TABLE II

BENZYLAMINE REACTION WITH *o*-BENZENEDISULFONYL CHLORIDE

No.	Mole ratio of amine:chloride	Solvent	Base[a]	Time/temp[b]	Product ratio[c] of imide:bis amide
1	4:1	THF	5% aq NaOH	0.5 hr/RT	80%[c]
2	3:1	C_6H_6	NaH[d]	0.5 hr/Δ	56%[c]
3	4:1	$(CH_3O)_3B$		2 hr/Δ	56%[c]
4	1:1	C_6H_6	$BF_3 \cdot Et_2O$ (4) + C_5H_5N (4)	4 hr/Δ	1:3
5	1:1	C_6H_6	Et_3N	5 min/RT	1:1
6	1:1[e]	C_6H_6	C_6H_5N	1 hr/RT	1:4
7	1:1	CH_2Cl_2	Et_3N (1)[f]	0.5 hr/RT	3:2
8	1:1[e]	*t*-BuOH	*t*-BuO^- (2)	3 hr/RT	1:1
9	1:1[e]	*t*-BuOH	*t*-BuO^- (2)	4 hr/Δ	1:1

[a] Excess base, except (no./equiv) in parentheses. [b] RT = room temp; Δ = reflux. [c] Isolated yield of bis amide noted. [d] Amine added first to NaH. [e] Slow addition of amine last, over 0.5–1 hr. [f] 1 equiv of base first (with chloride), then slow addition of amine followed by excess base.

cooled. 42 mg (36%) crystalline ZCH_2CH_2Ph sublimed to colorless crystals, mp 112–3°. Ir: 7.40, 8.42, 8.62 μ. Nmr: τ 2.05 (d, 4 H), 2.68 (s, 5 H), 5.89–6.92 (m, 4 H). Second crop 17 mg (14%) ZCH_2CH_2Ph (total yield 50%).

Reactions of ZCH_2CH_2Ph.—84% recovery from 24 hr/100°/C_5H_5N + 1 equiv Et_3N. At 170°/N_2/2 hr in 1,5-diazabicyclo-[4.3.0]-5-nonene, ZCH_2CH_2Ph was destroyed. Residue + Br_2 yielded 5% $PhCHBrCH_2Br$.

161 mg (0.5 mmol) ZCH_2CH_2Ph + 112 mg (2 mmol) KOH ground + Δ/N_2/180°/80 mm/2 hr. Distillate + $Br_2/CHCl_3 \rightarrow$ 14 mg (11%) $PhCHBrCH_2Br$, recryst/aq EtOH to mp 72–3° (lit.[13] 74°).

***o*-Benzenedisulfonhydrazide.**—0.30 g 95% NH_2NH_2/8 ml EtOH. Added disulfonyl chloride (0.8 g)/15 ml C_6H_6/0°. After 5 min filtered crystals, washed/H_2O + C_6H_6. 0.45 g (67%), mp 123–6°; recryst/THF–petrol ether, mp 126–8°. Ir: 2.92, 3.03, 7.50, 8.58 μ. Nmr: τ 1.8–2.4 (m, 4 H), 6.3 (m, ~5 H), disappears/D_2O).

Anal. Calcd for $C_6H_{10}S_2O_4N_4$: C, 27.05; H, 3.77; N, 21.05; S, 24.05. Found: C, 27.32; H, 3.80; N, 21.23; S, 23.81.

Suspension/hydrazide (50 mg)/H_2O slowly bubbles + soln overnight. Evap/vac/RT to 42 mg (98%) white solid, mp ~70° (bubbles), insol/$CHCl_3$. Ir: 3–4 (br), 7.5, 8.6, 9.9, 10.5 μ. Solid goes gummy in 2 days or on recryst. Hydrazide/H_2O + Br_2: bubbles, decolorizes. Evap to crystals, ir identical with *o*-benzenedisulfonic acid.

22 mg white solid/CH_3OH + 13 mg *p*-$MeOC_6H_4CHO \rightarrow$ 19 mg (76%) azine (*p*-$MeOC_6H_4CH{=}N)_2$ identified with authentic sample.

***o*-Benzenedisulfonyl Azide.**—30 mg hydrazide + 5 ml/20% aq H_2SO_4. Added 50 mg $NaNO_2/H_2O$. Ppt 25 mg, mp 112–4°, identical with authentic sample from disulfonyl Cl with NaN_3. Ir: 4.60, 7.24, 7.32, 8.5 μ. Ms: 246 (p − 42) but no parent at 288.

Anal. Calcd for $C_6H_4S_2O_4N_6$: C, 25.05; H, 139; N, 29.21; S, 22.22. Found: C, 24.79; H, 1.41; N, 29.03; S, 22.51.

Registry No.—ZH, 4482-01-3; Z-Cl, 21691-08-7; Z-Br, 21691-09-8; Z-OCH_3, 21691-10-1; Z-$OCOCH_3$, 21691-11-2; ZCH_2Ph, 21748-37-8; ZCH_2CH_2Ph, 21691-12-3; Z-Cl, cyclohexene adduct, 21691-13-4; *o*-benzenedisulfinic acid, 21691-14-5; N,N′-dibenzyl-*o*-benzenedisulfonamide, 21691-15-6; *o*-benzenedisulfonhydrazide, 21691-16-7; *o*-benzenedisulfonyl azide, 21691-17-8.

Acknowledgment.—We wish to extend our gratitude to the National Science Foundation for a research grant (GP-5525) partially supporting these studies.

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(13) C. Glaser, *Ann. Chem.*, **154**, 154 (1870).

The Preparation and Reactions of Perfluoro-β-oxa-δ-valerolactone

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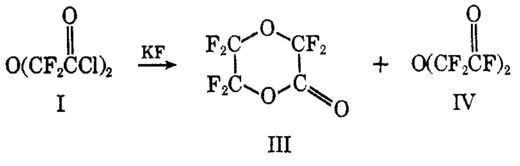
The preparation of perfluoro-β-oxa-δ-valerolactone (III) from perfluorooxydiacetyl chloride (I) and fluoride (IV) and metal fluorides is described. Reaction of III with excess water, methanol, and ammonia gives perfluorooxydiacetic acid, dimethylperfluorooxy diacetate, and perfluorooxydiacetamide, respectively. Ultraviolet irradiation of III gives perfluoro-1,3-dioxolane (V).

In a study of the chemistry of certain perfluoroacyl halides, it has been found that perfluoro-β-oxa-δ-valerolactone is formed when perfluorooxydiacetyl chloride or fluoride is allowed to react with metal fluorides. It is the purpose of this paper to describe the preparation and some chemical reactions of perfluoro-β-oxa-δ-valerolactone, and to describe the formation of perfluoro-1,3-dioxolane from the photolytic decarbonylation of this new lactone.

The reaction of perfluorooxydiacetyl chloride (I) with anhydrous potassium fluoride (eq 1) proceeded smoothly giving a 90% yield of perfluorinated product which was found to contain 44% perfluoro-β-oxa-δ-valerolactone (III) and 56% perfluorooxydiacetyl fluoride[1] (IV). Fractional distillation afforded pure samples of the two isomeric products which were readily differentiated by spectroscopic analyses, and further characterized by elemental analysis.



(1)

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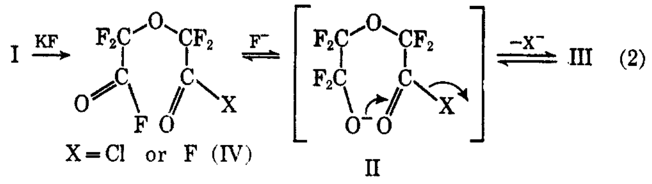
(1) J. L. Warnell, U. S. Patent 3,250,806 (1966).

Formation of a lactone in the reaction of I with KF (eq 1) may be rationalized by postulating the formation of a perfluoroalkoxide intermediate (II, X = F) by reaction of IV with fluoride ion followed by cyclization of this fluoroformyl-substituted perfluoroalkoxide to give III (eq 2). The formation of perfluoroalkoxides in similar situations is well documented.[2] In support of the intermediacy of II (X = F), it was found that both III and IV react with fluoride ion, *e.g.*, as provided



(2)

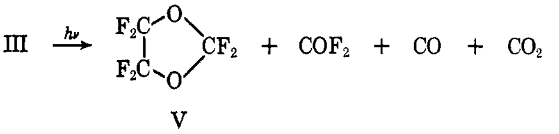
by cesium fluoride, to give an equilibrium mixture containing 36–42% III and 58–64% IV. These results are entirely consistent with the known ability of perfluoro acid fluorides and metal fluorides to exist in equilibrium[2] with perfluoroalkoxides and the generally inherent tendency of six-membered intermediates to cyclize.

Attempts were made to extend the lactone formation reaction to perfluoroglutaryl, perfluoroadipyl, and perfluorooxydipropionyl chlorides and fluorides, but in each case the only isolable product was the corresponding acid fluoride. Although the failure of perfluoroadipyl and perfluorooxydipropionyl fluorides to cyclize into the respective seven- and eight-membered-ring lactones was not entirely unexpected, the failure of perfluoroglutaryl fluoride to yield a six-membered-ring lactone as did IV is surprising. However, examination of space filling models (Stuart–Breglieb) reveals considerably more flexibility, because of less crowding, in segments of CF_2OCF_2 compared to $CF_2CF_2CF_2$, and suggests that cyclization of IV could be expected to proceed more readily than cyclization of perfluoroglutaryl fluoride. Interestingly, Banks and Mullen have recently reported[3] that perfluorosuccinyl fluoride also failed to give perfluorobutyrolactone on treatment with fluoride ions, but that the reverse reaction, conversion of the lactone to the acid fluoride, was readily achieved.

Although III is sensitive to moisture and must be handled under anhydrous conditions in order to prevent partial hydrolysis and subsequent equilibration with IV, it has exhibited excellent storage stability. For example, III has been stored in glass bulbs at room temperature for periods as long as 4 months without noticeable change. However, in the presence of excess water III is converted in essentially quantitative yield to perfluorooxydiacetic acid. Similarly, reaction of III with excess methanol or ammonia affords near quantitative yields of dimethyl perfluorooxydiacetate and perfluorooxydiacetamide, respectively.

While the photochemistry of hydrocarbon esters[4] and lactones[4,5] has been described, photolyses of perfluoroesters or perfluorolactones have not been reported. Since III was readily available from reaction of I or IV with fluoride ions, it was of interest to investigate the photolysis of this perfluorolactone.

The ultraviolet irradiation of either gaseous III or an FC-75[6] solution of III gives perfluoro-1,3-dioxolane (V), carbonyl fluoride, carbon monoxide, and carbon dioxide (eq 3). Vapor phase chromatography afforded



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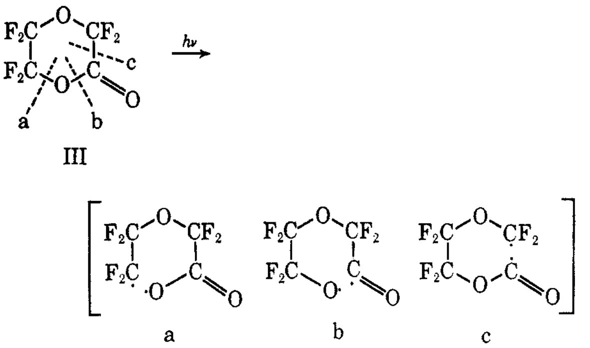
a pure sample of V which was characterized by elemental and spectroscopic analyses and which is inert to mineral acids and to concentrated base solutions.

As with the hydrocarbon lactones,[4,5] irradiation of III probably results initially in breakage of any of three different bonds (labeled a, b, and c in eq 4) and thence



(4)

to product. While the present data are insufficient for a mechanistic interpretation, isolation of V in 70% yield from the solution photolysis would appear to favor bond breakage at b and/or c over bond breakage at a as the main course of reaction.

Experimental Section

Infrared spectra were measured on a Perkin-Elmer Model 21 double-beam instrument using a 2.5-cm gas cell fitted with NaCl windows. The ultraviolet spectra were taken on a Beckman DK-2 spectrometer using a 5-cm quartz gas cell. Nuclear magnetic resonance measurements were made with a Varian V-4300-2 instrument operating at 40.0 Mc and utilizing an internal standard of $CFCl_3$ for the determination of chemical shifts. The values reported are ϕ^* values at a dilution of 10–25%. Trifluoroacetic acid is ϕ^* 76.5 on this scale. Mass spectra were measured utilizing a C.E.C. 21-103c instrument with an inlet temperature of 30°, ion chamber temperature of 250°, ion voltage of 70 V, and ion current of 10 μA. Molecular weights were determined by effusion. Peaks reported are the strongest and/or most significant ones and are described by *m/e* (relative intensity) assigned ion. Vapor phase chromatographic separations of III and IV were made using a 3 ft × 0.25 in. column of FS-1265 on Chromosorb P and by condensing the products in the effluent gas at −196° in a trap filled with glass beads. Vapor phase chromatographic separation of V was made using a 3 m × 0.5 in. column of FC-43 on Chromosorb P.

Perfluorooxydiacetyl Chloride.—Perfluorooxydiacetic acid (212 g, 1.03 mol) and phthaloyl chloride (529 g, 2.6 mol) were combined and refluxed for 8 hr. Distillation of the reaction mixture afforded 235 g (94%) of crude acid chloride, bp 72–90°. Redistillation gave 199 g (80%) of pure perfluorooxydiacetyl chloride, bp 95°: ir (neat) 5.56 μ (C═O); ^{19}F nmr, ϕ^* 76.8[7] (CF_2, s).

Anal. Calcd for $C_4Cl_2F_4O_3$: C, 19.77; Cl, 29.19; F, 31.28. Found: C, 19.8; Cl, 29.1; F, 31.0.

Perfluoro-β-oxa-δ-valerolactone.—A mixture of I (304 g, 1.25 mol) and anhydrous potassium fluoride (185 g, 3.2 mol) was

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[2] J. A. Young, *Fluorine Chem. Rev.*, **1**, 389 (1967).

[3] R. E. Banks and K. Mullen, *J. Chem. Soc., C*, 2333 (1967).

[4] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, New York, N. Y., 1966.

[5] R. Simonaitis and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **90**, 1389 (1968).

[6] 3M Brand Inert Fluorochemical Liquid.

[7] G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

placed in a three-necked flask fitted with a stirrer, thermometer, and condenser connected to a −78° trap, and stirred and heated under reflux until the reflux temperature decreased to a constant value (68–35°). Addition of small amounts of KSO_2F (<10%) is advantageous in the event of a slow reaction. Distillation at atmospheric pressure, bp 25–38° (178 g), and finally under vacuum (59 g collected in the −78° trap) yielded 237 g (90%) of product which, by vapor phase chromatographic analysis, consisted of 44% III and 56% IV. Fractionation of the product on a spinning-band distillation column gave three fractions: fraction 1, bp 23–34°, 64% III and 36% IV by vapor phase chromatography; fraction 2, bp 34–37°, 20% III and 80% IV by vapor phase chromatography; and fraction 3, bp 37–38.5°, 8% III and 92% IV by vapor phase chromatography.

Redistillation of fraction I gave pure III, bp 29–30°, 99.7% by vapor phase chromatography. An analytical sample was obtained by vapor phase chromatography of redistilled material: ir (gas) 5.36 μ (C=O); uv max (gas) 225 mμ (ε ~40); ^{19}F nmr, ϕ^* 70.0 (CF_2 C=O, complex), 89.7 ($CF_2OC{=}O$, complex), 86.6 ($CF_2CF_2OC{=}O$, complex). The mass spectrum is summarized as follows: 28 (10.2) CO, 31 (43.8) CF, 47 (73.8) CFO, 50 (100) CF_2, 69 (58.6) CF_3, 75 (8.8) C_2FO_2, 78 (7.4) C_2F_2O, 97 (24.5) C_2F_3O, 100 (72.1) C_2F_4, 116 (12.7) C_2F_4O, 163 (2.5) $C_3F_5O_2$, 191 (0.6) $C_4F_5O_3$.

Anal. Calcd for $C_4F_6O_3$: C, 22.87; F, 54.28; mol wt, 210.04. Found: C, 22.70; F, 54.30; mol wt, 210.8.

Redistillation of fraction 3 gave purified IV,[1] pb 37–38° (98%), which was chromatographed to obtain an analytical sample: ir (gas) 5.28 μ (C=O); uv max (gas) 214.5 mμ (ε ~130); ^{19}F nmr, ϕ^* −13.3 (-COF; 5-fold, J = 2.1 cps) and 76.7 (CF_2, t, J = 2.1 cps). The mass spectrum is summarized as follows: 28 (10.0) CO, 31 (25.1) CF, 47 (63.0) CFO, 50 (26.0) CF_2, 69 (100) CF_3, 97 (53.4) C_2F_3O, 100 (1.1) C_2F_4, 116 (1.7) C_2F_4O, 163 (10.5) $C_3F_5O_2$.

Anal. Calcd for $C_4F_6O_3$: C, 22.87; F, 54.28; mol wt, 210.04. Found: C, 22.80; F, 53.80; mol wt, 208.3.

B. From IV.—A mixture of IV (93%, 0.018 CFO equiv), III (3.5%), and perfluorooxydiacetic anhydride (3.5%) was condensed onto anhydrous cesium fluoride (0.8 g, 0.005 mol) in a glass ampoule containing a stirring bar and fitted with a Fischer–Porter Teflon valve. The mixture was stirred until the ratio of the carbonyl absorption bands of III and IV was constant (*ca.* 24 hr). Vapor phase chromatography of the product revealed a mixture of IV (60%), III (36%), and anhydride (3%).

Perfluorooxydiacetyl Fluoride.[1] **A. From III.**—A mixture of III (90%), IV (6.5%), and perfluorooxydiacetic anhydride (3.5%) was condensed onto cesium fluoride in a glass ampoule containing a stirring bar and fitted with a Fischer–Porter Teflon valve, and the mixture stirred until the infrared indicated a mixture of III and IV of constant composition. Transferal of the product to an ampoule cooled to −196° followed by vapor phase chromatography of the product revealed a mixture of 54% IV, 43% III, and 3% anhydride.

Reaction of III with Water, Methanol, and Ammonia.—In each case, III was condensed onto excess water, methanol, or ammonia contained in a glass ampoule fitted with a Fischer–Porter Teflon valve; the reactor was then warmed to room temperature with shaking and the product worked up. Extraction of the water solution with ether followed by drying ($CaSO_4$) and then sublimation of the residue from evaporation of the ether gave 0.7 g of sublimed acid from 0.9 g of III. Evaporation of the methanol gave 1.3 g of ester from 1.2 g of III from which 1.0 g of distilled ester was obtained. The excess ammonia was allowed to evaporate and the amide taken up in acetone and the insoluble ammonium fluoride removed by filtration. Evaporation of the acetone afforded 0.75 g of amide from 0.8 g of III. The infrared and ^{19}F nmr spectra of the acid, ester, and amide prepared in the described way were found to be identical with the spectra of authentic samples. The preparation and properties of these authentic samples is described below.

Perfluorooxydiacetic Acid.—Diethyl perfluorooxydiacetate, which may be obtained by the method of Banks and Burling,[8] was hydrolyzed with dilute base and processed to the acid in the usual way. The acid was recrystallized from benzene and an analytical sample obtained by sublimation: ir (Nujol) 5.69 μ (C=O); ^{19}F nmr (acetone), ϕ^* 78.1 (CF_2, s).

Anal. Calcd for $C_4H_2F_4O_5$: C, 23.34; H, 0.97; F, 36.88; equiv wt, 103.03. Found: C, 23.5; H, 1.1; F, 37.1; equiv wt, 104.

Dimethyl Perfluorooxydiacetate is prepared by addition of methanol to the acid chloride and the product distilled, bp 76–77° (11 mm): ir (neat) 5.59 μ (C=O); ^{19}F nmr, ϕ^* 77.7 (CF_2, s).

Anal. Calcd for $C_6H_6F_4O_5$: C, 30.78; H, 2.58; F, 32.46. Found: C, 30.9; H, 2.6; F, 32.7.

Perfluorooxydiacetamide is prepared by passing ammonia through an ether solution of dimethyl perfluorooxydiacetate and recovering the insoluble product by filtration. Purification, if required, may be effected by recrystallization from water: ir (Nujol) 2.95 and 3.13 μ (NH), 5.79 μ (C=O); ^{19}F nmr, ϕ^* 78.0 (CF_2, s).

Anal. Calcd for $C_4H_4F_4N_2O_3$: C, 23.54; H, 1.97; F, 37.24; N, 13.74. Found: C, 23.7; H, 1.9; F, 37.3; N, 13.9.

Perfluoro-1,3-dioxolane (V). **A. Gas Phase.**—A 500-ml quartz bulb was charged with 250 mm of III and irradiated with a 140-W Hanovia ultraviolet lamp. After 2 hr, the infrared spectrum of the bulb contents suggested the presence of CO, CO_2, large amounts of COF_2, and small amounts of III. The gases were passed through −78 and −196° traps and V isolated from the −196° trap by vapor phase chromatography: ir (gas) 7.90 and 8.30 (CF_2 and CO), 9.70 and 10.25 μ (weak and unassigned); ^{19}F nmr, ϕ^* 57.40 (OCF_2O; 5-fold, J = 3.8 cps) and 87.7 (CF_2CF_2, t, J = 3.8 cps). The mass spectrum is summarized as follows: 28 (3.6) CO, 31 (22) CF, 47 (68) CFO, 50 (100) CF_2 69 (27.8) CF_3, 97 (9.8) C_2F_3O, 116 (14.9) C_2F_4O, 119 (10) C_2F_5, 163 (1.5) $C_3F_5O_2$.

Anal. Calcd for $C_3F_6O_2$: C, 19.79; F, 62.63; mol wt, 182.03. Found: C, 19.6; F, 62.4; mol wt, 183.

B. FC-75 Solution.—A mixture of III (14.7 g, 0.07 mol), IV (0.6 g, 0.003 mol), and FC-75 (233 g) was added to a three-necked quartz photoreactor fitted with a quartz immersion well and a water condenser which was connected in series to a −78° gas trap and a −183° gas trap protected with a Drierite drying tube. This stirred mixture was irradiated at 40° with a 450-W medium pressure mercury vapor ultraviolet lamp until the reaction mixture stopped bubbling (5 hr).

A total of 8.9 g (70%) of V was obtained by distillation of the FC-75 solution (5.2 g condensed in a −78° trap connected to the water condenser), and by vacuum line distillation of the −78° trap from the photolysis reaction through a −78° trap and a −196° trap (3.7 g).

Registry No.—I, 21297-62-1; III, 21297-63-2; IV, 21297-64-3; V, 21297-65-4; perfluorooxydiacetic acid, 6535-10-0; perfluorooxydiacetamide, 21297-67-6.

Acknowledgment.—The author wishes to express his gratitude to Dr. J. J. McBrady for infrared and ^{19}F nmr spectra, to Mr. S. Kulver for mass spectra, and to Mr. P. B. Olson and Mr. J. G. Gagnon for elemental analyses.

[8] R. E. Banks and E. D. Burling, *J. Chem. Soc.*, 6077 (1965).