and other 8-fluoropurines,[2g] are readily hydrolyzed in dilute acid.

Since both 3(5)-nitro-1,2,4-triazoles and certain 8-nitropurines[7] are readily available, this method should provide a general route to the corresponding fluoro heterocycles.

Experimental Section

Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. Nmr spectra were recorded at 60 MHz for ^{1}H and at 56.4 MHz for ^{19}F with a Hitachi Perkin-Elmer R20A spectrometer in DMSO-d_6 solutions. Analytical data were determined by Galbraith Laboratories, Inc., Knoxville, Tenn.

General Procedure.—The nitro heterocycle (20 mmol) was heated with excess (*ca.* 30 ml) liquid hydrogen fluoride in a Monel or Teflon-lined bomb under the conditions given in Table I. At the end of the reaction the bomb was cooled and volatile material was removed under a stream of nitrogen. The residue was dried in a plastic vacuum desiccator over potassium hydroxide pellets. The products were crystallized directly or in some cases were purified by chromatography over silica gel as follows. The crude product (2 g) was dissolved in methanol, and silica gel (10 g) was added to the solution. The mixture was evaporated to dryness under reduced pressure and the silica gel mixture was slurried in chloroform and applied to a small silica gel column packed in chloroform. Elution with chloroform containing 1–10% methanol provided the pure products.

Completion of the reaction and purity of the products were determined by tlc on silica gel using 9:1 chloroform–methanol. The nitro compounds and the purines were visualized under a uv light. The fluoro-1,2,4-triazoles were detected as purple spots by spraying the tlc plate first with a 1% solution of *tert*-butyl hypochlorite[8] in cyclohexane, drying the plate at room temperature, and then spraying with potassium iodide–starch solution.

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(7) J. W. Jones and R. K. Robins, *J. Amer. Chem. Soc.*, **82**, 3773 (1960).

(8) Available as Unispray Aerosol Reagent from Nutritional Biochemicals Corp.; this reagent detects NH compounds.

Communications

See Editorial, *J. Org. Chem.*, **37**, No. 13, 4A (1972).

Synthesis of 1-Hydroxybicyclo[*n*.1.0]alkanes from Silyl Alkenyl Ethers. A Novel Class of Cyclopropanols[1]

Summary: The reaction of trimethylsilyl cycloalkenyl ethers (1) with Simmons–Smith reagent gave the corresponding silyl cyclopropyl ethers (2), which on hydrolysis afforded 1-hydroxybicyclo[*n*.1.0]alkanes (3, $n = 3$–5) which are a novel class of cyclopropanols having the hydroxy groups at the bridgehead carbon.

Sir: Very recently Rubottom and Lopez have reported in this journal[2] the synthesis of silyl cyclopropyl ethers and cyclopropanols by the reaction of silyl alkenyl ethers with Simmons–Smith reagent. This note has prompted us to disclose our results on the synthesis of 1-hydroxybicyclo[*n*.1.0]alkanes. The synthetic method is operationally simpler and much more useful than one might evaluate it from the result of Rubottom and Lopez.

Although there has been a good deal of interest in the chemistry of cyclopropanols,[3] little has been known about 1-hydroxybicyclo[*n*.1.0]alkanes, which are a novel class of cyclopropanols having the hydroxy group at the bridgehead carbon. Aside from having intrinsic interest, this class of cyclopropanols is important as the intermediate in the Clemmensen reduction of difunctional ketones[4] and in some other rearrangements.[5] Only several isolated examples of more highly substituted, but not the parent, 1-hydroxybicyclo[*n*.1.0]alkanes have been reported in the literature,[6] except those described by Rubottom and Lopez[2] which will be mentioned later. Although a wide variety of methods have been developed for the synthesis of cyclopropanols,[3,7] most of them are not suitable or inherently not applicable for the synthesis of such cyclopropanols as 1-hydroxybicyclo[*n*.1.0]alkanes.[8]

We have now established that the transformation shown in eq 1 is an exceedingly convenient way of

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(1) Synthesis *via* Silyl Alkenyl Ethers. IV. For part III see S. Murai, Y. Kuroki, K. Hasegawa, and S. Tsutsumi, *J. Chem. Soc., Chem. Commun.*, 946 (1972). A part of this work has been presented at the Symposium on Small Ring Compounds, Oct 1972, Nagoya, Japan.

(2) G. M. Rubottom and M. I. Lopez, *J. Org. Chem.*, **38**, 2097 (1973).

(3) C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968); U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **7**, 588 (1968); H. H. Wasserman, R. E. Cochoy, and M. S. Baird, *J. Amer. Chem. Soc.*, **91**, 2375 (1969); H. H. Wasserman, H. W. Adickes, and O. E. de Ochoa, *ibid.*, **93**, 5586 (1971); B. A. Howell and J. G. Jewett, *ibid.*, **93**, 798 (1971); P. v. R. Schleyer, W. F. Sliwinski, G. W. VanDine, U. Schöllkopf, J. Paust, and K. Fellenberger, *ibid.*, **94**, 125 (1972); W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *ibid.*, **94**, 133 (1972); J. R. Salaün and J. M. Conia, *Tetrahedron Lett.*, 2849 (1972); C. H. DePuy, H. L. Jones, and W. M. Moore, *J. Amer. Chem. Soc.*, **95**, 478 (1973).

(4) B. R. Davis and P. D. Woodgate, *J. Chem. Soc.*, 5943 (1965); E. Wenkert and E. Kariv, *Chem. Commun.*, 570 (1965); J. G. St. C. Buchanan and P. D. Woodgate, *Quart. Rev.*, **23**, 522 (1969).

(5) R. H. Eastman and A. V. Winn, *J. Amer. Chem. Soc.*, **82**, 5908 (1960); W. von E. Doering, M. R. Willcott, III, and M. Jones, Jr., *ibid.*, **84**, 1224 (1962); W. F. Erman, R. S. Treptow, P. Bakuzis, and E. Wenkert, *ibid.*, **93**, 657 (1971); M. L. Rueppel and H. Rapoport, *ibid.*, **94**, 3877 (1972).

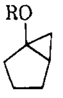
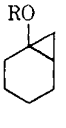
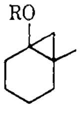
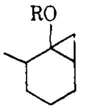
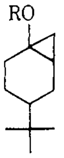
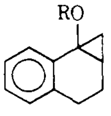
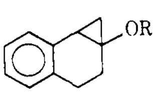
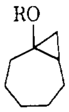
(6) (a) A. J. Birch and R. Keeton, *Aust. J. Chem.*, **24**, 331 (1971); (b) J. F. Templeton and W. Wie, *Tetrahedron Lett.*, 3955 (1971); (c) W. Reusch and D. P. Priddy, *J. Amer. Chem. Soc.*, **91**, 3677 (1969); (d) P. S. Venkataramani, J. E. Karoglan, and W. Reusch, *ibid.*, **93**, 269 (1971); (e) I. T. Harrison, R. J. Rawson, P. Turnbull, and J. H. Fried, *J. Org. Chem.*, **36**, 3515 (1971); (f) J. V. Paukstelis and J. Kao, *J. Amer. Chem. Soc.*, **94**, 4784 (1972).

(7) J. L. Magrane, Jr., and D. L. Cottle, *J. Amer. Chem. Soc.*, **64**, 484 (1942); J. P. Freeman, *J. Org. Chem.*, **29**, 1379 (1964); H. H. Wasserman and D. C. Clagett, *Tetrahedron Lett.*, 341 (1964), and *J. Amer. Chem. Soc.*, **88**, (1966); D. T. Longone and W. D. Wright, *Tetrahedron Lett.*, 2859 (1969); H. C. Brown and S. P. Rhodes, *J. Amer. Chem. Soc.*, **91**, 4306 (1969); R. Köster, S. Arora, and P. Binger, *Angew. Chem., Int. Ed. Engl.*, **8**, 205 (1969); C. H. DePuy and R. A. Klein, *Org. Syn.*, **47**, 108 (1967); U. Schöllkopf, J. Paust, and M. R. Patsch, *ibid.*, **49**, 88 (1969).

(8) Two interesting approaches to substituted 1-hydroxybicyclo[4.1.0]-heptanes starting from alkyl enol ethers have been reported. In these studies, tetrahydropyranyl[6a] and β-chloroethyl[6b] groups were employed as the "removable" alkyl groups.

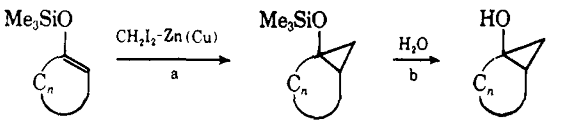
TABLE I

SYNTHESIS OF SILYL CYCLOPROPYL ETHERS AND CYCLOPROPANOLS ·

	Silyl cyclopropyl ethers (R = $SiMe_3$)[a]			Cyclopropanols (R = H)[b]				
Structure	Compd	Bp, °C (mm)[c]	Yield, %	Compd	Bp, °C (mm)[c] [mp, °C][c]	Ir, cm^{-1} [d]	Nmr, δ[e]	3,5-DNB mp, °C[f]
	**2a**	66–68 (13)	76	**3a**	63–65 (20)	3280 3080	0.41–2.27 (9 H), 3.05 (1 H)[g]	131–132
	**2b**	84–87 (17)	71	**3b**	55–56 (4)	3300 3090	0.05–0.30 (1 H), 0.55–2.60 (10 H), 4.32 (1 H)[g]	113–115
	**2c**	72–75 (7)	78	**3c**	71–73 (8)	3300 3060	0.37 (2 H), 0.85–2.60 (11 H),[h] 3.80 (1 H)[g]	144–145
	**2d**[i]	78–85 (6)	64[j]	**3d**[i]	76–79 (9)	3280 3050	0.00–2.50 (13 H),[k] 3.87 (1 H)[g]	129–147[i]
	**2e**[i]	120–123 (12)	80	**3e**[i]	77–78 (0.5)	3300 3080	0.57–0.85 (1 H), 0.95–3.10 (18 H),[l] 4.57 (1 H)[g]	114–132[i]
	**2f**	139–143 (16)	58	**3f**	[106.5–107.5][m]	3350	0.90–2.92 (7 H), 2.60 (1 H),[g] 7.03–7.93 (4 H)	102–104
	**2g**	82–86 (0.2)	64[j]	**3g**	93–94 (0.2)	3300	0.85–1.26 (2 H), 1.56–2.73 (5 H), 4.36 (1 H),[g] 6.68–7.18 (4 H)	136–138
	**2h**	97–99 (16)	77	**3h**	[47–48.5][n]	3200 3100	0.03–0.37 (1 H), 0.50–2.50 (12), 3.58 (1 H)[g]	131–132

[a] Complete spectral characterization and elemental composition confirm the structural assignment. [b] Yields of the hydrolysis of **2** to **3** were quantitative. Satisfactory microanalytical data were obtained for the cyclopropanols and/or their 3,5-dinitrobenzoates. [c] Melting and boiling points were not corrected. [d] Neat liquid except for **3f** and **3h** (Nujol). The characteristic bands for hydroxy groups and cyclopropyl hydrogens are listed. [e] In CCl_4 except for **3f** ($CDCl_3$). [f] 3,5-Dinitrobenzoates were recrystallized from a water–acetone mixture. [g] Disappeared by D_2O addition. [h] Includes a singlet at 1.18 (CH_3). [i] Mixture of ~1:1 cis and trans isomers, based on nmr. [j] For complete cyclopropanation, the reaction was repeated twice. [k] The spectra of the mixture of isomers exibited a singlet at 0.08 and two overlapping doublets at 1.02 and 1.12 (CH_3). [l] Includes two singlet at 0.81 and 0.82 [$(CH_3)_3C$]. [m] Recrystallized from benzene–hexane. [n] Sublimed at 25° (0.2 mm).

synthesizing 1-hydroxybicyclo[*n*.1.0]alkanes (**3**, *n* = 3–5). The trimethylsilyl alkenyl ethers **1** can be readily



1, $n = 3$-5 **2** **3** (1)

prepared from the corresponding ketones[9] and have electron-rich double bonds for carbenoid addition to give the silyl cyclopropyl ethers **2**, which then can be easily hydrolyzed to **3** under mild conditions without opening the acid- and base-sensitive cyclopropane ring of the products **3**.[10] Difficulty may be encountered in step a for the corresponding reaction of enol esters and in step b in the case of alkyl enol ethers.[8]

The general experimental procedure is as follows. To a suspension of zinc-copper couple[12] (0.09 mol) in anhydrous ether (110 ml) were added methylene iodide (0.08 mol) and **1** (0.05 mol). The mixture was maintained at reflux for 40 hr and worked up[13] to give **2** of

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(9) (a) Yu. I. Baukov and I. F. Lutsenko, *Organometallic Chem. Rev. A*, **6**, 355 (1970); (b) H. O. House, L. J. C. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).

(10) Recently, the use of trimethylsilyl group in the synthesis of a cyclopropanol has been reported by Denis and Conia.[11] They prepared 1,1′-dihydroxydicyclopropyl from 2,3-bis(trimethylsiloxy)butadiene (i), which was obtained by pyrolysis of 1,2-bis(trimethylsiloxy)cyclobutene. Independently, we had obtained the same result, but were able to prepare the diene i more conveniently from biacetyl (unpublished work). See also ref 2.

(11) J. M. Denis and J. M. Conia, *Tetrahedron Lett.*, 4593 (1972).

(12) R. J. Rawson and I. T. Harrison, *J. Org. Chem.*, **35**, 2057 (1970).

(13) The solution was filtered and washed successively with cold aqueous NH_4Cl, aqueous $NaHCO_3$, and water and then dried and distilled. It is desirable to remove zinc salts by washing with NH_4Cl, while treatment with hydrochloric acid has resulted in the decomposition of **2**.

high purity (Table I). In this reaction, the amount of the solvent (*i.e.*, the reactant to ether ratio) is very important. When the Simmons-Smith reaction was carried out using the smaller amount of the solvent (*i.e.*, under higher concentration) a considerable amount of the isomer[14] of **2** was also formed. For hydrolysis to **3**, **2** (0.01 mol) was added to a mixture of methanol (30 ml) and 0.1 *N* aqueous sodium hydroxide (3 ml), and the mixture was stirred for 30 min at room temperature, evaporated under reduced pressure, taken up with ether, and dried. Removal of the ether left the practically pure **3** in quantitative yields (Table I). These cyclopropanols **3** are reasonably stable when they are pure. They remained unchanged for a few days at room temperature and can be distilled under reduced pressure. Boiling points of **3** are shown in Table I. However, they isomerize to the corresponding α-methyl ketones when heated above $\sim$130°, dissolved in solvents, or treated with acid.[15] Therefore, it is recommended that they are best stored at the stage of stable compounds **2** and generated just before use. This is one of the principal advantages of the present method.

Rubottom and Lopez have reported very recently the similar synthesis of silyl cyclopropyl ethers **2b** and **2f** as well as cyclopropanols **3b** and **3f**.[2] However, on the work up of the Simmons-Smith reaction mixture, as well as on the hydrolysis of **2** to **3**, they treated the mixture with hydrochloric acid,[13] a reagent which, as we have observed, rapidly decomposes **2** or **3**. Consequently, they did not obtain **2** in a pure form and chromatographic separation was required. Moreover, they have described no physical constants for all compounds which they reported except the melting point of **3f**, 100–104°, whose wide range may show insufficient purity compared with that of ours, mp 106.5–107.5°. We have also synthesized 1-phenylcyclopropanol, bp 119–121° (26 mm), and 1-*tert*-butylcyclopropanol, bp 90–92° and mp 36–37°, the cyclopropanols reported in their paper[2] without any physical data.

It should be noted that the present synthesis may suggest that various types of cycloaddition reactions of **1** will provide new synthetic methods for preparing alcohols. In addition, because of high reactivity of **2** toward electrophilic reagents, **2** is also promising synthetic intermediate. For example, the reaction of **2** with bromine gave the corresponding α-bromomethyl ketones quantitatively.[16] Further study of the chemical properties of **3**, as well as those of **2**, is in progress.

Acknowledgment.—We wish to thank Emeritus Professor Shigeru Tsutsumi for his helpful discussions and encouragement. We are also grateful to Shin-Etsu Chemical Industry Co., Ltd., for providing the trimethylsilyl choloride.

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[14] The isomers were found to be the trimethylsilyl ethers of 2-methylenecycloalkanols. Details will be reported in the near future.

[15] NOTE ADDED IN PROOF.—A recent report describes the conversion of silyl cyclopropyl ethers to α-methyl ketones and also to a steroidal cyclopropanol which has a 1-hydroxybicyclo[4.1.0]heptane structure; see J. M. Conia and C. Girard, *Tetrahedron Lett.*, 2767 (1973).

[16] Unpublished work.

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