Preparation of 6,11-Dihydropyrido[3,2-*b*][4,1]benzoxazepine

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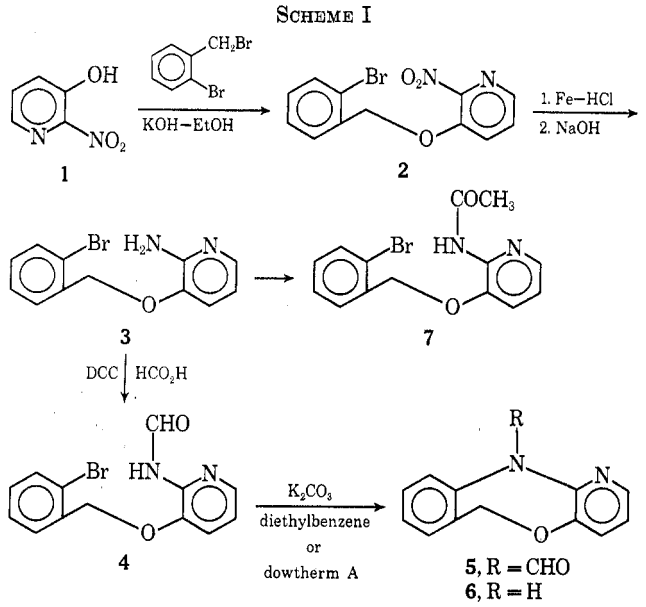
In earlier work it was found that *o*-[(*o*-bromobenzyl)-oxy]anilines and -acetanilides could not be cyclized to dihydrodibenzoxazepines, but that cyclization could be effected with the formyl derivatives.[1] In developing a synthetic route to the pyridobenzoxazepine **6**, the amine **3** and the acetamide **7** were similarly incapable of cyclization, and the formyl derivative **4** was therefore required.

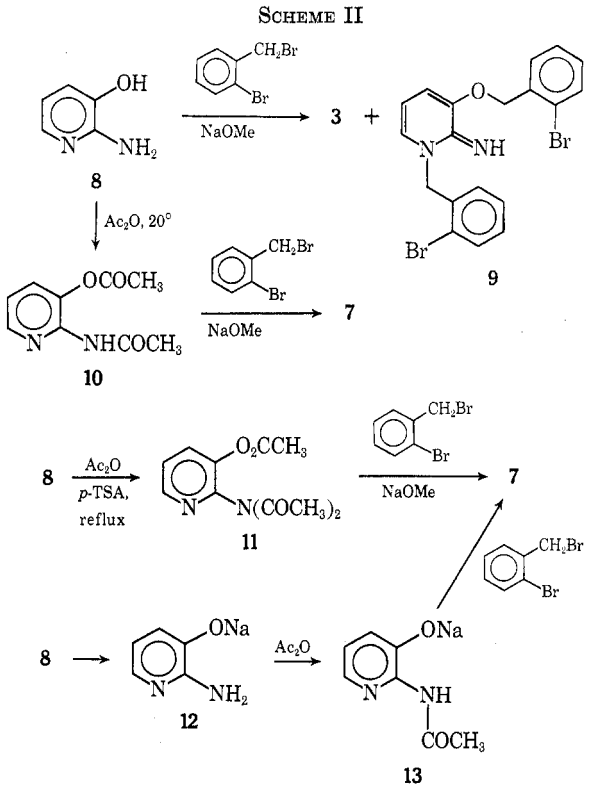
Direct formylation of **3** could not be accomplished by standard procedures, although the acetamide **7** was readily obtained from **3**. The formamide **4** was eventually prepared by the novel reaction of the amine **3**, formic acid, and dicyclohexylcarbodiimide (DDC) at 5°. This reaction is unique; under the same conditions with DCC, 2-amino-3-pyridinol was not formylated, and **3** was not acetylated by acetic acid (Scheme I).

SCHEME I



Alternative methods for preparing **3** are shown in Scheme II. Since (3-hydroxy-2-pyridyl)formamide could not be obtained, 2-amino-3-pyridinol (**8**) was employed for alkylation.[2] As a consequence, the yields of **4** were only 36%, due to concurrent alkylation at nitrogen[3] to give **9**. To minimize this side reaction, use was made of *N*-(3-hydroxy-2-pyridyl)acetamide acetate (**10**), obtained from **8** and acetic anhydride at room temperature, or 2-(diacetylamino)-3-pyridinola cetate (**11**), formed from **8** and acetic anhydride at reflux temperature; one acetyl group was retained in the reaction with sodium methoxide, and the anion reacted readily with *o*-bromobenzyl bromide to give **7**. Alkaline hydrolysis of **7** gave **3**. In the final sequence beginning with **8**, there was difficulty in preparing pure **12** and **13**, and, consequently, the yield of **7** by this method was low.

SCHEME II



Experimental Section

3-(*o*-Bromobenzyloxy)-2-nitropyridine (2).—To 11.6 g (0.18 mol) of 85% KOH in 100 ml of 95% EtOH was added dropwise, a solution of 25.0 g (0.18 mol) of **1** in 100 ml of 95% EtOH. To the resulting suspension of the sodium salt was added 36.5 g (0.18 mol) of *o*-bromobenzyl bromide in 100 ml of 95% EtOH. The mixture was refluxed for 0.5 hr, and 275 ml of EtOH was then distilled. To the residual solution was added 100 ml of H_2O; the solid was collected and air-dried to give 41.2 g of product, mp 86–88°. Recrystallization from 2-PrOH gave 32.9 g (60%) of **2**, mp 91.5–92.5°.

Anal. Calcd for $C_{12}H_9BrN_2O_3$: Br, 25.85; N, 9.07. Found: Br, 25.58; N, 9.14.

2-Amino-3-(*o*-bromobenzoyloxy)pyridine (3).—To a solution of 32.6 g (0.11 mol) of **2** in 500 ml of 2-PrOH and 50 ml of H_2O, heated to 60°, was added, with stirring, at 10-min intervals, five portions of 12.5 g of Fe powder and 1.3 ml of concentrated HCl (density 1.18). Subsequent to the final addition, the mixture was heated under reflux for 1 hr and filtered hot. To the filtrate was added 18 ml of concentrated HCl and the solution was concentrated to dryness *in vacuo*. The residual solid weighed 32.2 g, mp 158–161°. Recrystallization from acetonitrile gave 27.7 g (87% yield) of **3-(*o*-bromobenzyloxy)-2-pyridylammonium chloride**: mp 172–173°; ν (KBr) 3280 (s), 3240 (s), 3160–3080 (s, broad), 2940–2730 (s, broad), 1700 (s), 1640 (s) cm^{-1}.

Anal. Calcd for $C_{12}H_{12}BrClN_2O$: Cl, 11.24; N, 8.87. Found: Cl, 11.39; N, 8.97.

A suspension of 4.5 g (0.014 mol) of this chloride, 20 ml of 20% aqueous NaOH, and 100 ml of ether was agitated at room temperature for 1 hr. Evaporation of the washed and dried ether solution gave 4.0 g of solid, mp 104–106°. Recrystallization

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(1) H. L. Yale, B. Beer, J. Pluscec, and E. Spitzmiller, *J. Med. Chem.*, **13**, 713 (1970).

(2) With *N*-(*o*-hydroxy)formanilide, the anion reacts almost exclusively with *o*-bromobenzyl bromide to give *N*-[*o*-(*o*-bromobenzyl)oxy] formanilide. In contrast, *o*-aminophenol gives *o*-[*N*,*N*-di(*o*-bromobenzyl)amino]phenol and polymeric products (*cf.* ref 1). It is assumed, consequently, if it could be prepared, that *N*-(3-hydroxy-2-pyridyl)formamide would be the preferred reactant in these alkylations.

(3) Alkylation, in the presence of base, of 2-aminopyridines is reported to occur only at the 1 position: see A. S. Tomcufcik and L. N. Starker, "Pyridine and its Derivatives," Part III, Interscience, New York, N. Y., 1962, p 12 ff. The structure of **11** is supported by its pmr spectrum (see Experimental Section).

from Skellysolve E or diisopropyl ether gave 3.6 g (91% yield) of **3**: mp 107.0–108.5°; ν (mineral oil) 3460 (s), 3290 (w), 3150 (m), 1660 (s) cm^{-1}; δ ($CDCl_3$) 4.57 (m, J = 25 Hz, NH_2), 5.13 (s, CH_2), and 6.42–7.9 ppm (m, 7).

Anal. Calcd for $C_{12}H_{11}BrN_2O$: C, 51.62, H, 3.97; N, 10.04; Br, 28.62. Found: C, 51.72; H, 4.02; N, 10.04; Br, 28.34.

N-[3-(*o*-**Bromobenzyloxy**)-2-pyridyl]**formamide** (**4**).—To 67.0 g (0.24 mol) of **3** in 1800 ml of EtOAc was added 100.0 g (0.48 mol) of *N*,*N*′-dicyclohexylcarbodiimide in 100 ml of EtOAc. The solution was cooled to 5°, and 22.5 g (0.48 mol) of 98–100% HCO_2H in 100 ml of EtOAc was added in 20 min. The mixture was stirred, allowed to come to room temperature, and filtered to remove 1,3-dicyclohexylurea, and the filtrate was concentrated *in vacuo* to *ca.* 80 ml and cooled. The solid was collected to give 42.0 g (67% yield) of product, mp 128–130°. An analytical sample of **4**, recrystallized from EtOAc, melted at 137–139°: ν ($CDCl_3$) 3390 (m), 3140 (w), 1760 (s), 1590 (m), 1575 (m) cm^{-1}; δ ($CDCl_3$) 5.17 (s, CH_2), 6.8–8 (m, 7 aromatic H plus NH), 9.43 ppm (d, J = 10 Hz, CHO).

Anal. Calcd for $C_{13}H_{11}BrN_2O_2$: C, 50.84; H, 3.61; N, 9.13. Found: C, 50.83; H, 3.60; N, 9.11.

The EtOAc filtrate was concentrated to dryness to give a residue of 38.0 g. Recrystallization from diisopropyl ether gave 19.2 g (28% recovery) of **3**. An ether solution of **4** and Et_2O–HCl gave a **hydrochloride**, mp 80–82°, but this evolved HCl during drying *in vacuo* to regenerate **4**.

6,11-Dihydropyrido[3,2-*b*][4,1]**benzoxazepine-11-carboxaldehyde** (**5**).—A mixture of 68.6 g (0.22 mol) of crude **4** (mp 125–131°), 138.0 g (1.0 mol) of K_2CO_3, 6.0 g of Cu bronze, and 1600 ml of diethylbenzene was stirred and heated at an internal temperature of 155–160° for 2 hr, cooled to 60°, and filtered. The filtrate was evaporated to give 40.1 g (80% yield) of product, mp 141–145°. An analytical sample of **5**, recrystallized from hexane, melted at 150–153°: ν (KBr) 1690 (s), 1604 (w), 1570 (m) cm^{-1}; δ ($CDCl_3$) 5.15 (d, J = 12 Hz, CH_2), 7.1–8.2 (7 aromatic H), and 9.17 ppm (s, H of CHO).

Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.06; H, 4.53; N, 12.39. Found: C, 69.16; H, 4.46; N, 12.43.

When an equal volume of Dowtherm A replaced the diethylbenzene, with all other conditions remaining unchanged, the yield of **5** was 70%. Replacement of the K_2CO_3 by an equivalent amount of powdered NaOH in the above experiment in diethylbenzene gave only **3**.

6,11-Dihydropyrido[3,2-*b*][4,1]**benzoxazepine** (**6**).—A mixture of crude **5** (mp 141–145°), 37.5 g, 700 ml of EtOH, and 70 ml of 50% aq NaOH was refluxed for 1 hr and concentrated *in vacuo*. The residue was stirred with 100 ml of H_2O, filtered, and dried to give 29.5 g (89% yield) of product, mp 111–113°. An analytical sample was recrystallized from hexane to give **6**: mp 111–113°; ν ($CDCl_3$) 3410 (s), 1590 (s), 1570 (s) cm^{-1} (the 3410-cm^{-1} band remained unchanged when the spectrum was run at 30 mg/ml in a 0.2-mm cell or at 3 mg/ml in a 5-mm cell); δ ($CDCl_3$) 5.05 (s, CH_2), 6.6–8.0 ppm (m, 7 aromatic H plus NH).

Anal. Calcd for $C_{12}H_{10}N_2O$: C, 72.72; H, 5.08; N, 14.14. Found: C, 72.68; H, 5.10; N, 14.17.

2-Amino-3-(*o*-**bromobenzyloxy**)**pyridine** (**3**) **and 1-**[(*o*-**Bromobenzyl**)-**3-**(*o*-**bromobenzyloxy**)-**1,2-dihydro-2-iminopyridine** (**9**).—To a suspension of 24.0 g (0.22 mol) of 2-amino-3-pyridinol (**8**) in 100 ml of absolute EtOH was added during 20 min a solution of 12.0 g (0.22 mol) of NaOMe in 200 ml of absolute EtOH and then, in another 20-min period, 54.2 g (0.22 mol) of *o*-bromobenzyl bromide. The whole was heated under reflux for 2.5 hr and then concentrated to dryness *in vacuo*. The residue was suspended in 150 ml of H_2O and extracted with two 150-ml portions of ether. The ether extracts were agitated for 1 hr with 50 ml of 20% aqueous NaOH, separated, washed with 20 ml of saturated aqueous NaCl, dried, and concentrated to give 22.3 g (36% yield) of product, mp 100–102°. A sample recrystallized from Skellysolve E gave **3**, mp 107.0–108.5°, and was identical with **3** prepared *via* Scheme I, by mixture melting point and infrared comparison of the base and the hydrochloride.

The aqueous phase from the extraction gradually deposited a gray solid. This was collected and air-dried to give 16.0 g (16% yield) of crude **9**, mp 98–102°. Recrystallization from Skellysolve E and then from ligroin gave **19**: mp 114–116°; ν (mineral oil) 3340 (s), 1680 (s), 1660 (m); δ ($CDCl_3$) 5.13 and 5.32 (two identical s, 2 H of each $-CH_2$) and 6.8–7.7 ppm (m, 11 aromatic H, 1 NH).

Anal. Calcd for $C_{19}H_{16}Br_2N_2O$: C, 50.92; H, 3.60; N, 6.25; Br, 35.67; neut equiv (phenolic OH) (KOMe in MeOH), 0.0. Found: C, 51.15; H, 3.83; N, 6.18; Br, 35.49; neut equiv, 0.0.

N-(**3-Hydroxy-2-pyridyl**)**acetamide Acetate** (**10**).—A solution formed promptly when 5.1 g (0.046 mol) of **8** was added to 25.0 ml of Ac_2O; the reaction was slightly exothermic but was allowed to proceed without cooling. After 18 hr at room temperature, the mixture was concentrated to dryness *in vacuo* to give the product, mp 125–127°. Recrystallization from C_6H_6–cyclohexane (1:1) gave 8.9 g (99% yield) of **10**: mp 131–133°; ν ($CDCl_3$) 3420 (s), 1765 (s), 1700–1670 (b, broad), 1600 (s) (note: 3-pyridinol acetate also shows ester carbonyl absorption at 1765 cm^{-1}); δ ($CDCl_3$) 2.30 (s, 6 H, from CH_3CO groups), 7.17 (m, 5 H), 7.58 (m, 4 H), 8.22 (m, 6 H), and 8.83 ppm (broad s, H of NH) (note: 3-pyridinol acetate in $CDCl_3$ showed a 3-proton singlet at 2.28 ppm while 2-pyridylacetamide in $CDCl_3$ gave a 3-proton singlet at 2.30 ppm).

N-[3-(*o*-**Bromobenzyloxy**)-2-pyridyl]**acetamide** (**7**).—To 8.8 g (0.045 mol) of **10** in 125 ml of 95% EtOH was added, in 22 min, 4.9 g (0.09 mol) of NaOMe in 50 ml of absolute EtOH. After stirring for 1 hr at room temperature (pH 8.3), 11.6 g (0.045 mol) of *o*-bromobenzyl bromide was added in 11 min; the pH was then 8.1. Heating under reflux for 16 min changed the pH to 5.3; the mixture was promptly poured into 500 ml of ice–water. The solid was collected and air-dried to give 12.0 g (82% yield) of product, mp 138–142°; recrystallization from 50% aqueous MeOH gave 7.8 g of **7**, mp 157–159°, identical with the **7** prepared as described below by mixture melting point and infrared comparison.

2-(**Diacetylamino**)**-3-pyridinol Acetate** (**11**). **A.**—A solution of 25.0 g (0.228 mol) of **8**, 100 ml of Ac_2O, and 0.5 g of *p*-Me$C_6H_4SO_3H$ was heated under reflux for 2 hr and then concentrated to dryness *in vacuo*. The residual oil crystallized when triturated with 100 ml of cyclohexane. This solid, 46.1 g, mp 75–109°, was heated under reflux with 5 l. of cyclohexane and the hot mixture was filtered. The insoluble material weighed 8.4 g and was shown to be **10**. From the cyclohexane filtrate was recovered on cooling, 35.5 g (66% yield) of **11**: mp 81–83°; ν ($CDCl_3$) 1760 (m), 1720–1695 (s, broad); pmr ($CDCl_3$) 2.30 (s, 9 H from 3-CH_3CO), 7.2–7.8 (m, 2 H at position 4 and 5), 8.45 ppm (q, 6 H).

Anal. Calcd for $C_{11}H_{12}N_2O_4$: C, 55.93; H, 5.13; N, 11.86; acetyl, 22.2. Found: C, 56.00; H, 5.21; N, 12.01; acetyl, 20.5.

B.—Compound **10** from A, 8.4 g, 35 ml of Ac_2O, and 0.7 g of *p*-Me$C_6H_4SO_3H$ was refluxed as above. The residue crystallized when triturated with ligroin, mp 75–77°. Recrystallization from 700 ml of cyclohexane gave 7.7 g (75% yield) of **11**, mp and mmp 81–83°.

Compound 7 from Compound 13.—To a solution of 35.5 g (0.15 mol) of **11** in 600 ml of 95% EtOH was added in 25 min a solution of 9.6 g (0.18 mol) of NaOMe in 200 ml of absolute EtOH; the pH was 9.2. To this solution was added 37.8 g (0.15 mol) of *o*-bromobenzyl bromide in 0.5 hr; the pH remained unchanged. At the boiling point, the mixture had a pH of 7.8 and after 10 min under reflux, the pH was 7.4. The mixture was heated an additional 5 min and poured into 2500 ml of ice–water. The solid was collected, air-dried, and triturated with 150 ml of ligroin to give 49.3 g (quantitative yield) of product, mp 152–154°. For comparison, a sample was recrystallized from 50% aqueous MeOH and then melted at 157–159°; it was identical by mixture melting point and infrared spectrum with **7** prepared from **12**: ν (mineral oil) 3270 (s), 3180 (w), 1710 (s) cm^{-1}; δ ($CDCl_3$) 2.47 (s, CH_3CO), 5.20 (s, CH_2), 6.7–7.7 (m, 4 H and 5 H), 8.00 ppm (q, 6 H).

Anal. Calcd for $C_{14}H_{13}BrN_2O$: C, 52.25; H, 4.08; N, 8.70. Found: C, 52.30; H, 4.15; N, 8.64.

Compound 7 *via* *N*-(**3-Hydroxy-2-pyridyl**)**acetamide Sodium Salt.**—To 5.5 g (0.05 mol) of **8** in 80 ml of absolute MeOH was added in 10 min at room temperature, a solution of 2.7 g (0.05 mol) of NaOMe in 20 ml of absolute MeOH. The solution was heated under reflux for 1 hr and concentrated *in vacuo*. The residual semisolid was very hygroscopic and could not be purified; it was shaken at room temperature with 5 ml of Ac_2O for 5 hr when there gradually formed a granular mass. This was filtered and weighed 4.3 g, but was still somewhat gummy. Recrystallization from 180 ml of absolute EtOH gave 2.5 g of crude **sodium salt** of 3-hydroxy-2-pyridylacetamide, mp 275–278°. To a solution of 4.2 g (0.024 mol) of the sodium salt in 50 ml of absolute MeOH was added 6.0 g (0.024 mol) of *o*-bromobenzyl bromide in 5 ml of absolute MeOH. The mixture was stirred and heated under reflux for 2.5 hr and poured into 200 ml of ice–water. Re-

crystallization from cyclohexane gave 1.6 g (10% yield) of **7**, mp 157–159°, identical by mixture melting point and infrared spectrum with **7** prepared from **12** or **13**.

Anal. Calcd for $C_{14}H_{18}BrN_2O_2$: C, 52.36; H, 4.08; N, 8.73. Found: C, 52.43; H, 4.06; N, 8.74.

Saponification of 7 to 3.—Compound **7**, 5.1 g (0.016 mol) in 75 ml of 2-PrOH and 20 ml of 50% aqueous NaOH formed a two-phase system. The mixture was stirred and heated under reflux for 1 hr and cooled, the lower aqueous solution separated, the 2-PrOH solution washed with 10 ml of saturated aqueous NaCl and filtered, and the filtrate concentrated to dryness *in vacuo* to give 3.2 g (91% yield) of **3**, mp 105–107°; a mixture melting point with **3** prepared *via* **8** was 106–107.5°, and their infrared spectra were identical.

Acetylation of 3 to Give 7.—When **3**, 0.50 g (0.018 mol), was mixed with 5 ml of Ac_2O, a clear solution formed after 0.5 hr. On keeping overnight at room temperature a crystalline mass separated. This was filtered to give 0.58 g (quantitative yield) of **7**, mp 157–158°; a mixture melting point with **7** prepared above was 157–159°, and their infrared spectra were identical.

Registry No.—**2**, 26372-71-4; **3**, 26419-18-1; **3** (HCl), 26372-55-4; **4**, 26372-72-5; **4** (HCl), 26372-73-6; **5**, 26372-74-7; **6**, 26372-75-8; **7**, 26372-76-9; **9**, 26372-77-0; **10**, 26372-53-2; **11**, 26372-54-3.

Deuterated Olefins from the Wittig Reaction

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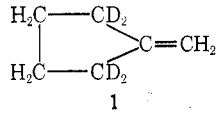
The usefulness of the Wittig reaction[2] for the preparation of deuterated olefins has been severely limited by the occurrence of large amounts of scrambling and exchange of label with the medium. Previous workers have used the anion of dimethyl sulfoxide[3] to generate ylides for this purpose. However, scrambling and loss of label make material so prepared unsuitable for use in mechanistic and spectroscopic studies. These problems are much less severe when alkyllithium reagents in ether[3,4] are used, but the yields in this case are low, and the procedures required for decomposition of the ylide are not convenient.

We have found that some α-deuterated olefins can be efficiently and conveniently prepared, using sodium hydride as the base, simply by changing the solvent to one not susceptible to hydrogen exchange. We have synthesized methylenecyclopentane-2,2,5,5-d_4 (**1**) and methylene-d_2-cyclopentane-2,2,5,5-d_4 (**2**). Our results



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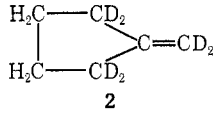

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also suggest that the intramolecular scrambling of the label is a function of the base, rather than a solvent effect. The procedure we describe is operationally simple and gives good yields of material of high isotopic purity.

The d_6 material **2** was prepared from methyl-d_3-triphenylphosphonium bromide and cyclopentanone-2,2,-5,5-d_4. The deuterium exchange reaction involving phosphonium salts has been previously described by Schlosser[5] and the deuterium exchange reaction of cyclopentanone in basic solution has been cited by several workers.[6] The exchange reactions were carried out in two steps and the final starting materials for the Wittig reaction were greater than 98 at. % D, in the appropriate positions, as estimated from integrated nuclear magnetic resonance (nmr) spectra.

Attempts to prepare the tetradeuterio compound **1** by a similar procedure with unlabeled phosphonium bromide gave a mixture of isotopic derivatives. This product retained virtually all the deuterium present in the starting material, but 20% of it wound up in the exocyclic position. However, when *n*-butyllithium was used as the base in place of sodium hydride, a good yield of specifically labeled product was obtained.

The use of ethers of ethylene glycol as solvents for the Wittig reaction effectively eliminates exchange of hydrogen with the medium. When sodium hydride is used as a base, intramolecular scrambling across the incipient double bond occurs, but with no noticeable loss of deuterium from the molecule. The use of an alkyllithium leads to specifically labeled product without scrambling. This modification of the Wittig reaction should make the synthesis of α-deuterated olefins, particularly where both the carbonyl and ylide precursors are α-deuterated, accessible, and convenient (Table I).

TABLE I
LABEL DISTRIBUTION IN WITTIG PRODUCTS FROM CYCLOPENTANONE-2,2,5,5-d_4 IN BIS(2-ETHOXYETHYL) ETHER

Ylide	Base	Product	At. % D: 2,5 ring position	At. % D: Exocyclic methylene
$Ph_3P{=}CH_2$	NaH	1	80	40
$Ph_3P{=}CH_2$	BuLi	1	98	0
$Ph_3P{=}CD_2$	NaH	2	98	97

Experimental Section

All of the products exhibited ir and nmr spectra which differed from those of authentic unlabeled analogs only in those respects expected as a result of deuterium incorporation. The use of undeuterated reagents gave materials identical in all respects measured with authentic samples.

Methyltriphenylphosphonium bromide was prepared by the method of Trippett.[7]

Methyl-d_3-triphenylphosphonium Bromide.—Methyltriphenylphosphonium bromide (25 g, 0.070 mol) was dissolved in 50 ml of heavy water (99.89 at. % D) and then 0.07 ml of 40% sodium deuterioxide in heavy water was added with stirring. The solution was stirred for 10 min and then immediately extracted with four 30-ml portions of methylene chloride. The combined methylene chloride layers were dried over sodium sulfate, filtered, concentrated under reduced pressure, and crystallized by addition of ether. This process was repeated with another 50-ml portion of heavy water; the crystals were dried in a vacuum oven overnight, to give 22.6 g (90%) of product which was estimated from the integrated nmr spectrum to have greater than 98 at. % D on the methyl group.

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(2) G. Wittig and U. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954).

(3) J. G. Atkinson, M. H. Fisher, D. Horley, A. T. Morse, R. S. Stuart, and E. Synnes, *Can. J. Chem.*, **43**, 1614 (1965).

(4) R. C. Cookson, D. P. G. Hamon, and R. E. Parker, *J. Chem. Soc.*, 5014 (1962).

(5) M. Schlosser, *Chem. Ber.*, **97**, 3219 (1958).

(6) (a) A. Streitwieser, Jr., R. H. Jagow, and S. Suzuki, *J. Amer. Chem. Soc.*, **77**, 6713 (1955); *ibid.*, **80**, 2326 (1958). (b) P. Natalis, *Bull. Soc. Chim. Belges*, **67**, 599 (1958). (c) C. L. Angell, P. J. Krueger, R. Lauzon, L. C. Leitch, K. Noack, R. J. D. Smith, and R. N. Jones, *Spectrochim. Acta*, 926 (1959).

(7) S. Trippett, "Advances in Organic Chemistry," Vol. 1, Interscience, 1960, pp 83–102.