was washed several times with water, dried over $MgSO_4$, and reduced to 30 ml, whereupon a white solid precipitated. An equal volume of pentane was added to give a total of 0.360 g (57%) of pure **10**, mp 168–169° (lit.[7] mp 168–169°).

Acid Hydrolysis of 5 to Form 6. A solution of **5** (0.163 g, 0.64 mmol) in 6 ml of dioxane was treated with 6 ml of 10% H_2SO_4. After 21 hr at room temperature, the mixture was diluted with 30 ml of water and extracted with methylene chloride. The organic layer was washed with water, dried over $MgSO_4$, and evaporated at reduced pressure to yield 0.150 g of an oily solid. Recrystallization from pentane afforded 0.120 g (73%) of **6**, mp 73–74° (lit.[4] mp 75°).

Acid Hydrolysis of 8 to Form 9. A solution of **8** (0.071 g, 0.29 mmol) in 3 ml of benzene was treated with 3 ml of 10% H_2SO_4 with stirring. Stirring was continued for 47 hr, after which time work-up as above gave **9** (0.035 g, 50%), mp 176–177° (lit.[7] mp 174–176°).[9]

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Registry No.—**1**, 886-38-4; **5**, 55991-26-9; **6**, 54108-62-2; **7**, 451-40-1; **8**, 55991-27-0; **9**, 35061-99-5; **10**, 22468-40-2; *N*-aminopyridinium iodide, 6295-87-0.

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Optically Active Heteroaromatic Compounds. VII. Synthesis of the Three Optically Active *sec*-Butylpyridines

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As a part of a synthesis project for optically active vinylpyridines, a relatively simple and expeditious method for obtaining chiral alkylpyridines with rather high enantiomeric purity was needed.

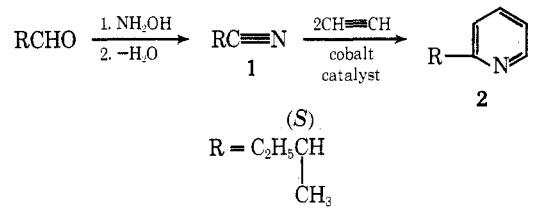
The only known optically active alkylpyridine is 2-*sec*-butylpyridine, which was obtained by resolution of racemic compound with dibenzoyl-(+)-tartaric acid.[1] The value of the specific rotation of the most highly resolved sample was rather high ($[\alpha]^{25}D$ −30°), but neither the absolute configuration of the prevailing enantiomer nor the minimum optical purity was reported.

In this paper we report results obtained (1) in the synthesis of all isomeric chiral *sec*-butylpyridines and (2) in the determination of the relationship between the sign of the rotatory power and the absolute configuration, and of the minimum optical purity.

The reaction sequence leading to (+)-(*S*)-2-*sec*-butylpyridine is depicted in Scheme I.

The necessary optically active nitrile **1** was obtained by dehydration of the known (+)-(*S*)-2-methylbutanal oxime[2] using *N,N'*-carbonyldiimidazole[3] with nearly quantitative yields; moreover, because of the very mild conditions used, the optical yield was very high (≥95%).

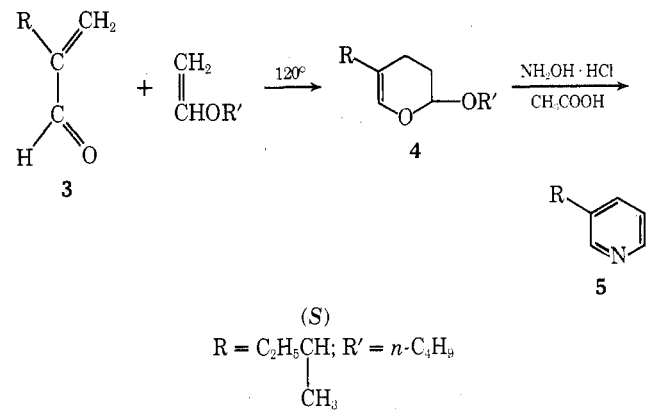
Scheme I



Cyclization of **1** with acetylene[4] at a pressure of ≥6 atm and 140° using π-cyclopentadienylcobalt cyclooctadiene[5] as the catalyst brought about the formation of the desired pyridine derivative in 95% yield.

Different reaction sequences are used for the preparation of (+)-(*S*)-3- (**5**) and (+)-(*S*)-4-*sec*-butylpyridine (**12**) (Schemes II and III). The chiral starting product for both

Scheme II



syntheses was (+)-(*S*)-2-methylene-3-methylpentanal (**3**).[6] In the first case **3** represented the diene partner for the well-known cycloaddition to vinyl butyl ether[7] to form (+)-2-butoxy-5-*sec*-butyl-3,4-dihydro-2*H*-pyran, which is a very suitable precursor for pyridine ring formation.[8] In a second case **3** was transformed through a five-step sequence (Scheme III) into (*S*)-3-*sec*-butylglutaraldehyde (**10**) and hence to the corresponding (+)-(*S*)-4-*sec*-butylpyridine (**12**). Some investigations on reaction conditions have been made in order to obtain higher yields of dihydropyran derivative **4** (Scheme II).

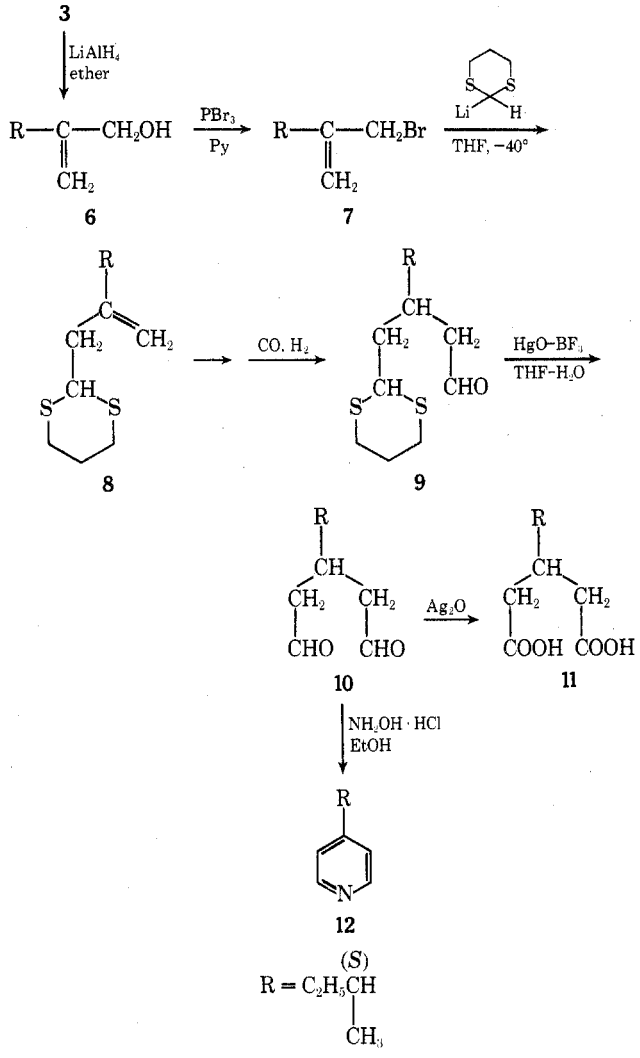
From the results obtained in several runs, it can be concluded that, with comparable conversion of the unsaturated aldehyde **3** (~90%), the best yield of **4** (70%) is achieved operating in a steel autoclave at 120° and 1–2 atm of nitrogen for 24 hr with a vinyl ether to acrolein molar ratio of 2.0. The secondary reactions, namely, isomerization and dimerization of the substrate, were under these conditions 20–22 and 7–8%, respectively.

Cyclization of **4** with hydroxylamine hydrochloride in acetic acid according to a known procedure[9] gave a high yield of the corresponding pyridine (**5**) (80–86%), free from isomeric products (GLC and NMR analysis).

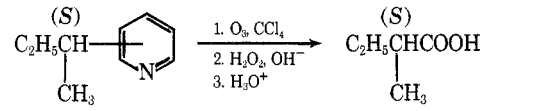
For the synthesis of optically active 4-*sec*-butylpyridine we preferred to develop a general route, not involving a dihydropyran derivative, because of the absence in the literature of any data about optically active β-*sec*-butyl acroleins necessary for cycloaddition to the vinyl ethers.

For the preparation of a suitable precursor to pyridine, e.g., an optically active alkyl-substituted glutaraldehyde, we considered the hydroformylation of acetal of β,γ-unsaturated aldehydes[10] as a concrete possibility, an analogous procedure having given good results in the synthesis of

Scheme III



Scheme IV



	$[\alpha]^{25}D$	$[\alpha]^{25}D$	Minimum optical purity, %
2	+25.78° (ethanol)	+15.8° (*n*-heptane)	80
5	+26.7° (neat)	+11.9° (neat)	60
12	+23.4° (*n*-heptane)	+17.9° (ethyl ether)	89

1,4-dialdehydes from acetal of α,β-unsaturated aldehydes.[12]

The suitable substrate for hydroformylation **8** was obtained by alkylation of 2-lithium-1,3-dithiane[13] with (+)-(*S*)-2-*sec*-butylallyl bromide (**7**) (Scheme III), easily obtained from (+)-(*S*)-2-*sec*-butylacrolein through the corresponding alcohol.[14] Hydroformylation of **8** was accomplished conveniently using $HRh(CO)(PPh_3)_3$ or $RhCl(CO)(PPh_3)_2$ as the catalyst,[12] and the monothioacetal of 3-*sec*-butylglutaraldehyde (**9**) was formed as the only reaction product (GLC and NMR analysis). Treatment of **9** with $HgO–BF_3·Et_2O$ system in $THF–H_2O$ solution at room temperature[15] resulted in rapid formation of the 3-*sec*-butylglutaraldehyde (**10**). An attempt to purify this compound by vacuum distillation was unsuccessful. To confirm its identity, **10** was converted by silver oxide oxidation into the corresponding (+)-(*S*)-3-*sec*-butylglutaric acid (**11**) (Scheme III).

Cyclization of crude **10** with hydroxylamine hydrochloride in boiling ethanol produced (+)-(*S*)-4-*sec*-butylpyridine (**12**) in 40–66% yield.[16] 3-Substituted isomer (up to 4%) also was found in the reaction product, as shown by comparison with the mass spectra, GLC analyses, and NMR spectra of an authentic sample.[17] The minimum optical purity of the prepared alkylpyridines was determined by the method of standard cleavage of the heterocyclic nucleus to (+)-(*S*)-2-methylbutanoic acid (Scheme IV).[2,19] The values of optical purity found for the recovered samples of this acid were assumed as the minimum for the optical purity of the relative pyridines, as the cleavage procedure employed by us should occur without remarkable racemization.[2,12]

Thus, it can be established that cyclization of (+)-(*S*)-2-methylbutanenitrile to (+)-(*S*)-2-*sec*-butylpyridine (Scheme I) takes place with ~9% racemization, indicating that the asymmetric center, even if directly bound with the cyano group, is not involved in the intermediary reaction complex.

Furthermore, while the reaction we have adopted for the synthesis of (+)-(*S*)-4-*sec*-butylpyridine (**12**) (Scheme III) occurs with a very low degree of racemization (~9%), we found for the (+)-(*S*)-3-*sec*-butylpyridine a minimum optical purity of 60%, corresponding to 35% loss of optical activity with respect to the starting (+)-(*S*)-2-*sec*-butylacrolein (**3**) (Scheme II).

It appears very unlikely that racemization takes place during the cycloaddition of **3** to butyl vinyl ether as shown by analogous reaction of (+)-(*S*)-*sec*-butyl-1,3-butadiene with ethylene, even under much more drastic reaction conditions.[21] Moreover, as **5**, when kept for 4 hr under the same conditions used for cyclization, does not racemize, it can be assumed that the loss of optical activity occurs practically only during the formation of pyridine ring from the dihydropyran **4**. Other examples illustrating improvements and extentions of these routes to alkylpyridines will be described in due course.

Experimental Section

Boiling points are uncorrected. GLC analyses were performed on the Perkin-Elmer F-11 and 990 gas chromatographs, using the columns and the temperatures specified. NMR spectra at 60 MHz were obtained with a Varian T-60 spectrometer, and at 100 MHz with a Varian HA-100 spectrometer, in CCl_4 solutions with tetramethylsilane as an internal standard (δ 0). Optical rotations were taken on a Perkin-Elmer 141 polarimeter in 1- or 0.1-dm tubes. Mass spectra were obtained with an Hitachi Perkin-Elmer RMU-6L mass spectrometer. Microanalyses were performed by the Microanalytical Laboratory of the Technical-Chemical Laboratory of the E. T. H. (Zurich, Switzerland).

Materials. Butyl vinyl ether from Fluka AG (purum grade) was distilled on sodium metal before use. (+)-(*S*)-2-*sec*-Butylacrolein (**3**) and (+)-(*S*)-2-*sec*-butylallyl alcohol (**6**) were prepared by methods described in the literature.[6,14] 1,3-Dithiane from Fluka AG (purum grade) was used without further purification. The synthesis of racemic 2-*sec*-butylpyridine was accomplished by the reaction of pyridine and *sec*-butyllithium.[1]

(+)-(*S*)-2-Methylbutanenitrile (1). To a solution of 18.6 g (0.114 mol) of 1,1-dicarbonylbiimidazole in 56 ml of CH_2Cl_2, 11.8 g (0.114 mol) of (+)-(*S*)-2-methylbutanal oxime,[2] $[\alpha]^{25}D$ + 23.1° (*c* 4.084, *n*-heptane), was added at room temperature during 0.5 hr.[3] After stirring for 0.5 additional hr the reaction mixture, solvent, and reaction product were distilled in vacuo (0.1 mm) and collected in a trap cooled at −70°. Fractional distillation gave a practically quantitative yield of pure (+)-(*S*)-2-methylbutanenitrile (**1**), bp 125° (750 mm), $[\alpha]^{25}D$ +34.18° (neat), corresponding to a minimum optical purity of 87.4%.[22] In another experiment, **1**, $[A]^{25}D$ +32.7° (neat) (83.4% optical purity), was prepared with 95% yield by dehydration of (+)-(*S*)-2-methylbutanal oxime, $[\alpha]^{25}D$ +23.5° (*c* 4.00, *n*-heptane).

(+)-(*S*)-2-sec-Butylpyridine (2). π-Cyclopentadienylcobalt cyclooctadiene[5] (0.700 g) was dissolved in 8 g (0.096 mol) of (+)-(*S*)-2-methylbutanenitrile (which was distilled under nitrogen), $[\alpha]^{25}D$ +33.2° (85.2% optical purity), at room temperature, still maintaining the nitrogen atmosphere. This brown solution was introduced by suction into a 0.2-l. autoclave, evacuated from air (0.1 mm). The autoclave was pressurized to 8 atm with acetylene and then shaken and heated to 140°. Reaction started immediately. Whenever the pressure (14 atm) dropped to 6 atm, acetylene was introduced to the upper pressure limit. Four hours was required for the adsorption of the theoretical amount of gas.

After cooling and releasing of residual gas, the brown reaction mixture was distilled under reduced pressure to give 12.3 g (0.091 mol, 95% yield) of pure **2**, bp 73° (15 mm) [lit.[1] bp 74° (18 mm) for the racemic compound], $[\alpha]^{25}D$ +31.96° (neat), d_4^{25} 0.904, $[\alpha]^{25}D$ +25.78° (*c* 1.706, ethanol).

2 gave one peak by GLC analysis (2 m × 2.5 mm column, SP 1000 2.5% on Chromosorb G at 130°) and was identified by comparison of mass spectrum and NMR spectrum with those of an authentic sample.

(+)-2-Butoxy-5-*sec*-butyl-2*H*-pyran (4). A typical procedure is described. A mixture of 5.2 g (0.05 mol) of (+)-(*S*)-2-*sec*-butylacrolein (**3**) (95–96% optical purity),[6] 10.2 g (0.1 mol) of freshly distilled butyl vinyl ether, and 0.150 g of hydrochinone was heated in a rocking steel autoclave at 120° and 2 atm of nitrogen for 24 hr. GLC analysis of the reaction mixture (on a 2 m × 2.2 mm 15% polyglycol 4000 on Kieselgur column, heated at 200°) showed that 90% of **3** had reacted and the following composition: 70% of cycloaddition product **4**, 20% of isomeric products derived from **3**, 7–8% of dimerization products of **3**. Fractional distillation gave 7.0 g of pure **4**, bp 116° (11 mm), $\alpha^{25}D$ +27.5° (*l* 1, neat). The mass spectrum showed the molecular ion *m/e* 212; NMR ($CDCl_3$) 6.12 (m, H-6), 4.95 (m, H-2), 1.9 ppm (m, 2 H-3 and 2 H-4).

In another experiment from 16.5 g (0.16 mol) of **3**, using the same reaction conditions but 130° reaction temperature, **4** was obtained with 69% yield, $\alpha^{25}D$ +31.05° (*l* 1, neat) after 15 hr reaction time.

(+)-(*S*)-3-sec-Butylpyridine (5). **4** (22.0 g, 0.103 mol), $\alpha^{25}D$ +31.0° (*l* 1, neat), in 200 ml of pure acetic acid was refluxed under nitrogen for 2 hr. After cooling, this solution was added to a boiling mixture of 21.5 g (0.31 mol) of hydroxylamine hydrochloride and 100 ml of acetic acid.[9] Heating was continued for 4 additional hr, then most of the solvent was evaporated in vacuo (12–13 mm). Cold water (100 ml) was added and the resulting mixture was alkalized with 10% sodium hydroxide (pH ~10). Extraction with ether, drying (Na_2SO_4), and fractional distillation yielded 11.0 g (80% yield) of pure **5**: bp 74° (15 mm); $n^{20}D$ 1.4942; d_4^{25} 0.914; $[\alpha]^{25}D$ +27.0° (neat). The mass spectrum showed the molecular ion *m/e* 135; NMR (100 MHz, CCl_4) 8.31 (m, H-2 and H-6), 7.38 (m, H-4), 7.11 (m, H-5), 2.62 (m, 1 H, CH), 1.28 (d, 3 H, CH_3), 0.84 ppm (t, 3 H, CH_3).

In another experiment, **5**, $[\alpha]^{25}D$ 26.7° (neat), was prepared in 80% yield by cyclization of **4**, $\alpha^{25}D$ 27.5° (*l* 1, neat), using the same reaction conditions.

(+)-(*S*)-2-*sec*-Butylallyl Bromide (7). Phosphorus tribromide (21.9 g, 0.08 mol) was added dropwise to a stirred solution of 23 g (0.2 mol) of (+)-(*S*)-2-*sec*-butylallyl alcohol (**6**), $[\alpha]^{25}D$ +20.3° (minimum optical purity ~95%[14]), and 5.5 g (0.06 mol) pyridine cooled to 0°. After stirring at 0° for 4 hr, then at room temperature for 2 hr, the mixture was poured into ice and the product was extracted with ether. The ether solution was neutralized with 5% sodium bicarbonate, dried over Na_2SO_4, and, after removal of the solvent, distilled in vacuo. The yield of **7** was 25.5 g (72%), bp 52° (12 mm), $[\alpha]^{25}D$ + 25.76° (*c* 4.27, *n*-heptane).

(+)-(*S*)-2-(2-*sec*-Butylallyl)-1,3-dithiane (8). 1,3-Dithiane (17 g, 0.14 mol) was treated with 5% excess of butyllithium in 430 ml of THF at −40°.[13] After addition of 25.5 g (0.14 mol) of **7**, the mixture was stirred at −40° for 6 hr and at −20 to −15° for 18 hr. Working up according to Seebach[13] and distillation gave 25.0 g (82% yield) of **8**, bp 112–114° (0.2 mm), $[\alpha]^{25}D$ +21.23° (*c* 3.344, *n*-heptane).

In another experiment **8**, $[\alpha]^{25}D$ +20.74° (*c* 2.3, *n*-heptane), was prepared from **7** (0.15 mol), $[\alpha]^{25}D$ +26.06° (*c* 1.174, *n*-heptane), with 75% yield.

(+)-(*S*)-3-*sec*-Butyl-4-(1,3-dithian-2-yl)butanal (9). **8** (23.8 g, 0.11 mol) in 100 ml of dry benzene was hydroformylated with a mixture of CO and H_2 (1:1) at 100 atm and 100° in the presence of 0.20 g of $HRh(CO)(PPh_3)_3$ according to the procedure described elsewhere.[12] After 30 hr, >90% of the substrate had reacted (GLC). After cooling and releasing of the pressure, the reaction mixture was evaporated under reduced pressure (20 mm) and the residual aldehyde was directly purified through its bisulfite derivative. Quite pure **9** (18.9 g, 70%) was recovered by distillation in vacuo as a pale yellow oil, bp 128–130° (0:04 mm), $[\alpha]^{25}D$ +4.65° (*c* 2.406, *n*-heptane).

In another preparation **8** (0.11 mol), $[\alpha]^{25}D$ +20.74° (*n*-heptane), was hydroformylated at 100° and 105 atm of a mixture of CO and H_2 (1:1) using 0.400 g of $RhCl(CO)(PPh_3)_2$ and 0.5 ml of triethylamine. After a reaction time of 40 hr **9** was obtained by usual working up of the reaction mixture with 66% yield.

(*S*)-3-*sec*-Butylglutaraldehyde (10). A typical procedure is described. Red mercuric oxide (4.3 g, 0.02 mol) and 2.8 g (0.02 mol) of boron trifluoride etherate in 24 ml of 15% aqueous THF were stirred vigorously under nitrogen. A solution of 2.5 g (0.01 mol) of the dithiane **9** in 2 ml of THF was added dropwise and the mixture was stirred at room temperature for 2 hr.[15] The crude reaction product (1.3 g, 80% yield) was obtained as a slightly yellow oil by working up of the reaction mixture[15] and gave one peak by GLC analysis (2 m × 2 mm column, silicone SF 96, 2.5% on Chromosorb G at 150°). The molecular weight was 156 (mass spectroscopy).

(+)-(*S*)-3-*sec*-Butylglutaric Acid (11). Crude dialdehyde **10** (1.0 g) was added slowly at 0° to a stirred suspensn of 12.5 g (5.3 mmol) of silver oxide in 20 ml of water containing 0.3 g of NaOH. After 8 hr the filtered solution was worked up in the usual way[23] to give a slightly yellow oil. After addition of dry pentane the crude acid was allowed to stand for 2 hr at room temperature. The white crystals formed were filtered, washed with pentane, and dried under vacuum. **11** (0.6 g) was obtained, mp 82°, $[\alpha]^{25}D$ +12.3° (*c* 2.048, chloroform), neut equiv 98 (lit.[24] mp 68–70° for racemic compound).

Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.34; H, 8.44.

(+)-(*S*)-4-*sec*-Butylpyridine (12). $NH_2OH{\cdot}HCl$ (1.2 g) was added to a boiling solution of 1.2 g (0.08 mol) of crude **10** in 20 ml of ethanol. After 0.5 hr the mixture was alkalized with 5% sodium hydroxide and the product was extracted with ether. Drying over Na_2SO_4 and distillation yielded 0.45 g (0.032 mol, 40% yield) of **12**, bp 128° (100 mm) [lit.[25] bp 128–130° (100 mm) for racemic compound], $[\alpha]^{25}D$ +23.36° (*c* 1.524, *n*-heptane), which was shown to contain ~4% of 3-*sec*-butylpyridine by GLC analysis (2 m × 2.5 mm column, SP 1000, 2.5% on Chromosorb G at 100°). The mass spectrum showed the molecular ion *m/e* 135; NMR (CCl_4) 8.4 (m, H-2 and H-6), 7.1 (m, H-3 and H-5), 2.58 (m, 1 H, CH), 1.27 (d, 3 H, CH_3), 0.85 ppm (t, 3 H, CH_3).

In another cyclization experiment **12** (containing ~4% of **5**), $[\alpha]^{25}D$ +23.8° (*c* 1.310, *n*-heptane), was obtained from **9** (0.038 mol) with 66% yield. Isomers **12** and **5** were separated by preparative GLC on a 5 m × 8 mm column, SP 1000, 15% on Chromosorb G at 180°. Pure **12** showed $[\alpha]^{25}D$ 20.2° (*c* 2.29, *n*-heptane).

Ozonization of (+)-(*S*)-*sec*-Butylpyridines to (+)-(*S*)-2-Methylbutanoic Acid. A typical experiment is described.[2] **12** (0.5 g, 3.7 mmol), $[\alpha]^{25}D$ 23.4° (*c* 1.524, *n*-heptane), in 15 ml of CCl_4 was ozonized at room temperature for 18 hr. After replacement of the solvent by the same volume of ethanol, 5 ml of 5% sodium hydroxide and 2 ml of 35% hydrogen peroxide were added slowly at 0°. The mixture was refluxed for 3 hr and the acid was isolated by the usual procedure.[2] (+)-(*S*)-2-Methylbutanoic acid (98 mg) was obtained (26% yield), $[\alpha]^{25}D$ +17.9° (*c* 0.91, ethyl ether) (89% minimum optical purity).

From **5** (4.0 g, 0.03 mol), $[\alpha]^{25}D$ +26.7° (neat), 0.5 g of the same acid was obtained, $[\alpha]^{25}D$ 11.9° (neat) (60% minimum optical purity). From **2**, $[\alpha]^{25}D$ +25.78° (*c* 1.706, ethanol), (+)-(*S*)-2-methylbutanoic acid was obtained, $[\alpha]^{25}D$ +15.8° (*c* 0.974, *n*-heptane) (80% minmum optical purity).

Racemization Experiment with (+)-(*S*)-3-*sec*-Butylpyridine (5). **5**, $[\alpha]^{25}D$ +25.75° (neat), was refluxed for 4 hr in 75 ml of dry acetic acid containing 5.3 g of 37% hydrochloric acid. The pyridine, recovered by already reported working up of the mixture, showed $[\alpha]^{25}D$ +25.53° (neat).

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Registry No.—**1**, 25570-03-0; **2**, 55740-78-8; **3**, 10203-77-7; **4**, 55740-79-9; **5**, 55740-80-2; **6**, 39497-65-9; **7**, 55740-81-3; **8**, 55740-82-4; **9**, 55740-83-5; **10**, 55740-84-6; **11**, 55740-85-7; **12**, 55740-86-8; (+)-(*S*)-2-methylbutanol oxime, 16885-26-0; phosphorus tribro-

mide 7789-60-8; 1,3-dithiane, 505-23-7; (+)-(S)-2-methylbutanoic acid, 1730-91-2.

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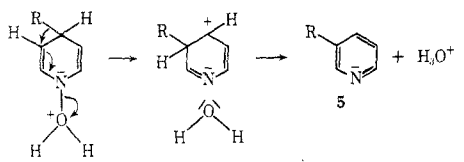
(16) An attempt to obtain **12** by direct cyclization of **9** afforded a very low yield of the expected alkylpyridine and other unidentified products.
(17) A sample containing ~80% of **5** was obtained by preparative GLC. The rotatory power of this sample ($[\alpha]^{25}D$ ~+30°) showed that **5** is also optically active. On this basis, and taking into account the reaction intermediates suggested for the cyclization of 1,4-dioxo compounds with hydroxylamine,[18] a possible pathway for the formation of **5** from **10** can be formulated as follows.



(18) See ref 8, p 279.
(19) The optical purity was determined in case of chiral 2-*sec*-butylpyridine (**2**) by NMR analysis in the presence of tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III).[20] From the NMR results obtained on a solution containing 35.3 mg of (−)-(*R*)-**2**, $[\alpha]^{25}D$ −12.8° (ethanol), prepared by resolution of racemic compound with dibenzoyl-(+)-tartaric acid,[1] and 59.9 mg of the europium complex, $[\alpha]D$ +196° (carbon tetrachloride), in 0.7 ml of carbon tetrachloride, looking at the signals of the H-2 ring proton and of the methyl group protons nearer to the asymmetric center, a value of 29 (ethanol) for the maximum rotatory power of **2** was extrapolated. This value is in satisfactory agreement with that obtained through the cleavage method, $[\alpha]^{25}D$ +32.2° (ethanol) (Scheme IV), considering that the precision of the NMR method is about ±10%.
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Reaction of Azomethine Ylides with Sulfur Ylides. A Novel Azetidine Synthesis

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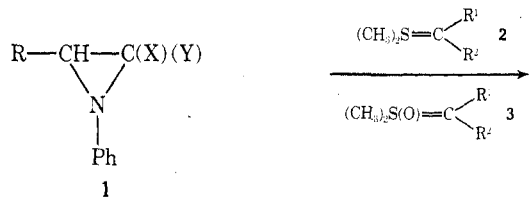
Aziridines represent versatile substrates which can serve as azomethine ylide precursors. We have shown an unusual feature of these ylides: they are able to react with both electrophilic and nucleophilic reagents.[1-4] Not the least interesting of these last are sulfur ylides which lead to azetidines in a novel way.[5] As a result of a continuing study of this last reaction we wish to report some new information and experimental details which were not given in the preliminary note.[5]

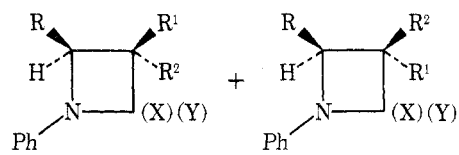
The various azetidines which were prepared are shown in Scheme I.

Scheme I[6]



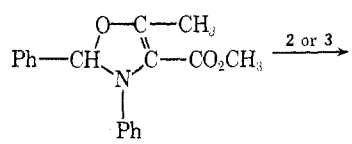
1a, R = Ph; X = Y = CO_2CH_3
1b, R = X = Y = CO_2CH_3
1c, R = Ph; X = H; Y = $CO_2C_2H_5$

2a or **3a**, $R^1 = R^2 = H$
2b, $R^1 = H$; $R^2 = CO_2CH_3$
2c, $R^1 = H$; $R^2 = CO_2C_2H_5$
2d or **3d**, $R^1 = H$; $R^2 = COPh$
2e, $R^1, R^2 = C_{13}H_{18}$[a]
2f, $R^1 = Cl$; $R^2 = CO_2C_2H_5$
2g, $R^1 = Br$; $R^2 = CO_2C_2H_5$

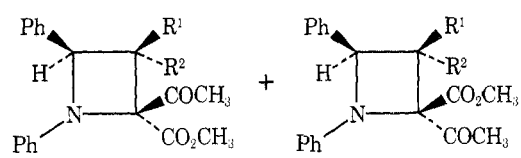


4 a-g
4′ R = Ph; X = Y = CO_2CH_3

4d and **4′d**, R = X = Y = CO_2CH_3



5



6b or **6′b**; **6d** or **6′d**; **6e** or **6′e**; **6f** or **6′f**

[a] Fluorenylidene.

In the reactions of ethyl chloro- (or bromo-) (dimethylsulfuranylidene)acetate (**2f** or **2g**) with aziridine **1a** and 4-oxazoline **5**, we expected competition between dimethyl sulfide (DMS) and bromide or chloride elimination. However, in each case, DMS is a better leaving group than the halide and we observe only formation of the epimeric halogenated azetidines **4f, 4′f; 4g, 4′g;** and **6f, 6′f.** In an attempt to prepare the C_2 monosubstituted azetidines, the sulfonium ylides were heated with aziridine **1c** in boiling benzene (under these conditions, **1c** is in equilibrium with the corresponding azomethine ylide[2,3,7]) but no reaction occurs, except the isomerization of **1c** and the partial decomposition of the sulfur ylide. We have no explanation for this failure; it is not due to instability of the sulfonium ylide, which is still present after 8 hr of reaction. Nevertheless it is possible to get the C_2 monosubstituted azetidines in good yield by demethoxycarbonylation of compounds **4** with piperi-