**Supplementary Material Available.** Chlorination of ethylbenzene with 1% $PCl_5$ at 30 °C with room light (Table III) and 1% peroxide (Table IV) and (α-chloroethyl)benzene and (α-chloroethyl)toluene with 1% $PCl_5$ at 40 °C with room light (Tables V and VIII) (2 pages). Ordering information is given on any current masthead page.

## References and Notes

(1) Dow Chemical, U.S. Patent 3 732 321, May 8, 1973.

(2) Euteco, U.S. Patent Applied 852 764, Nov. 18, 1977; British Patent 792 860, April 2, 1958; U.S. Patent, 2 780 604, Feb. 5, 1957.

(3) (a) B. Fell, *Angew. Chem., Int. Ed. Engl.*, **4**, 522 (1965); (b) B. Fell and L. H. Kung, *Chem. Ber.*, **98** (9), 2871 (1965); *Chem. Abstr.*, **63**, 13018 (1965).

(4) D. P. Wyman, J. Y. Wang, and W. R. Freeman, *J. Org. Chem.*, **28**, 3173 (1963).

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(6) G. A. Russel, A. Ito, and D. G. Hendry, *J. Am. Chem. Soc.*, **85**, 2976 (1963).

(7) C. Walling and N. F. Mayahi, *J. Am. Chem. Soc.*, **81**, 1485 (1959), have found the following relative selectivities in normal butyl chloride and butane:

$$\begin{array}{ccc} CH_3\text{–}CH_2\text{–}CH_2\text{–}CH_3 & \qquad & CH_3\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}Cl \\ 1^a \quad 3.8 \quad 3.8 \quad 1^a & & 1^a \quad 3.8 \quad 1.8 \quad 0.6 \end{array}$$

[a] Arbitrary assumed value.

(8) H. G. Haring and H. W. Knoll, *Chem. Process Eng. (London)*, **46**, 38 (1965); **45**, 560–690 (1964).

(9) G. A. Russel, *Free Radicals 1973*, **1**, 293 (1973), discusses the polar effect in chlorination of para- and meta-substituted alkylbenzenes.

(10) G. A. Olah and T. R. Hokswender, Jr., *J. Org. Chem.*, **38**, 3478 (1973), have acknowledged increased yields of anti-Markownikoff HBr addition, catalyzed by $PBr_3$, while using an olefin not previously purified of contained peroxides.

(11) K. B. Wiberg and E. L. Slaugh, *J. Am. Chem. Soc.*, **80**, 3033 (1958).

(12) C. Walling and B. Miller, *J. Am. Chem. Soc.*, **79**, 4181 (1957).

(13) G. A. Russel, *J. Am. Chem. Soc.*, **80**, 5002 (1958).

(14) C. L. Thomas, "Catalytic Processes and Proven Catalysts", Academic Press, 1970, pp 98–99.

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# Structure and Conformation of Heterocycles. 11.[1] *cis-* and *trans*-2,3-Difluoro-1,4-dioxane. Gauche and Anomeric Effects of Fluorine

Benzion Fuchs* and Aviyakar Ellencweig

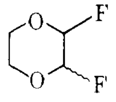
*Department of Chemistry, Tel-Aviv University, Ramat-Aviv, Tel-Aviv, Israel*

*Received November 29, 1978*

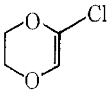
The title compounds were synthesized along with *trans*-2-fluoro-3-chloro-1,4-dioxane and conformationally analyzed using $^1H$, $^{19}F$, and $^{13}C$ NMR spectroscopic methods. The trans compound was concluded to occur in better than 96% as diaxial conformers. This is discussed in terms of the "anomeric effect" and "gauche effect" of fluorine.

We are currently investigating systems derived from 1,4-dioxanes, in particular such which bear polar substituents[1,2] and exhibit anomeric and related effects.[3] These effects have been for some time now the subject of intense experimental and theoretical probing.[3,4]

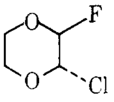
In this framework we undertook to examine the stereoisomeric 2,3-difluoro-1,4-dioxanes (1), a system which is of interest both for its reactivity as well as for its conformational features. For one, while the anomeric effect of fluorine was found and well studied in fluorinated carbohydrates,[5] it is otherwise poorly documented, and although it has been discussed in theoretical terms,[4] a somewhat controversial character emerges from some of these discussions as to the magnitude of this effect relative to other halogens.[4e]



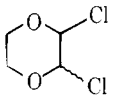
**1a**, *trans*
**b**, *cis*



**2**



**3**



**4a**, *trans*
**b**, *cis*

As to the synthetic aspects of this study, the alleged preparation of 1, without mentioning any configurational features, was cursorly mentioned in a literature procedure[6] which we found irreproducible in our hands. Furthermore, indiscriminate fluorination of 1,4-dioxane has been shown[7a] to give a plethora of highly fluorinated derivatives, but 1 was not isolated. We solved the synthetic problem by reacting *trans*-2,3-dichloro-1,4-dioxane (**4a**)[8] with the "naked" fluoride ion from KF and 18-crown-6 ether in acetonitrile.[9] A mixture of products was obtained containing both stereoisomers of **1**, 2-chloro-1,4-dioxene (**2**), and 2-fluoro-3-chloro-1,4-dioxane (**3**), all in variable amounts, the reaction being very temperature and concentration dependent. While we have not exhausted the study of the various reaction conditions, we were able to optimize the latter in order to obtain mostly **1a** (38%) and **1b** (55%), accompanied by some **2** (7%) but with complete absence of **3**, which appears to be an intermediate in the transformation. The starting material was completely consumed in all cases. The product mixture was readily resolved in GLC, and GC/MS measurements provided nice confirmation of the molecular structures and their fragmentation pattern.

The configurational as well as conformational assignments were made following the acquisition of extensive $^1H$, $^{13}C$, and $^{19}F$ NMR data as assembled in Table I, together with those of **4a** and **4b** for the sake of comparison. The latter stereoisomers have been analyzed in the past[10–12] (and our data are almost identical with the published ones), and their conformations are well established.[3c]

The first step toward an unequivocal assignment was made possible by the LAOCN 3[13] analysis of the AA′BB′ pattern of the $O\text{–}CH_2\text{–}CH_2\text{–}O$ moiety in **1a** (Figure 1 and Table I). The well-defined parameters and the resulting $R$ value[20] of $J_{\text{trans}}/J_{\text{cis}} = 2.2$ (i.e., a dihedral angle of ca. 58.5°) indicate a noninverting chair conformation, in line with other substituted 1,4-dioxanes.[2,3c] While **1b** was not similarly analyzed by simulation, its $O\text{–}CH_2\text{–}CH_2\text{–}O$ spectrum (Figure 2) exhibits an unmistakably much narrower AA′BB′ pattern as compared to that of **1a** (a half-width ca. 20 vs. 80 Hz, respectively) as commonly encountered in the rapidly inverting cis-2,3-disubstituted dioxans vs. the fixed trans isomers.[1b,2] This configurational assignment was supported by the half-widths $w_{1/2}$ of the $^{19}F$ decoupled CHF signals in **1a** and **1b** which are 1.8

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**Table I. $^1$H, $^{19}$F, and $^{13}$C NMR Data of 1a, 1b, and 3**

| | **1a**[b] | **1b** | **3** | **4a**[c] | **4b**[c] |
|---|---|---|---|---|---|
| $\delta(\mathrm{C\mathbf{H}F})$ | 5.34 | 5.32 | 5.40 | | |
| $\delta(\mathrm{C\mathbf{H}Cl})$ | | | 5.86 | 5.95 | 5.60 |
| $\delta(\mathrm{C\mathbf{H}_2})$[d] | 4.02 | 3.96 | 4.34; 3.78 | 4.04 | 3.95 |
| $\delta(^{19}\mathbf{F})$ | −141.6 | −150.7 | −125.6 | | |
| $\delta(^{13}\mathrm{\mathbf{C}HF})$ | 100.28 | 101.13 | | | |
| $\delta(^{13}\mathrm{\mathbf{C}H_2})$ | 58.77 | 61.04 | | 59.5 | |
| $^2J(\mathrm{C\mathbf{H}_2})$ | −11.78 | | | −12.17 | −12.25 |
| $^3J_{\mathrm{aa}}(\mathrm{C\mathbf{H}_2C\mathbf{H}_2})$ | 12.99 | | | 12.43 | |
| $^3J_{\mathrm{ee}}(\mathrm{C\mathbf{H}_2C\mathbf{H}_2})$ | 0.98 | | | 0.96 | 6.45[e] |
| $^3J_{\mathrm{ae}}(\mathrm{C\mathbf{H}_2C\mathbf{H}_2})$ | 3.08 | | | 3.16 | 3.10 |
| $^3J(\mathrm{C\mathbf{H}FC\mathbf{H}F})$[f] | | 1.1 | 1 | | |
| | ca. −8[g,i] | | | | |
| $^3J(\mathrm{CH\mathbf{F}CH\mathbf{F}})$[f] | | −18.3 | | | |
| $^2J(\mathrm{C\mathbf{HF}})$[f] | | 52.5 | 52.3 | | |
| | 52.2[g] | | | | |
| $^3J(\mathrm{C\mathbf{H}FCH\mathbf{F}})$[f] | | 8.3 | 3.7[j] | | |
| $^1J(\mathrm{\mathbf{C}H\mathbf{F}})$ | 221.2 | 227.5 | 225.5 | | |
| $^2J(\mathrm{\mathbf{C}HFCH\mathbf{F}})$ | 47.0 | 26.0 | 44.0 | | |
| $w_{1/2}(\mathrm{C\mathbf{H}FC\mathbf{H}F})$[h] | 1.8 | 0.9 | | 1.5 | 0.8 |

[a] $\delta$ (ppm), positive sign measuring downfield from the respective internal reference; $J$ in Hz. $^1$H NMR and $^{13}$C NMR spectra were measured in $CD_3Cl/Me_4Si$ and $^{19}$F spectra in $CDCl_3/CFCl_3$. Values are given to the last significant figure. [b] The AA′BB′ proton spectrum was analyzed by theoretical simulation using the LAOCN 3 program.[13] [c] The 2,3-dichlorodioxanes (**4**) were measured and are given for the sake of comparison; cf. ref 10 for **4a** and ref 10–12 for **4b.** [d] Center of AA′BB′ multiplet. [e] ½ ($J_{\mathrm{aa}} + J_{\mathrm{ee}}$). [f] These AA′XX′ spectra were calculated manually after appropriate peak assignments. [g] In **1a** the CHF–CHF spectra[f] are deceptively simple and we could only evaluate $^3J_{\mathrm{FF}} + {}^3J_{\mathrm{HH}} \approx 8$ Hz and $^2J_{\mathrm{HF}} + {}^3J_{\mathrm{HF}} = 52.2$ Hz.[14] [h] Half-width of the $H_{2,3}$ singlet with reference to the $CHCl_3$ signal ($w_{1/2}$ = 0.35 Hz). [i] Negative signs were assigned to the vicinal F–F coupling constants, following Hall's assertion.[17] [j] $^3J(\mathrm{CHCl\mathbf{C}H\mathbf{F}})$.

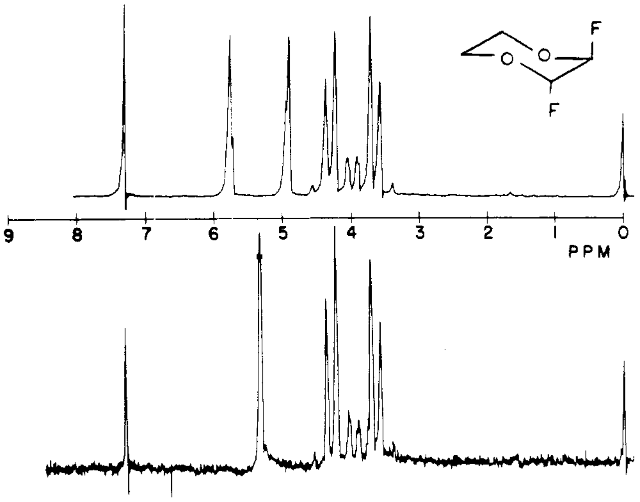


**Figure 1.** $^1$H NMR spectrum of *trans*-2,3-difluoro-1,4-dioxane (**1a**) (a, top); the same as (a) only $^{19}$F decoupled (b, bottom).

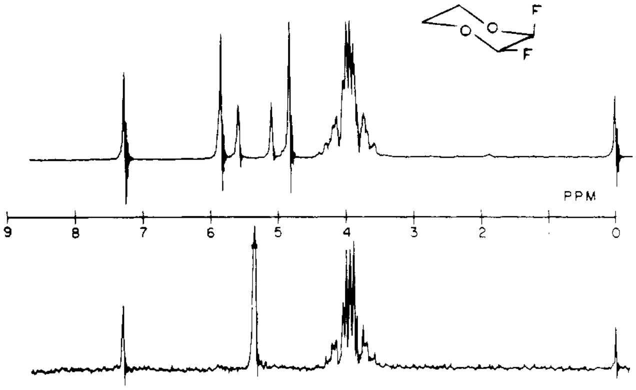


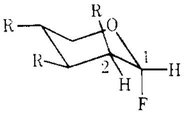
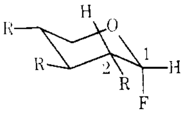
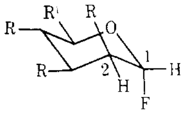
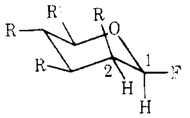
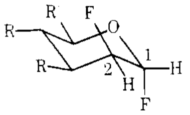
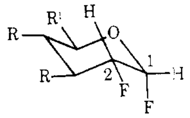
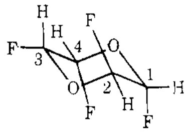
**Figure 2.** $^1$H NMR spectrum of *cis*-2,3-difluoro-1,4-dioxane (**1b**) (a, top); the same as (a) only $^{19}$F decoupled (b, bottom).

and 0.9 Hz, respectively, again characteristic of trans- and cis-2,3-disubstituted 1,4-dioxans,[1b,2] where the higher value of $w_{1/2}$ = 1.8 Hz in the trans isomers is due to long-range interaction of the equatorial protons. This fits well with the coupling constants between these protons as extracted from the $^{13}$C-satellite signals and which are all <2 Hz for trans-diaxially-2,3-disubstituted dioxans in contrast with 7–8 Hz for the two axial protons in trans-diequatorially-substituted 1,4-dioxans.[21,22] This, in fact, introduces us to the conformational analysis of the system after having established the configuration.

We have come to the conclusion[1b,2] that the only reliable approach in conformational problems of this sort is to seek converging results from a multitude of probes, in our case three types of nuclear magnetic resonance measurements, viz., $^1$H, $^{13}$C, and $^{19}$F. Both chemical shifts and coupling constants were used as criteria, and we sought and found supporting data from a number of recent investigations. Two very informative $^{19}$F NMR reviews[15,16] provided much general support to our assignments, but most useful in this direction were the extensive data on specifically fluorinated carbohydrates obtained and reported by Hall and his associates[5,17] concerning $^1$H and $^{19}$F chemical shifts as well as FH and FF coupling constants involving anomeric fluorine atoms. The reports of Burdon and Parsons[7b] and Phillips and Wray[19] were also helpful in this area whereas for $^{13}$C data we found support in the results of Bock and Pedersen.[18] To facilitate reading and comprehension, we tabulate some particularly instructive samples from the cited literature (Table II).

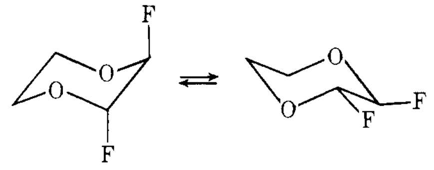
To summarize briefly the most important points which support our assignments: from $\delta(^{19}\mathrm{F})$ in Table I one sees that the vicinal diaxial fluorines are deshielded relative to the axial–equatorial ones in accord with data on known compounds (Table II) where axial $F_1$ is considerably deshielded by a vicinal–trans-axial F or even OAc. A sensitive probe, namely the geminal coupling constant $^2J(F_1H_1)$, is known[5,19] to decrease following vicinal–axial polar substitution; also, the vicinal coupling constants $^3J(F_1H_2)$ are smaller by an order of magnitude in the gauche arrangement relative to the trans

**Table II. Relevant NMR Data of Selected Literature Compounds**[a]

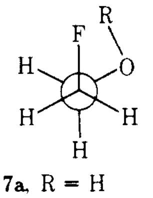
| compd R = OAc; R′ = CH$_2$OAc | ref | $\delta(^{19}F)$ | $\delta(^{13}C)$ | $\delta(^1H_1)$ | $^2J(F_1H_1)$ | $^3J(F_1H_2)$ | $^3J(F_2H_1)$ | $^3J(H_1H_2)$ | $^3J(F_1F_2)$ | $^1J(C_1F_1)$ | $^2J(C_2F_1)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  | 5b | −141.1 | | 5.46 | 49.1 | <2 | | 2.0 | | | |
|  | 5b | −152.1 | | 5.67 | 53.5 | 23.7 | | 2.8 | | | |
|  | 5c, 18 | −138.8 | $C_1$ 104.71<br>$C_5$ 70.82 | 5.57 | 48.6 | ~1.5 | | 1.7 | | 223.1 | 39.7 |
|  | 18 | | $C_1$ 104.05<br>$C_5$ 72.71 | | | | | | | 223.6 | 25.0 |
|  | 17 | −143.4 | | 5.76 | 48.0 | 0 | 4.0 | 2.0 | −20.0 | | |
|  | 17 | −151.5 | | 5.80 | 53.3 | 23.8 | 0 | 2.9 | −18.8 | | |
|  | 19 | $F_1$ −140.9;<br>$F_2$ −132.3;<br>$F_3$ −157.6;<br>$F_4$ −151.3 | | 5.9 | 51 [$^2J(F_4H_4)$53] | | | | | | |

[a] See footnote *a* in Table I for specification of internal references and units; solvents were largely similar.

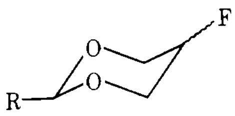
arrangement; furthermore, $^3J(F_1F_2)$ which is known not to obey any Karplus-type relationship[16] is negative[17] and slightly larger for the trans-diaxial arrangement (Table II). The corresponding analysis for our case is somewhat hampered by the fact that from the deceptively simple CHF spectrum of **1a** we were able to extract only combined values (Table I, footnote *g*), and except for the somewhat low $^3J_{FF} + ^3J_{HH} \approx -8$ Hz the data fit nicely the known trends. Finally, the $^{13}C$ chemical shifts for $CH_2$ and CHF as well as the $^2J(CF)$ values show the expected trend.[18] It was rewarding to see how all the recorded data were largely corroborative toward assigning a diaxial conformation (**5**) to the trans isomer **1a**; the very high value of $^3J_{aa}$ = 12.99 Hz is taken to indicate that this assignment is practically exclusive, in particular after comparing it with $^3H_{aa}$ = 11.30 Hz of the >95% diaxial *trans*-2,3-dimethoxy-1,4-dioxane;[1b2] hence for **5**, $K_{g/t} > 24$ and $\Delta G°_{5\text{-}6} > 2$ kcal/mol. By the same token, the 2-fluoro-3-chloro derivative also exhibits NMR spectral data which indicate a clear trans-diaxial conformation (**3aa**). As to the cis compound **1b**, it occurs as expected in the rapidly inverting axial–equatorial form.



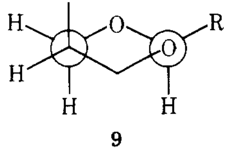
**5** **6**



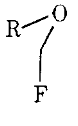
**7a**, R = H
**b**, R = COCX$_3$



**8**



**9**



**10a**, R = H
**b**, R = CH$_3$

In conclusion, a short interpretative discussion is in order. We would like to dissect the energetics in **1a** into three types of interactions: (1) two O–C–C–F interactions, which are gauche in the diaxial form **5** and anti in the diequatorial form **6**; (2) two C–O–C–F interactions, which are again gauche in **5** and anti in **6**; and (3) an F–C–C–F interaction, which is anti in **5** and gauche in **6** (the O–C–C–O moiety is gauche in both **5** and **6**, canceling out the difference). Following more than a decade of investigation of related systems, one may attempt to put the above on a semiquantitative basis. Thus, 2-fluoroethanol (**7a**) has been consistently found to occur in better than 95% gauche conformation in the liquid phase (and >90–95% in the vapor phase).[23,24] While part of this strong preference had been attributed to the O–H- - -F hydrogen bond, the latter has been shown, in fact, to influence very little the gauche ⇄ anti equilibrium from NMR spectroscopic evaluation of the hydrogen bond in **7a**[24] as well as the conformation of a species (**7b**) devoid of intramolecular hydrogen bond and still >95% gauche![25] A fair evaluation of this interaction would then be $\Delta G°_{g\text{-}t} \sim 2$ kcal/mol. Interestingly, investigation of a related, though more complex system (**8**), viz., conformational equilibrium in **8a**[26] and chemical equilibrium in **8b**,[27] shows albeit a preference of fluorine for the axial position but to a considerably lesser extent ($\Delta G°_{\text{ax-eq}} \sim 0.8$ kcal/mol). This occurs even though a system with two O–C–C–F apparent interactions is on hand. One cannot help but conclude that the geometry with the second substituent on oxygen turned inside, as in the hydrogen-bonded 2-fluoroethanol (**7a**), is essential for the gauche effect to come into full display. Notably, in *cis*-**8** ≡ **9**, the second substituent on oxygen is turned half-way out due to annelation, and so it is also in our case **5**, for which then a gauche effect[4a,28] of only ca. 0.8 kcal/mol is also expected.

Turning now to the second C–O–C–F interaction, we find that this is in fact a typical example of the well known "anomeric effect".[3] Its lower homologue, fluoromethanol, has undergone extensive theoretical study leading to a concensus for a considerably favored gauche form (**10a**).[4] Fortunately, an even better experimental model for our compound recently became available, namely fluoromethyl methyl ether, which has been reported to be practically only in the gauche form (**10b**) with a dihedral angle of 69°.[29] An approximation for $\Delta G°_{g-t}$ of ca. 1.8 kcal/mol would then also be acceptable in this case.

Finally, the F–C–C–F moiety can be conveniently compared with 1,2-difluoroethane, which exists in an undisputed gauche form[30,31] with $\Delta E_{g-t}$ ca. 2 kcal/mol for the liquid phase.[30] Hence, **5** is *destabilized* by this amount. This leads us to a summation of $1.6 + 3.6 - 2 = 3.2$ kcal/mol in favor of the diaxial form **5** over **6**, which confirms that our evaluation (vide supra) was a safe lower limit for our system (**1a**).

## Experimental Section

$^1$H NMR spectra of $CD_3CN/Me_4Si$ solutions were recorded on a JEOL C-60 HL spectrometer at 60 MHz, using a JNM SD-HC heterodecoupler for irradiation of the $^{19}$F nuclei.

Natural abundance $^{13}$C NMR spectra of $CDCl_3/Me_4Si$ solutions were measured on a Bruker FTWH-90 spectrometer operating in the pulsed Fourier transform mode, using the D-heteronuclear lock and proton noise decoupling.

$^{19}$F NMR spectra of $CDCl_3/CFCl_3$ solutions were recorded on a Bruker FT-EH 90 spectrometer.

Theoretical simulation of NMR spectra was done with the LAOCN 3 program[13] using the CDC-6600 computer of Tel-Aviv University's computation center.

The GLC (analytical and preparative) runs were performed on Varian Aerograph Model 1800, using a column of 15% Carbowax 20 M on Chromosorb W at 80 °C. The mass spectra were performed on a DuPont 21-491 B mass spectrometer operating in the GC/MS mode.

**Fluorination Procedure.** A solution of *trans*-2,3-dichloro-1,4-dioxane[8] (**4a**) in dry acetonitrile was added to a well-stirred mixture of 6 g of 18-crown-6 ether and 41.4 g of KF (anhydrous) in 60 mL of dry acetonitrile, and the mixture was heated to 65 °C with stirring for 48 h. Another portion of 1.5 g of 18-crown-6 ether and 10.3 g of KF in 20 mL of acetonitrile was added, and the reaction mixture was heated for an additional 48 h. After being cooled to room temperature and filtered, the solids were washed with 70 mL of dry acetonitrile, and the combined filtrate was distilled through a small fractionating column.[32] The solvent distilled at 32 °C (120 torr), and then two fractions were collected: at 32–46 °C (20 torr) (16.4 g) and at 18–40 °C (0.02 torr) (4.2 g).

These fractions were resolved by preparative gas chromatography following a GC/MS analysis of the acetonitrile solution prior to distillation, and four components were obtained and characterized.

1. ***trans*-2,3-Difluoro-1,4-dioxane (1a):** $R_t$ 14 min; 17%; $\nu_{max}$ ($CHCl_3$) 2990, 2950, 2900, 1278 (s), 1200 (s), 1041, 997 (s), 915 (s), 880 (s) cm$^{-1}$; *m/e* 124 (100), 105 (1), 86 (25), 64 (68).

Anal. Calcd for $C_4H_6O_2F_2$: C, 38.71; H, 4.85; F, 30.62. Found: C, 38.55; H, 4.97; F, 30.41.

2. **2-Chloro-1,4-dioxene (2):** $R_t$ 71 min; 52%; physical properties as published.[8b]

3. ***cis*-2,3-Difluoro-1,4-dioxane (1b):** $R_t$ 86 min; 23%; $\nu_{max}$ ($CHCl_3$) 2980, 2900, 1450, 1350, 1282, 1178 (s), 1145 (vs), 1070 (s), 1030, 1010, 915, 880 cm$^{-1}$; *m/e* 124 (36), 105 (5), 86 (1), 64 (100).

4. ***trans*-2-Fluoro-3-chloro-1,4-dioxane (3a):** $R_t$ 100 min; 8%; $\nu_{max}$ ($CHCl_3$) 2990, 2950, 2890, 1455, 1400, 1365, 1345, 1275 (s), 1175 (vs), 1125, 1040, 970 (vs), 905, 880; *m/e* 142 (14), 140 (41), 123 (3), 121 (8), 105 (100), 104 (50), 86 (12), 82 (18), 80 (56).

The composition of the product mixture can be varied. Thus a typical reaction of **4a** (0.05 moles), anhydrous KF (0.1 moles), and 18-crown-6 ether (0.02 moles) in 10 mL of dry acetonitrile at reflux gave after 90 h 38% **1a**, 55% **1b**, and 7% **2**. On the other hand, 2-fluoro-3-chloro-1,4-dioxane (**3a**) could be enriched in the product mixture (up to 90%) by judicious variation of the reaction conditions, viz., increasing dilution and decreasing temperature and reaction time.

**Registry No.**—**1a**, 69912-56-7; **1b**, 69912-57-8; **2**, 57253-40-4; **3a**, 69912-58-9; **4a**, 3883-43-0.

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