1,3-Bridged Aromatic Systems. XII. Hydrogen–Deuterium Exchange Reactions in 1-Substituted 12,13-Benzo-16-chloro[10](2,4)pyridinophanes [1]

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Deuterium exchange reactions have been studied with a variety of *syn*- and *anti*-pyridinophanes of type **1** and **2**, both in acetic acid-d_4 and in alcohol with added alkoxide or hydroxide. Deuterium exchange at the methine carbon in acetic acid-d_4 is highly specific for syn and anti acetates (**1a** and **2a**) and for syn bromide **1b** with retention of configuration; epimerization was observed for the anti bromide **2b**. Exchange reactions in more basic media at the methine carbon are also stereospecific, with retention of configuration, with the exception of the anti bromide **2b** which leads to some epimerization. Reaction of syn alcohol **1b**, but not anti alcohol **2b**, with ethoxide in ethanol results in appreciable dechlorination of aryl halide.

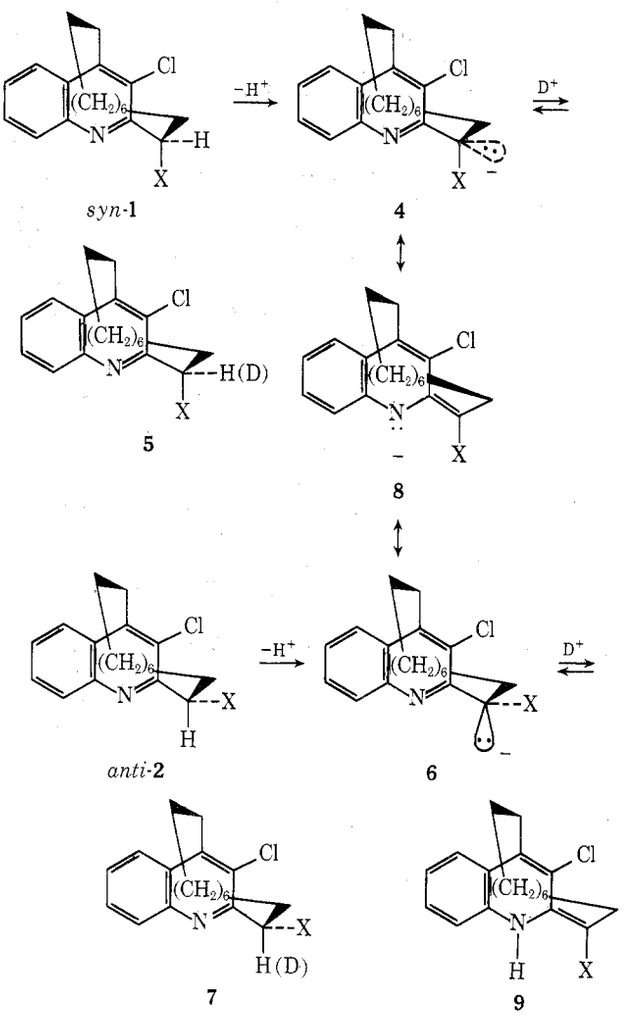
Since it is known that 2- and 4-alkylpyridines undergo H–D exchange in the presence of base[2] or by action of hot acetic acid,[3,4] we have examined such exchange with *syn*- and *anti*-pyridinophanes[5] of type **1** and **2** in order to gain insight into the stereochemical consequence of such exchange (Scheme I). It is known[6] that syn and anti diastereomers **1** and **2** do not interconvert by rotation of the methylene bridge to the other face of the aromatic ring; consequently, one would expect exchange with retention of syn or anti configuration if intermediates of type **4** and **6** resist rehybridization to **8**, due possibly to steric constraint.[5] Nonstereospecific exchange would be expected (syn ⇄ anti interconversion) if intermediates **4** and **6** either invert configuration at the α carbon or if they rehybridize to intermediate **8**. In cases involving exchange in acetic acid medium, and perhaps even in alcohol under base catalysis, it is assumed[3,4] that **4** and **6** would exist as the corresponding zwitterions (N-protonated), and that **8** would exist as the anhydro base **9**.

I. Exchange Reactions in Acetic Acid-d_4. It was shown that syn and antiacetates **1a** and **2a** do not interconvert (epimerize) in hot (118°, 48 hr) acetic acid.[6] Significantly, both *syn*-**1a** and *anti*-**2a** undergo exchange of benzylic hydrogen by deuterium in hot acetic acid-d_4 (118°, 48 hr), and in neither case was any interconversion (epimerization) detected by liquid chromatography (less than 1% interconversion). Thus, *syn*-**1a** gave recovered syn acetate **5a** which contained 71% deuterium at the methine position and 28% deuterium at the benzylic methylene position; no anti acetate was detected. Similarly, *anti*-**2a** gave recovered anti acetate **7a** which contained 29% deuterium at the methine position and 20% deuterium at the benzylic methylene position.

These results conclusively establish that an intermediate such as **8** [X = OC(=O)CH_3], or more likely the corresponding anhydro base **9** (X = $OCOCH_3$), is not an intermediate in these exchange reactions.[7] Retention of configuration in exchanges observed for **1a** and **2a** suggest that exchange is more rapid from **4** or **6** (or the corresponding N-protonated zwitterions) than rehybridization to an intermediate **8** (or **9**).

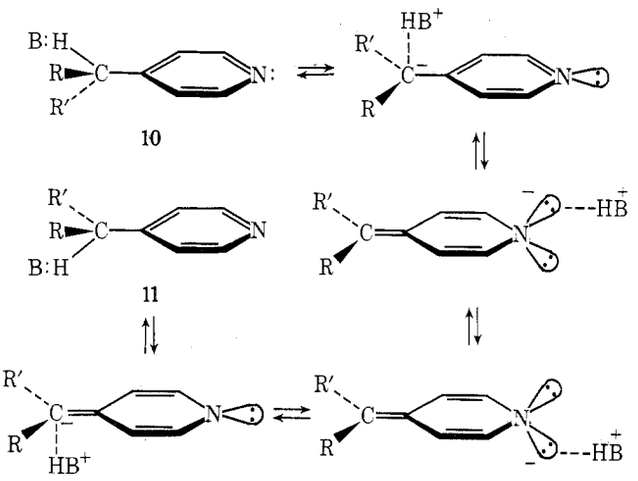
Base-catalyzed exchange in asymmetric carbon atoms has been studied in great detail[8,9] and can occur with retention of configuration, racemization, inversion of configuration, isoracemization, or a combination of these processes depending on structure and polarity of solvent. Exchange with racemization or isoracemization is usually observed[9] for those derived anions which can be stabilized (resonance) by an electronegative group. The only prior case studied which involves stereochemistry of exchange in alkylpyridines was carried out by Cram (Scheme II). In this

Scheme I



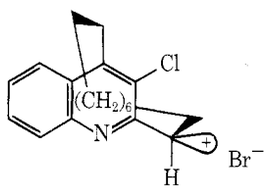
a, X = $OCOCH_3$
b, X = Br
c, X = OSO_2Ar
d, X = OH
e, X = OC_2H_5

Scheme II



case it was observed[8] that exchange in **10** occurred, accompanied by a "conducted tour mechanism" to give **10** and **11** with both racemization and inversion.

Exchange reactions in the syn and anti bromides **1b** and **2b** are of interest, but gave less definitive stereochemical results. Reaction of **1b** and **2b** with acetic acid-d_4 were carried out under identical conditions (118°, 48 hr) and recovered bromides (>70% in each case) were separated by high pressure liquid chromatography; deuterium exchange was determined by pmr.[10] Bromide recovered from *syn*-**1b** contained only a trace (detected only by lc) of anti bromide **7b;** recovered pure *syn*-**5b** (80% recovery) showed complete deuterium incorporation at the methine carbon atom and 35% deuterium incorporation at the benzylic methylene position. Bromide recovered from anti bromide **2b** was a mixture of syn bromide **5b** (18%) and anti bromide **7b** (52%); recovered *syn*-**5b** was essentially completely deuterated at the methine carbon and contained 17% deuterium at the benzylic methylene position while recovered anti bromide **7b** showed essentially no deuterium incorporation at the methine carbon but ~30% deuterium at the benzylic methylene position. Obviously syn bromide (anti H) undergoes more rapid deuterium exchange at the methine position than does the anti bromide (syn H). These results do not unequivocally differentiate epimerization and subsequent exchange through an anhydro base **9** (X = Br) which protonates (or adds D^+) to give the more stable[6] syn bromide, or through an ion pair of type **12,** which epimerizes to the



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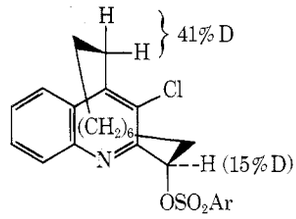
more stable syn bromide which subsequently undergoes exchange. The comparative inertness to solvolysis or replacement of the anti bromide relative to syn bromide has been previously noted.[6]

II. Exchange Reactions in Basic Media. Although syn and anti tosylates **1c** and **2c** undergo slow hydrolysis, by O–S bond cleavage, to syn and anti alcohols (**1d** and **2d,** respectively) by action of KOH in methanol, we have reconfirmed the observation[6] that there is no epimerization either in recovered starting material or in the derived alcohols when either **1c** or **2c** is treated in this manner. Both *syn*-**1c** and anti-**2c** were treated under identical conditions (20 hr, reflux) with KOD in methanol-*O*-*D;* recovered tosylate in each case was separated from the corresponding alcohol by tlc, and deuterium label was determined by pmr. The results are summarized in **13** and **14.** It was observed



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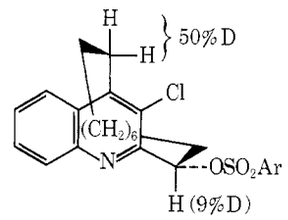

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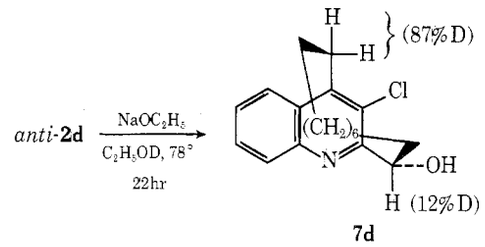
that (1) in both cases exchange occurred at the methine position without epimerization, (2) exchange is much more rapid at the benzylic methylene position,[2b] (3) exchange is somewhat more rapid at the methine hydrogen of syn tosylate **13** than at the methine hydrogen of anti tosylate **14.**

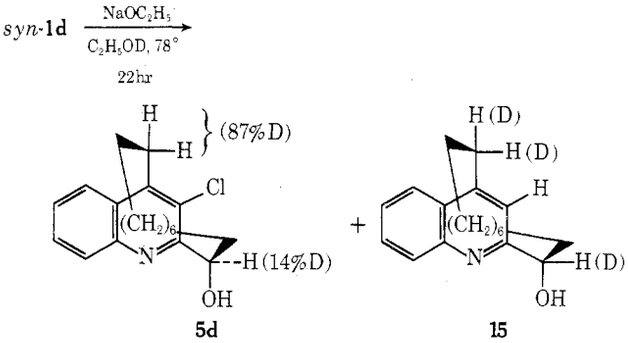
These results are interpreted by arguments essentially identical with those presented above for exchange with acetic acid-d_4. It is clear that base-catalyzed exchange at the methine position occurs with retention of configuration under these conditions.

Similar results were obtained with other cyclophanes; however, in some cases results are less definitive because of side reactions.

Reaction of anti alcohol **2d** with sodium ethoxide in hot ethanol-*O*-*D* gave recovered anti alcohol **7d** (83%) labeled as shown in **7d,** below; there was no evidence for formation of epimeric syn alcohol **5d.** Reaction of syn alcohol under



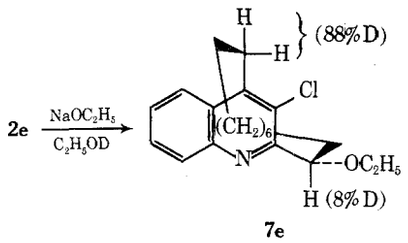
7d



5d **15**

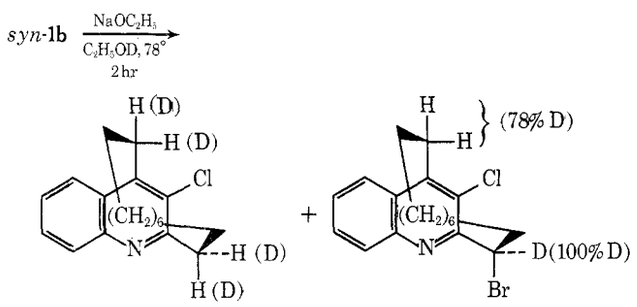
identical conditions gave *syn*-**5d,** labeled as shown in the accompanying formula, together with a dechlorinated alcohol (~45% yield, completely deuterated at methine and benzylic methylene positions) to which structure **15** is assigned. Repetition of the reaction with **1d** with unlabeled solvent gave unlabeled **15** (~60% yield) and its structure was assigned by composition and spectra (pmr and mass spectrum).

Reaction of anti ether **2e** with sodium ethoxide in ethanol-*O*-*D* (48 hr, reflux) gave 70% recovery of anti ether labeled as shown in **7e.** Examination of the mother liquor from which **7e** was obtained by tlc showed a possible trace of syn ether **5e.**



7e

Finally, examination of exchange of syn and anti bromides **1b** and **2b**, respectively, was examined in hot ethanol-*O-D* with ethoxide (2 hr, reflux). The reaction was complicated by debromination, a reaction previously reported,[6] to give **16**. Reaction of **1b** under these conditions gave **16** (~49% yield, which was not further examined as to label) and recovered syn bromide **5d** labeled as shown in **17**; there was no evidence for formation of anti bromide **7d**.



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Reaction of the anti bromide **2b** under these same conditions gave a complex mixture which was not resolved; however, tlc analysis showed reduced pyridinophane **16**, anti bromide **7b**, epimeric **5b** (appreciable, but considerably less than **7b**).

In summary it is concluded that (1) in basic media the anti-substituted pyridinophanes **1** (syn H) undergo exchange somewhat less readily at the methine position than the *syn*-pyridinophanes (anti H), and (2) in all cases studied except the anti bromide **2b**, exchange is highly specific with retention of configuration.

Our data on these exchange reactions[3] suggest that the reactivity ratio of 2- and 4-alkyl hydrogens of pyridines (k_2/k_4) is generally ≥1 for acid-catalyzed exchange, whereas k_2/k_4 is generally <1 for base-catalyzed exchange. While k_2/k_4 <1 for basic exchange is in agreement with the literature,[2b] $k_2/k_4 \geq 1$ has no precedent of which we are aware.

Experimental Section

Starting Materials. Syn and anti acetates **1a** and **2a** were prepared from the corresponding pure alcohols[11] by conversion into the lithium salt (in THF by titration with 2 *M* butyllithium in hexane) with subsequent treatment of the derived salts with acetyl chloride (77% yield of **1a**, mp 118–119°, lit.[12] 116–118°; 50% yield of **2a**, mp 149.5–150°, lit.[12] 144–146°). Alternatively, the mixed acetates[11] were separated by high pressure liquid chromatography [8 ft × 2.2 mm i.d., Porasil A, eluted with chloroform–petroleum ether[13] (1:1) at 0.75 ml/min]. The retention times of **1a** and **2a** under these conditions are 16 and 22.5 min, respectively.

Syn[11] and anti[6] bromides **1b** and **2b** can be separated by tlc (silica gel, multiple developments with petroleum ether[13]–ether); however, they are more efficiently purified by high pressure liquid chromatography (8 ft × 2.2 mm i.d., Porasil A, eluted with 5% chloroform–petroleum ether[13] at 2.7 ml/min). The retention times of **1b** and **2b** under these conditions are 3.8 and 5.7 min, respectively.

All materials used in exchange studies contained no trace of epimeric impurities as judged by characteristic pmr resonances of methine hydrogens.[5,6,11]

Exchange Reactions in Acetic Acid-d_4. A mixture of syn acetate (**1a**, 144.5 mg, 0.402 mmol) and acetic acid-d_4 (4.94 g, 77.2 mmol, Stohler Isotopic Chemicals, Inc.) was heated at the reflux temperature for 48 hr under an atmosphere of dry nitrogen. After most of the acetic acid was removed by distillation, the residue was dissolved in chloroform which was subsequently extracted with aqueous sodium bicarbonate and dried ($MgSO_4$). Analysis of the oil (143 mg) obtained from the chloroform by high pressure liquid chromatography (see starting materials) showed the absence of anti acetate **7a**. Preparative tlc separation of the mixture (silica gel developed twice with 15% ether in petroleum ether[3]) gave recovered syn acetate **5a** as an oil (93 mg, 64.4% recovery; mp 114–116°[12] from petroleum ether[14]), and syn alcohol **5d** (39.6 mg, 31%, mp 154–155°, mixture melting point with sample mp 160° was 155–157°; pmr identical with authentic sample except for decreased intensity of methine resonance due to deuterium incorporation) which was not further examined. Deuterium analysis of recovered syn acetate[10] showed 71% deuterium incorporation at the benzylic methine position at δ 6.55 and 28% deuterium incorporation at the benzylic methylene position (δ 3.8–3.0).

The anti acetate 2a was treated as described above. Analysis of the crude product, as described above, showed no syn acetate **5a** to be present; recovered anti acetate [78% recovery, mp 138–140°, from chloroform–petroleum ether,[14] mp 149.5–150° (pure) by high pressure liquid chromatography]. The pmr spectrum showed[10] 29% deuterium incorporation at the methine position (δ 6.08) and 20% deuterium incorporation at the benzylic methylene position (δ 3.8–3.3)

Syn Bromide[11] **1b** (70.8 mg) was treated with acetic acid-d_4 as described above. Analysis of the crude yellow solid by high pressure liquid chromatography (see starting materials) showed syn bromide **5b** and a trace (less that 2% assuming equal extinction coefficients of **1b** and **2b** at 254 nm) of anti bromide **7b**. Recovered syn bromide (**5b**, mp and mmp 145–145.5°, lit. 149–151°,[11] obtained by recrystallization of the crude bromide from petroleum ether,[14] 80% recovery) showed ~100% deuterium incorporation at the benzylic methine position (no resonance at δ 6.05)[11] and 35% deuterium incorporation at the benzylic methylene position (1.29 H at δ 3.7–3.3).[11]

Anti Bromide 2b.[6] Analysis of the crude product (83.1 mg, 80%, mp 130–135°), obtained by treatment of pure **2b** (103.9 mg) with acetic acid-d_4 as described above, by high pressure liquid chromatography (see starting materials, except 2% chloroform in petroleum ether[13] was employed) showed the presence of syn bromide **5b** (retention time 7.7 min) and anti bromide **7b** (retention time 13 min). Preparative separation by high pressure liquid chromatography (conditions as described above for analysis) gave syn bromide **5b** (16.6% yield, mp 143–145°, mmp 142–144°, lit.[11] 149.5–151°) and anti bromide **7b** (52.7% recovery, mp 149–151°, mmp 148–149°, lit.[6] 152–153°). The syn bromide showed[10] 90–100% deuterium incorporation at the benzylic methine carbon (integration of the small signal at δ 6.05 did not permit a more accurate estimate) and 17% deuterium at the benzylic methylene position (δ 3.7–3.3). The anti bromide **7b** showed[10] essentially no deuterium exchange at the benzylic methine position (0.97 H at δ 5.50) and 30% deuterium incorporation at the benzylic methylene position (δ 3.8–3.0).

Exchange Reactions with Syn and Anti Tosylates (1c and 2c). Syn Tosylate 1c.[5] Potassium hydroxide (0.36 g) was dissolved in deuterium oxide (5.71 g, 99.8% D, Aldrich) and D_2O was removed by distillation; the exchange process was repeated with 3.31 g of additional D_2O. The resulting potassium deuterioxide was dissolved in methanol-*O-D* (9.7 g, Stohler Isotope Chemicals, Inc.), syn tosylate **1c** (200 mg) was added, and the mixture was heated for 20 hr at the reflux temperature protected from atmospheric moisture. The methanol was removed by distillation and the residue was treated with aqueous ammonium chloride and was then extracted with chloroform. The oil, obtained from the dried ($MgSO_4$) chloroform, showed (pmr) the presence of syn tosylate (δ 6.46) and syn alcohol (δ 5.35) and the absence of anti tosylate (δ 5.72) and anti alcohol and was purified by preparative tlc [silica gel; eluent petroleum ether[3] (3:1)] to give, in order of increasing R_f, (1) recovered syn tosylate **5c** (123 mg, 61.5% recovery, mp 120–121° from ether; lit.[5] 105–107° from chloroform–petroleum ether,[13] 120–121°[12b] from ether) showing[10] 15% deuterium incorporation at the benzylic methine position (δ 6.46) and 41% deuterium incorporation at the benzylic methylene position (δ 3.6–3.2); and (2) syn alcohol **5d** (44.3 mg, 33% yield, slightly impure, mp 152–153°, lit.[11] mp 160–162°). This material was not examined further.

Anti tosylate 2c was treated as described above for **1c**. The

crude oil showed the presence of anti tosylate **7c**, anti alcohol **7d**, and the absence of syn tosylate **5c** and syn alcohol **5d**. The oil was recrystallized from chloroform–petroleum ether[14] to give recovered **7c** (mp 119–121°, lit. 121–123°, 93% recovery) which showed[10] 9% deuterium incorporation at the methine position (δ 5.72) and ~50% incorporation at the benzylic methylene position (δ 3.7–2.5).

Preparation of 15. Syn alcohol **1d**[11] (100 mg, 0.314 mmol) was treated with sodium ethoxide (from 0.18 g, 7.85 mg-atoms of sodium) in absolute ethanol (25 ml) at the reflux temperature (90 hr) under a dry nitrogen atmosphere. Excess ethanol was removed *in vacuo*, and saturated aqueous NH_4Cl was added to the cold residue. The product was extracted with chloroform and the oil (97.3 mg) obtained from the dried ($MgSO_4$) extract was separated into two components by preparative tlc [silica gel with petroleum ether[13]–ether (3:1) as eluent].

(1) Crude **15**, 64% by wt, mp 136–138°, was recovered from carbon tetrachloride–petroleum ether.[14] The solid was further purified by multiple injections into a high pressure liquid chromatograph (8 ft × 2.2 mm i.d., Porasil A, eluted with 40% chloroform–petroleum ether[14] at a flow rate of 2.7 ml/min), mp 139–140°. The mass spectrum of **15** showed *m/e* (relative intensity) 283 (91), 254 (56.5), 185 (100), 172 (56.5) [the M^+ is consistent with **15** (no chlorine)]; pmr ($CDCl_3$) δ 8.2–7.4 (m, 4, aromatic H), 7.26 (s, 1, isolated aromatic H), 5.00 (q, 1, methine H, X portion of ABX system $J_{AX} + J_{BX}$ = 10 Hz), 3.40 (octet, 1, benzylic H), 2.78 (octet, 1, benzylic H), 2.2–0.4 (m, ~16, bridge CH_2); ir (KBr disk) ν_{OH} 3225 cm^{-1} (broad).

Anal. Calcd for $C_{19}H_{25}NO$: C, 80.57; H, 8.89; N, 4.94. Found: C, 80.81; H, 8.74; N, 4.79.

(2) Impure syn alcohol **1d** (35 mg, 35% recovery, pmr methine at δ 5.35[11]) was recovered but was not processed further.

Exchange Reactions of Syn and Anti Alcohols (1d and 2d). Anti Alcohol 2d.[11] The anti alcohol **2d** (109.9 mg) was treated in a manner similar to that described for the preparation of **15**; however, anhydrous ethanol-*O-D* (3.45 g, Stohler Isotope Chemicals) was employed (26-hr reflux). Trituration of the residue (121.7 mg) with methanol gave 90.6 mg (83% recovery) of **7d** (mp and mmp 203–205°, lit.[11] 205.5–207°); the product[10] contained 12% deuterium at the methine position (δ 5.05) and 87% deuterium at the benzylic methylene position.

Examination of the mother liquor by tlc [silica gel with petroleum ether–petroleum ether[13] (3:1)] showed no detectable amounts of epimeric alcohol **5d** although there were some other minor byproducts formed.

Syn Alcohol 1d. Reaction of *syn*-**1d**[11] (103.5 mg) with sodium ethoxide in ethanol-*O-D* was carried out as described for **2d**. Examination of the product by tlc (as described for **2d**) showed no detectable quantity of anti alcohol **7d**, but rather two major components listed in order of increasing R_f: (1) ~45% by wt of impure **15** (completely deuterated at benzylic positions[10]) and (2) slightly impure recovered syn alcohol **5d** (mp 153–154°, pmr methine at 5.34, lit.[11] mp 160–162°, 32 mg, 32% recovery). The pmr analysis[10] of this slightly impure sample of **5d** showed 14% deuterium incorporation at the methine position (δ 5.35) and 74% deuterium incorporation at the benzylic methylene position (δ 3.6–3.2).

Reaction of Anti Ether 2e with Sodium Ethoxide in Ethanol-*O-D*. A sample of **2e** (108.5 mg, 0.314 mmol) was treated essentially as described for **1d** and **2d** (48-hr reflux) to give 110.3 mg of crude crystalline product. Recrystallization of this product from absolute ethanol gave 75.9 mg (70%) of recovered **7e** (mp 107–108°, mmp 106–107°, lit.[15] 107.5–110°); analysis for deuterium by pmr[10] showed 8% deuterium incorporation at the methine position (δ 4.76) and ~88% deuterium incorporation at the benzylic methylene position. (δ 3.8–3.2, under CH_2 resonance of ethyl group).

Examination of the mother liquor by tlc showed principally additional **7e**; however, six trace materials were detected, one of which had an R_f corresponding to syn ether **5e**.[15]

Exchange of Syn and Anti Bromides 1b and 2b with Sodium Ethoxide in Ethanol-*O-D*. These reactions were conducted essentially as described for **1d** and **2d**.

From syn bromide 1b[11] (131.3 mg) there was obtained 104.4 mg of crude product. Preparative tlc [silica gel, petroleum ether[13]–ether (3:1)] showed no detectable quantities of anti bromide **7b**, but two major products listed in order of increasing R_f: (1) reduced pyridinophane[6,11] **16** (51.2 mg, 49% yield, mp 77–78° from petroleum ether,[4] lit. 81.2–82.5°), and (2) recovered syn bromide **5b** [21 mg, 16% yield, mp 140–141°; mp 147° from petroleum ether,[14] lit. 149.5–151°; nmr ($CDCl_3$) methine H at δ 6.05] showed[10] 100% deuterium incorporation at the methine position and 78% incorporation at the benzylic methylene position (δ 3.6–3.0).

From anti bromide 2b (106.5 mg, 0.28 mmol) there was obtained 82.7 mg of a solid product. Analysis of this material by high pressure liquid chromatography [8 ft × 2.2 mm i.d., Porasil A, chloroform–petroleum ether[13] as eluent (9:1) at 2.7 ml/min] showed it to be a complex mixture containing at least six components; syn and anti bromides **5b** (major) and **7b** were shown to be present by injection (lc) of authentic samples. Attempts to resolve the mixture by tlc [silica gel with petroleum ether[13]–ether (9:1) as eluent] were not successful; reduced pyridinophane **16** was shown to be present.

Registry No.—**1a**, 51933-62-1; **1b**, 25859-37-4; **1c**, 37781-25-2; **1d**, 25866-36-8; **2a**, 52078-88-3; **2b**, 42880-45-5; **2c**, 37781-31-0; **2d**, 25907-82-8; **2e**, 34844-97-8; **5a**, 52437-22-6; **5b**, 52437-23-7; **5c**, 52437-24-8; **5d**, 52437-25-9; **7a**, 52151-91-4; **7b**, 52437-26-0; **7c**, 52437-27-1; **7d**, 52079-43-3; **7e**, 52437-28-2; **15**, 52438-79-6.

References and Notes

(1) Supported in part by National Science Foundation Grant No. 35429.
(2) (a) J. A. Zoltewicz and P. E. Kandetzki, *J. Amer. Chem. Soc.*, **93**, 6562 (1971), and references cited therein; (b) "Heteroaromatic Nitrogen Compounds: Pyrroles and Pyridines," K. Schofield, Ed., Butterworths, London, 1967, pp 325–327, and references cited therein.
(3) W. E. Parham and P. E. Olson, *Tetrahedron Lett.*, **48**, 4783 (1973).
(4) 2- and 4-alkylpyridines also undergo exchange in HCl–ethanol-*O-D* and deuterium oxide: *cf.* ref 2a, and A. I. Shatenshtien, "Isotopic Exchange and the Replacement of Hydrogen in Organic Compounds," translated by C. N. Turton and T. I. Turton, Consultants Bureau, New York, N. Y., 1962, pp 33–37.
(5) W. E. Parham, K. B. Sloan, K. R. Reddy, and P. E. Olson, *J. Org. Chem.*, **38**, 927 (1973).
(6) W. E. Parham, P. E. Olson, K. R. Reddy, and K. B. Sloan, *J. Org. Chem.*, **39**, 172 (1974).
(7) While it is clear that intermediates **8** or **9** cannot be involved as such in these exchange reactions, some contribution from structures implied by **8** and **9** is possible. Resonance stabilization of this type does not require coplanarity but is a function of the cosine of the angle and is rather at a maximum when the atoms involved are coplanar.
(8) D. A. Jaeger, M. D. Broadhurst, and D. J. Cram, *J. Amer. Chem. Soc.*, **95**, 7525 (1973), and references cited in footnotes 2 and 4 of that communication.
(9) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N.Y., 1965, pp 85–114, and references cited therein.
(10) Deuterium isotope analyses performed by pmr were calculated by comparison of the integral of aromatic hydrogens, which were assigned the theoretical value, *vs.* the integral of benzyl methylene hydrogen and/or benzyl methine hydrogen. In no case where an additional standard was used (methylene chloride) was there any observed aromatic hydrogen–deuterium exchange.
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