Experimental Section[10,11]

Ethyl 3,4,5,6-tetrahydroanthranilate (1) was prepared following the procedure of Prelog and Geyer,[12] mp 73–74.5 (lit.[12] mp 72–73.5). The product amino ester from the hydrogenation was isolated as the HCl salt, mp 128–129° (lit.[8] mp 131–133°).

Methyl 4-carbomethoxy-3,4,5,6-tetrahydroanthranilate (2) was prepared in quantitative yield from 2,4-dicarbomethoxycyclohexanone[13] by the procedure described by Becker,[14] mp 58–60.5° (hexane–benzene–ether, 10:1:1).

Anal. Calcd for $C_{10}H_{15}NO_4$: C, 56.33; H, 7.09; N, 6.57. Found: C, 56.22; H, 7.22; N, 6.74.

Dimethyl β-N-Methylamino Glutaconate (3).—In a three-necked flask equipped with a gas inlet tube, mechanical stirrer, and a Dean–Stark water separator was placed 17.4 g (0.1 mol) of dimethyl acetone–dicarboxylate dissolved in 250 ml of dry benzene. The solution was heated to 60–70° and methylamine gas was bubbled in slowly. The temperature of the reaction mixture was kept between 70–75° and the gas flow continued until the theoretical amount of water was trapped in the water separator. The benzene was removed under reduced pressure giving a viscous oil which slowly crystallized. After washing thoroughly with anhydrous ether 14 g of white crystals, mp 83–90°, was obtained. Repeated recrystallization from ether gave a mixture of *cis* and *trans* isomers, mp 92–99°.

Anal. Calcd for $C_8H_{13}NO_4$: C, 51.33; H, 7.00; N, 7.48. Found: C, 51.18; H, 6.86; N, 7.49.

The product amino diester, dimethyl β-N-methyl glutarate, was purified as its 3,5-dinitrobenzamide, mp 86–88° (pentane–chloroform).

Anal. Calcd for $C_{15}H_{17}N_3O_9$: C, 46.98; H, 4.47; N, 10.97. Found: C, 47.07; H, 4.67; N, 11.01.

Recommended Procedure for the Hydrogenation of Vinylogous Urethans. The Hydrogenation of 2.—To 8 g of 5% palladium on charcoal was added, carefully, 35 ml of dry dioxane so that the catalyst was thoroughly moistened with the solvent. To this paste was added, carefully, 65 ml of absolute methanol. (Direct addition of methanol to a dry hydrogenation catalyst can result in severe fires.[3]) This mixture was poured into the hydrogenation apparatus and 12.5 g of the vinylogous urethan 2 in 125 ml of methanol added. The hydrogenation was run for 18–24 hr at 85° and 1000–1500 psi. After this time the reaction mixture was cooled, the catalyst filtered off, and the solvent removed under reduced pressure at 30–35°. The cloudy residue was taken up in ether and filtered. Evaporation of the ether from the filtrate gave 11.25 g (90%) of the product amino diester as a colorless oil. The 3,5-dinitrobenzamide had mp 175–176° (ether–methanol).

Anal. Calcd for $C_{17}H_{19}N_3O_9$: C, 49.88; H, 4.68; N, 10.26. Found: C, 49.77; H, 4.93; N, 9.99.

Registry No.—2, 15649-59-9; 3,5-dinitrobenzamide of hydrogenated 2, 15649-60-2; 3 (*cis*), 15649-63-5; 3,5-dinitrobenzamide of hydrogenated 3, 15717-42-7; 3 (*trans*), 15983-53-6.

(10) Infrared spectra were recorded on a Beckman IR-10 spectrophotometer. The extent of hydrogenation was determined in some cases by product isolation and in others it was estimated by observing the decrease in adsorption at 1655 ($NH_2C{=}CC(=O)OR$) and at 1620 cm^{-1} ($C{=}C$)[11] and the corresponding increase in adsorption at 1730 ($CH_2(O{=})COR$) as well as by tlc.

(11) F. Korte and K. Trautner, *Chem. Ber.*, **95**, 295 (1962).

(12) V. Prelog and U. Geyer, *Helv. Chim. Acta*, **28**, 1677 (1945).

(13) H. T. Openshaw and R. Robinson, *J. Chem. Soc.*, 912 (1946).

(14) H. G. O. Becker, *J. Prakt. Chem.*, **12**, 294 (1961).

Synthesis of *exo,exo*-5,6-Dideuterio-*syn*-7-acetoxynorbornene and *exo,exo*-5,6-Dideuterio-2-norbornene

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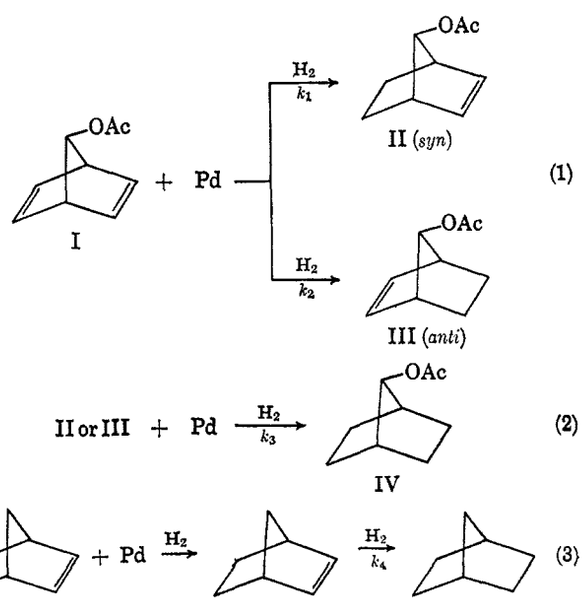
In a previous publication in which the synthesis of *syn*-7-acetoxynorbornene (II) by the platinum-catalyzed reduction of 7-acetoxynorbornadiene (I) was described, the isolated yield of *syn*-acetate was reported to be 22%.[1] During a subsequent study of reductions in the 7-substituted norbornadienyl system and the effect of various transition metal catalysts,[2] 7-acetoxynorbornadiene was hydrogenated over a palladium catalyst in the presence of an equal molar amount of norbornadiene.[3] The utilization of this technique increased the yield of *syn*-7-acetoxynorbornene (II) to ~40% (~70% by glpc). When deuterium was substituted for hydrogen in this reduction, a comparable yield of *exo,exo*-5,6-dideuterio-*syn*-7-acetoxynorbornene was realized. Furthermore, this method has led to a procedure for achieving the deuterium reduction of norbornadiene to *exo,exo*-5,6-dideuterionorbornene (V) with high selectivity and conversion. These useful synthetic procedures are presented in detail in the Experimental Section of this Note.

The significantly increased yield of the *syn*-acetate (II) is attributed to two factors that operate in this reduction. One of these is the preferential reduction of the less sterically hindered *anti* double bond of the dienyl acetate (I). The other is the competitive hydrogenation on the catalyst surface of the various diolefinic and monoolefinic species present in the reaction mixture. The relative amounts of the various reduction products as a function of per cent reduction are illustrated by Figure 1. It is apparent that norbornadiene is rapidly reduced to norbornene while the reduction of dienyl acetate (I) to the isomeric *syn*- (II) and *anti*-acetates (III) proceeds at a somewhat slower rate. The norbornene produced, however, which reduces more slowly than the dienyl acetate (I), is reduced more rapidly than either the *syn* (II) or the *anti* (III) isomer. This rate differential effectively suppresses the subsequent conversion of II and III to saturated acetate product (IV). The data of Figure 1 may be rationalized by consideration of eq 1–3. The



(1) B. Franzus, W. C. Baird, Jr., E. I. Snyder, and J. H. Surridge, *J. Org. Chem.*, **32**, 2845 (1967).

(2) The results of this work will be fully described in forthcoming publications.

(3) This experiment was performed at the suggestion of Professor H. C. Brown in order to investigate several anomalies that had been observed regarding the stereochemistry of these reductions.[2] The synthetic utility of this reduction was not anticipated.

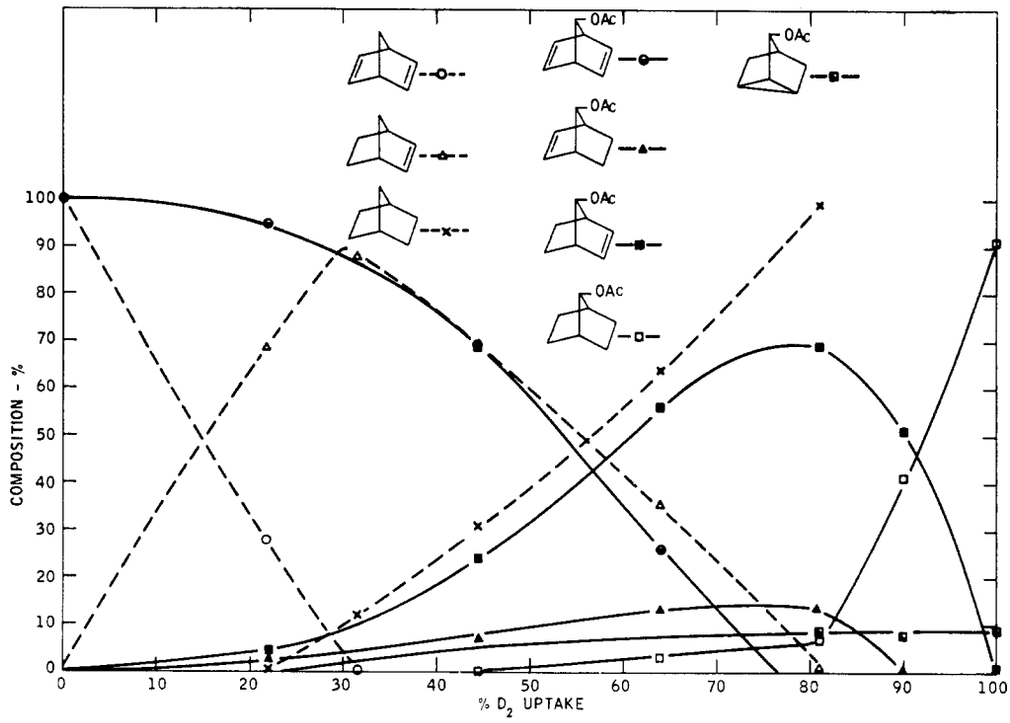
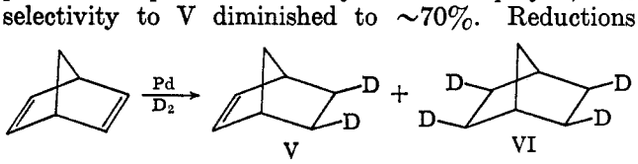


Figure 1.—Competitive reduction of norbornadiene and 7-acetoxynorbornadiene.

yields of II and III are obviously optimized when reaction 3 is faster than reaction 2 but slower than reaction 1 ($k_3 < k_4 < k_1$ or k_2). For purposes of synthesizing *syn*-7-acetoxynorbornene (II) or *exo,exo*-5,6-dideuterio-*syn*-7-acetoxynorbornene, one can take advantage of these rate differentials by stopping the reduction at the point where 7-acetoxynorbornadiene is no longer present. At this stage of the reduction the amount of II present as a percentage of all acetates is 63–73% (by glpc analysis); the amount of III present is 7–17%. In order to achieve this degree of selectivity it is necessary to use an initial norbornadiene to catalyst mole ratio of at least 25:1 when norbornadiene and dienyl acetate are present in equimolar amounts. Lower norbornadiene to catalyst ratios produce significantly smaller amounts of II and larger amounts of III. Furthermore, selectivity to the *syn* isomer (II) cannot be realized by substituting norbornene for norbornadiene or by using a platinum catalyst. However, the course of the reduction is not dependent on reducing the palladium catalyst with hydrogen (deuterium) before exposing it to the diolefins.

During this study it was noted that high yields of norbornene could be obtained by the hydrogenation of norbornadiene over a prereduced palladium catalyst. If deuterium were substituted for hydrogen, this method would afford a convenient synthesis of *exo,exo*-5,6-dideuterionorbornene (V). A typical reduction gave (by glpc analysis) 91.7% V, 5.9% *exo,exo,exo,exo*-2,3,5,6-tetradeuterionorbornane (VI), and 2.4% unreacted norbornadiene. The isolated yield of dideuterionorbornene amounted to ~50%. If a nonprereduced palladium catalyst was employed, the selectivity to V diminished to ~70%. Reductions performed over platinum catalysts were totally nonselective; typical reactions gave 37.6% V, 30.2% VI, and 32.2% unreacted norbornadiene.



V VI

Experimental Section

7-Acetoxynorbornadiene was purchased from Frinton Laboratories, Vineland, N. J., and was used without further purification. Norbornadiene and palladium on powdered charcoal were obtained from Matheson Coleman and Bell.

Analytical glpc was performed with a Perkin-Elmer Model 154-D vapor fractometer. The 7-acetoxy compounds were analyzed on a 2 m × 0.25 in. column packed with 30% FFAP (Varian Aerograph) on acid-washed Chromosorb W at 136° with a 100 ml/min helium flow. The norbornyl hydrocarbons were analyzed on a 2 m × 0.25 in. Perkin-Elmer "U" (squalane) column at 100° with a 95 ml/min helium flow. Varian Aerograph Autoprep Model A-700 was used for the preparative scale glpc.

Nmr spectra were determined with a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard. Mass spectral data were determined with the Esso Chemical Physics mass spectrometer using both chemical ionization[4] and electron-impact techniques.

Competitive Reduction of Norbornadiene and 7-Acetoxynorbornadiene.—For purposes of following the changes in composition of a reduction mixture, 0.301 g of 10% palladium on powdered charcoal in 5 ml of methanol was saturated with deuterium in a gas buret apparatus at atmospheric pressure. Into this slurry 5 ml of a methanol solution of 0.889 g (5.92 mmol) of 7-acetoxynorbornadiene (I) and 0.647 g (7.04 mmol) of norbornadiene were injected with a syringe. Periodically 0.1-ml samples were withdrawn from the reduction mixture and were analyzed by glpc. When 487 ml (21.8 mmol at STP) of D_2 had been consumed, the gas uptake ceased. Glpc analysis at this point showed no unsaturated compounds remaining. The results of this experiment are plotted in Figure 1 where the *y* axis is the per cent of each compound present when the acetate esters and the hydrocarbons are each considered separately to be 100%.

Preparation of *exo,exo*-5,6-Dideuterio-*syn*-7-acetoxynorbornene (II).—In 20 ml of methanol 0.486 g of 10% palladium on powdered charcoal was saturated with 5.1 ml of deuterium. Into this slurry was injected a mixture of 2.40 g (16.0 mmol) of 7-acetoxynorbornadiene (I) and 1.52 g (16.5 mmol) of norborna-

(4) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 2621 (1966).

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).
(6) E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964).
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(8) H. Tanida and Y. Hata, *J. Org. Chem.*, **30**, 977 (1965).
(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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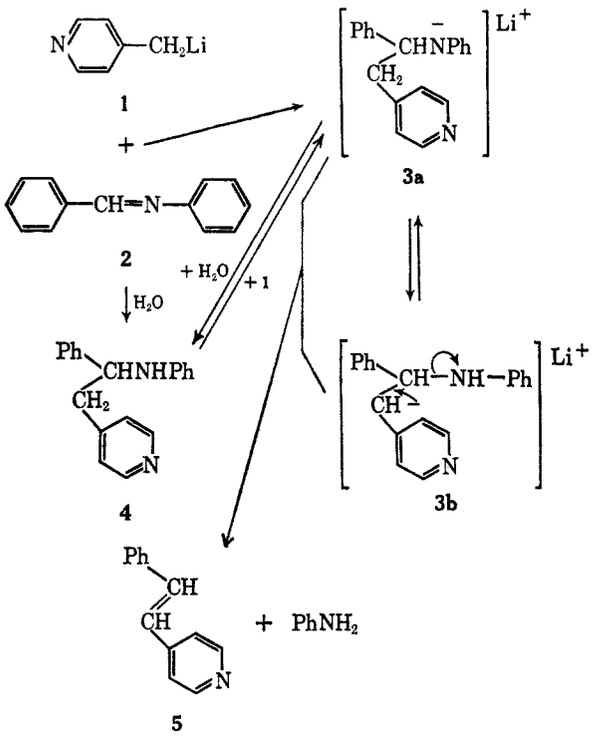
Our interest in the synthesis of compounds derived from 4-picolyllithium[1] led us to synthesize some N,1-diphenyl-2-(4-pyridyl)ethylamines. These compounds were prepared by treating arylideneanilines with 4-picolyllithium (**1**). During the course of this work we observed two elimination reactions (Scheme I). When a solution of benzylideneaniline (**2**) was

SCHEME I



treated at low temperature with **1**, rapid hydrolytic work-up afforded the desired pyridylethylamine **4** in excellent yield.[2,3]

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).