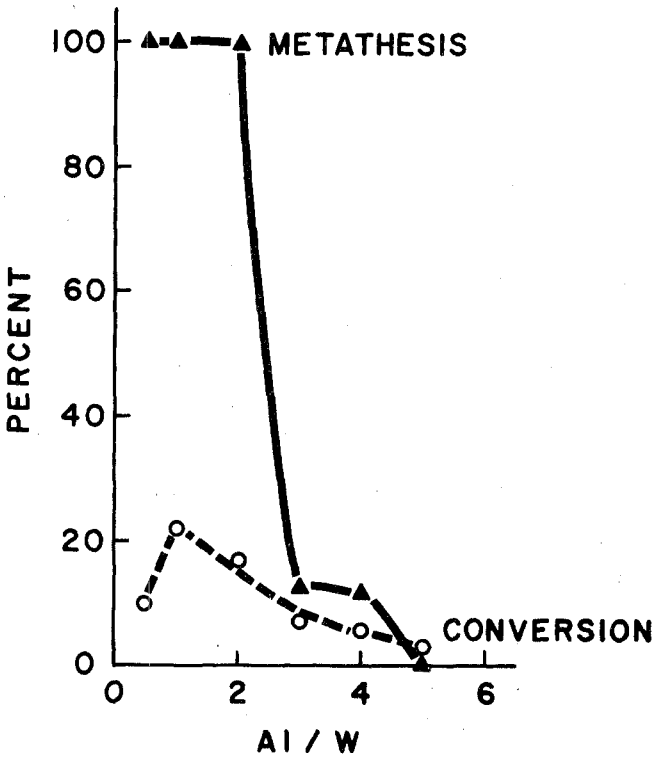

Figure 3. 2-Pentene-2 and $Et_3Al_2Cl_3$.

where intermediate C, with one less ligand, would allow more facile coordination of an internal olefin than B.

Similar results would be observed if the terminal olefin sustained a nonproductive metathesis, such as the exchange of methylene groups only. However, this possibility seems unlikely.

When the tungsten atom of intermediate A is in a relatively high oxidation state (perhaps IV or V), the pathway to the carbene C affords relief to electron-deficient tungsten by expulsion of H^+. When tungsten has been reduced further (perhaps III or IV), the route through intermediate B, where W is relatively electron rich, affords stabilization of the olefin complexes shown. Somewhere in between, A becomes stable and little reaction occurs. Complexes of the type A and B have been reported,[8] and the carbene mechanism for metathesis has been suggested.[9] The route to metathesis should be favored by small amounts of Lewis acid, and we have observed such an effect previously.[5] More basic reductants such as butyllithium may abstract the α proton from A first, followed by ejection of chloride ion.

Experimental Section

2-Pentene was distilled from sodium bisulfite under nitrogen, and propylene was dried through a bed of 3-A molecular sieves. Aniline was vacuum distilled from sodium. Solvents were carefully dried over sodium or silica gel. Tungsten hexachloride was dissolved and used as received, and the ethylaluminum chlorides were diluted to 2 *M* in benzene or chlorobenzene.

Propane as an internal standard was added to the propylene–chlorobenzene solutions, which were about 0.5 *M*.

Transfers of olefin solutions and chemical reagents were done by hypodermic syringes. Reactions were carried out for 1 hr in 4-oz glass bottles at room temperature, agitated on a Burrell shaker, and terminated by 1 ml of isopropyl alcohol. Then the reaction mixtures were cooled before VPC analysis.

For 2-pentene, analyses were done on a 42-ft Tergitol column at 60°, using *n*-pentane as internal standard. For the propylene work, analyses were done on a 60-ft β,β-oxydipropionitrile column at 30° or Tergitol at 30°. Using propane as an internal standard, the weight of propylene converted (expressed in peak area) was calculated and compared to ½ the observed areas for the 2-butene isomers (since some of the ethylene went on to form 1-butene, etc.). Thus, conversion and total selectivities were simply calculated.

Acknowledgment. We would like to thank Mr. Frank Cinocca for his capable assistance in performing much of the work described here, and also The Goodyear Tire & Rubber Co. for permission to publish. Thanks to Drs. J. G. Bryson and M. F. Farona for a helpful discussion on mechanism.

Registry No.—*trans*-2-Pentene, 646-04-8; *cis*-2-pentene, 627-20-3; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; propylene, 115-07-1; WCl_6, 13283-01-7; $PhNH_2$, 62-53-3; $Et_3Al_2Cl_3$, 12075-68-2; ethanol, 64-17-5; $EtAlCl_2$, 563-43-9.

References and Notes

(1) N. Calderon, E. A. Ofstead, J. P. ward, W. A. Judy, and K. W. Scott, *J. Am. Chem. Soc.*, **90**, 4133 (1968).
(2) C. P. C. Bradshaw, E. J. Howman, and L. Turner, *J. Catal.*, **7**, 269 (1967).
(3) G. C. Bailey, *Catal. Rev.*, **3**, 36 (1969).
(4) N. Calderon, *Acc. Chem. Res.*, **5**, 127 (1972).
(5) J. L. Wang, H. R. Menapace, and M. Brown, *J. Catal.*, **26**, 455 (1972).
(6) D. L. Crain, *J. Catal.*, **13**, 110 (1969).
(7) J. L. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968).
(8) F. W. S. Benfield, B. R. Francis, and M. L. H. Green, *J. Organomet. Chem.*, **44**, C13 (1972).
(9) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **96**, 7808 (1974).

Reaction of Diphenylcyclopropenone with Pyridinium *N*-Imine in Protic Media. The Quenching of a Reactive Intermediate

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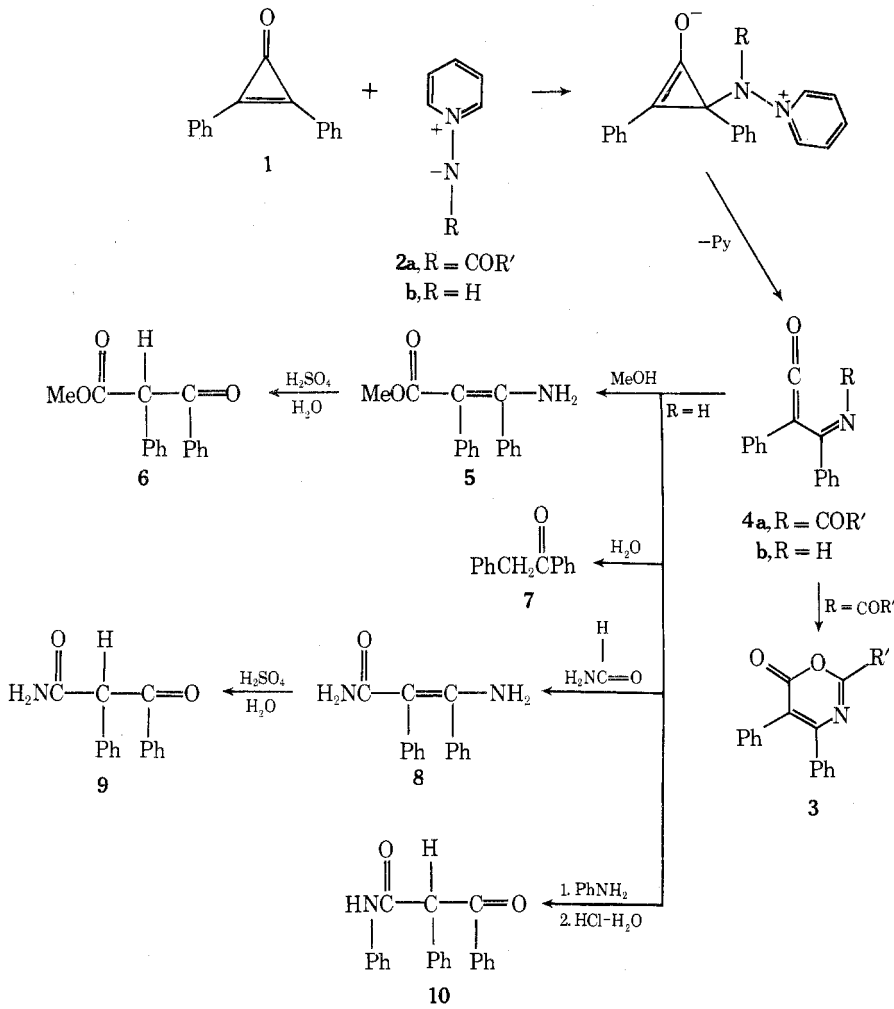
The reaction of diphenylcyclopropenone (**1**) with *N*-acyl pyridinium imines (**2a**) has been reported to produce 2,4,5-trisubstituted 6*H*-1,3-oxazin-6-ones (**3**).[1,2] A pathway involving formation of a ketene[3] intermediate (**4a**) was suggested for the process. However, attempts to quench this intermediate with methanol were unsuccessful, possibly because the intramolecular cyclization process is rapid compared with intermolecular reaction of the ketene with solvent.[1] In this case, absence of the N substituent should permit addition of a protic solvent to the intermediate.

We have, therefore, investigated some reactions of diphenylcyclopropenone with *N*-aminopyridinium iodide, in protic media, in the presence of a tertiary amine (diisopropylethylamine and triethylamine were found to be equally effective). A methanol solution of these reagents developed a wine-red coloring during several hours at room temperature. After 17 hr, the methanol was evaporated and the residue was purified by extraction and precipitation to give **5** as a crystalline solid in 95% yield. The structure assignment was suggested by the NMR spectrum ($CDCl_3$) which showed a sharp 3 H singlet at δ 3.65 (methyl ester), and by the infrared spectrum ($CHCl_3$), which exhibited prominent absorption at 3490, 3304, and 1660 cm^{-1}. A mild acid hydrolysis of **5** produced the known[4] β-keto ester **6**. Primary enamines analogous to **5** have been reported in the reactions of diphenylcyclopropenone with aziridines[5] and ammonia,[6] the cis configuration being assigned in both cases. Evidence has been presented[6] to suggest that the trans isomer, if formed in the reaction, would be expected to isomerize readily in solution.

The formation of **5** in the present study may be visualized as occurring by way of a 1,2 or 1,4 addition of methanol to an iminoketene intermediate (**4b**), formed by initial conjugate addition of **2b** on **1**. The general applicability of the reaction was demonstrated by considering various protic media. Thus, reaction in aqueous dioxane gave deoxy-



benzoin (7, 30%), the expected decarboxylation–hydrolysis product of H_2O addition to **4b**. Reaction in formamide produced amide **8** (50%), presumably via a decarbonylation of the formamide adduct under the reaction conditions. The structure of **8** was confirmed by mild acid hydrolysis to the known[7] β-keto amide **9**. Some deoxybenzoin (**7**) always accompanied the formation of **8**, and probably arises from the presence of traces of water in the formamide. Finally, reaction in aniline, followed by a work-up with concentrated HCl, afforded directly the hydrolysis product **10** (57%), an alternate preparation of which has been described elsewhere.[7]

Experimental Section

All melting points were obtained on a Mettler FP52 melting point apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer 337 spectrophotometer. NMR spectra were recorded with a Varian T-60 spectrometer using tetramethylsilane as an internal standard. The elemental analyses were performed by Alfred Bernhardt Laboratories, West Germany.

Reaction of Diphenylcyclopropenone (1) with *N*-Aminopyridinium Iodide in the Presence of Triethylamine. A. In Methanol. A solution of *N*-aminopyridinium iodide[8] (0.444 g, 2 mmol), triethylamine (0.6 ml, 4 mmol), and diphenylcyclopropenone (0.206 g, 1 mmol) in 60 ml of dry methanol was allowed to stand at room temperature. After 17 hr, the solvent was evaporated at reduced pressure, and the resulting residue was extracted with methylene chloride (60 ml). The extract was concentrated to 30 ml and pentane (30 ml) was added to precipitate dissolved salts. Evaporation of the solvent left a pale yellow solid, which upon recrystallization from cyclohexane afforded 0.240 g (95%) of **5** as white needles: mp 113–114°; ir ($CHCl_3$) 3490, 3304, 1660, 1600, 1575 cm^{-1}; NMR ($CDCl_3$) δ 3.65 (3 H, singlet), 7.00 and 7.10 (singlets, the region 6.0–8.0 integrating as 12 H, diminishing to 10 H upon D_2O exchange).

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.73; H, 6.04; N, 5.69.

B. In Aqueous Dioxane. A solution of *N*-aminopyridinium iodide (0.666 g, 3 mmol), triethylamine (1.2 ml, 8 mmol), and diphenylcyclopropenone (0.412 g, 2 mmol) in 20 ml of 50% aqueous dioxane was allowed to stand at room temperature. After 20 hr, water (50 ml) was added and the resulting mixture was extracted with methylene chloride. The organic layer was washed several times with water, dried over $MgSO_4$, and evaporated at reduced pressure to yield 0.500 g of a yellow oil. Addition of benzene (50 ml) left an insoluble solid residue (0.100 g), which was not identified. The benzene-soluble material was chromatographed on a neutral alumina column (benzene) to afford 0.120 g (30%) of pure **7**, mp 56°.

C. In Formamide. A solution of *N*-aminopyridinium iodide (0.222 g, 1 mmol), triethylamine (0.3 ml, 2 mmol), and diphenylcyclopropenone (0.128 g, 0.62 mmol) in 30 ml of formamide (Fisher reagent grade, dried over type 3A molecular sieve) was allowed to stand at room temperature. After 17 hr, the solution was treated with 100 ml of water and worked up as in B to give 0.121 g of a solid residue which was recrystallized from methylene chloride–pentane to afford 0.074 g (50%) of **8**: mp 149–151°; ir ($CHCl_3$) 3525, 3480, 3405, 1630, 1600, 1565 cm^{-1}; NMR ($CDCl_3$) δ 5.20 (2 H, broad), 7.10 and 7.13 (sharp singlets, the region 6.5–7.5 integrating as 12 H).

Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.92; N, 11.76. Found: C, 75.65; H, 6.07; N, 11.62.

Evaporation of the mother liquor left a yellow oil which was crystallized from cyclohexane to give 0.012 g (10%) of **7**, mp 55–56°. The infrared spectrum of this material ($CHCl_3$) was identical with that of an authentic sample.

D. In Aniline. A solution of *N*-aminopyridinium iodide (0.666 g, 3 mmol), triethylamine (1.2 ml, 8 mmol), and diphenylcyclopropenone (0.412 g, 2 mmol) in 30 ml of freshly distilled aniline was allowed to stand at room temperature. After 20 hr, 200 ml of ether was added followed by the dropwise addition of concentrated HCl (21 ml). The salts were removed by filtration. The organic layer

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.

References and Notes

(1) J. W. Lown and K. Matsumoto, *Can. J. Chem.*, **50**, 584 (1972).
(2) T. Sasaki, K. Kanematsu, and A. Kakehi, *J. Org. Chem.*, **36**, 2451 (1971).
(3) For a recent review of cyclopropenone chemistry see K. T. Potts and J. S. Baum, *Chem. Rev.*, **74**, 189 (1974).
(4) E. P. Kohler, *J. Am. Chem. Soc.*, **46**, 1743 (1924).
(5) E. V. Dehmlow, *Chem. Ber.*, **102**, 3863 (1969).
(6) F. Toda, T. Mitote, and K. Akagi, *Chem. Commun.*, 228 (1969).
(7) S. D. Work, D. R. Bryant, and C. H. Hauser, *J. Org. Chem.*, **29**, 722 (1964).
(8) R. Gösl and A. Meuwsen, *Org. Synth.*, **43**, 1 (1963).
(9) A mild, heterogeneous hydrolysis of **5**, as described for **8**, gave a mixture of **5** and **6**, even after 47 hr at room temperature. The possibility that such a mixture forms in the case of **8** cannot be ruled out, inasmuch as only 50% of the material was recovered.

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.

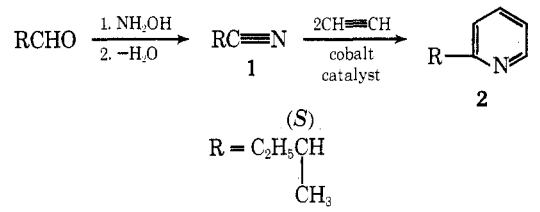
The only known optically active alkylpyridine is 2-*sec*-butylpyridine, which was obtained by resolution of racemic compound with dibenzoyl-(+)-tartaric acid.[1] The value of the specific rotation of the most highly resolved sample was rather high ($[\alpha]^{25}D$ −30°), but neither the absolute configuration 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%).

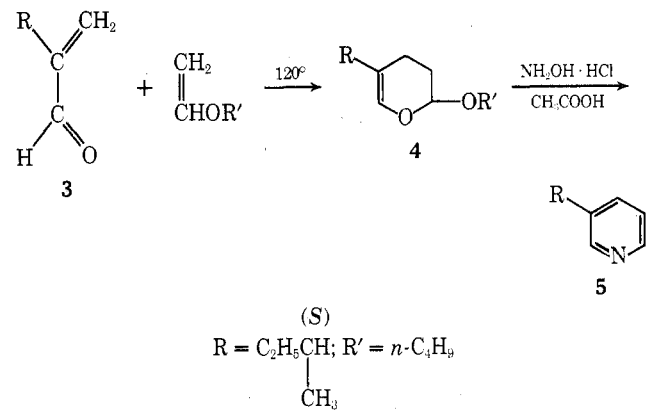
Scheme I



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