diene. This mixture was reduced with 1130 ml (46.3 mmol at STP) of deuterium or 71% of the amount required for complete reduction. Glpc analysis showed the acetate composition to be 72.4% *syn*-7-acetoxynorbornene (II), 12.9% *anti*-7-acetoxynorbornene (III), 7.2% 7-acetoxynorbornane (IV), and 7.5% 3-acetoxynortricyclene.(5) Isolation of II was accomplished *via* the silver nitrate technique previously described(1) and gave 1.08 g (41%) which by glpc analysis was 93% II, 5% III, and 2% an unidentified impurity. *syn*-7-Acetoxynorbornene(6) (II) has previously been identified. The nmr spectra (in $CDCl_3$) of *exo,exo*-5,6-dideuterio-*syn*-7-acetoxynorbornene (II) exhibits the characteristic "doublet of triplets" for vinyl hydrogens (δ 6.05, area 2) typical of *syn* compounds,(6-9) bridge hydrogen (multiplet, δ 5.05, area 1), bridgehead hydrogens (multiplet, δ 3.1, area 2), $OC(=O)CH_3$ hydrogens (singlet, δ 2.05, area 3), and *endo* hydrogens (singlet, δ 1.05, area 1.8). The nmr spectrum also shows *exo* hydrogens (multiplet, δ 2.28, area 0.2). The small amount of *exo* hydrogen arises from both incomplete deuteration (see mass spectral data) and some *endo* addition.(2) The mass spectral data (*via* the chemical ionization technique(4)) were obtained by Dr. Frank H. Field of these laboratories; the data showed that compound II was about 90% d_2 and 10% d_1.

Preparation of *exo,exo*-5,6-Dideuterio-2-norbornene (V).—In 15 ml of methanol 0.325 g of 10% palladium on powdered charcoal was saturated with 4.8 ml of deuterium. Into this mixture was injected 2.93 g (31.9 mmol) of norbornadiene which was partially reduced with 802 ml (32.8 mmol at STP) of deuterium. Glpc analysis of this mixture showed 86% norbornene, 7% norbornadiene, and 7% norbornane. The reduction mixture was filtered, added to 30 ml of H_2O, and extracted three times with 15-ml portions of pentane. The combined pentane extracts were dried over anhydrous $MgSO_4$ and reduced in volume to 3 ml by atmospheric distillation on a Todd fractionation assembly equipped with a Monel spiral column. Injections of 0.28 ml of the concentrated solution were chromatographed on a 20 ft × $^3/_8$ in. column packed with 30% silicone SE-30 on 60/80 Chromosorb P at 110° with 80 ml/min helium flow. Norbornene had a retention time of 12 min from air and was collected in Dry Ice–isopropyl alcohol cooled traps, giving 1.48 g (46%) which by glpc analysis was 95% norbornene and 5% of an unidentified impurity. The nmr spectrum of compound V has previously been described.(10) Mass spectra of compound V by the chemical ionization method(4) indicates 5% d_1 and 95% d_2. By electron impact compound V analyzes 99% d_2 and 1% d_1.

Registry No.—II (5,6-dideuterio), 15649-38-4; V, 3675-40-9.

Acknowledgment.—The authors are indebted to Dr. Frank H. Field for his aid in obtaining and interpreting the mass spectral data.

(5) Identified by comparison with an authentic compound: L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Amer. Chem. Soc.*, **78**, 2819 (1956).

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(7) G. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966).

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(9) H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **31**, 3941 (1966).

(10) W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *J. Amer. Chem. Soc.*, **89**, 410 (1967).

Base-Catalyzed Elimination Reactions of Substituted 2-(4-Pyridyl)ethylamines

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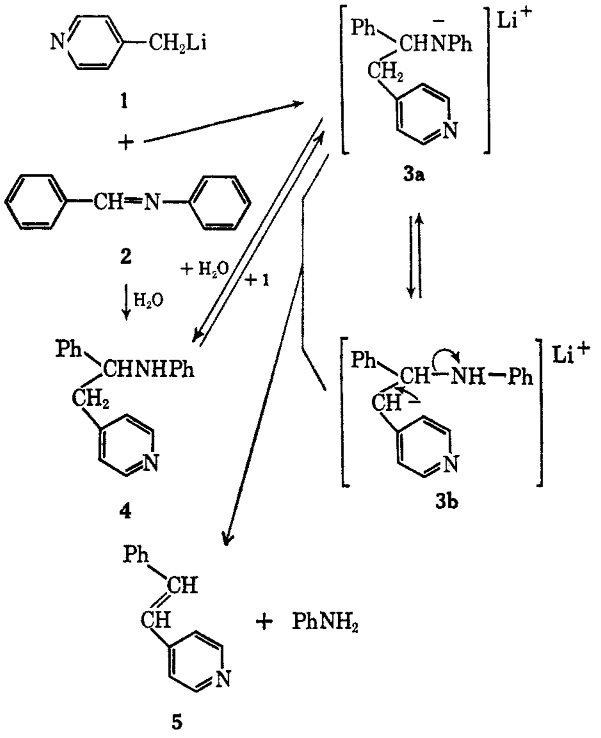
Our interest in the synthesis of compounds derived from 4-picolyllithium(1) led us to synthesize some N,1-diphenyl-2-(4-pyridyl)ethylamines. These compounds were prepared by treating arylideneanilines with 4-picolyllithium (**1**). During the course of this work we observed two elimination reactions (Scheme I). When a solution of benzylideneaniline (**2**) was treated at low temperature with **1**, rapid hydrolytic work-up afforded the desired pyridylethylamine **4** in excellent yield.(2,3)

SCHEME I



If, however, the reaction mixture was heated or allowed to stir at room temperature for a prolonged time, only the stilbazole (**5**) was isolated. That compound **4** was an intermediate in the formation of **5** could be demonstrated by treating a solution of **4** with either **1** or phenyllithium and warming the reaction mixture. Again, aniline was eliminated and **5** was the isolated product. A plausible mechanism for the elimination of aniline would involve a shift of the negative charge from the initial anion **3a** to give the carbanion **3b**.(4) Either of these intermediates could readily rearrange as shown to form **5** with the expulsion of the aniline anion.

In an attempt to find evidence for the existence of the carbanion **3b**, the reaction mixture was allowed to stand at room temperature until visual estimation of a thin layer chromatogram indicated that the product **5** was present in about 30% yield. At this time the reaction mixture was quenched with deuterium oxide. An examination of the nmr spectrum of the product **4** showed the deuterium to be located only on the nitrogen. Thus, the proposed carbanion **3b** is either very short-lived and undergoes immediate elimination to give **5** or compound **5** is formed directly from the anion **3a** *via* a concerted elimination.

(1) (a) R. I. Fryer, B. Brust, J. V. Earley, and L. H. Sternbach, *J. Org. Chem.*, **31**, 2415 (1966); (b) M. E. Derieg, B. Brust, and R. I. Fryer, *J. Heterocycl. Chem.*, **3**, 165 (1966).

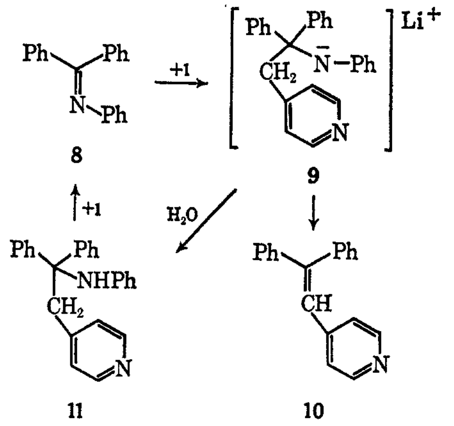
(2) The structure of compound **4** was confirmed by an independent synthesis described in the Experimental Section.

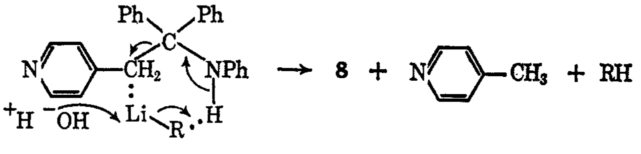
(3) F. F. Shuman and E. D. Amstutz, *Rec. Trav. Chim.*, **84**, 441 (1965).

(4) H.-D. Becker, *J. Org. Chem.*, **29**, 2891 (1964).

The same reaction sequence was next carried out on compound **8** (Scheme II) and the initial results were in agreement with those observed for the previous sequence in that rapid work-up of the reaction mixture gave **11** while prolonged standing gave the analogous phenylstilbazole **10**. The structure of **10** was confirmed by an independent synthesis involving the dehydration of 1,1-diphenyl-2-(4-pyridyl)ethanol which in turn was prepared from benzophenone by treatment with **1**. The mechanism of the formation of **10** from **8** presumably would be analogous to the sequence **3a,b** to **5**. However, when compound **11** was treated with **1** or with phenyllithium, picoline was eliminated on hydrolysis giving the Schiff base **8** in very high yield instead of the expected stilbazole **10**. Therefore, in this reaction, neither **9** nor the corresponding carbanion could be an intermediate since the product would then be compound **10**. The failure of **11** to react with either sodium hydride or lithium hydride in tetrahydrofuran further demonstrates the difficulty of the deprotonation of **11** to **9** in a nonaqueous system. The possibility of a retro-aldol type of reaction can also be discounted since the expected products, *i.e.*, compounds **8** and **1**, would then recombine to yield **9** and ultimately either **11** and/or **10**. One explanation for the elimination of picoline could be that a stable complex,[5] such as **12**, is initially formed and that upon the addition of water it is decomposed into **8**, picoline, and RH.

SCHEME II





12

Experimental Section

All melting points were determined microscopically on a hot stage and are corrected. Spectra were obtained for all compounds and were compared in order to confirm or exclude the expected structural changes. Tetrahydrofuran (THF) was dried over Woelm grade I neutral alumina.

1-Anilino-1-phenyl-2-(4-pyridyl)ethane (4).—A mixture of 19.7 g (0.1 mol) of 4-phenacylpyridine,[1a] an excess of aniline (0.25 mol), 100 ml of pyridine, 100 ml of benzene, and 15 ml of concentrated hydrochloric acid was heated under reflux for 48 hr using a Dean–Stark trap to remove water. The reaction mixture was cooled and filtered to give 25.5 g (82.8%) of 4-(β-phenyliminophenethyl)pyridine hydrochloride. Recrystallization from ethanol gave the analytically pure compound as yellow prisms, mp 261–271°.

Anal. Calcd for $C_{19}H_{16}N_2 \cdot HCl$: C, 73.90; H, 5.55; Cl, 11.48. Found: C, 74.02; H, 5.89; Cl, 11.56.

A solution of 15 g of 4-(β-phenyliminophenethyl)pyridine hydrochloride (48.5 mmol) in 200 ml of ethanol and 5 ml of concentrated ammonium hydroxide was treated with 7.0 g of sodium borohydride. The reaction mixture was diluted with water, cooled, and filtered to give 11.65 g (87.5%) of **4**, mp 115–118°. Recrystallizations from a mixture of methylene chloride and hexane gave the pure material as colorless plates, mp 118–119°.

Anal. Calcd for $C_{19}H_{18}N_2$: C, 83.17; H, 6.61; N, 10.21. Found: C, 82.98; H, 6.63; N, 10.39.

The dihydrochloride of **4** was prepared from an ethereal solution of **4** and dry hydrogen chloride. Recrystallizations from a mixture of methanol and ether gave colorless plates, mp 182–186°.

Anal. Calcd for $C_{19}H_{18}N_2 \cdot 2HCl$: C, 65.71; H, 5.80; Cl, 20.42. Found: C, 65.69; H, 5.71; Cl, 20.18.

Reaction of Benzylideneaniline (2) with 4-Picolyllithium (1).—A solution of 49.5 g (0.5 mol) of **1**[1a] in 300 ml of THF, under dry nitrogen and at −25°, was stirred during the dropwise addition (20 min) of a solution of 88 g (0.49 mol) of **2** in 240 ml of THF. Stirring was continued for 30 min and the reaction was quenched by the addition of 150 ml of water. The reaction mixture was extracted with 6 *N* hydrochloric acid; the acid layer was washed with ether and poured into an excess of ammonium hydroxide and ice. A yellow gum formed and slowly solidified. The solid was removed by filtration and was washed well with water giving, after air drying, 108.1 g of crude **4**.

When the reaction was performed on a 0.1-mol scale (18 g of **2**) at room temperature and allowed to stir overnight, work-up as described above afforded 6.5 g (36%) of 4-stilbazole (**5**). Recrystallizations from dilute acetone gave the pure product, mp 131.5–132° (lit.[6] mp 131°). By heating the reaction mixture at reflux for 2.5 hr the yield of **5** was increased from 36% to approximately 65%.

1,1-Diphenyl-2-(4-pyridyl)ethylene (10).—A solution of 10 g of 1,1-diphenyl-2-(4-pyridyl)ethanol[7] (36.4 mmol) in 50 ml of 70% H_2SO_4 was stirred and heated at 75° for 22 hr. The reaction mixture was treated with ice, made basic with ammonium hydroxide, and extracted with methylene chloride. The organic phase was dried over sodium sulfate and the solvent was evaporated. The residue was crystallized from hexane to give 7.6 g (81.4%) of **10**. Recrystallizations from a mixture of methylene chloride and hexane gave the analytical sample as colorless prisms, mp 74–76°.

Anal. Calcd for $C_{19}H_{15}N$: C, 88.68; H, 5.88. Found: C, 88.71; H, 5.91.

Reaction of N-Benzohydrylideneaniline (8) with 1.—A solution of 9.9 g (0.1 mol) of **1** in 200 ml of THF at −30° was stirred under dry nitrogen during the dropwise addition (30 min) of a solution of 25.7 g (0.1 mol) of **8** in 200 ml of THF. Stirring was continued for 30 min at −30° when the reaction was quenched with 60 ml of water. The reaction mixture was worked up as described for the isolation of compound **4** to give 24.8 g (70.6%) of 1-anilino-1,1-diphenyl-2-(4-pyridyl)ethane (**11**). Recrystallizations from methylene chloride gave an analytically pure sample as colorless prisms, mp 234–236°.

Anal. Calcd for $C_{25}H_{22}N_2$: C, 85.68; H, 6.33; N, 7.99. Found: C, 85.99; H, 6.45; N, 7.79.

The salt was prepared by treating a solution of **11** in chloroform with dry hydrogen chloride. Recrystallizations from a mixture of ethanol and ether gave the hydrochloride as yellow plates, mp 199–201°.

Anal. Calcd for $C_{25}H_{22}N_2 \cdot HCl$: C, 77.60; H, 5.99; Cl, 9.16. Found: C, 77.76; H, 5.90; Cl, 9.25.

When the reaction mixture (36.4 g of **8**, 0.14 mol) was heated under reflux for 18 hr, the usual work-up yielded an oil which was separated from the aqueous phase by ether extraction. The organic phase was washed with water, dried over magnesium sulfate, and evaporated to give an oily residue which was then extracted with petroleum ether (bp 30–60°). Removal of the

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(5) This is compatible with the observations that the addition of the organometallic compound to **11** results in a black solution and **8** could not be detected in the reaction mixture until the addition of water.

(6) E. A. Wagstaff, *J. Chem. Soc.*, 276 (1934).

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solvent and recrystallization from dilute acetone gave 9.15 g (25.6%) of pure **10**, mp 74–76°. The combined mother liquors contained **8**, **10**, and **11** in approximately equal amounts as seen by visual estimation on a thin layer chromatogram.

Reaction of 11 with 1.—A solution 3.5 g (10 mmol) of **11** in 50 ml of THF was treated with a solution of 10 mmol of **1** in 50 ml of THF and the resulting black solution was stirred under dry nitrogen overnight at room temperature. The reaction mixture was then poured over ice and 2.5 g (97.4%) of yellow crystalline **8**, devoid of **11** and **10** (mp 109–113°, lit.[3] 115–116°), was removed by filtration. The same result was obtained when the reaction mixture was heated under reflux and also when phenyllithium was substituted for **1** in the reaction.

Registry No.—4-(β-Phenylmonophenethyl)pyridine hydrochloride, 15813-15-7; **4**, 15856-53-8; **4** 2HCl, 15813-16-8; **10**, 15814-97-8; **11**, 15814-98-9; **11** HCl, 15813-17-9.

Acknowledgment.—We are indebted to Dr. A. Steyermark and his staff for the microanalyses and to Mr. S. Traiman for the determination of infrared spectra.

The Chlorination of Diethyl Acetylenedicarboxylate with Ferric Chloride

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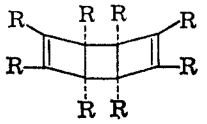
We recently became interested in the synthesis of *syn*-octacarbethoxytricyclo[4.2.0.$0^{2,5}$]octadiene (I) in connection with some photochemical studies. Since the aluminum chloride catalyzed tetramerization of 2-butyne to the octamethyl derivative II had been reported,[1] it was felt that a similar Lewis acid catalyzed reaction of diethyl acetylenedicarboxylate (III) should lead to the desired tetramer (I). To avoid the possibility of undesirable side reactions between aluminum chloride and the diester,[2] ferric chloride was chosen as the Lewis acid. Instead of producing I, however, ferric chloride served as a stereospecific chlorinating agent to yield diethyl dichlorofumarate (IV).



I, R = $-CO_2C_2H_5$
II, R = $-CH_3$

When a solution of III in cyclohexane was added to a stirred suspension of anhydrous ferric chloride in the same solvent, a viscous, amorphous complex which adhered to the walls of the flask was formed. Complex formation could be monitored by gas chromatography of the supernatant liquid, and appeared to be essentially complete after 1.5 hr. Continued stirring of the reaction mixture, followed by hydrolysis, produced a mixture of starting material and one major volatile product. That this product was not the expected tetramer (I) was demonstrated by its mass spectrum, which displayed a peak for the molecular ion at 239.9947, and suggested the formula $C_8H_{10}O_4Cl_2$. This formula was confirmed by combustion analysis and additional molecular weight data. The nmr spectrum exhibited *only* the characteristic signals for the grouping $-OCH_2CH_3$. Only two structures accommodated this data, diethyl dichloromaleate and diethyl dichlorofumarate (IV). Unequivocal proof that the product was not the maleate derivative was obtained by comparison of its glpc retention time with that of authentic diethyl dichloromaleate, prepared from the commercially available dichloromaleic anhydride. Earlier workers[3] had demonstrated that the acid-catalyzed esterification of this anhydride proceeds without isomerization. In addition, the well-defined separation of the two isomeric esters on gas chromatography gave assurance of the stereospecificity of the chlorination.

The chlorination of benzene derivatives,[4] alcohols,[5] and esters[5] by ferric chloride have been reported. Since there appeared to be no previous reports of chlorination of acetylenic compounds by ferric chloride,[6] however, a cursory investigation of the reaction mechanism was made. The dependence of the yield of diethyl dichlorofumarate (IV) upon reaction parameters is summarized in Table I.

Table I

Reaction time, hr	Moles of $FeCl_3$/mole of III	% yield of IV
1.5	8.71	4.3
17	2.03	7.7
17	4.13	20.5
16	8.42	19.7
45	9.76	30.4

The physical state of the intermediate complex makes extreme emphasis upon the effect of varying the $FeCl_3$/III ratio on the yield of IV unjustifiable. It is not inconceivable that a significant amount of ferric chloride became occluded in the sticky complex during the early stages of the reaction, and was thereby effectively removed from the reaction media.

From the low yield of IV after a reaction time of 1.5 hr (complex formation complete), it was inferred that chlorination was not simply a result of the hydrolysis of the complex. This experiment also demonstrated that chlorination occurred more slowly than complex formation, a hypothesis which was substantiated by the dependence of the yield of IV on reaction time. Finally, when diphenylacetylene was treated with ferric chloride for 22 hr, no reaction occurred. Thus it appeared that the carbethoxy groups were involved in the chlorination reaction.

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(1) H. M. Rosenberg and E. C. Eimutis, *Can. J. Chem.*, **45**, 2263 (1967).

(2) A. F. Dobryanskiĭ and Yu. I. Kornilova, *Sb. Statei Obsch. Khim. Akad. Nauk SSSR*, **1**, 320 (1953); *Chem. Abstr.*, **49**, 867*d* (1955).

(3) N. R. Eldred and D. M. Yound, *J. Amer. Chem. Soc.*, **75**, 4338 (1953).

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(5) M. Dangyan, *J. Gen. Chem. USSR*, **8**, 1780 (1938); *Chem. Abstr.*, **33**, 4957 (1939).

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