was heated under reflux for 16 h under a dry nitrogen atmosphere. The reaction mixture was cooled, quenched with ice–water, neutralized with aqueous sodium bicarbonate, and extracted with dichloromethane (2 × 50 mL). The combined organic extracts were washed with saturated sodium thiosulfate solution and dried over anhydrous magnesium sulfate. The solvent was evaporated and the crude product chromatographed on a silica gel column with hexane. Removal of the solvent afforded *p*-tolyl disulfide as a colorless crystalline solid (1.25 g, 96%) mp 48 °C (lit.[7] mp 48 °C).

Reduction of *p*-Chlorobenzenesulfonyl Chloride to *p*-Chlorophenyl Disulfide with BF_3/I^-. A mixture of *p*-chlorobenzenesulfonyl chloride (2.0 g, 9.5 mmol) and potassium iodide (16.7 g, 100 mmol) in 1,2-dichloroethane (30 mL) was placed in a high-pressure stainless-steel bomb (125-mL capacity). The bomb was charged with boron trifluoride gas (Matheson) to a pressure of 1000 psi and the reaction mixture shaken at 80 °C for 16 h. The bomb was cooled, boron trifluoride was vented, and the reaction mixture quenched with ice–water. Workup and purification as described above yielded *p*-chlorophenyl disulfide (1.3 g, 95%) as a colorless crystalline solid, mp 72 °C (lit.[7] mp 73 °C).

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

Registry No. Benzenesulfonyl chloride, 98-09-9; 4-methylbenzenesulfonyl chloride, 98-59-9; 4-bromobenzenesulfonyl chloride, 98-58-8; 4-chlorobenzenesulfonyl chloride, 98-60-2; 4-methylbenzenesulfonyl fluoride, 455-16-3; methyl 4-methylbenzenesulfonate, 80-48-8; 4-methylbenzenesulfonic acid, 104-15-4; 2-methylbenzenesulfonic acid, 88-20-0; benzenesulfonic acid, 98-11-3; Ag(I) 4-methylbenzenesulfonate, 16836-95-6; butanesulfonic acid, 2386-47-2; propanesulfonic acid, 5284-66-2; diphenyl disulfide, 882-33-7; bis(4-methylphenyl) disulfide, 103-19-5; bis(4-bromophenyl) disulfide, 5335-84-2; bis(4-chlorophenyl) disulfide, 1142-19-4; bis(2-methylphenyl) disulfide, 4032-80-8; dibutyl disulfide, 629-45-8; dipropyl disulfide, 629-19-6; BI_3, 13517-10-7; BCl_3, 10294-34-5; BBr_3, 10294-33-4; KI, 7681-11-0; TBAI, 311-28-4.

(7) Reid, E. E. "The Organic Chemistry of Bivalent Sulfur"; Chemical Publishing Company, Inc.: New York, 1960.

Elimination Reactions in 1-Amino-2-phenylhexahydroazepine Derivatives

Stanley Wawzonek* and Jan Michael Shradel[1]

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242

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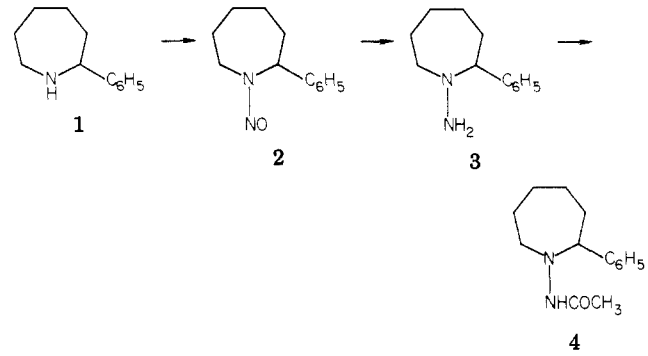
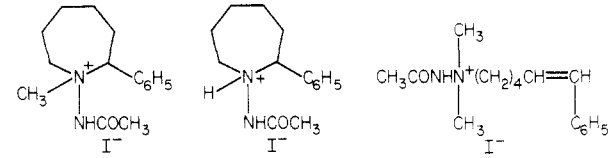
Aminimides derived from 2-phenylpyrrolidine[2] and 2-phenylpiperidine[3] upon being heated undergo ring expansion to the phenylhexahydropyridazine and phenylhexahydrodiazepine derivatives, respectively, and cleavage to the corresponding amine and isocyanate. Studies aimed at extending this reaction to the 2-phenylperhydroazepine series reveal a different behavior which is reported here.

The reaction sequence used for preparation of the key intermediate **4** paralleled that used for the homologues. The next reaction, which involved treating 1-acetamino-2-phenylperhydroazepine (**4**) with methyl iodide, did not give the desired 1-acetamino-1-methyl-2-phenylperhydroazepinium iodide (**5**) but yielded instead 1-(acetyl-



1 2 3 4

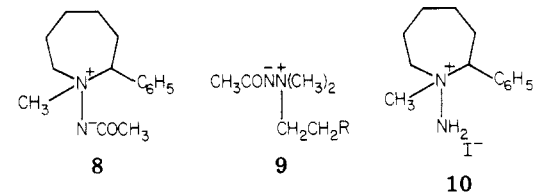
amino)-2-phenylperhydroazepine hydroiodide (**6**) and 1-



5 6 7

acetyl-2,2-dimethyl-2-(6-phenyl-5-hexenyl)hydrazinium iodide (**7**). The structure of the hydroiodide **6** was shown by its synthesis from **4**, and that of **7** was based on its IR and NMR spectra. The coupling constant of 16 Hz for the olefinic protons suggested trans stereochemistry about the double bond.

These results indicated that methylation of **4** occurred normally and that the resulting salt **5** was converted by **4** into the hydroiodide **6** and the desired aminimide (**8**).



8 9 10

This product (**8**) is not stable at the boiling point of acetonitrile but undergoes elimination and forms 1-acetyl-2-methyl-2-(6-phenyl-5-hexenyl)hydrazine which upon methylation gave the salt **7**, which was isolated. None of the rearranged product from the aminimide **8**, 1-methyl-2-acetyl-3-phenylperhydro-1,2-diazocine,[4] or fragmentation product 1-methyl-2-phenylperhydroazepine were detected among the reaction products.

Eliminations have been reported with aminimides of type **9** in the alicyclic series, usually at the melting point of the compound.[5] The facile elimination observed in the present work is unusual since the five- and six-membered homologues are isolable and show little propensity for elimination. A possible explanation for this behavior is the ability of the seven-membered ring to attain the proper stereochemical relationship for intramolecular elimination. Assuming that the perhydroazepine ring system will not differ greatly from cycloheptane, a twisted chair form[6] would be the preferred arrangement over other alternatives. An axial acetamino group in the 1-position would allow excellent overlap of a hydrogen on the 3-carbon by the carbonyl group.

An intramolecular process has likewise been proposed to explain the facile elimination observed with 1-methyl-

(1) Abstracted in part from the Ph.D. Thesis of J.M.S.
(2) S. Wawzonek and R. C. Gueldner, *J. Org. Chem.*, **30**, 3031 (1965).
(3) S. Wawzonek and J. G. Stephanie, *J. Org. Chem.*, **36**, 2467 (1971).
(4) S. Wawzonek and J. M. Shradel, *J. Org. Chem.*, **45**, 5216 (1980).
(5) D. G. Morris, B. W. Smith, and R. J. Wood, *Chem. Commun.*, 1134 (1968).
(6) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).

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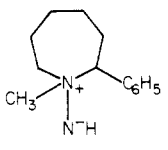
perhydroazepine *N*-oxide; thermolysis at 165 °C caused the Cope elimination and production of the unsaturated hydroxylamine. *N*-Methylpiperidine oxide, on the other hand, was stable up to 215 °C where it decomposed explosively.[7]

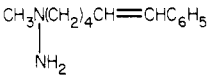
A Hoffmann-type elimination on 8 cannot be completely excluded. Studies[8] of the reaction of *N,N*-dimethyl cyclic ammonium ions with sodium methoxide have shown that ring-opening elimination is greatly enhanced in the seven-membered ring over that found for the five- and six-membered rings.

The facility with which elimination occurred with the aminimide 8 suggested that acetonitrile may lower the energy of activation for this reaction. This concept could not be tested since an attempt to methylate 1-(acetylamino)-2-phenylperhydroazepine (4) at room temperature was not successful. Periodic monitoring by NMR of a mixture of methyl iodide and 4 showed no reaction after 115 h.

Other methods tried for preparing the aminimide 8 were dependent upon reactions of 1-amino-1-methyl-2-phenylperhydroazepinium iodide (10) which was prepared by methylation of the amine 3 and occurs as a mixture of two geometric isomers. This salt (10) was not affected by acetic anhydride at 25 and 85 °C. The reaction with ethyl acetate in the presence of potassium *tert*-butoxide likewise caused no acetylation. Infrared and NMR spectra of the reaction product indicated that both elimination and rearrangement involving the aminimine 11 had occurred and



11



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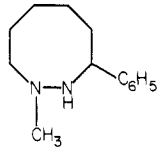

13

formed 1-methyl-1-(6-phenyl-5-hexenyl)hydrazine (12) and 1-methyl-3-phenylperhydro-1,2-diazocine (13) in a 12/13 ratio of 1:1.4. No attempt was made to separate 12 from 13.

Rearrangement and elimination in aminimines in the alicyclic series[9,10] also occurs.

Experimental Section

NMR spectra were obtained by using tetramethylsilane as an internal standard with a Varian-A60 NMR spectrometer. IR spectra were recorded with a Perkin-Elmer Infracord spectrometer. Melting points and boiling points are not corrected.

1-Nitroso-2-phenylperhydroazepine (2). A solution of 2-phenylperhydroazepine (1; 45 g, 0.026 mol)[11] in a mixture of glacial acetic acid (45 mL) and 2 N hydrochloric acid (130 mL) was cooled in an ice bath and treated dropwise with a solution of sodium nitrite (23.8 g, 0.33 mol) in water (400 mL) at a rate which maintained the temperature between 0 and 5 °C. The reaction mixture was stirred for 6 h at 0 °C and 12 h at room temperature. Extraction with methylene chloride gave, after washing with water and sodium bicarbonate solution and removal of the solvent, 53.1 g of a yellow oil. Distillation at reduced pressure gave 47.6 g (0.23 mol, 88.5%) of 1-nitroso-2-phenylperhydroazepine (2): bp 138 °C (0.02 mm); n^{20}_D 1.5602; IR (neat) 6.96 (NO), 14.3 (C_6H_5) μm; NMR ($CDCl_3$) δ 0.76–5.00 (m, 10 H, 3,4,5,6,7-CH_2), 5.30–6.00 (m, 1 H, 2-CH), 6.95–7.48 (m, 5 H, aromatic H's); mass spectrum, *m/e* 204 (M^+).

Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.89; N, 13.71. Found: C, 70.74; H, 7.74; N, 13.77.

This compound may be a carcinogen.

1-Amino-2-phenylperhydroazepine (3). A mixture of lithium aluminum hydride (7.5 g) and ether (300 mL) was treated with a small amount of a solution of 1-nitroso-2-phenylperhydroazepine (2, 27.1 g) in ether (50 mL). After an induction period of 1 h the remainder of the solution was added dropwise over 2.5 h, and the resulting reaction mixture was heated at reflux for 16.5 h. The reaction mixture was treated with ether (100 mL) and sequentially with water, 6 N sodium hydroxide, and water. The ether layer upon removal of the solvent gave 1-amino-2-phenylperhydroazepine (3): 22.0 g; bp 102–105 °C (0.7 mm); n^{20}_D 1.5474; IR (neat) 2.98, 3.13 (NH_2), 14.23 (C_6H_5) μm; NMR ($CDCl_3$) δ 1.07–2.22 (m, 8 H, 3,4,5,6-CH_2), 2.90 (s, 2 H, NH_2), 2.40–3.50 (m, 3 H, 2-CH, 7-CH_2), 7.0–7.51 (m, 5 H, 3 H, 2-CH, 7-CH_2), 7.02–7. 51 (m, 5 H, aromatic H's), singlet at δ 2.90 underwent exchange with D_2O; mass spectrum, *m/e* 190 (M^+).

Anal. Calcd for $C_{12}H_{18}N_2$: C, 75.74; H, 9.54; N, 14.72. Found: C, 75.62; H, 9.53; N, 14.72.

1-(Acetylamino)-2-phenylperhydroazepine (4). The amine 3 (15.0 g) in benzene (70 mL) was treated with a solution of acetic anhydride (8.4 g) in benzene (40 mL) dropwise with cooling over a period of 1.3 h. The resulting solution was stirred at 0 °C for 1.7 h and at room temperature for 15.5 h. Neutralization of the acetic acid with sodium bicarbonate was followed by separation of the benzene layer. Removal of the benzene gave a solid which was recrystallized from hexane: yield 14.5 g; mp 81.5–83 °C; IR (Nujol) 3.07 (NH), 6.00 (CO), 14.21 (C_6H_5) μm; NMR ($CDCl_3$) δ 1.17–2.30 (m, 8 H, 3,4,5,6-CH_2), 1.50, 1.72 (2 s, 3 H, CH_3CO), 2.87–3.43 (m, 2 H, 7-CH_2), 3.43–4.45 (2 m, 1 H, 2-CH), 7.00–7.53 (m, 5 H, aromatic H's), 7.70 and 8.12 (br absorptions, 1 H, NH), last absorptions underwent exchange with D_2O; mass spectrum, *m/e* 232 (M^+).

Anal. Calcd for $C_{14}H_{20}N_2O$: C, 72.38; H, 8.68; N, 12.06. Found: C, 72.13; H, 8.56; N, 11.94.

Reaction of 1-(Acetylamino)-2-phenylperhydroazepine (4) with Methyl Iodide. A solution of 1-(acetylamino)-2-phenylperhydroazepine (4, 2.70 g) and methyl iodide (5.1 mL) in acetonitrile (25 mL) was heated at reflux under nitrogen for 49 h. Thin-layer chromatography of the resulting solution with silica gel and ethyl acetate indicated the presence of two major components and a small amount of the starting material. The reaction mixture gave after concentration and addition of ether a light yellow solid (3.44 g). Recrystallization from a mixture of acetonitrile and absolute ether gave 1.27 g of 1-(acetylamino)-2-phenylperhydroazepine hydroiodide (6): mp 158–159 °C dec; IR (Nujol) 3.23 (NH), 5.88 (CO), 14.26 (C_6H_5) μm; NMR (Me_2SO) δ 1.32–2.48 (m, 9 H, 3,4,5,6-CH_2), 1.73 (s, 3 H, CH_3CO), 3.40–3.98 (m, 2 H, 7-CH_2), 4.48–4.90 (m, 1 H, 2-CH), 7.18–7.75 (m, 5 H, aromatic), 10.60–11.33 (br s, 2 H, CONHN$^+$H, exchangeable with D_2O).

Anal. Calcd for $C_{14}H_{21}IN_2O$: C, 46.68; H, 5.88; N, 7.78. Found: C, 46.83; H, 5.91; N, 7.85.

The filtrate from the above recrystallization was evaporated to dryness, and the resulting gummy residue upon recrystallization from a mixture of isopropyl alcohol and ether gave 1.47 g of 1-acetyl-2,2-dimethyl-2-(6-phenyl-5-hexenyl)hydrazinium iodide (7): mp 100–101 °C; IR (Nujol) 3.20 (NH), 5.82 (CO), 14.35 (C_6H_5) μm; NMR ($CDCl_3$) δ 1.23–2.04 (m, 4 H, $(CH_2)_2$, 6 H, $(CH_3)_2N^+$), 4.03–4.57 (m, 2 H, N^+CH_2), 6.17 (dt, 1 H, olefinic, J_{ab} = 16 Hz, J_{bx} = 6 Hz), 6.57 (d, 1 H, olefinic, J_{ab} = 16 Hz, J_{ax} = 6 Hz), 7.07–7.67 (m, 5 H, C_6H_5), 10.40–10.93 (br s, 1 H, CONH–N^+).

Anal. Calcd for $C_{16}H_{25}IN_2O$: C, 49.49; H, 6.49; N, 7.21. Found: C, 49.58; H, 6.61; N, 7.20.

The original filtrate from the iodides was found to contain 0.1 g of starting material. None of the rearrangement product from the intermediate aminimide, 1-methyl-2-acetyl-3-phenyloctahydro-1,2-diazocine,[4] or the cleavage product 1-methyl-2-phenylperhydroazepine[12] was found.

(7) A. C. Cope and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 4656 (1960).
(8) G. Cerichelli, G. Illuminati, and C. Lillocci, *J. Org. Chem.*, **45**, 3952 (1980).
(9) P. A. S. Smith and G. L. DeWall, *J. Am. Chem. Soc.*, **99**, 5791 (1977).
(10) Y. Tamura, J. Minamikawa, O. Nishikawa, and M. Ikada, *Chem. Pharm. Bull.*, **22**, 1202 (1974).
(11) S. Wawzonek and J. M. Shradel, *Org. Prep. Proced. Int.*, **9**, 281 (1977).
(12) W. Carruthers and R. A. W. Johnstone, *J. Chem. Soc.*, 1653 (1965).

°C and identical with the sample isolated in the methylation studies.

1-Amino-1-methyl-2-phenylperhydroazepinium Iodide (10). A solution of 1-amino-2-phenylperhydroazepine (3, 7.24 g) in acetonitrile (20 mL) was heated at reflux with methyl iodide (5 mL) for 17 h under nitrogen. Removal of the solvent gave a solid which was recrystallized from absolute ethanol: yield 3.55 g; mp 165–167 °C; IR (Nujol) 3.07, 3.18 (NH), 14.16 (C_6H_5) μm; NMR ($CDCl_3$–Me_2SO-d_6) δ 1.50–2.50 (m, 8 H, 3,4,5,6-CH_2), 3.07, 3.29 (2 s, 3 H, CH_3), 3.67–4.48 (m, 2 H, 7-CH_2), 4.85–5.33, (m, 1 H, 2-CH), 5.45–5.87 (br singlets, 2 H, NH_2), 7.32–7.90 (m, 5 H, C_6H_5). The singlets at δ 5.45 and 5.87 underwent slow exchange with D_2O.

Studies on the Acetylation of 1-Amino-1-methyl-2-phenylperhydroazepinium Iodide (10). (A) The iodide 10 was not affected by heating with acetic anhydride in acetonitrile for 6 h.

(B) The iodide 10 (2.66 g) was heated under nitrogen with ethyl acetate (0.71 g) and potassium *tert*-butoxide (0.90 g) in *tert*-butyl alcohol (50 mL) at 85–90 °C for 42 h. The resulting reaction mixture was filtered, and the filtrate upon removal of the solvent gave a yellow oil which distilled at 117–120 °C (0.5 mm); yield 0.34 g. The product, on the basis of its IR and NMR spectra, appeared to be a mixture of 1-methyl-1-(6-phenyl-5-hexenyl)-hydrazine (12) and 1-methyl-3-phenylperhydro-1,2-diazocine (13) in a ratio of 1:1.4: IR (neat) 3.05 (weak), 3.27, 3.41, 3.51, 3.58, 5.93 (weak), 6.23, 6.68, 6.79, 6.96, 7.40, 8.35, 9.35, 9.81, 9.97, 10.36, 11.45, 12.02, 13.10, 13.45, 13.85, 14.27 μm; NMR ($CDCl_3$) δ 1.17–2.00 (m, 10.3 H, CH_2, NH, NH_2, CH_2N, $CH_2C{=}C$), 2.00–3.00 (m, 10.3 H, CH_2, NH, NH_2, CH_2N, $CH_2C{=}C$), 2.40 (s, 3 H, NCH_3), 4.02 (t, 0.7 H, CHC_6H_5, J = 5 Hz), 6.13 (dt, 0.5 H, olefinic, J = 15, 6 Hz), 6.44 (d, 0.5 H, olefinic, J = 15 Hz), 7.00–7.62 (m, 5 H, aromatic).

The absorptions in the IR fingerprint region (8.35, 9.35, 9.81, 9.97, 11.45, 12.02, 13.10, 13.85, and 14.27 μm) were identical with those found for an authentic sample of 13.[4] The triplet in the NMR spectrum at δ 4.02 (J = 5 Hz) for the benzylic proton of 13 occurs at the same point as that reported in the spectrum of an authentic sample.[4]

Registry No. 1, 3466-82-8; 2, 77153-75-4; 3, 77153-76-5; 4, 77153-77-6; 6, 77153-78-7; (*E*)-7, 77153-79-8; 10, 77153-80-1; 12, 77172-41-9; 13, 49868-87-3.

Ring Opening of Cyclopropyl Ketones by Trimethylsilyl Iodide

Robert D. Miller* and Dennis R. McKean

IBM Research Laboratory, San Jose, California 95193

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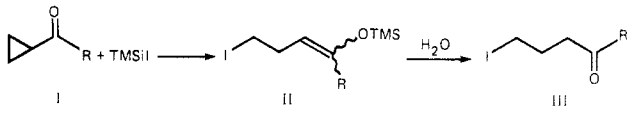
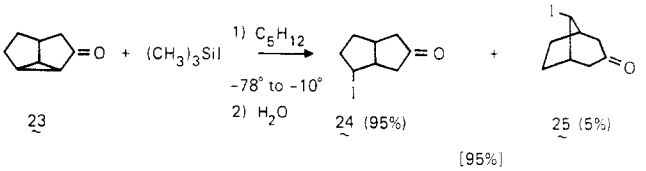
Recent advances in the generation of three-membered rings have led to the steadily increasing usage of cyclopropyl derivatives as reagents for organic synthesis.[1] In this respect, the nucleophilic ring opening of electron-deficient cyclopropane derivatives has received considerable attention and has been recently reviewed.[2] Similarly, the acid-catalyzed ring opening of cyclopropylcarbinyl alcohols has also been successfully employed for the synthesis (often stereoselective) of a variety of useful olefin derivatives.[3]

Scheme I



Scheme II



Unlike the ring opening of cyclopropyl ketones and esters by nucleophiles which usually requires diactivation, a number of electrophilically initiated ring openings of monofunctional cyclopropyl derivatives have been reported.[4] These have traditionally employed acidic reagents and often require reaction conditions which are not compatible with sensitive functionality. In addition, the regioselectivity of the ring opening, particularly in polycyclic systems, is somewhat unpredictable and may be a sensitive function of reaction conditions, structure, substituents, etc.[4h] Nevertheless, in spite of the many uncertainties, the electrophilic ring opening of cyclopropyl carbonyl derivatives has been successfully utilized in a number of natural product syntheses.[5]

Trimethylsilyl iodide (Me_3SiI) is a highly electrophilic reagent of considerable synthetic importance.[6] The reactivity of this reagent with α,β-unsaturated enones[6f] suggested that cyclopropyl ketones could be similarly transformed to generate either γ-iodo ketones or the corresponding iodotrimethylsilyl enol ethers (see Scheme I), depending on the reaction conditions. We describe here in some detail the general utility of this reagent for the former purpose.

The ring opening which proceeds rapidly under very mild conditions ultimately generates the corresponding γ-iodo ketones upon hydrolytic workup (Table I).[7,8] In-

(1) (a) Seebach D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239. (b) de Meijere, A. *Ibid.* **1979**, *18*, 809.

(2) Danishefsky, S. *Acc. Chem. Res.* **1979**, *12*, 66.

(3) (a) Julia, M.; Julia, S.; Guegan, R. *Bull. Soc. Chem. Fr.* **1960**, 1072. (b) Julia, M.; Julia, S.; Tchen, S.-Y. *Bull. Soc. Chem. Fr.* **1961**, 1849. (c) Brady, S. F.; Ilton, M. A.; Johnson, W. S. *J. Am. Chem. Soc.* **1968**, *90*, 2882. (d) Miller, R. D.; McKean, D. R.; Kaufmann, D. *Tetrahedron Lett.* **1979**, 587. (e) Descoins, C.; Samain, D. *Ibid.* **1976**, 745. Olah, G. A.; Schleyer, P. v. R. "Carbonium Ions"; Vol. III, Wiley-Interscience: New York, 1972; Vol. 3, p 1201 ff.

(4) (a) Stork, G.; Grieco, P. A. *Tetrahedron Lett.* **1971**, 1807. (b) Dasgupta, S. K.; Sarma, A. S. *Ibid.* **1973**, 309. (c) Nakai, T.; Wada, E.; Okawara, M. *Ibid.* **1975**, 1531. (d) Ruppert, J. F.; White, J. D. *J. Chem. Soc., Chem. Commun.* **1976**, 976. (e) Walz, W.; Habermehl, G. *Z. Naturforsch.* **1976**, *31b*, 983. (f) Tunemoto, D.; Kondo, K. *Yuki Gosei Kagaku Kyoksishi* **1977**, *35*, 1070 and references cited therein. (g) Tardella, P.; Bello, N.; Pellacani, L. *Synthesis* **1978**, 227. (h) Caine, D.; Boucugnani, A.; Chu, C.-Y. *Tetrahedron Lett.* **1978**, 2667. (i) Giacomini, E.; Loreto, M. A.; Pellacani, L.; Tardella, P. A. *J. Org. Chem.* **1980**, *45*, 519. (j) Demuth, M.; Raghavan, P. R. *Helv. Chim. Acta* **1979**, *62*, 2338.

(5) (a) Mongrain, M.; LaFontaine, J.; Belanger, A.; Deslongchamps, P. *Can. J. Chem.* **1970**, *48*, 3273. (b) White, J. D.; Torii, S., Nogami, J., *Tetrahedron Lett.* **1974**, 2879. (c) McCurry P. M., Jr.; *Tetrahedron Lett.* **1971**, 1845.

(6) (a) Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761. (b) Jung, M. E.; Andrus, W. A.; Ornstein, P. L. *Tetrahedron Lett.* **1977**, 4175. (c) Ho, T.-L.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 774. (d) Jung, M. E.; Lyster, M. A. *J. Chem. Soc., Chem. Commun.* (1978), 315. (e) Miller, L. L.; Stewart, R. F. *J. Org. Chem.* **1978**, *43*, 3078. (f) Miller, R. D.; McKean, D. R. *Tetrahedron Lett.* **1979**, 2305.

(7) Consistent spectral data were obtained for all compounds. The iodo ketones were reduced by using tri-*n*-butyltin hydride for comparison with authentic samples. Satisfactory analytical and/or high-resolution mass spectroscopic data were obtained for new compounds or suitable derivatives.

(8) Under these reactions conditions, simple cyclopropylcarboxylic acid esters were unreactive. Reactivity was, however, observed for diactivated esters such as 1,1-dicarbethoxycyclopropane and 6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione, which yielded the expected iodo esters in good yield after 6–48 h at 25 °C.

(9) Under the stated conditions, less than 5% of 4-iodocyclohexanone was produced (NMR analysis). When the Me_3SiI was added at higher temperatures (i.e., 25 °C), the ring opening became slightly less regioselective.

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