rapidly, and the solution was warmed to room temperature. The solution was neutralized with 3 N HCl, the solvent was removed, and the yellow oil was taken up in CH_2Cl_2, washed with brine, and dried over $MgSO_4$. Purification of the yellow oil (2.7 g) by medium-pressure preparative liquid chromatography (silica gel column, 1:1 ethyl acetate–hexane eluent) gave 8-(1-hydroxyethyl)quinoline: 1.6 g (64%); mp 48–52 °C (ether–hexane); IR (film) 3380, 1594, 1497, 901, 832, 797, 762 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.73 (dd, J = 4, 2 Hz, 1 H, 2 position), 8.07 (dd, J = 8, 2 Hz, 1 H, 4 position), 7.8–7.2 (m, 4 H, ring), 6.04 (br, 1 H, OH), 5.62 (q, J = 7 Hz, 1 H, HC–O), 1.80 (d, J = 7 Hz, 3 H, CH_3). Anal. Calcd for $C_{11}H_{11}NO$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.47; H, 6.44; N, 7.83.

8-Allylquinoline via the Cuprate. 8-Lithioquinoline was prepared from 8-bromoquinoline (2.08 g, 10 mmol) as above, except the solvent was diethyl ether. It was added rapidly, via a double-tipped needle packed in dry ice, to a suspension of CuI (0.952 g, 5 mmol) in 20 mL of ether at −20 °C under argon. After warming to −5 °C over 20 min, the clear brown solution was quenched with allyl bromide (1.2 g, 10 mmol) and stirred at −5 °C for 1 h and then at 25 °C for 1 h. The solution was washed three times with ammonium hydroxide solution, once with ammonium chloride solution, and once with brine and dried over $MgSO_4$, and solvent was removed to give a yellow oil. Medium-pressure preparative liquid chromatography (silica gel column, 3:1 hexane–ethyl acetate) gave 8-allylquinoline as a clear oil: 0.55 g (65%); IR (film) 1635, 1594, 1496, 910, 825, 792, 757 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.93 (dd, J = 5, 2 Hz, 1 H, 2 position), 8.10 (dd, J = 8, 2 Hz, 1 H, 4 position), 7.8–7.2 (m, 4 H, ring), 6.6–6 (m, 1 H, HC= allyl), 5.1 (m, 2 H, $=CH_2$ allyl), 4.15 (m, 2 H, CH_2 allyl). Anal. Calcd for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.19; H, 6.50; N, 8.18.

Registry No. 8-(1-Hydroxyethyl)quinoline, 73038-00-3; 8-bromoquinoline, 16567-18-3; acetaldehyde, 75-07-0; 8-lithioquinoline, 73038-01-4; allyl bromide, 106-95-6; 8-allylquinoline, 73038-02-5; 8-(formyl-*d*)quinoline, 73038-03-6; 8-formylquinoline, 38707-70-9; 8-(diphenylphosphino)quinoline, 28225-52-7; 8-methylquinoline, 611-32-5; 8-(tetramethylstannyl)quinoline, 73038-04-7; 8-(2-hydroxyethyl)quinoline, 73048-42-7; perfluoro-*N*,*N*-dimethylformamide, 4472-41-7; *N*,*N*-dimethylformamide, 68-12-2; diphenylphosphinous chloride, 1079-66-9; iodomethane, 74-88-4; chlorotrimethylstannane, 1066-45-1; ethylene oxide, 75-21-8.

Regioselective 2-Alkylation and 2-Arylation of Piperidine and Pyrrolidine via Organolithiation of Cyclic Imines[1]

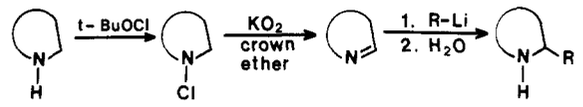
Frank E. Scully, Jr.

Department of Chemical Sciences, Old Dominion University, Norfolk, Virginia 23508

Received May 24, 1979

Recently, we reported a reaction of potassium superoxide with primary and secondary organic *N*-chloramines which produces imines in good yield.[2] In our subsequent studies of the mechanism and limitations of this reaction we have examined the reaction of alicyclic *N*-chloramines and found, as expected, that the cyclic imines are formed. In an attempt to characterize these cyclic imines we have taken advantage of the aprotic solvent in which they are generated to study their reaction with organometallics. This paper describes the successful addition of organolithium reagents to the cyclic imines and a new approach to the regioselective alkylation of piperidine and pyrrolidine.

Scheme I

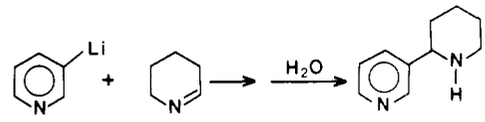


Cyclic imines **1** and **2** can be generated from cyclic

1 2

N-chloramine precursors by reaction with potassium superoxide in ether solution. The solution then can simply be filtered and added dropwise to a solution of excess organolithium. Reaction appears to be immediate at room temperature so that after the addition of a minimum amount of water and subsequent drying of the ether solution, the product can be isolated by distillation. The overall reaction scheme is shown in Scheme I. The yields of 2-alkyl- and 2-arylpiperidines range from 44 to 63% based on the amount of *N*-chloropiperidine used. All attempts to isolate *N*-chloropyrrolidine resulted in its rapid, exothermic decomposition. Thus it was necessary to carry out the reaction without isolation of the chloramine. The yields of 2-substituted pyrrolidines reported here are therefore lower (25–29%). However, if we assume that the yield of *N*-chloropyrrolidine generated in situ is comparable to that of the isolated yield of *N*-chloropiperidine (60%), then the yields of 2-substituted pyrrolidines compare favorably with those of the piperidines. Grignard reagents give no noticeable alkylation or arylation of the cyclic imines under similar conditions.

One of the most interesting applications of our reaction involves the synthesis of the tobacco alkaloid *dl*-anabasine (**7**) or 2-(3′-pyridyl)piperidine (see eq 1). 3-Pyridyllithium



1 7 (1)

is usually generated by metal–halogen exchange between 3-bromopyridine and *n*-butyllithium at low temperature. However, the yields of anabasine are only about 10% when this method is used. The majority of material formed is considerably higher boiling than anabasine. When *tert*-butyllithium is used for the metal–halogen exchange at −120 °C and **1** added to the resulting slurry of pyridyllithium at −100 °C, the yield rises significantly to 44%, and very little high-boiling material is produced. We suspect that the *n*-butyl bromide formed when *n*-butyllithium is used alkylates the piperidide anion but that *tert*-butyl bromide undergoes elimination.

In examining the factors which limit the yields to about 50%, we found that when **1** is the limiting reagent and is added to an excess of *n*-butyllithium, a yield of 58% is obtained. Since the dehydrohalogenation of 40 mmol of *N*-chloropiperidine usually takes about 8 h, we suspected that trimerization accounted for a significant decrease in yield under these conditions. We therefore attempted to quantitate it by allowing a 0.4 M solution of *N*-chloropiperidine to react with KO_2 for 8 h. After removal of the KO_2 by filtration the ether solution was concentrated under vacuum with slight warming. The residue, piperideine trimer, which crystallized overnight, accounted for 35% of the theoretical amount of piperideine formed.

(1) Presented in part before the Division of Organic Chemistry at the 178th National Meeting of the American Chemical Society, Washington, DC, Sept 9–14, 1979.

(2) F. E. Scully, Jr., and R. C. Davis, *J. Org. Chem.*, **43**, 1467 (1978).

0022-3263/80/1945-1515$01.00/0

Unreacted chloramine does not account for much, if any, of this residue as determined in a separate experiment which measured the amount of chloramine remaining at the end of an 8-h reaction. This suggests that when the organolithium is in excess, the most serious hindrance to the yield of this reaction is trimerization.

The five- and six-membered cyclic imines, Δ^1-piperideine (1) and 1-pyrroline (2), possess interesting synthetic potential in their monomeric form. In solution these imines slowly trimerize,[3-6] but the elegant work of Schöpf and others has shown that α-tripiperideine is a stable shelf reagent that can be used as a precursor for the condensation of 1 or 2 with ester enolates in alcohol solutions.[3-7] However, we have found that the trimer is not suitable for reaction with organometallics in ether solvents and that stirring piperideine trimer with *n*-butyllithium in ether–hexane for 60 h gave less than a 2% yield of 2-butylpiperidine and approximately 80% recovery of pure unreacted trimer.

This observation is not unexpected in light of Schöpf's report that detrimerization is catalyzed by acid.[3] Although the detrimerization is slow in basic solution, it appears that as long as the solvent is protic it will occur. Thus, piperideine trimer is a suitable precursor for the condensation of 1 with ester enolates in alcoholic solvents but is inert in ether solvent.

We attempted to reduce the amount of trimerization by reducing the reaction time and therefore used 1 equiv of crown ether instead of a catalytic amount. However, the reaction time monitored by the loss of the yellow superoxide color was not significantly affected.

In preparation for the synthesis of more complex piperidine alkaloids, we examined the conditions necessary to optimize the yield of this reaction when the organolithium compound is the limiting reagent. In this case the order of addition significantly affects the product yields. For example, when *n*-butyllithium is added to excess 1, the yield of butylpiperidine drops to 34%. We believe the developing solution of the highly basic piperidide anion is enhancing formation of the inert trimer. By contrast, when excess 1 is added to the *n*-butyllithium, the yield returns to the value typically observed (54%).

Syntheses of 2-substituted piperidines and pyrrolidines have commonly involved two approaches: (a) cyclization of an appropriately constructed acyclic precursor and (b) alkylation of a pyridine or pyrrole followed by reduction of the aromatic heterocycle. Many of these methods suffer from too many steps, lack of generality, or low yields. We have presented here a new, general, and simple approach to the synthesis of these compounds that involves C-alkylation of the corresponding cyclic imine precursors in fair yield. We believe this approach will prove valuable in the total synthesis of larger piperidine and pyrrolidine alkaloids.

Experimental Section

General Methods. NMR spectra were recorded on a Varian T-60 in $CDCl_3$ or CCl_4 and are reported in δ units (parts per million) relative to tetramethylsilane. High-resolution mass spectra were recorded by the Mass Spectroscopy Center of the Chemistry Department, Purdue University, on a CEC 21-100B mass spectrometer and exact mass measurements determined by the peak-matching technique. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer. Melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected. The purity of samples was determined on a Varian Model 920 gas chromatograph with a thermal conductivity detector. A 10 ft × $^1/_4$ in. column of 10% SE-30 on acid-washed Chromosorb W was used from 120 to 160 °C at a helium flow rate of 85 mL/min both for purity determination and for purification of samples. Anhydrous ethyl ether (Mallinckrodt) was used freshly opened without futher drying or was distilled from benzophenone ketyl. Aldrich 18-crown-6 ether and piperidine were used as received. Pyrrolidine (Eastman) was distilled from calcium hydride before use. Potassium superoxide (Alfa, used as received) was stored and weighed in a drybox (phosphorus pentoxide). *n*-Butyllithium (1.5 M in hexane, Aldrich) and *tert*-butyllithium (1.2 M in pentane, Aldrich) were stored in a refrigerator and used under an atmosphere of dry nitrogen. Phenyllithium was prepared in ether from bromobenzene (Fisher, used as received) and lithium wire (Fisher). Aldrich 3-bromopyridine was distilled from calcium hydride prior to use and *tert*-butyl hypochlorite was prepared by the method of Mintz and Walling.[8]

***N*-Chloropiperidine.** A variation of the method of Bachmann et al.[9] as detailed elsewhere by us[2] was used to prepare ether solutions (0.5–2 M) of *N*-chloropiperidine. After the solution was dried, it was filtered and concentrated at atmospheric pressure by using a 20-cm Vigreaux column until the distillation head reached a temperature of 42 °C. The solution was cooled before a vacuum was applied, and concentration was continued until the head temperature reached 58 °C at 46 mm. The solution was cooled again and the Vigreaux column replaced with a short-path distillation column. Pure *N*-chloropiperidine was collected in about 60% yield at 62–64 °C (46 mm) and stored below 0 °C in the dark over a small amount of anhydrous potassium carbonate until it was used.

Solutions of Δ^1-Piperideine (1). Solutions of 0.4–1.5 M *N*-chloropiperidine were used to prepare solutions of 1. In a typical experiment, the chloramine (4.84 g, 40 mmol) in 100 mL of anhydrous ether and 18-crown-6 ether (100 mg) were slurried with potassium superoxide (6.16 g, 87 mmol) for 9 h, during which the yellow color of the KO_2 faded to a beige. The solution of 1 was filtered before addition to the appropriate organolithium.

2-*n*-Butylpiperidine (4). A 250-mL three-necked flask was fitted with a dropping funnel, reflux condenser, nitrogen inlet, drying tube, and Teflon stirring bar. The apparatus was flame-dried, cooled, and charged with *n*-butyllithium (53 mL of a 1.5 M solution, 80 mmol). A 0.4 M solution of 1 prepared from the chloramine (4.84 g, 40 mmol) in 100 mL of ether was added dropwise with stirring at ambient temperature over 40 min. When addition was complete, the solution was stirred an additional 30 min and the reaction quenched cautiously with water (2 mL). The ether was decanted, dried, filtered, and concentrated at atmospheric pressure through a 20-cm Vigreaux column. 2-*n*-Butylpiperidine was distilled through a micro distilling head and 3.28 g collected at 106–112 °C (52 mm). VPC analysis showed it to be 97% pure (58% yield of pure material). Preparative VPC provided a pure sample: NMR ($CDCl_3$) δ 3.3–2.0 (m, 3), 2.0–1.6 (m, 16); IR (neat) 3400 (w), 2950, 1440, 1325, 1115, 735 cm^{-1}; mass spectrum, *m/e* 141.152 (M^+, calcd for $C_9H_{19}N$, 141.151); hydrochloride, mp 178–180 °C (lit.[10] mp 181–182 °C).

2-Phenylpiperidine (6). Phenyllithium (80 mmol) was prepared from lithium metal (1.17 g, 170 mmol) and bromobenzene (12.56 g, 80 mmol) in ether (200 mL) at reflux in a flask fitted as above. After the mixture cooled, a 0.4 M solution of 1 prepared from the chloramine (4.84 g, 40 mmol) in 100 mL of ether was added dropwise with stirring at ambient temperature over 30 min. The reaction was treated as above, and 3.73 g of 2-phenylpiperidine was distilled at 112–117 °C (7 mm). NMR analysis showed that it contained 5% biphenyl (55% yield of pure material). After removal of the biphenyl by extraction into 20% aqueous hydrochloric acid, followed by basification and reex-

(3) C. Schöpf, A. Komnak, F. Braun, E. Jacobi, M. L. Borgmuth, M. Bullnheimer, and I. Hagel, *Justus Liebigs Ann. Chem.*, **559**, 1 (1948).
(4) D. W. Fuhlhage and C. A. VanderWerf, *J. Am. Chem. Soc.*, **80**, 6249 (1958).
(5) J. Quick and R. Oterson, *Synthesis*, 745 (1976).
(6) J. M. Grisar, G. P. Claxton, and K. T. Stewart, *Synthesis*, 284 (1974).
(7) D. Bender, L. Bjeldanes, D. Knapp, and H. Rapoport, *J. Org. Chem.*, **40**, 1264 (1975).
(8) M. J. Mintz and C. Walling, *Org. Synth.*, **49**, 9 (1969).
(9) W. E. Bachmann, M. P. Cava, and A. S. Drieding, *J. Am. Chem. Soc.*, **76**, 5554 (1954).
(10) K. Löffler and P. Plöcker, *Chem. Ber.*, **40**, 1310 (1907).

traction into ether, pure 2-phenylpiperidine was isolated by preparative VPC: NMR ($CDCl_3$) δ 7.35 (s, 5, aromatic), 3.8–2.5 (m, 3), 2.05–1.25 (m, 7); IR (neat) 3350 (w), 2950, 1440, 1100, 750, 695; mass spectrum, *m/e* 161.120 (M^+, calcd for $C_{11}H_{15}N$, 161.120).

Solutions of 1-Pyrroline (2). Solutions of 1-pyrroline were prepared by reacting freshly distilled pyrrolidine (2.84 g, 40 mmol) with *tert*-butyl hypochlorite in ether (100 mL) by the method of Bachmann et al. as detailed elsewhere by us.[2] *N*-Chloropyrrolidine was not isolated, but its ether solution was slurried with potassium superoxide (6.25 g, 88 mmol) and 18-crown-6 ether (80 mg) for 9 h. The solution was filtered before addition to the appropriate organolithium.

2-*n*-Butylpyrrolidine (3). A solution of *n*-butyllithium (53 mL of a 1.5 M solution, 80 mmol) was introduced into a flask fitted as described in the synthesis of **4**. A solution of 1-pyrroline prepared as described above was added dropwise with stirring at ambient temperature over 30 min. The reaction was treated as in the usual manner, and 1.41 g of 2-butylpyrrolidine was distilled at 65–72 °C (18 mm) VPC analysis showed that it contained 10% hexane (25% yield of pure material). Preparative VPC provided pure sample: NMR ($CDCl_3$) δ 3.2–2.6 (m, 3), 2.1–1.7 (complex m, 14); IR (neat) 3300, 2900, 1460, 1400; mass spectrum, *m/e* 127.137 (M^+, calcd for $C_8H_{17}N$, 127.136).

2-Phenylpyrrolidine (5). Phenyllithium (60 mmol) was prepared from bromobenzene and lithium metal in ether at reflux in a flask fitted as described in the synthesis of **4**. After the solution of phenyllithium was cooled, a solution of 1-pyrroline (prepared as above from 30 mmol of pyrrolidine) was added in the usual manner. The reaction mixture was treated as in the synthesis of **4** to yield 2.22 g of 2-phenylpyrrolidine (58% pure by NMR, contained biphenyl as the impurity): bp 98–100 °C (2.5 mm); 29% yield of pure material. Preparative VPC provided a pure sample: NMR ($CDCl_3$) δ 7.35 (m, 5), 4.12 (t, 1), 3.40–2.73 (m, 2), 2.40–1.42 (m, 5); IR (neat) 3300, 2950, 1600, 1480, 1440, 1060, 1020, 750, 695; mass spectrum, *m/e* 147.105 (M^+, calcd for $C_{10}H_{13}N$, 147.105); picrate, mp 150–151 °C (lit.[11] mp 148–149 °C).

***dl*-Anabasine (7).** 3-Pyridyllithium was prepared by the dropwise addition over 1 h of 3-bromopyridine (12.6 g, 80 mmol) in ether (100 mL) to *tert*-butyllithium (66 mL of a 1.2 M solution in pentane, 80 mmol) in ether (100 mL) under a nitrogen atmosphere in a −120 °C bath [pentane–2-propanol–acetone (4:1:1), liquid N_2]. The resulting yellow slurry was stirred an additional 0.5 h before a solution of piperideine (40 mmol) in ether (125 mL) was added dropwise over 1 h at −100 °C. The mixture was stirred an additional 0.5 h before warming over 1 h to −40 °C. Water (15 mL) was added dropwise with stirring, and the reaction mixture warmed rapidly to room temperature with a warm-water bath. The ether was decanted, and 2 mL of a 50% aqueous KOH solution was added to the residue which was then extracted with ether (20 mL, three times). After the ether extracts were combined with the product mixture and the ether dried over anhydrous sodium sulfate and concentrated, the residue was distilled, and 2.96 g of 97% pure *dl*-anabasine was collected at 100–112 °C (2 mm) (44% yield of pure material by NMR). Preparative VPC provided a pure sample: NMR ($CDCl_3$) δ 8.51 (m, 2), 7.73 (dt, 1), 7.22 (dd, 1) 3.62 (m, 1), 3.42–2.46 (m, 2), 2.12–1.0 (m, 7); IR (neat) 3300, 2940, 1570, 1420, 1310, 1100, 1020, 710; mass spectrum, *m/e* 162.115 (M^+, calcd for $C_{10}H_{14}N_2$, 162.115).[12]

2-*tert*-Butylpiperidine (8). A 0.36 M solution of **1** in ether prepared from *N*-chloropiperidine (4.84 g, 40 mmol) was added dropwise to a solution of *tert*-butyllithium in pentane (1.2 M, 80 mmol) at −80 °C. After the mixture was stirred for 1 h, water (10 mL) was added dropwise over 10 min and the mixture warmed to room temperature with a warm-water bath. The product mixture was filtered and dried over anhydrous sodium sulfate. After filtration the solution was concentrated at atmospheric pressure through a 6-in. Vigreaux column. When the head temperature reached 160 °C, the Vigreaux head was removed, and the product (3.74 g) was distilled with a microcondenser and collected from 168 to 175 °C (lit.[13] bp 173–174 °C). VPC analysis showed it to be 95% pure (63% yield). Preparative VPC provided a pure sample. The spectra were identical with those of 2-*tert*-butylpiperidine prepared by the method of Grundon and Reynolds:[13] NMR (CCl_4) δ 3.40–0.94 (m, 10), 0.86 (s, 9); IR (neat) 3350 (w), 2950, 1470, 1430, 1350, 1320, 1190, 1110, 1050, 857, 842, 747; mass spectrum, *m/e* 141.154 (M^+, calcd for $C_9H_{19}N$, 141.152); hydrochloride, mp 257–259 °C.[14]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corp. for the support of this research. We are grateful to Professor R. Graham Cooks and the Mass Spectroscopy Center of the Chemistry Department, Purdue University, for providing us with high- and low-resolution mass spectra of the compounds described here and to Dr. Michael Lusch of Polaroid Corp. for many helpful discussions.

Registry No. 1, 505-18-0; 2, 5724-81-2; 3, 3446-98-8; 4, 72939-22-1; 4·HCl, 72939-23-2; 5, 1006-64-0; 5 picrate, 1689-55-0; 6, 3466-80-6; 7, 13078-04-1; 8, 72939-24-3; 8·HCl, 72939-25-4; *N*-chloropiperidine, 2156-71-0; bromobenzene, 108-86-1; pyrrolidine, 123-75-1; 3-bromopyridine, 626-55-1.

(11) S. Gabriel and J. Colman, *Chem. Ber.*, **41**, 513 (1908).

(12) NMR and IR spectra were identical with those of an authenic sample. We are grateful to Dr. Edward Sanders of the Philip Morris Research Center for providing us with spectra for comparison.

(13) M. F. Grundon and B. E. Reynolds, *J. Chem. Soc.*, 2445 (1964).

(14) The melting point of the hydrochloride reported by Grundon and Reynolds[13] is 229–232 °C. We have repeated their synthesis and found a melting point for the hydrochloride (acetone) of 257–259 °C.

New Synthesis of (±)-Menthofuran[1]

Sadao Tsuboi, Kazuo Shimozuma, and Akira Takeda*

Department of Synthetic Chemistry, School of Engineering, Okayama University, Tsushima, Okayama 700, Japan

Received September 13, 1979

Syntheses of menthofuran, one of the important aromatics, have been carried out by many groups.[2a-k] They mostly used naturally occuring pulegone or isopulegone as a starting material. Wenkert et at.[2j] synthesized (±)-menthofuran in about 18% overall yield in five steps from ethyl 4-methyl-2-oxo-1-cyclohexanecarboxylate (**1**),[3] via the thermal interaction of dimethyl diazomalonate with 1-methoxy-5-methyl-1-cyclohexene, which was derived from **1** as a key intermediate. Overall yields of menthofuran in these procedures appear to be no higher than 20%. For example, Zalkow et al.[2g] prepared optically pure (+)-menthofuran from pulegone by a two-step sequence in about 20% yield. Bedoukian [2b] also obtained (+)-menthofuran via pulegenol sulfonic ester[2a] in 20% yield. In this paper, we wish to report a new synthesis of (±)-menthofuran, in about 45% overall yield in a three-step sequence from **1**, via the direct C-alkylation with ethyl 2-iodopropionate. The reaction sequence of the present

(1) Presented in part at the 22nd Symposium on the Chemistry of Terpenes, Essential Oils, and Aromatics, the Chemical Society of Japan, Yokohama, Oct 1978.

(2) (a) W. Treibs, *Chem. Ber.*, **70**, 85 (1937); (b) P. Z. Bedoukian, *J. Am. Chem. Soc.*, **70**, 621 (1948); (c) W. Treibs, G. Jucivs, H. Kogler, and H. Breslander, *Justus Liebigs Ann. Chem.*, **581**, 59 (1953); (d) H. Fritel and P. Baranger, *C. R. Hebd. Seances Acad. Sci.*, **241**, 674 (1955); (e) H. Fritel and M. Fetizon, *J. Org. Chem.*, **23**, 481 (1958); (f) H. Stetter and R. Lauterbach, *Chem. Ber.*, **93**, 603 (1960); (g) L. H. Zalkow, J. W. Ellis, and S. M. R. Brennan, *J. Org. Chem.*, **28**, 1705 (1963); (h) L. H. Zalkow and J. W. Ellis, *ibid.*, **29**, 2626 (1964); (i) K. Ohkata, T. Sakai, Y. Kubo, and T. Hanafusa, *J. Chem. Soc., Chem. Commun.*, 581 (1974); (j) E. Wenkert, M. E. Alonso, B. L. Buckwalter, and K. J. Chou, *J. Am. Chem. Soc.*, **99**, 4778 (1977); (k) B. Harirchian and P. D. Magnus, *Synth. Commun.*, **7**, 119 (1977).

(3) C. Djerassi, J. Burakevich, J. W. Chamberlin, D. Elad, T. Toda, and G. Stork, *J. Am. Chem. Soc.*, **86**, 465 (1964).

0022-3263/80/1945-1517$01.00/0