and $Co_3(CP)_9CCl$ has the lowest activity. In the series of acetylenic cobalt carbonyl complexes, an increase in activity was detected with increase in the nuclearity of the cluster (for $Ph_2C_2Co_2(CO)_6$ the conversion is 12% and for $Ph_2C_4Co_4(CO)_{12}$ it is 30%). The activity of the catalyst decreases with increase in the distance between the cobalt pairs.

Studies on these catalysts by physical methods are being carried out, and will be reported later.

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