Other crystallization and sublimation fractions had infrared absorption bands characteristic of cyanotriphenylmethane (2230 cm.$^{-1}$, potassium bromide disk), triphenylmethyl peroxide, and mercuric cyanide. No attempt was made to isolate all products from these fractions.

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Reaction of 2-Aminopyridine with Propiolic Acid

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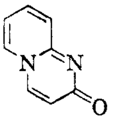
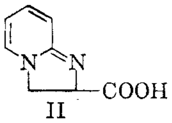
In a previous paper[2] it was shown that 2-aminopyridine reacts with α-bromoacrylic acid at the ring nitrogen atom to produce 2*H*-pyrido[1,2-*a*]-pyrimidin-2-one (I). A by-product, considered to be 2,3-dihydroimidazo-[1,2-*a*]pyridine-2-carboxylic acid (II) on the basis of analogy to previous work[3] was also obtained.

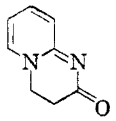
Subsequently, Lappin[4] showed that 2-aminopyridine reacts with acrylic esters at both the ring and α-amino nitrogen atoms to form 3,4-dihydro-2*H*-pyrido[1,2-*a*]pyrimidin-2-one (III) and esters of *N*-(2-pyridyl)-β-alanine (IV).



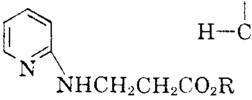
I



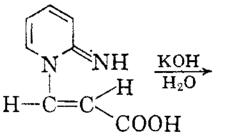
II



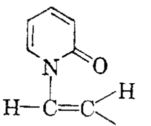
III



IV



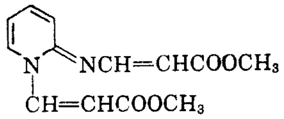
V



VI

In extending these studies on the addition of 2-aminopyridine to derivatives of unsaturated acids, the reaction with propiolic acid was investigated. Two colorless compounds were obtained, one of which is 2*H*-pyrido[1,2-*a*]pyrimidin-2-one (I). The second product, an amino acid, fails to cyclize when heated and must therefore be a *trans* adduct. It is the *ring* nitrogen derivative, *trans*-2-imino-1-(2*H*)-pyridineacrylic acid (V), as treatment with alkali results in evolution of ammonia and formation of *trans*-2-oxo-1(2*H*)pyridineacrylic acid (VI). No evidence for reaction of propiolic acid at the α-amino nitrogen atom was obtained.

Lappin[5] recently reported the reaction of 2-aminopyridine with methyl propiolate. He found that the highly exothermic reaction produced I and the colored diadduct VII. Although none of the monoadduct corresponding to V was obtained in the reaction, such adducts could be obtained when certain substituted 2-aminopyridines were used.



VII

EXPERIMENTAL

Reaction of 2-aminopyridine with propiolic acid. To 7.0 g. of propiolic acid was added 10.0 g. of 2-aminopyridine. Heat was evolved as 2-aminopyridinium propiolate formed. Upon heating to 100°, reaction occurred with evolution of gas and spontaneous temperature rise to 150°. The mixture was kept at this temperature for 5 min. and then cooled. The resulting solid was broken up and extracted three times with 25-ml. portions of hot 2-propanol. The insoluble residue was recrystallized from water to give 5.5 g. of *trans*-2-imino-1-(2*H*)-pyridineacrylic acid (V), m.p. 255° (dec.). The compound is a monohydrate.

Anal. Calcd. for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.53; N, 15.38. Found: C, 52.78; H, 5.62; N, 15.19.

Evaporation of the aqueous mother liquor from the crystallization of V left a residue which largely dissolved in hot 2-propanol. The 2-propanol solution was combined with the extracts previously obtained and the total was evaporated to dryness. The residue was dissolved in methanol and the resulting solution diluted with chloroform. An additional 0.3 g. of V separated. The methanol-chloroform solution, upon concentration, gave 4.0 g. of 2*H*-pyrido[1,2-*a*]pyrimidin-2-one (I), m.p. 245°, which was identified with a previously obtained sample.

trans-2-Oxo-1(2H)-pyridineacrylic acid (VI). To 1.0 g. of *trans*-2-imino-1(2*H*)pyridineacrylic acid (V) was added 0.5 g. of potassium hydroxide and 10 ml. of water. The solution was heated under reflux for 30 min. It turned red in color and ammonia was evolved. The solution was acidified with dilute sulfuric acid and a solid separated Recrystallization from ethanol with charcoal treatment gave 0.53 g. of needles of VI which, after one further recrystallization from ethanol, melted at 220–225° dec.

Anal. Calcd. for $C_8H_7NO_3$: C, 58.18; H, 4.27; N, 8.48. Found: C, 57.70; H, 4.26; N, 8.24.

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(1) Present address: Research and Development Division, Smith Kline and French Laboratories, Philadelphia 1, Pa.

(2) R. Adams and I. J. Pachter, *J. Am. Chem. Soc.*, **74**, 5491 (1952).

(3) R. Adams and I. J. Pachter, *J. Am. Chem. Soc.*, **74**, 4906 (1958).

(4) G. R. Lappin, *J. Org. Chem.*, **23**, 1358 (1958).

(5) G. R. Lappin, *Distillation Products Industries Organic Chemical Bulletin*, **33** (1), 1961, and private communication.

Direct Synthesis of *p*-Styryldiphenylphosphine

Robert Rabinowitz and Ruth Marcus

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A recent article[1] describes a multistep synthetic route to *p*-styryldiphenylphosphine, I. The proce-

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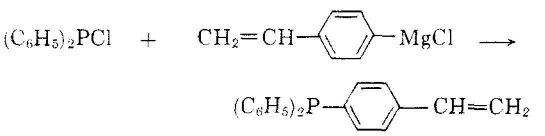
(1) A. E. Senear, W. Valient, and J. Wirth, *J. Org. Chem.*, **25**, 2001 (1960).

dure involves treating the Grignard reagent of the ketal from ethylene glycol and *p*-bromoacetophenone with diphenylchlorophosphine, followed by hydrolysis of the ketal, sodium borohydride reduction of the ketone to the alcohol, and finally dehydration to the desired product, I. An over-all yield of 22% based on diphenylchlorophosphine was reported.

We have investigated a simpler and more direct route to I, the reaction of *p*-styrylmagnesium chloride[2] with diphenylchlorophosphine.



(I)

Reactions of this Grignard reagent with triphenylgermanium bromide,[3] triphenyllead chloride,[3] triphenyltin chloride,[2,3] diphenyldibromogermane, and trimethylchlorosilane[4] are reported to give the corresponding substituted styrene. However, Senear, Valient, and Wirth[1] report that their attempts to prepare I from direct reaction of diphenylchlorophosphine with the Grignard led to immediate polymerization.

We wish to report that the direct reaction to prepare I can be carried out in good yield with only slight modification of the published procedures[2-4] for the synthesis of the tin, germanium, lead, and silicon substituted styrenes. These procedures involve adding the organometalloid halide compound to a solution of the Grignard[2] reagent maintained at 50–60°. We also, using these conditions, could not isolate any I. However, at 0–10° a 51% yield was obtained on a small scale and 31% on a larger scale. An even greater improvement was realized through the use of the inverse technique of addition. Under these conditions, small scale experiments at 50–60° gave 50% of I and a large scale experiment gave a 76% yield at 0–10°.

EXPERIMENTAL[5,6]

Reaction of p-styrylmagnesium chloride and diphenylchlorophosphine at 50° using inverse addition. The *p*-styrylmagnesium chloride was prepared by the method of Leebrick and Ramsden[2] using 9.7 g. of magnesium, 3 ml. of ethyl bromide, 27.6 g. (0.20 mole) of *p*-chlorostyrene, and 55 ml. of tetrahydrofuran, with the exception that the temperature was never allowed to exceed 60°. After adding an additional 50 ml. of tetrahydrofuran to the mixture on completion of the reaction, a 2-ml. sample was removed, hydrolyzed in water and the hydrolysate extracted with a few milliliters of carbon tetrachloride. Gas phase chromatography of the extract revealed mainly styrene plus a trace of *p*-chlorstyrene, indicating that the Grignard formation went to virtual completion. Dropping the extract into methanol revealed that some polymer was present.[7] The Grignard was slowly added to a solution of 31.5 g. (0.142 mole) of diphenylchlorophosphine in 150 ml. of tetrahydrofuran. The reaction was exothermic and the temperature was maintained between 50–60° using external cooling. The mixture was stirred for 10 min. after the addition was complete and was then poured nto 200 ml. of cold water containing 33 g. of ammonium chloride. This was extracted with tetrahydrofuran, 0.25 g. of *t*-butylcatechol added as an inhibitor, the extract was dried over sodium sulfate and reduced in volume to 75 ml. This was added to hexane resulting in the precipitation of 15 g. of polymer.[8] The tetrahydrofuran was removed from the filtrate leaving a mixture of solid and oil. The addition of 95% ethanol and subsequent filtration gave 20.25 g. (50%) of I, m.p. 65–75°. It was recrystallized from 95% ethanol, m.p. 77–8.°[9]

Anal. Calcd. for $C_{20}H_{17}P$: C, 83.31; H, 5.94; P, 10.74. Found: C, 82.63; H, 6.12; P, 11.06.

Reaction of p-styrylmagnesium chloride with diphenylchlorophosphine at 0–10° using inverse addition. The Grignard was prepared as before using 3.5 ml. of ethyl bromide, 29.1 g. of magnesium, 81.8 g. (0.59 mole) of *p*-chlorostyrene, and 165 ml. of tetrahydrofuran. After dilution with an additional 50 ml. of tetrahydrofuran this mixture was added to a solution of 111 g. (0.50 mole) of diphenylchlorophosphine in 400 ml. of tetrahydrofuran. The temperature was maintained at 0–10° during the addition and when complete it was allowed to warm to room temperature. It was worked up as before. The volume of the extract prior to addition into 1400 ml. of hexane was 400 ml. Only 7.0 g. of polymer was found. The filtrate, upon removal of solvent, revealed 109 g. of I, m.p. 65–75° which was readily purified by recrystallization from 95% ethanol.

Reaction of p-styrylmagnesium chloride with diphenylchlorophosphine using direct addition at 0–10°. The Grignard was prepared as previously described from 9.7 g. of magnesium, 3 ml. of ethyl bromide, 27.6 g. (0.20 mole) of *p*-chlorostyrene, and 150 ml. of tetrahydrofuran. It was then cooled to 0° and 31.5 g. (0.142 mole) of diphenylchlorophosphine was slowly added while maintaining the temperature at 0–10°. The mixture was allowed to warm to room temperature and was then worked up as already described. Only 4.2 g. of polymer was obtained. From the precipitation filtrate, upon removal of the solvent, was isolated 20.9 g. (51%) of I.

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(2) J. R. Leebrick and H. E. Ramsden, *J. Org. Chem.*, **23**, 935 (1958).

(3) J. G. Noltes, H. A. Budding, and G. J. M. Van Der Kerk, *Recueil*, **79**, 408 (1960).

(4) A. E. Senear, J. Wirth, and R. Neville, *J. Org. Chem.*, **25**, 807 (1960).

(5) All melting points are uncorrected.

(6) The *p*-chlorostyrene was obtained from the Monomer-Polymer Laboratories of the Borden Co. and the diphenylchlorophosphine from Victor Chemicals. They were distilled prior to use.

(7) In every preparation of *p*-styrylmagnesium chloride, some polymer was noted at this stage.

(8) As polymer is always present, even at the Grignard stage, this technique of separating polymer from monomer is valuable in preparing the other known substituted styrenes—*i.e.*, Ge, Pb, Si, Sn, etc.—provided a medium can be found in which only the polymer is insoluble.

(9) Ref. 1 reports 74–76° for the crude product.

Thermal Decarboxylation of Diaryl Fumarates to Stilbenes

Sydney M. Spatz

Received March 23, 1961

Stilbene derivatives are useful in such varied fields as azo dyestuffs, optical brighteners, and