tracted with ether. No attempt was made to isolate the free aldehyde but it was at once converted to the *semicarbazone*, white crystals from ether; m.p. 155–156°. The yield was poor.

Anal. Calcd. for $C_{15}H_{26}N_6O$ (mol. wt. 306.41); C, 58.79; H, 8.55. Found: C, 58.98; H, 8.32.

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A Convenient Method for the Preparation of Di-*n*-butylfluoroborane

E. J. De Witt

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Hennion, McCusker, and Rutkowski[1] have recently reported the preparation of diisobutylfluoroborane by treatment of the corresponding chloroborane with antimony trifluoride. Antimony trifluoride is known to replace the other halides for fluoride, but it is unusual for this reagent to replace an alkyl group for fluoride. Such a reaction was used to prepare di-*n*-butylfluoroborane in a very convenient one step process. Tri-*n*-butylborane was heated with antimony trifluoride. At about 135°, the di-*n*-butylfluoride began to distill, and an antimony mirror formed on the flask walls. The reaction was completed by heating to 180°. The lower boiling butyldifluoroborane might be expected to form, but none was detected.

Buls, Davis, and Thomas[2] have reported the di-*n*-butylfluoroborane to boil at −5°/100 mm. The material reported here had a much higher boiling point, 48°/20 mm. (d_4^{24} 0.783). Hennion *et al.* reported their isobutyl isomer to boil at 49°/52 mm. (d_4^{25} 0.7662). The higher boiling point (48°/20 mm.) would be expected since it lies between the monoalkyldifluoroborane (36.3°/742 mm.)[3] and the tri-*n*-butylborane (90°/9 mm.).[3]

EXPERIMENTAL

Di-n-butylfluoroborane. The reaction system consisted of all glass connections, and all operations were carried out under nitrogen. A flask was charged with 32 g. of antimony trifluoride and 50 g. of tri-*n*-butylborane. On heating to 135°, a volatile material began to distill and was collected in a cooled receiver. The temperature was gradually increased to 180°, and when distillation ceased, the heat was removed. The water-white product weighed 41.3 g. This material was distilled twice through a 1-ft. × 1/4-in spiral wire packed column. The water-white mobile liquid weighed 25 g. and was flammable in air. The product distilled at 47°/20 mm. (d_4^{24} 0.783).

Anal. Calcd. for $C_8H_{18}BF$: F, 13.18. Found: F, 12.91, 13.09.

Acknowledgment. The author wishes to thank Dr. L. Kreider for obtaining some of the physical data on this reaction; and the Goodrich analytical staff for the fluorine analysis.

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(1) G. F. Hennion, P. A. McCusker, and A. J. Rutkowski, *J. Am. Chem. Soc.*, 80, 617 (1958).

(2) V. W. Buls, O. L. Davis, and R. L. Thomas, *J. Am. Chem. Soc.*, 79, 337 (1957).

(3) M. F. Lappert, *Chem. Rev.*, **56**, 1053, 1028 (1956).

Synthesis of Cyanotriphenylmethane from Hexaphenylethane

C. W. Schimelpfenig

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The postulation of the involvement of the cyanyl radical in the reaction of mercuric cyanide with disilicon hexachloride[1] has prompted a search for further examples in which a carbon-nitrogen pair might react as an uncharged unit. By the reaction of hexaphenylethane and mercuric cyanide, cyanotriphenylmethane has been formed in 15% yield.

Whether this reaction has involved the cyanyl radical or the cyanide ion is not certain. It is of interest to note earlier reactions between organic radical precursors and mercury salts other than mercuric cyanide[2] and to note reactions between hexaphenylethane and several inorganic salts.[3]

EXPERIMENTAL

A solution of 0.09 mole of hexaphenylethane in 250 ml. of benzene was prepared.[4] Silver chloride and excess silver were removed by filtration under nitrogen. A suspension composed of the benzene solution and 0.1 mole of mercuric cyanide was stirred magnetically for 10 days at room temperature beneath an atmosphere of nitrogen. The suspension was filtered. The filtrate was extracted with water. The washed benzene filtrate containing the crude product was evaporated to dryness. This residue was extracted with boiling ethanol. From the ethanol-soluble portion was isolated by fractional sublimation and fractional crystallization (ethanol solvent) 7.55 g. (0.028 mole) of cyanotriphenyl methane. This product was shown to be identical with an authentic sample prepared by the method of Fischer[5] by the identity of their infrared spectra and on the basis of a mixture melting point.

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(1) A. Kaczmarczyk and G. Urry, *J. Am. Chem. Soc.*, 81, 4112 (1959).

(2) A. D. Ainley, L. A. Elson, and W. A. Sexton, *J. Chem. Soc.*, 776 (1946); Z. M. Manulkin, *Zhur. Obshcheĭ Khim.*, **16**, 235 (1946); G. A. Razuvaev, Yu. A. Ol'dekop, and N. A. Maĭer, *Zhur. Obshcheĭ Khim.*, **25**, 697 (1955); G. A. Razuvaev Yu. A. Ol'dekop, and N. A. Maĭer, *Doklady Akad. Nauk, S.S.S.R.*, **98**, 613 (1954); Yu. A. Ol'dekop and N. A. Maĭer, *Doklady Akad. Nauk, S.S.S.R.*, **131**, 1096 (1960); B. S. Wildi and J. S. Dunn, U. S. Patent **2,957,935** (Oct. 25, 1960).

(3) M. Gomberg and H. R. Gamrath, *Trans. Faraday Soc.*, **30**, 24 (1934); H. D. Hetzner, Dissertation, University of Michigan, 1939.

(4) M. Gomberg, *J. Am. Chem. Soc.*, **22**, 757 (1900).

(5) E. Fischer and O. Fischer, *Ann.*, **194**, 242 (1878).

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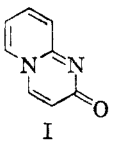
In a previous paper[2] it was shown that 2-aminopyridine reacts with α-bromoacrylic acid at the ring nitrogen atom to produce 2*H*-pyrido[1,2-*a*]-pyrimidin-2-one (I). A by-product, considered to be 2,3-dihydroimidazo-[1,2-*a*]pyridine-2-carboxylic acid (II) on the basis of analogy to previous work[3]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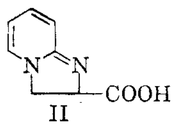
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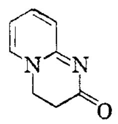
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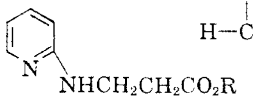
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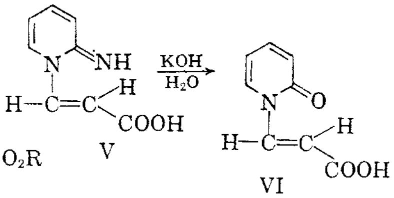
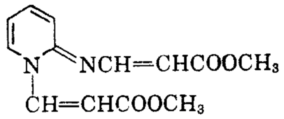

V

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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(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).