temperature for a period of 1 day. The brown product mixture was partitioned between water and ether. The layers were separated, and the organic phase was washed with two 15-mL portions of water (small emulsion broken up with solid sodium chloride). The aqueous washings were extracted with two 10-mL portions of ether. The combined organic fractions were dried over $MgSO_4$. The solvent was removed with a rotary evaporator, and the resulting yellow oil was subjected to silica gel column chromatography to obtain ca. 55 mg (82%) of recovered iodide **50**, 12 mg (16%) of recovered sulfone **49**, 11.4 mg (15%) of sulfone **51**, and 8.9 mg of unidentified materials. Compound **51**: IR (film) 3060, 2925, 2850, 1440, 1375, 1305, 1250, 1140, 1110 cm^{-1}; ^1H NMR δ 0.04 (s, 6), 0.85 (s, 9), 1.34 (m, 2), 1.89 (m, 2), 3.15 (dd, 1, J = 3.4, 14.6), 3.32 (s, 3), 3.43 (dd, 1, J = 8.1, 14.6), 4.06 (m, 1), 4.36 (tt, 1, J = 5, 10), 4.70 (d, 1, J = 2.9), 7.57 (m, 3), 7.94 (d, 2, J = 7.0). Anal. Calcd for $C_{19}H_{32}O_5SSi$: C, 56.96; H, 8.05. Found: C, 57.04; H, 7.99.

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Registry No. **1**, 73573-88-3; **2**, 6322-07-2; **3**, 67642-42-6; **3** hydroxycarboxylate deriv., 91312-46-8; **4**, 91312-47-9; **5**, 91312-48-0; **7**, 78039-08-4; **8**, 68198-85-6; **9**, 91312-49-1; **10** α-D-gulo deriv., 91312-50-4; **10** β-D-gulo deriv., 91312-51-5; **11**, 91312-52-6; **14**, 5055-09-4; **15**, 32233-43-5; **16**, 32233-44-6; (3*R*)-**17**, 91312-53-7; (3*S*)-**17**, 91312-54-8; (3*R*)-**18**, 91312-55-9; (3*S*)-**18**, 91312-56-0; (3*R*)-**19**, 91312-57-1; (3*S*)-**19**, 91312-58-2; **20**, 91312-59-3; **21**, 91327-64-9; **22**, 2873-29-2; **23**, 73541-95-4; **24**, 73573-78-1; **25**, 13145-22-7; **26**, 73541-94-3; **27**, 86030-92-4; **28**, 91312-60-6; **29**, 91312-61-7; **31**, 91312-62-8; **32**, 91312-63-9; **33**, 91312-64-0; **34**, 91312-65-1; **35**, 91312-66-2; **36**, 91312-67-3; **37**, 91312-68-4; **41**, 91312-69-5; **42**, 91312-70-8; (*E*)-**44**, 91327-65-0; (*Z*)-**44**, 91383-94-7; **45**, 91312-71-9; **46**, 91312-72-0; **47** (isomer 1), 91312-73-1; **47** (isomer 2), 91383-67-4; **48**, 86031-05-2; **49**, 91312-74-2; **50**, 91312-75-3; **51**, 91312-76-4; CS_2, 75-15-0; SEM-Cl, 76513-69-4; ethyl acetate, 141-78-6; cyclohexylmethyl bromide, 2550-36-9; cyclohexylmethyl iodide, 5469-33-0.

1-Oxa-4-decalone Derivatives. Synthesis and Structure

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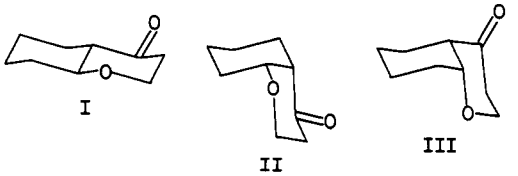
The synthesis of some 1-oxa-4-decalone derivatives is described. Both epimers at C-4a were isolated and their configurations and conformations were inferred by ^1H and ^{13}C NMR studies.

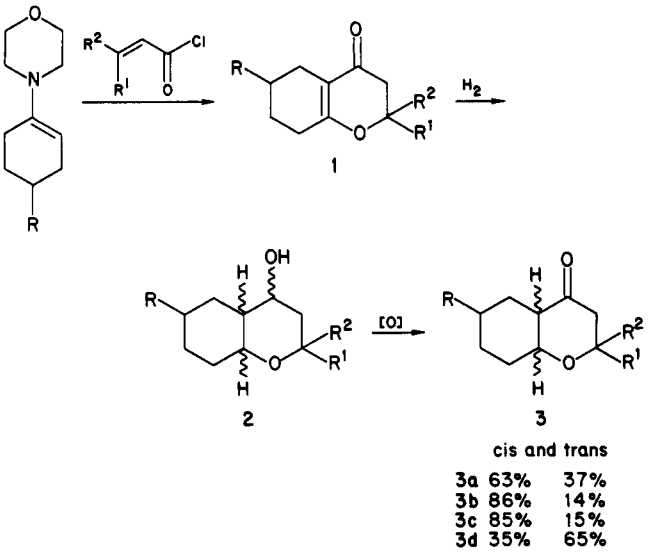
Our purpose was to synthesize a series of 1-oxa-4-decalone derivatives (octahydrobenzo-4-pyranones) **3** in an effort to investigate by ^1H and ^{13}C NMR spectroscopy both their configurations and their preferred conformations. These compounds are nearly unknown. *cis*- and *trans*-1-oxa-4-decalones, and some 6- and 7-methoxycarbonyl derivatives, have been prepared and identified by ^1H NMR.[1]

It is generally accepted that tetrahydro-4-pyranones exist in a chair form.[2,3] However, tetrahydropyran has a chair conformation that is slightly flattened from the shape of cyclohexane. The somewhat larger C–O–C bond angle and shorter C–O bond length cause this distorsion.[4] Chair-like conformations of 1-oxa-4-decalone derivatives could be anticipated by analogy with *cis*- and *trans*-decalones.[5] Thus the trans compounds are uncomplicated since they can all be expected to be based on conformation I. In the cis series, the two possible conformations II and



III have to be considered. However, II is clearly less favorable than III because of the greater 1,3-diaxial interactions in the former.[6]

Scheme I[a]



[a] a, R = H; R¹ = R² = H; b, R = H; R¹ = Me; R² = H; c, R = H; R¹ = R² = Me; d, R = *t*-Bu, R¹ = R² = Me.

1-Oxa-4-decalones Synthesis. Path A. Earlier, we reported on the synthesis of 2,3,5,6,7,8-hexahydrobenzo-

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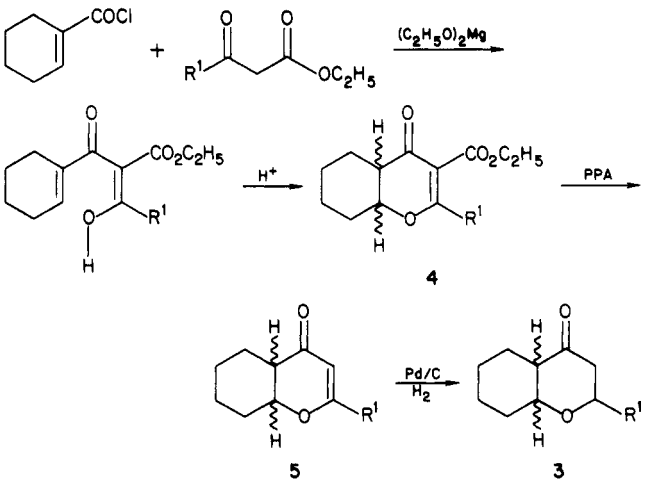
0022-3263/84/1949-4003$01.50/0

Table I. Pertinent ^{1}H NMR Spectral Data

compd	junction	δ H-8a	$W_{1/2}$, Hz H-8a	J, Hz H-4a,H-8a	J, Hz H-8a,H-8	J, Hz H-2,H-3	CH_3(C-2)
3a	trans	3.20	24	10		10, 4[a]	
3b	trans	3.21	24	10	10.5, 3.8	9.9, 4.2	1.32
3c	trans	3.38	24	10.5	9.6, 4		1.17, 1.32
3d	trans	3.33	24	9.6	10, 4		1.17, 1.32
3e	trans	3.14	24	10	10.5, 3.8	9.2, 4.9	
3a	cis	3.75	*b*				
3b	cis	3.78	8	3	3, 3	12, 3	1.30
3c	cis	4.00	8	3	3, 3		1.17, 1.33
3d	cis	3.95	8	3	3, 3		1.18, 1.33
3e	cis	3.69	8	3	3, 3	12, 3	

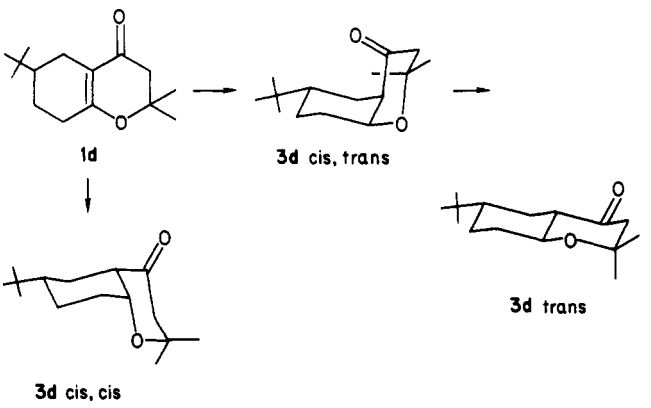
[a] Lit.[1] 11.5 and 3.5 Hz. [b] Overlapped with H-2.

Scheme II[a]



[a] b, R^1 = Me; e, R^1 = *t*-Bu.

Scheme III



4-pyranones **1a–c** by acylation of 1-morpholino-1-cyclohexene by α,β-unsaturated acyl chlorides.[7,8] Compound **1d** was prepared by this route. Catalytic hydrogenation (Raney nickel) of compounds **1** afforded a mixture of four diastereoisomeric 1-oxa-4-decalols **2**. Oxidation of these mixtures with Jones reagent gave mixtures of both the cis- and trans-fused 1-oxa-4-decalones **3** (Scheme I).

Path B. Acylation of ethyl acetoacetate and ethyl pivaloylacetate by 3,4,5,6-tetrahydrobenzoyl chloride afforded a mixture of cis- and trans-fused 4a,5,6,7,8,8a-hexahydrobenzo-4-pyranone derivatives **4**. The reaction of ethyl acetoacetate and tetrahydrobenzoyl chloride was first investigated by Kidd and co-workers,[9] but they did not recognize that their product was a mixture of cis and trans isomers. However, the pure trans isomer was isolated by recrystallization of the crude reaction mixture. Decarbethoxylation of compounds **4** using polyphosphoric acid[10] afforded **5** which was subjected to catalytic hydrogenation to give a mixture of epimeric compounds **3b,e** (Scheme II).

Stereochemical product ratios were obtained by ^{1}H NMR analysis and GLC (Table I). The cis and trans isomers were obtained in a pure state by gas chromatography. The first and second eluted isomers were shown by ^{1}H NMR spectroscopy (see below) to be the cis- and trans-fused isomers, respectively.

Catalytic hydrogenation of **1a–d** (path A) would be expected to yield only a cis ring junction, so the formation of the trans isomers correspond to a partial epimerization of the cis enolizable ketones **3**. The detection of four isomeric alcohols **2** suggests that this epimerization occurs during the hydrogenation from the cis ketones **3** initially formed from **1**.[11] On the other hand, oxidation of alcohols **2** with Jones' reagent was accomplished under nonequilibrating conditions.

When the mixture of epimeric ketones **3**, obtained from path A or B was submitted to base-catalyzed equilibration a trans/cis ratio of 9:1, respectively, was obtained from **3a–c,e**. Under the same conditions, the initial ratio of trans/cis for **3d**, substituted in the 6 position of the cyclohexane ring by a *tert*-butyl group, remains unaffected, indicating that only in this case, the epimerization of the cis isomer does not occur. It will be noted that there were two possible approaches for hydrogen at the double bond of the unsaturated ketone **1d** to yield **3d** cis,cis and **3d** cis,trans. In a chair conformation, the compound **3d** cis,cis should be stable since epimerization at C-4a would require that the *tert*-butyl group adopts an axial position; in the contrary, **3d** cis,trans being destabilized by 1,3-diaxial interactions underwent complete epimerization into **3d** trans. This isomerization occured without interconversion of the cyclohexane ring.

The similarity in the coupling constants between **3d** cis and **3a–c,e** cis allows exclusion of the possibility of a twist conformation of the cyclohexane ring containing the *tert*-butyl group. Our equilibration results were in good agreement with the trans/cis ratios obtained from the 1-decalone system.[12–15]

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(11) Attempts of specific hydrogenation of the double bond of compound **1b** using 10% Pd/C as a catalyst afforded a mixture of *cis*- and *trans*-2-methyl-1-oxa-4-decalone **3b** (30%) in a ratio 3:2, respectively, **2b** (30%), and starting material (40%).
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Table II. ^{13}C Chemical Shifts for Octahydrobenzo-4-pyranones (3)[a]

compd	junction	C-2	C-3	C-4	C-4a	C-8a	C-8	Me	t-Bu	other C
3a	trans	67.7	43.0	207.8	56.4	82.5	33.4			24.5, 23.3, 24.9
3b	trans	74.0	49.8	207.8	55.1	80.9	33.1	22.1		24.4, 23.0, 24.7
3c	trans	76.0	53.6	208.6	55.4	75.4	33.6	24.1, 31.2		24.5, 23.0, 24.8
3d	trans	76.0	53.3	208.4	55.1	75.3	33.5	24.0, 31.1	32.4, 27.5	46.6 (C-6) 25.2, 23.7
3e	trans	85.2	43.2	209.0	55.5	80.8	33.0		34.2, 25.6	24.7, 24.3, 23.1
3a	cis	66.3	39.0	210.0	53.3	75.5	30.0			24.4, 20.5, 25.0
3b	cis	74.0	45.8	210.9	52.6	73.4	30.2	22.1		24.9, 20.0, 25.1
3c	cis	74.7	49.4	211.8	52.5	67.4	30.4	24.6, 31.2		24.8, 19.9, 25.0
3d	cis	74.6	49.3	212.0	53.0	66.8	31.0	24.5, 31.1	32.5, 27.3	46.8 (C-6) 26.2, 21.0
3e	cis	84.2	38.9	211.8	52.8	73.6	30.2		34.3, 25.5	25.0, 24.9, 20.1

[a] No attempt was made to assign C-5–C-7 resonances.

Identification of Products, NMR Spectra. Configuration of the products **3** rests both on ^1H and ^{13}C NMR spectra. Determination of the stereochemistry at the ring junction was easily deduced by ^1H NMR by a first-order approach, as found in previous work on 1-oxa-4-decalone **3a**.[1] The H-8a signal appeared at a lower field in the cis isomer than in the trans. A relatively narrow resonance $W_{1/2}$ = 8 Hz was observed for this proton in a cis junction as compared to the wider signal for a trans junction ($W_{1/2}$ = 24 Hz). Additional information was gleaned from 350 ^1H NMR spectra by ^1H spin decoupling experiments. In the trans series, the coupling constants of ~10 Hz between H-8a and H-4a denote a trans diaxial relationship.

The magnitude of the vicinal coupling constants between H-2 and H-3 for **3b** and **3e**, 9.9–9.2 and 4.2–4.9, shows an equatorial position for the 2-methyl or 2-*tert*-butyl substituent. In the cis series, the coupling constants for **3b** and **3e**, H-8a and H-8, with J values of 3 and 3 Hz were only consistent with a cis fusion of the ring with H-8a equatorial to the cyclohexane ring (and axial with respect to the heterocyclic ring). The coupling constants H-2 and H-3 of 12 and 3 Hz, $J_{2ax,3eq}$, respectively, show that both the 2-methyl and the 2-*tert*-butyl groups are attached equatorially. On the other hand, the cis ketone **3d** in which the equatorial 6-*tert*-butyl group is fixed exhibited the same nonequivalence of the geminal 2-methyl groups as the 6-unsubstituted ketone **3c**. These findings strongly suggest that all these cis compounds prefer the conformation with an axial position of the C–O bond (conformation III). From Table I, a difference between the vicinal coupling constants H-2 and H-3 in the trans and cis series is observed (**3b** and **3e**). The ratio $R = J_{H\text{-}2ax,H\text{-}3ax}/J_{H\text{-}2ax,H\text{-}3eq}$ was found to be about 2 for the trans compounds, in agreement with an undistorted heterocycle. The R value of 4 for the cis series suggests a puckering of the heterocyclic ring.[4]

Although ^{13}C chemical data of some tetrahydro-4-pyranones have been reported,[3,16-18] there is no literature available on the ^{13}C chemical shifts of epimeric 1-oxa-4-decalones. The ^{13}C chemical shifts of compounds **3a–e** are presented in the Table II. The assignments were made on the basis of off-resonance decoupling, by analogy to literature assignments of the known tetrahydro-4-pyrone derivatives[16-18] and by using similarities with substituent effect parameters in decaline or cyclohexane.[19,20] Changes in chemical shifts by introduction of a substituent at C-2 on cis and trans 1-oxa-4-decalone **3a** are in good agreement with the values observed from 1,3-dioxane derivatives.[21] The remarkable similarity in the chemical shifts of the geminal 2-methyl groups between cis-**3d** (6-*tert*-butyl) in rigid conformation and cis-**3c** clearly suggests that the cis-fused compounds are conformationally homogeneous (Tables II and III). On the other hand, it is interesting to compare the differences observed on the chemical shifts on going from the trans to the cis isomer (Table IV). The methylene substituent at C-4a changes from equatorial in the trans isomer to axial in the cis isomer. As expected, the ≃4 ppm upfield differences at C-3 reflect well 1,3 syn-axial interactions as compared to the equatorial ones.

Significant upfield shifts were observed from the carbons at the ring junctions on going from the trans to the cis isomers. This is probably due to steric perturbations. Similar differences were found between trans and cis decalins (–7.3 ppm).[22] On the other hand, by comparing the

Table III. Effects on ^{13}C Shifts in Octahydrobenzo-4-pyranones Caused by Replacement of Ring Hydrogen by Methyl and *tert*-Butyl Substituents[a]

substituent	ring C affected	effect	trans	cis
2-Me	2	α_{eq}	6.3	7.7
	3	β_{eq}	6.8	6.8
	4	γ_{eq}	0	0.9
	8a	γ_{eq}	–1.6	–2.1
	4a	δ_{eq}	–1.3	–0.7
$2(Me)_2$	2	α_{ax}	2	0.7
	3	β_{ax}	3.8	3.6
	4	γ_{ax}	0.8	0.9
	8a	γ_{ax}	–5.5	–6
	4a	δ_{ax}	0.3	–0.1
2-*t*-Bu	2	α_{eq}	17.5	17.9
	3	β_{eq}	0.2	–0.1
	4	γ_{eq}	1.2	1.8
	8a	γ_{eq}	–1.7	–1.9
	4a	δ_{eq}	–0.9	–0.5

[a] The differences reported are obtained by comparing **3a** and **3b**, **3b** and **3c**, and **3a** and **3e**. The plus sign indicates downfield from the signal in **3a**.

Table IV. $\Delta\delta$ from the Trans to the Cis Isomer

compd	C-2	C-3	C-4	C-4a	C-8a
3a	–1.4	–4	2.2	–3.1	–7
3b	0	–4	3.1	–2.5	–7.5
3c	1.3	–4.2	3.2	–2.9	–8
3d	–1.4	–4	3.6	–2.1	–8.5
3e	–1	–4.3	2.8	–2.7	–7.2

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shifts of the C-4 carbonyl in the trans and cis ketone **3a** respectively δ 207.8 and 210, with those of *cis*- and trans-1-decalone, 211.9 and 212.7,[23,24] it can be seen that the γ shielding effect of the oxygen atom in the trans compound is −4.1 ppm. The same effect (−4.3 ppm) is observed between tetrahydro-4-pyranone and cyclohexanone.[3,17] It is not clear why this effect is weakened in all the cis-fused compounds (−2.7 ppm).

In summary, the configuration and conformation of epimeric 1-oxa-4-decalone derivatives were analyzed by ^1H and ^{13}C NMR studies. Thus, axial attachment of the ether bond with respect to the carbocyclic ring (III) is preferred in the cis series. This conformation (III) is not affected by the nature of the substituent at C-2 (*t*-Bu, Me, or H) or at C-6 (*t*-Bu or H). This conclusion is consistent with results obtained from conformational analysis of *cis*-1-oxadecalins.[25,26]

Experimental Section

Melting points were recorded on a Kofler hot plate. Boiling points are uncorrected. IR spectra were obtained with a Beckman model Acculab 2 spectrometer. ^1H NMR spectra were recorded by using a Brucker WP-80 80 MHz or 350 MHz Cameca spectrometers. ^{13}C NMR spectra were performed on a Varian XL-100 12FT or a Brucker WP-80. All spectra were obtained in deuteriochloroform as solvent and the chemical shifts are recorded in δ units downfield from Me_4Si. Gas chromatographic analyses and separations were performed on a Varian Aerograph 90P (TC detector) equipped with a 6 m × 4 mm column packed with 20% DEGS on 60/80 mesh Chromosorb W. Elemental analyses were determined by Microanalytical Laboratory, Centre National de la Recherche Scientifique 69390 Vernaison, France.

6-*tert*-Butyl-2,2-dimethyl-2,3,5,6,7,8-hexahydrobenzo-4-pyranone (1d). This was prepared as in the general procedure described for **3a–c**[8] using 4-*tert*-butyl-1-morpholino-1-cyclohexene and 3-methyl-2-butenoyl chloride: yield 51%; bp 154–156 °C (6 mmHg); mp 56–58 °C (hexane); ^1H NMR δ 0.92 (s, 9 H), 1.33 (s, 3 H), 1.39 (s, 3 H), 1.20–2.50 (m, 9 H). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24. Found: C, 76.38; H, 10.22.

1-Oxa-4-decalones (3a–d). Path A. General Procedure. (a) Catalytic Reduction of 1a–d. A solution of 1 (30 mmol) in ethanol (60 mL) was hydrogenated over Raney nickel W4 at 80 °C under a pressure of 100 atm (about 6 h). After the catalyst was filtered off, ethanol was removed and the residue either distilled under reduced pressure (for **2a–c**) or recrystallized (**2d**) to afford four isomers of 1-oxa-4-decalols **2a–d**, as evidenced by GLC analysis. **2a**: yield 76%; bp 118–128 °C (3 mmHg). **2b**: yield 83%; bp 125–130 °C (3 mmHg). **2c**: yield 82%; bp 120–130 °C (3 mmHg). **2d**: yield 90% (by recrystallization from cyclohexane).

(b) Oxidation of 2 to 3. To a stirred solution of 2 (10 mmol) in acetone (30 mL) at 0 °C was added dropwise Jones reagent (1.23 M)[27] (10.6 mL, 13 mmol). The reaction mixture was stirred at 0 °C for 1 h and diluted with ether (60 mL). The ether extract was washed with 5% aqueous sodium bisulfite, dried (Na_2SO_4), and evaporated. The resultant oil was distilled under reduced pressure to give an epimeric mixture of cis- and trans-fused ketones **3a–d**. 1-Oxa-4-decalone (**3a**): yield 65%; bp 92–95 °C (2 mmHg); cis/trans ratio 63:37. 2β-Methyl-1-oxa-4-decalone[28] (**3b**): yield 75%; bp 76–78 °C (0.5 mmHg);[29,31] cis/trans ratio 86:14. 2,2-Dimethyl-1-oxa-4-decalone (**3c**): yield 86%; bp 84–86 °C (0.1 mmHg);[30,31] cis/trans ratio 85:15. 6β-*tert*-Butyl-2,2-dimethyl-1-oxa-4-decalone[28] (**3d**): yield 84%; bp 98–100 °C (0.3 mmHg); cis/trans ratio 35:65. Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. Found: C, 75.39; H, 11.11.

A portion of the isomeric mixture was further chromatographed (GLC, DEGS, 150 °C) so as to separate the epimers. The cis isomers were first eluted. For spectral data see Tables.

Path B. General Procedure. (a) 3-(Ethoxycarbonyl)-4a,5,6,7,8,8a-hexahydrobenzo-4-pyranones (4b,e). To a solution of ethyl acetylacetate or ethyl pivaloylacetate (0.1 mol) was added magnesium ethylate (11.4 g, 0.1 mol). The mixture was heated to reflux for 3 h. The solvent was then evaporated in vacuo to dryness. The residue was diluted with toluene (50 mL) in the case of **4b** or tetrahydrofuran (50 mL) in the case of **4e**. The resultant mixture was cooled to 0–5 °C and 3,4,5,6-tetrahydrobenzoyl chloride (15.9 g, 0.11 mol) was added dropwise with stirring. The reaction mixture was stirred at room temperature for 1 h and refluxed for 2 h. The mixture was then poured on to cold 10% hydrochloric acid (200 mL) and extracted with ether. The organic phase was washed twice with saturated aqueous sodium bicarbonate and water and then dried (Na_2SO_4). The solvent was removed and the residue (ethyl ((tetrahydrobenzoyl)acyl)acetate) was refluxed for 12 h with ethanolic hydrogen chloride prepared from absolute ethanol (50 mL) and acetyl chloride (2 mL). After distillation of ethanol the residue was distilled under reduced pressure to afford **4a,e** as a mixture of cis and trans isomers as determined by ^1H NMR. The cis compounds showed their C-8a protons at lower field than those of the trans isomers.[1]

3-(Ethoxycarbonyl)-2-methyl-4a,5,6,7,8,8a-hexahydrobenzo-4-pyranone (4b): yield 73%; bp 120–160 °C (2 mmHg); the cis/trans isomer ratio was 45:55; IR 1730, 1680, 1600 cm^{-1}; ^1H NMR δ 1.33 (t, J = 7 Hz, 3 H), 1.30–2.50 (m, 9 H), 2.20 (s, 0.55 H, CH_3 trans), 2.21 (s, 0.45 H, CH_3 cis), 4.04 (m, $W_{1/2}$ = 26 Hz, 0.55 H, H-8a trans), 4.30 (q, J = 7 Hz, H), 4.58 (m, $W_{1/2}$ = 8 Hz, 0.45 H, H-8a cis).

The cis–trans mixture partly crystallized on standing; recrystallization of the solid material from hexane afforded the pure trans isomer: mp 65 °C (lit.[9] mp 66 °C).

2-*tert*-Butyl-3-(ethoxycarbonyl)-4a,5,6,7,8,8a-hexahydrobenzo-4-pyranone (4e): yield 65%; bp 120–125 °C (0.5 mmHg); the cis/trans isomer ratio was 75:25; IR 1735, 1675, 1590 cm^{-1}; ^1H NMR δ 1.25 (s, 9 H), 1.33 (t, J = 7 Hz, 3 H), 1.20–2.50 (m, 9 H), 3.85 (m, $W_{1/2}$ = 26 Hz, 0.25 H, H-8a trans), 4.25 (q, J = 7 Hz, 2 H), 4.43 (m, $W_{1/2}$ = 8 Hz, 0.75 H, H-8a cis). Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.67; H, 8.79.

(b) 4a,5,6,7,8,8a-Hexahydrobenzo-4-pyranones (5b,e). Compound **4b,e** (10 mmol) was added dropwise to polyphosphoric acid (10 g) preheated to 120–130 °C. After being stirred at that temperature for 30 min, the mixture was poured on to ice/water and extracted with chloroform (4 × 50 mL). The combined extracts were washed with water (2 × 30 mL) and dried (Na_2SO_4). After evaporation of the solvent the residue was distilled under reduced pressure to afford a cis and trans mixture of isomers **5b,e**.

2-Methyl-4a,5,6,7,8,8a-tetrahydrobenzo-4-pyranone (5b): yield 57%; bp 90–100 °C (1 mmHg); the cis/trans isomer ratio was 45:55, IR 1645, 1620 cm^{-1}; ^1H NMR δ 1.00–2.35 (m, 9 H), 2.00 (s, 0.55 H, CH_3 trans), 2.03 (s, 0.45 H, CH_3 cis), 3.98 (m, $W_{1/2}$ = 28 Hz, 0.55 H, H-8a trans), 4.50 (m, $W_{1/2}$ = 8 Hz, 0.45 H, H-8a cis), 5.28 (s, 0.45 H, H-3 cis), 5.30 (s, 0.55 H, H-3 trans). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.29; H, 8.65.

2-*tert*-Butyl-4a,5,6,7,8,8a-tetrahydrobenzo-4-pyranone (5e): yield 59%; bp 100–105 °C (0.5 mmHg); the cis/trans isomer ratio was 75:25; IR 1665, 1595 cm^{-1}; ^1H NMR δ 1.15 (s, 0.25 H, *t*-Bu trans), 1.18 (s, 0.75 H, *t*-Bu cis), 1.00–2.50 (m, 9 H), 3.87 (m, J = 13, 10.5 and 4 Hz, 0.25 H, H-8a trans), 4.43 (m, $W_{1/2}$ = 8 Hz, 0.75 H, H-8a cis), 5.34 (s, 0.75 H, H-3 cis), 5.39 (s, 0.25 H, H-3 trans). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.91; H, 9.76.

(c) 1-Oxa-4-decalones (3b,e). A mixture of **4b,e** (10 mmol) and palladium/charcoal (10%, 1 g) in methanol (30 mL) was stirred in a hydrogen atmosphere at room temperature. After uptake of the calculated amount of hydrogen, the catalyst was

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filtered off and the solvent was evaporated. The mixture was distilled under reduced pressure to give a mixture of *trans*- and *cis*-**3b,e**.

2β-Methyl-1-oxa-4-decalone[29,31] (**3b**): yield 85%; bp 76–78 °C (0.5 mmHg); cis/trans ratio 45:55.

2β-*tert*-Butyl-1-oxa-4-decalone[28] (**3e**): yield 83%; bp 82–84 °C (0.5 mmHg); cis/trans ratio 75:25. Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.23; H, 10.55. Pure epimers were obtained by GLC as described above.

Equilibration of 1-Oxa-4-decalones 3. A solution of cis and trans isomers **3** (10 mmol) in ethanol (15 mL) and triethylamine (1.46 g, 15 mmol) was refluxed for 48 h and concentrated in vacuo. The residue was distilled under reduced pressure and analyzed by GLC. The trans/cis ratios were 9:1 for **3a–c,e** and 65:35 for **3d**.

Registry No. **1a**, 29798-89-8; **1b**, 13738-56-2; **1c**, 29798-90-1; **1d**, 91743-36-1; **2a**, 51599-61-2; **2b**, 91743-37-2; **2c**, 91743-38-3; **2d**, 91743-39-4; *trans*-**3a**, 51600-19-2; *cis*-**3a**, 51600-16-9; **3b**, 55023-43-3; *trans*-**3c**, 91743-40-7; *cis*-**3c**, 91743-43-0; **3d**, 91743-41-8; **3e**, 91743-42-9; *trans*-**4b**, 91743-44-1; *cis*-**4b**, 91743-48-5; *trans*-**4e**, 91743-45-2; *cis*-**4e**, 91743-49-6; *trans*-**5b**, 91743-46-3; *cis*-**5b**, 91743-50-9; *trans*-**5e**, 91743-47-4; *cis*-**5e**, 91743-51-0; 4-*tert*-butyl-1-morpholino-1-cyclohexene, 16963-28-3; 3-methyl-2-butenoyl chloride, 3350-78-5; ethyl acetylacetate, 141-97-9; ethyl pivaloylacetate, 17094-34-7; 3,4,5,6-tetrahydrobenzoyl chloride, 36278-22-5.

Catalytic Conversion of Fluoroalkyl Alkyl Ethers to Carbonyl Compounds

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Fluoroalkyl alkyl ethers are generally available by attack of alkoxide ion on fluoro olefins. In the presence of Lewis acid catalysts, such methyl and ethyl ethers have now been found to lose methyl or ethyl fluoride, respectively, to give fluorinated carbonyl compounds. The carbonyl compounds include acid fluoride, ketone, keto ester, vinyl ketone, acyl ketene, ketene, and acryloyl fluoride.

Fluorine atoms attached to carbon which also bears an alkyl ether group are known to be labile to electrophilic reagents. They are readily hydrolyzed in concentrated sulfuric acid, thus providing a route to some esters of fluoroacids.[2] The use of sulfur trioxide or fluorosulfonic acid gives acid fluorides, and chlorosulfonic acid gives acid chlorides.[3]

$$R_fCOF + CH_3OSO_2F \xleftarrow{SO_3} R_fCF_2OCH_3 \xrightarrow[H_2SO_4]{H_2O} R_fCOOCH_3 + HF$$

$$\xrightarrow{ClSO_3H} R_fCOCl + CH_3OSO_2F + HF \qquad \xrightarrow{FSO_3H} R_fCOF + CH_3OSO_2F + HF$$

The use of sulfur trioxide has been especially valuable to prepare, from methyl ethers, acid fluorides which were desired in our research. However, sulfur trioxide (bp 42 °C) and the toxic byproduct, methyl fluorosulfate (bp 92 °C), are difficult to handle and must be separated from the desired acid fluoride product.

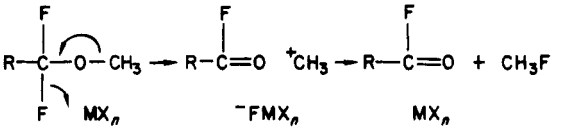
Results and Discussion

In an early experiment,[4] 1 mol of 3-methoxyperfluoropropionyl fluoride[5] was heated with 1.5 mol of titanium tetrafluoride in a sealed vessel at 175 °C to give a 77% yield of perfluoromalonyl fluoride (**2**) and methyl fluoride.

$$\underset{\mathbf{1}}{CH_3OCF_2CF_2COF} \xrightarrow{TiF_4} \underset{\mathbf{2}}{CF_2(COF)_2} + CH_3F$$

It was subsequently shown that this reaction is catalytic and can be carried out exothermally at atmospheric pressure and at low temperatures in high yield on a number of related compounds.[4] Antimony pentafluoride is one of many effective metal halide, Lewis acid type catalysts.[4] Because the reaction is clean and gives only a gas, methyl fluoride (bp −80 °C), as byproduct, it provides an excellent replacement for the use of sulfur trioxide to prepare acid fluorides from methyl fluoro ethers.

The mechanism may involve abstracting fluorine from a C–F bond giving the acid fluoride, a metal fluoride anion, and a methyl cation. The latter two unite to give methyl fluoride and regenerate the catalyst. Alternately, a concerted, cyclic transition state may be involved.[6] If a metal halide other than fluoride is used as catalyst, that methyl halide is evolved in initial stages of the reaction along with methyl fluoride.



The exothermic reaction is best controlled by regulating addition of the ether with stirring into a pot containing the neat catalyst. The product can often act as a moderating solvent; boiling lower than starting material, it can be fractionated from the mixture. Methyl fluoride is evolved as gas. Fresh catalyst can be added as required.

In addition to the preparation of acid fluorides by removal of CH_3F from the $-CF_2OCH_3$ group, ketones can be prepared from the $-CF(OCH_3)-$ group and ketenes and/or acryloyl fluorides from $FC(OCH_3)=C(F \text{ or } CF_3)CF_3$ where

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(6) The author is indebted to referees for this suggestion which avoids formation of a methyl cation. One has suggested that the use of a butyl ether would be informative, since the cation would be expected to rearrange to give *sec*-butyl fluoride.

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