127–128.5°, $[\alpha]^{20}D$ +51° (*c* 2.00, chloroform). The mixture melting point with authentic cholestan-2-one (mp 130–131°, $[\alpha]^{23}D$ +51°) was undepressed. Tlc alongside authentic **6** gave a single spot with the same R_f 0.35 when developed in reagent grade chloroform.

Registry No.—**1**, 1452-34-2; pyridine, 110-86-1; γ-picoline, 108-89-4; β-picoline, 108-99-6; α-picoline, 109-06-8; 2,4-lutidine, 108-47-4; 2,6-lutidine, 108-48-5; γ-collidine, 108-75-8; γ-picolinium salt of **1**, 10294-04-9; **5**, 2042-01-5.

Chromic Acid Oxidation of *endo*-5,6-Trimethylenenorbornyl Alcohols

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Solvolysis studies of the tosylate esters of the *endo*-5,6-trimethylenenorbornane[1] system have recently been the subject of much interest.[2] In connection with this work, comparisons of nonbonded interactions being relieved by movement of the oxygen atom would be of value. Some of these ground-state interactions which could be relieved in the transition state assuming a decrease in steric strain have been estimated,[2a] but not experimentally evaluated. If the chromic acid oxidation of these alcohols behaves normally, that is, if the rate is increased by greater steric strain in the ground state, then this should permit an evaluation of free-energy differences.[3,4] The rates of oxidation are given in Table I.

Table I

Chromic Acid Oxidation Rates (25.0° in 75% Acetic Acid and 0.1 *M* Perchloric Acid)

Alcohol	$k_2 \times 10^2$, l. mole^{-1} sec^{-1}	Relative rate
exo-2-Norbornanol	4.08	1.00
endo-2-Norbornanol	26.4	6.47
endo-5,6-Trimethylene-*exo*-2-norbornanol (**1**)	8.43	2.07
endo-5,6-Trimethylene-*endo*-2-norbornanol (**2**)	1270	311
exo-5,6-Trimethylene-*exo*-2-norbornanol (**3**)	4.43	1.09
exo-5,6-Trimethylene-*endo*-2-norbornanol (**4**)	35.8	8.77
Cyclopentanol	4.03	1.00
endo-5,6-Trimethylene-*exo*-8-norbornanol (**5**)	4.93	1.22
endo-5,6-Trimethylene-*endo*-8-norbornanol (**6**)	124	30.8
endo-5,6-Trimethylene-*exo*-9-norbornanol (**7**)	9.33	2.31
endo-5,6-Trimethylene-*endo*-9-norbornanol (**8**)	7.22	1.79

The results indicate that the oxidation rates are normal. *endo*-5,6-Trimethylene-*endo*-2-norbornanol (**2**) is oxidized 151 times faster than its epimer (**1**), representing a Δ*F* difference of 3.0 kcal/mole. *endo*-Trimethylene-*endo*-2-norbornanol (**2**) is oxidized 48 times faster than *endo*-2-norbornanol. We believe that this difference is due almost entirely to steric effects corresponding to a free-energy difference of 2.3 kcal/mole. Comparison of **3** with *exo*-2-norbornanol shows that the inductive effect of the *exo*-trimethylene bridge is negligible and comparison of **4** with *endo*-2-norbornanol shows only a very slight rate increase, part of which may be due to greater rigidity of the *endo*-5,6-hydrogens because of the attached trimethylene ring. There are reactions where *exo* and *endo* substituents have different effects,[5] but the considerably lower value of the ρ expected here[6] and the relatively poor electron-donating ability of the uncharged methylene groups should lead to very small differences. *endo*-5,6-Trimethylene-*endo*-8-norbornanol (**6**) is oxidized 25 times faster than its less strained epimer (**5**), which corresponds to a free-energy difference of 1.9 kcal/mole. Comparison of the epimers **7** and **8** shows that there is essentially no difference in their ground-state nonbonded interactions.

Comparison of **1** with *exo*-2-norbornanol and **5** with cyclopentanol shows that, as steric strain becomes greater on the methine hydrogen, the rate becomes more rapid with the ease of approach of solvent apparently playing no major role in determining the rate of oxidation.[7] The rate of **7** is 1.89 times faster than **5**. This was unexpected because both steric and inductive effects would have predicted the opposite result. Possibly this is due to conformational differences. In summary, the results with one exception of minor magnitude appear to be self-consistent and to provide experimental evaluation of the ground-state differences due to nonbonded interactions. In the compounds where comparisons can be made, the experimental values are in reasonable agreement with the values previously estimated.[2a]

Experimental Section

The alcohols are known compounds and the properties agreed with those reported in the literature.[2a,e,f,8]

Rate studies were carried out using essentially the procedure of Stewart and Lee[9] in 75% acetic acid and 0.10 *M* in perchloric acid. Treatment of the slope of a plot of Cr(VI) concentration *vs.* time by the procedure of Benson[10] for second-order reactions with stoichiometric concentration yielded the rate constants. The rate plots all gave straight lines up to 70% of reaction. All

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[1] The nomenclature used is described by P. v. R. Schleyer and M. M. Donaldson [*J. Am. Chem. Soc.*, **82**, 4645 (1960)] and in ref 2a.

[2] (a) H. C. Brown, I. Rothberg, P. v. R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1653 (1966); (b) H. C. Brown, "Chemistry in Britain," Vol. 2, 1966, p 199; (c) J. A. Berson, in "Molecular Rearrangements," Part 1, P. DeMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3; (d) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966); (e) P. D. Bartlett and R. S. Barnes, Abstracts of the 12th National Organic Symposium of the American Chemical Society, June 1951, p 1; (f) K. Takeuchi, T. Oshika, and Y. Koga, *Bull. Chem. Soc. Japan*, **38**, 1318 (1965); (g) M. M. Donaldson, Ph.D. Thesis, Princeton University, Princeton, N. J., 1958; *Dissertation Abstr.*, **22**, 738 (1961); (h) P. v. R. Schleyer, Ph.D. Thesis, Harvard University, Boston, Mass., 1956.

[3] For discussion of the use of chromic acid oxidations as a measure of free-energy differences, see (a) E. L. Eliel, S. H. Schroeter, T. J. Brett, F. J. Biros, and J. C. Richer, *J. Am. Chem. Soc.*, **88**, 3327 (1966); (b) J. C. Richer and C. Gilardeau, *Can. J. Chem.*, **43**, 538 (1965); (c) C. F. Wilcox, M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, **28**, 1079 (1963); (d) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, pp 81–85.

[4] For an example of abnormal behavior, see ref 3d, p 271.

[5] H. Kwart and L. J. Miller, *J. Am. Chem. Soc.*, **83**, 4552 (1961).

[6] A ρ value of −1.06 was found by J. Rocek [*Collection Czech. Chem. Commun.*, **25**, 1052 (1962)] for an aliphatic system where the distance separating reaction site from substituents was shorter than in our compounds.

[7] For discussion on the mechanism of chromic acid oxidation, see (a) K. B. Wiberg in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, Chapter 2; (b) R. Stewart, "Oxidation Mechanisms," W. A. Benjamin Inc., New York, N. Y., 1964, Chapter 4.

[8] H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **67**, 723 (1945); S. J. Cristol, W. K. Seifert, and S. B. Soloway, *ibid.*, **82**, 2351 (1960).

[9] R. S. Stewart and D. G. Lee, *Can. J. Chem.*, **42**, 439 (1964).

[10] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 20.

rates were run at least in duplicate and many in triplicate. The average deviations were less than 6% with one exception. The rapid rate of oxidation of **2** led to experimental difficulties and here the average deviation was 10%. In addition, relative rates were run on a preparative scale using a modification of the Brown and Garg oxidation procedure[11] comparing **1** and **3** with *exo*-2-norbornanol and **5** with **8**. In all cases, the relative rates were in good agreement with the results reported and the products checked by vapor phase chromatography (vpc) were present in high yield with no rearrangement.

Registry No.—**1**, 10271-42-8; **2**, 10271-43-9; **3**, 10271-44-0; **4**, 10271-45-1; **5**, 10271-46-2; **6**, 10271-47-3; **7**, 10271-48-4; **8**, 10271-49-5; *exo*-2-norbornanol, 497-37-0; *endo*-2-norbornanol, 497-36-9; cyclopentanol, 96-41-3.

Acknowledgment.—The authors are grateful to the Rutgers Research Council for financial support.

[11] H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

Fluorocarbon Nitrogen Compounds. XII. Catalytic Perfluoroalkylation of Halotriazines[1]

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Perfluoro olefins react with carbonyl fluoride in the presence of fluoride ion to give perfluoroacyl fluorides and perfluoro ketones.[2] Compounds containing fluorine atoms whose reactivity is comparable to that of an acid fluoride, in structures otherwise inert toward fluoride ion, should undergo analogous reactions. The halotriazines are in some respects similar to acid halides, and fluorotriazines readily undergo fluoride-catalyzed reaction with polyfluoro compounds containing carbon–carbon or carbon–nitrogen unsaturation.

Cyanuric fluoride, heated under autogenous pressure with perfluoropropene and cesium fluoride at 100° for 12 hr, was converted almost quantitatively (>90%) to a mixture of mono-, bis-, and tris(perfluoroisopropyl)-triazines, easily separable by fractionation. Although three compounds were formed, the reaction could be directed toward any one of the three by altering the reactant ratio. With a $C_3F_6:(CNF)_3$ ratio of approximately 2:1, the ratio of mono-, di-, and trisubstitution products was 8:10:1, while a reactant ratio of 1:1.25 led to a product ratio of 28:6:1.

All of the products showed the characteristic triazine absorption band near 1550 cm^{-1}. Both the complexity of this band and its intensity relative to absorption by the $(CF_3)_2CF$ groups decreased with increasing degree of substitution. In nuclear magnetic resonance (nmr) spectra, chemical shifts for the ring fluorine, the CF_3 of $(CF_3)_2CF$ and the CF of $(CF_3)_2CF$ were, respectively, 30.4–30.6, 74.4–75.4, and 183.8–186.5 ppm upfield from $CFCl_3$, as perfluoroisopropyl groups were added. Fine structure and area ratios for the three different types of fluorine were consistent with the assigned structures.

Functionally active perfluoroalkyl side chains can be introduced into a triazine ring in the same manner, as long as these functions are inert to fluoride ion. Perfluoroallyl cyanide, made by dehalogenation of $CF_2ClCFClCF_2CN$, reacted under the same conditions with a slight excess of 2,4-bis(perfluoroisopropyl)-6-fluoro-*s*-triazine to give a 62% yield of perfluoro-[2-(β-cyanoisopropyl)-4,6-diisopropyl]triazine.

Compounds containing unsaturation other than carbon–carbon can also be utilized. Perfluoro-2-azapropene ($CF_3N{=}CF_2$) reacted with cyanuric fluoride in a manner entirely analogous to that of perfluoropropene and produced a mixture of mono-, bis-, and tris(perfluorodimethylamino)-substituted triazines, a 2:1 $CF_3N{=}CF_2:(CNF)_3$ ratio giving a product ratio of 1:2:1. Infrared spectra showed the same sequential behavior of the 1550-cm^{-1} band as with the perfluoroisopropyl series; in the monosubstituted compound this band was a multiplet, in the disubstituted compound a doublet, and in the symmetrical trisubstituted compound a singlet. Nmr spectra showed peaks for the $(CF_3)_2N$ and ring fluorine atoms at 55.1, 55.0, and 32.4, 32.9 ppm, relative to $CFCl_3$, for the mono- and disubstituted compounds, while the trisubstituted compound showed only a 55.2-ppm peak. Area ratios for (side chain:ring) fluorine were in the correct ranges, 6:2 and 12:1, respectively. As was the case with the perfluoroisopropyl series, the trisubstituted compound was a low-melting solid.

Physical constants of the substituted triazines are given in Table I.

A fluorine atom on an aromatic or heterocyclic ring must apparently be fairly labile for the alkylation to succeed. Neither perfluorobenzene nor bromopentafluorobenzene reacted with either $CF_3CF{=}CF_2$ or $CF_3N{=}CF_2$ when heated in the presence of cesium fluoride, either alone or in acetonitrile solution, at temperatures up to 175°. It is possible that the *p*-fluorine atom in nitropentafluorobenzene might be reactive enough to permit alkylation, although this compound was not investigated. Cyanuric chloride could probably be substituted for cyanuric fluoride, since the former is converted to the latter by alkali metal fluorides, although this technique would obviously require the use of sufficient fluoride for both halogen exchange and catalysis.

The carbanion reaction mechanism advanced by Smith[2] to explain the carbonyl fluoride–olefin reactions seems consistent with the present results as well. Attack of fluoride ion on the terminal carbon atom of the unsaturated group would lead to a branch at the α carbon (or nitrogen) of the substituent group in the substituted triazine, as has been observed in every case.

Experimental Section

Perfluoroalkylation of Cyanuric Fluoride.—Cesium fluoride (50 g) was dried in an autoclave at 200–300° overnight under continuous evacuation. The bomb was cooled and loaded by vacuum transfer with 45 g (0.33 mole) of cyanuric fluoride and 87.5 g (0.58 mole) of hexafluoropropene, then sealed and rocked at 100° for 16 hr.

The cooled bomb was vented into an evacuated system, giving <1 g of volatile material. The crude product was decanted and the residual solid extracted with Freon 113, 126 g (95%) of the

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[1] Presented in part at the 150th National Meeting of the American Chemical Society, New York, N. Y., Sept 12–16, 1966. Previous paper: J. A. Young and R. L. Dressler, *J. Org. Chem.*, in press.

[2] R. D. Smith, F. S. Fawcett, and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 4285 (1962).