was irradiated for 4 hr. under nitrogen at 17–27°. N.m.r. analysis of the raw product showed that 85% of the allyl chloride had reacted. Fractional distillation of the crude product yielded 671 g. (73%) of 3-chloropropyl ethyl sulfide between 58 and 64° at 10 mm. Kretov and Toropova[20] reported b.p. 58–72° (18 mm.). An n.m.r. spectrum of the product in carbon tetrachloride showed signals (parts per million from internal tetramethylsilane) as follows: 3.43 t (chloromethylene), 2.38 m (mercaptomethylenes), 1.80 p (middle methylene), and 1.11 t (methyl).

3-Chloropropyl Phenyl Sulfide.—A stirred mixture of 550 g. (5.0 moles) of benzenethiol and 382.5 g. (5.0 moles) of allyl chloride was irradiated for 9 hr. at 17–30° under a nitrogen atmosphere. N.m.r. analysis indicated that 66 mole % of the allyl chloride had been consumed. Fractional distillation of the crude product *in vacuo* produced 413.8 g. (44%) of 3-chloropropyl phenyl sulfide, b.p. 95–96° (0.45 mm.), n^{26}_{D} 1.5717 [lit.[21] b.p. 124–125° (7 mm.), n^{26}_{D} 1.5714]. An n.m.r. spectrum of the product in carbon tetrachloride showed signals (parts per million from internal tetramethylsilane) as follows: 7.17 s, 7.20 s (phenyl), 3.49 t (chloromethylene), 2.93 t (mercaptomethylene), and 1.91 p (middle methylene).

Unsymmetrical 1,3-Bis(substituted thio)propanes from 3-Chloropropyl Ethyl Sulfide.—The appropriate thiol (0.4 mole) was slowly added to a solution of 21.6 g. (0.4 mole) of sodium methylate in 200 ml. of methanol contained in a four-neck flask under a nitrogen atmosphere. Then 54.6 g. (0.4 mole) of 3-chloropropyl ethyl sulfide was slowly added to the mercaptide solution. The resulting mixture was refluxed for 2 hr. while a white precipitate formed. Methanol was then distilled from the reaction mixture, and water (150 ml.) and ether (100 ml.) were added to the distillation residue. The organic phase was separated and washed three times with water and dried over anhydrous sodium sulfate. Ether was stripped from the solution and the residue was distilled under high vacuum to obtain the purified product (Tables II and III).

1-Benzylthio-3-phenylthiopropane was prepared from 3-chloropropyl phenyl sulfide by the general procedure given above using benzylmercaptan and sodium methylate. After solvent removal, n.m.r. indicated greater than 95% purity of the crude product. Analytical and n.m.r. data of a distilled sample are shown in Tables II and III, respectively.

Acknowledgment.—The authors wish to thank G. J. Hart and A. M. Palmer for valuable technical help. The analytical work of Dr. W. Naegele (n.m.r.), E. R. Quiram, Miss M. J. Doolan (g.l.p.c.), and P. B. Gerhardt (elemental) is gratefully acknowledged.

---

(20) A. E. Kretov and E. M. Toropova, *J. Gen. Chem. USSR*, **7**, 2009 (1937); *Chem. Abstr.*, **32**, 518 (1938).

(21) W. H. Vinton, U. S. Patent 2,604,657 (1952); *Chem. Abstr.*, **47**, 1516*d* (1953).

Fluoro Ketones. III. Preparation and Thermal Decomposition of Fluoroacetone Hemiketal Esters[1]

PETER E. NEWALLIS AND PASQUALE LOMBARDO

General Chemical Research Laboratory, General Chemical Division, Allied Chemical Corporation, Morris Township, New Jersey

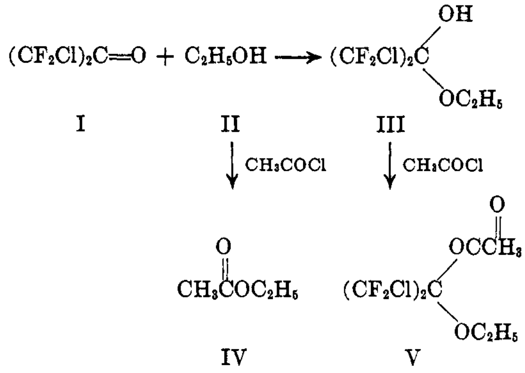
Received June 9, 1965

The preparation and properties of novel fluoroacetone hemiketal esters and carbonates are reported. Thermal decomposition of these esters gave the corresponding fluoroacetones and simple esters. A possible mechanism for these decompositions is presented.

The facile reaction of fluoroacetones with a wide variety of nucleophiles has been reported to give good yields of the corresponding adducts.[1b,2-4] These adducts are hydrolytically unstable, giving the fluoroacetone hydrate and starting nucleophile. For practical reasons, it was desired to convert these adducts to more stable derivatives.

Attempts to prepare esters of the amide–fluoroacetone adducts were unsuccessful,[1b] but esters, sulfonates, and carbamates of fluoroacetone cyanohydrins have recently been synthesized.[5] These results are in accord with the findings of Mill and co-workers.[4d]

Alcohols are known to react with fluoroacetones in an equilibrium reaction to give hemiketals such as III.[3b]



Distillation of these hemiketals was tedious and always accompanied by a considerable amount of the fluoroacetone (recovered from a cold trap). Consequently, crude hemiketals were largely used in the work reported in this paper.

Acetylation of III with acetyl chloride and pyridine was carried out in dry diethyl ether or tetrahydrofuran,[6] with distillation of the crude product at atmospheric pressure giving both IV and V. The formation of IV could be rationalized either by the acetylation of II (using the principle of microscopic reversibility) or by the decomposition of V. Distillation of the

---

(1) (a) Part I: B. Farah and S. Horensky, *J. Org. Chem.*, **28**, 2494 (1963); (b) part II: P. E. Newallis and E. J. Rumanowski, *ibid.*, **29**, 3114 (1964); (c) presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964; Abstracts, p. 23K.

(2) (a) C. Woolf, Abstracts, 132nd National Meeting of the American Chemical Society, New York, N. Y., Sept. 1957, p. 23 M; (b) A. L. Henne, J. W. Shepard, and E. J. Young, *J. Am. Chem. Soc.*, **72**, 3577 (1950); (c) A. T. Morse, P. B. A. Ayscough, and L. C. Leitch, *Can. J. Chem.*, **33**, 453 (1955).

(3) (a) I. L. Knunyants and Yu. A. Cherburkov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 678 (1960); (b) H. E. Simmons and D. W. Wiley, *J. Am. Chem. Soc.*, **82**, 2288 (1960); (c) I. L. Knunyants, C. Ch'ing-yun, and N. P. Gambaryan, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 686 (1960); (d) R. G. Koshyanovskii, *Proc. Acad. Sci. USSR, Chem. Sect.*, **137**, 379 (1961).

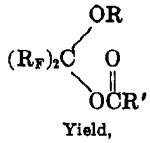
(4) (a) I. L. Knunyants, Yu. M. Rokhlin, N. P. Gambaryan, Yu. A. Cherburkov, and C. Tsin-Yun, *Khim. Nauka i Promy.*, **4**, 802 (1959); (b) F. W. Hoover, H. B. Stevenson, and H. S. Rothrock, *J. Org. Chem.*, **28**, 1825 (1963); (c) S. Andreades, *ibid.*, **27**, 4157 (1962); (d) T. Mill, J. O. Rodin, R. M. Silverstein, and C. Woolf, *ibid.*, **29**, 3715 (1964).

(5) E. J. Rumanowski, unpublished results.

(6) Dissolving III in ether or tetrahydrofuran liberated a considerable amount of heat, probably due to the formation of strong hydrogen bonds. Hexafluoroisopropyl alcohol, for example, has been recently reported to form strong hydrogen bonds with tetrahydrofuran [see W. J. Middleton and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **86**, 4948 (1964)].

TABLE I

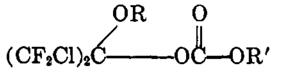
FLUOROACETONE HEMIKETAL ESTERS

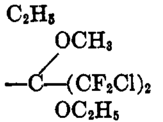
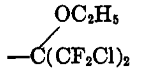

$(R_F)_2C(OR)OC(=O)R'$

R_F	R	R′	B.p., °C. (mm.)	Yield, %	$n^{25}D$	Calcd., % C	Calcd., % H	Calcd., % F	Found, % C	Found, % H	Found, % F
CF_2Cl	C_2H_5	CH_3	42–43 (1.2)	84	1.3917	29.3	2.81	26.5	29.5	2.90	27.0
CF_2Cl	$(CH_3)_3C$	CH_3	47–48 (2.0)	46	1.4062	34.3	3.85	24.1	34.5	3.94	24.5
CF_2Cl	$C_6H_5CH_2$	CH_3	106 (0.95)	64.5	1.4628	41.3	2.89	21.8	41.2	2.78	22.0
CF_2Cl	$C_6H_5CH_2CH_2$	CH_3	111–114 (0.2)	66	1.4602	43.0	3.34	20.9	42.8	3.50	21.1
CF_2Cl	$ClCH_2CH_2$	CH_3	67 (0.8)	66	1.4130	26.1	2.19	23.6	25.8	2.18	24.4
CF_2Cl $CFCl_2$	$CH_3OCH_2CH_2$	CH_3	84 (0.8)	42	1.4284	28.8	3.01	17.1	28.3	2.97	18.4
CF_2Cl	Cyclopentyl	CH_3	66 (0.5)	63	1.4223	36.7	3.70	23.2	36.5	3.73	23.5
CF_2Cl	2-*exo*-Norbornyl	CH_3	101 (1.6)	61	1.4377	40.8	3.98	21.5	40.9	3.74	21.3
CF_3	C_2H_5	CH_2Cl	160–161	65	1.3584	29.2	2.44	39.5	29.2	2.84	39.0
CF_2Cl	$(CH_3)_2CH$	CH_2Cl	95–96 (4.3)	42	1.4171	28.6	2.70	22.6	29.0	2.70	23.0
CF_2Cl	n-$C_{10}H_{21}$	CH_2Cl	122–124 (0.2)	32	1.4318	41.5	5.35	17.5	41.9	4.30	17.3
CF_2Cl	C_2H_5	C_6H_5	103 (1.1)	50	1.4655	41.3	2.89	21.8	41.3	2.78	22.4
CF_2Cl	C_2H_5	CH_2Cl	64 (1.4)	80	1.4136	26.1	2.19	23.6	26.2	2.00	23.4
CF_2Cl	C_2H_5	$CHCl_2$	56–70 (0.65)	39	1.4210	23.0	1.70	20.8	23.4	1.62	22.0
CF_2Cl	C_2H_5	CCl_3	52 (0.75)	0.5	1.4265	21.6	1.29	19.6	21.8	1.49	20.1

TABLE II

sym-TETRAFLUORODICHLOROACETONE HEMIKETAL CARBONATES


$(CF_2Cl)_2C(OR)—OC(=O)—OR'$

R	R′	B.p., °C. (mm.)	Yield, %	$n^{25}D$	Calcd., % C	Calcd., % H	Calcd., % F	Found, % C	Found, % H	Found, % F
C_2H_5	C_2H_5	53 (0.45)	67	1.3975	30.3	3.19	24.8	29.6	3.13	25.0
CH_3	 $—C(OCH_3)(CF_2Cl)_2$	86.7 (1.0)	13	1.3985	22.1	1.24	31.1	22.5	1.22	30.8
C_2H_5	 $—C(OC_2H_5)(CF_2Cl)_2$	92 (0.45)	8	1.3996	25.6	1.96	29.5	25.5	2.00	29.8

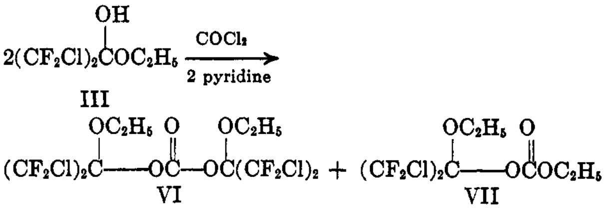
crude product under reduced pressure afforded a good yield of V with only a small amount of IV. This suggests that most of IV must have arisen from the thermal decomposition of V during the distillation at atmospheric pressure. Other acid chlorides reacted similarly with hemiketals to give the appropriate esters as shown in Table I.

The hemiketal esters were usually prepared by the dropwise addition of pyridine to a cooled ethereal solution of the hemiketal and the acid chloride. Preformation of the pyridine salt of III followed by the addition of acetyl chloride resulted in a slower rate of reaction.[7]

Substitution of chlorine in the α-position of acetyl chloride produced a marked decrease in the yield of corresponding ester, the magnitude of this effect being proportional to the degree of substitution. Several attempts to prepare the trichloroacetate of III gave a maximum yield of only 0.5%.[8]

The infrared spectra of the hemiketal esters exhibited characteristic bands at 5.5 to 5.65 μ (C = O) and intense bands at 8.0 to 9.0 μ (C–F). The F^{19} n.m.r. spectra gave sharp singlets at 59 to 61 p.p.m. from $CFCl_3$.

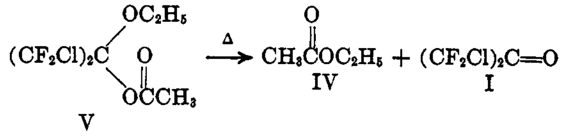
The reaction of phosgene with III (1:2 molar ratio) afforded a low yield of the anticipated carbonate VI and the mixed carbonate VII. Ethyl chloroformate, however, gave a good yield of VII (see Table II). Both VI and VII were quite unstable, decomposing


$$2(CF_2Cl)_2C(OH)OC_2H_5 \xrightarrow[\text{2 pyridine}]{COCl_2} (CF_2Cl)_2C(OC_2H_5)—OC(=O)—OC(OC_2H_5)(CF_2Cl)_2 + (CF_2Cl)_2C(OC_2H_5)—OC(=O)OC_2H_5$$

III VI VII

slowly on standing at ambient temperatures. These carbonates exhibited infrared bands at 5.5–5.6 μ (C=O) and intense bands at 8.0–9.0 μ (C–F).

Although hemiketal esters are both thermally and hydrolytically more stable than the corresponding hemiketals, they could be readily pyrolyzed to the fluoroacetones and nonfluorinated esters. These decompositions occurred smoothly at moderate temperatures (97–230°) compared with normal ester pyrolyses (*ca.* 500°).[9] The apparent driving force is the elimina-


$$(CF_2Cl)_2C(OC_2H_5)OC(=O)CH_3 \xrightarrow{\Delta} CH_3C(=O)OC_2H_5 + (CF_2Cl)_2C{=}O$$

V IV I

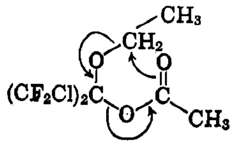
---

[7] Other amine salts of hemiketals were also found to be surprisingly stable: P. Lombardo, unpublished observations.

[8] In order to obtain satisfactory analysis, it was necessary to purify this compound by preparative gas chromatography. An F & M Model 720 with an 8-ft. preparative column packed with 10% silicone rubber SE-30 on 60–80-mesh Diatoport W was used.

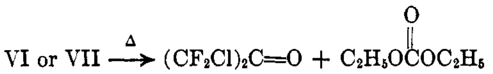
[9] C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

tion of the volatile fluoroacetone, and it seems likely that a mechanism similar to that of normal ester pyrolyses is operative,[9] *e.g.*, VIII. Preliminary evidence



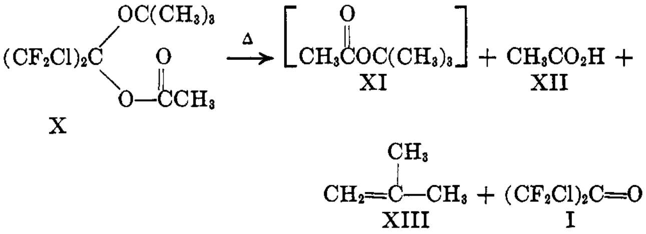
VIII

indicates that the relative rates of decomposition of the hemiketal esters are similar to normal ester pyrolyses (tertiary > secondary > primary). Furthermore, the hemiketal carbonates VI and VII decompose more rapidly than V. This again is comparable to the relative stabilities of normal carbonates and esters.

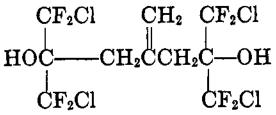


$$\text{VI or VII} \xrightarrow{\Delta} \underset{\text{I}}{(CF_2Cl)_2C{=}O} + \underset{\text{IX}}{C_2H_5O\overset{\displaystyle O}{\overset{\|}{C}}OC_2H_5}$$

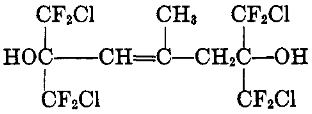
Decomposition of the *t*-butyl hemiketal acetate X took a different course, giving none of the expected *t*-butyl acetate (XI), but rather acetic acid (XII) and isobutylene (XIII). The effluent gases were passed into 50% H_2SO_4 to give *t*-butyl alcohol, indicating



isobutylene to be one of the reaction products. Examination of samples stored in closed containers at room temperature indicated considerable decomposition had taken place. After removal of volatiles from a 10-month-old sample, a tan solid, XIV, was obtained. G.c. analysis resolved XIV into two isomeric compounds, XIVa (35%) and XIVb (65%).[10] Presumably, isobutylene was liberated, which subsequently reacted with the fluoroacetone in the sealed system to form XIV.



XIVa



XIVb

It appears that more than one decomposition mechanism may be operative, depending on the structure of the hemiketal ester. A detailed study of the mechanistic aspects of these decompositions is currently under investigation in our laboratories.

Experimental Section

1-Ethoxy-1-(chlorodifluoromethyl)-2-chloro-2,2-difluoroethyl Acetate. Method A.—To 99.5 g. (0.5 mole) of *sym*-dichlorotetrafluoroacetone was added dropwise with moderate cooling, 23 g. (0.5 mole) of anhydrous ethanol. After the addition was complete, 100 ml. of anhydrous ethyl ether was added and the reaction mixture was cooled to 5°. A solution of 39.3 g., (0.5 mole) of acetyl chloride in 100 ml. of ether was then added rapidly, followed by dropwise addition of a solution of 39.5 g. (0.5 mole) of pyridine in 100 ml. of ether. During the addition the reaction temperature was kept below 10°, and the mixture was stirred overnight at room temperature. After washing with water and drying over anhydrous magnesium sulfate, the ether was distilled, leaving 148 g. of an oil.[11] Distillation of the crude reaction mixture gave 120 g. (84%) of a water-white liquid, b.p. 43–45° (1.2 mm.).

Method B.—To 10 g. (0.05 mole) of *sym*-dichlorotetrafluoroacetone dissolved in 20 ml. of methylene chloride was slowly added 2.3 g. (0.05 mole) of anhydrous ethanol and 4.0 g. (0.05 mole) of pyridine. The additions were exothermic, and removal of the volatiles at 25° (15 mm.) left 16 g. (100%) of a colorless oil: b.p. 49–50° (3.5 mm.); $\lambda_{\max}^{\text{film}}$ 3.36, 3.95 (NH^+, very broad), 6.27, 6.94, 8.81 (C–F, very broad), 9.37, 9.92, 10.41, 12.10, 13.31, 13.55, 14.24 μ; n.m.r. (p.p.m. from TMS), singlet at 5.72 ($\geqslant NH^+$), multiplets at 4.23, 3.78 (aromatic protons), multiplets centered at 2.04, 0.65 (ethyl).

Anal. Calcd. for $C_{10}H_{11}Cl_2F_4NO_2$: C, 37.0; H, 3.16; F, 23.5; N, 4.32. Found: C, 36.6; H, 3.45; F, 23.8; N, 4.1.

To 7 g. (0.022 mole) of the pyridine salt was added 20 ml. of anhydrous ethyl ether. A solution of 1.7 g. (0.022 mole) of acetyl chloride in 10 ml. ether was added slowly with stirring, maintaining the reaction temperature below 20°. The mixture was stirred for 30 min. after completion of the addition and then washed with water. Removal of the solvent left 5.5 g. of an oil which was found to be 87% pure in desired ester by g.c. analysis. Yield of the hemiketal ester was therefore 77%. This was identical with the sample prepared by method A.

1-Ethoxy-1-trifluoromethyl-2,2,2-trifluoroethyl Chloroacetate.—Hexafluoroacetone ethyl hemiketal, 142 g. (0.67 mole), was dissolved in 200 ml. of isopropyl ether. To this was rapidly added a solution of 75 g. (0.67 mole) of chloroacetyl chloride in 50 ml. of isopropyl ether and the solution was cooled to 10°. A solution of 52.4 g. (0.67 mole) of pyridine in 50 ml. of isopropyl ether was then slowly added with stirring, maintaining the temperature below 10°. Salt formation was immediate. After washing with water and drying over $MgSO_4$, the solution was distilled to give a water-white liquid, b.p. 160–161°, 65%.

Ethyl 1-Ethoxy-1-(chlorodifluoromethyl)-2-chloro-2,2-difluoroethyl Carbonate.—To 24.5 g. (0.1 mole) of *sym*-dichlorotetrafluoroacetone ethyl hemiketal was added 60 ml. of anhydrous ethyl ether and the mixture was cooled to 5°. A solution of 10.9 g. (0.1 mole) of ethyl chloroformate in 50 ml. of ether was added rapidly, followed by dropwise addition of 7.9 g. (0.1 mole) of pyridine in 60 ml. of ether with stirring. The temperature was maintained below 10° during the addition, and the mixture was allowed to stand overnight. After washing with water and drying over anhydrous magnesium sulfate, the ether was distilled, leaving 32.5 g. of an oil. Distillation gave 22 g. (67%) of a water-white liquid, b.p. 53° (0.45 mm.).

Bis[1-methoxy-1-(chlorodifluoromethyl)-2-chloro-2,2-difluoroethyl] Carbonate.—To a solution of 46.4 g. (0.2 mole) of *sym*-dichlorotetrafluoroacetone in 100 ml. of anhydrous ethyl ether was added a solution of 10 g. (0.1 mole) of phosgene in 50 ml. of ether. The solution was cooled to 15° and 15.8 g. (0.2 mole) of pyridine in 50 ml. of ether was added slowly with stirring and cooling. Precipitation of pyridine hydrochloride was immediate, and the mixture was stirred at room temperature for 2 hr. After washing with water, drying over anhydrous magnesium sulfate, and removal of the solvent, the mixture was distilled, affording 6 g. (13%) of a water-white liquid, b.p. 86–87° (1.0 mm.).

Thermal Decomposition Studies.[12] Decomposition of 1-Ethoxy-1-(chlorodifluoromethyl)-2-chloro-2,2-difluoroethyl Acetate.—Ten grams (0.035 mole) of the above ester was placed in a distillation flask equipped with a distillation head. The liquid was heated to reflux and distillate was removed periodically at a head temperature of not greater than 93°. The pot temperature varied from 124 to 139° over the course of 30 hr.

The distillate was redistilled at atmospheric pressure, affording 2 g. (0.023 mole), 65%, of ethyl acetate, b.p. 80°.

Decomposition of Isopropoxy-1-(chlorodifluoromethyl)-2-chloro-2,2-difluoroethyl Chloroacetate.—The ester, 2.65 g.

---

(10) This mixture was found to be identical with that obtained by Dr. J. J. Murray of our laboratories from the reaction of I with XIII. We are indebted to Dr. Murray for supplying us with a sample of this mixture.

(11) G.c. analysis indicated that the desired ester comprised 95% of the mixture.

(12) The products obtained in the decomposition studies were identified by comparison with authentic samples.

(0.079 mole) was placed in a distillation flask equipped with a distillation head. The liquid was heated to reflux and a fraction boiling at 48–71° was removed over 7 hr. G.c. and the infrared spectrum indicated this to be the fluoroacetone (λ_{max}^{film} 5.55 μ) containing a small amount of isopropyl chloroacetate. The flask residue (0.8 g.) was identified as a mixture of isopropyl chloroacetate (λ_{max}^{film} 5.81 μ) and the undecomposed hemiketal ester in a 89:11 ratio, indicating that the decomposition had occurred to the extent of 89%. The flask temperature varied from 164 to 212°.

Decomposition of 1-Benzyloxy-1-(chlorodifluoromethyl)-2-chloro-2,2-difluoroethyl Acetate.—Ten grams (0.029 mole) of the above acetate was placed in a distillation flask equipped with a distillation head. The liquid was heated to reflux and a fraction boiling at 46–47° (4.5 g.) was removed periodically over a 0.5-hr. period, followed by a fraction boiling at 203–221° (4.5 g.) A residue (0.5 g.) was left in the flask. The flask temperature varied from 206 to 229° during the distillation. Examination by g.c. and infrared spectroscopy indicated that the first fraction was the fluoroacetone (λ_{max}^{film} 5.55 μ) and that the second fraction was 95% benzyl acetate (λ_{max}^{film} 5.73 μ). The residue consisted of benzyl acetate containing a trace of the hemiketal ester.

Decomposition of 1-(β-Phenylethoxy)-1-(chlorodifluoromethyl)-2-chloro-2,2-difluoroethyl Acetate.—Ten grams (0.0275 mole) of the above acetate was placed in a distillation flask equipped with a distillation head. The liquid was heated to reflux and a fraction boiling at 46–60° (4.7 g.) was collected in 0.5 hr. A second fraction boiling at 226–233° (4.0 g.) followed, leaving a residue of approximately 1 g. G.c. and infrared analyses indicated the first fraction to be the fluoroacetone (λ_{max}^{film} 5.55 μ) and the second fraction and residue to be β-phenethyl acetate (λ_{max}^{film} 5.75 μ) containing a small amount of the fluoroacetone. The flask temperature varied from 188 to 240° during the course of the decomposition.

Decomposition of 1-(*t*-Butoxy)-1-(chlorodifluoromethyl)-2-chloro-2,2-difluoroethyl Acetate.—Twenty grams (0.0635 mole) of the above acetate was placed in a distillation flask equipped with a distillation head. The liquid was heated to reflux (97°) and a distillate boiling at 50–67° was collected in 30 min. Refluxing stopped at this point and the flask temperature rose to 117° with no further distillation. The liquid remaining in the flask (3.6 g., theoretical 3.8 g.) was identified as acetic acid containing a small amount of the fluoroacetone. The distillate (11 g., theoretical 12.5 g.) was approximately 90% pure fluoroacetone. No *t*-butyl acetate was obtained.

In another decomposition experiment, the exit gas was passed through 50% H_2SO_4, and work-up of the solution gave some *t*-butyl alcohol, indicating isobutylene to be a decomposition product.

Examination of a 10-month-old sample of the hemiketal ester (stored at room temperature) indicated that extensive decomposition had taken place. Evaporation of the acetic acid from a portion of the sample (8.0 g., 0.025 mole) left 4.0 g. of a dark oil which solidified on standing. This was identified as the 2:1 reaction product of *sym*-dichlorotetrafluoroacetone and isobutylene, m.p. 81–93° (70%).

Anal. Calcd. for $C_{10}H_8Cl_4F_8O_2$: C, 26.4; H, 1.78. Found: C, 26.4; H, 2.08.

G.c. analysis resolved the crude product into two isomeric compounds (XIVa and XIVb) in a 35:65 ratio, and preparative gas chromatography (10% silicone rubber SE-30 on 60–80-mesh Diatoport W) separated the major isomer (XIVb): m.p. 72–74°; λ_{max}^{Nujol} 2.97 (OH), 6.00 (C=C), 8.60 (very broad, C–F) μ; n.m.r. (p.p.m. from TMS), singlet 2.08 ($-CH_3$), singlet 3.26 ($-CH_2-$), singlet 5.53 (vinyl proton).

Anal. Calcd. for $C_{10}H_8Cl_4F_8O_2$: C, 26.4; H, 1.78. Found: C, 26.2; H, 2.06.

Studies on Nitroso Compounds. II. Dimerization of 4-Substituted 2,6-Dichloronitrosobenzenes. An Equilibrium Controlled by the Resonance Effect of *para* Substituents[1]

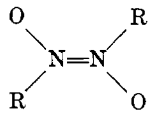
RICHARD R. HOLMES,[2] RAYMOND P. BAYER, LOUIS A. ERREDE, HORACE R. DAVIS,
ARNOLD W. WIESENFELD, PAUL M. BERGMAN, AND DAVID L. NICHOLAS

Department of Chemistry, Hofstra University, Hempstead, New York

Received May 3, 1965

A previous report that *m*-trifluoromethylnitrosobenzene, unlike other nitroso compounds substituted in the *meta* or *para* positions only, is highly dimerized is shown to be in error. The compound reported as *m*-trifluoromethylnitrosobenzene is found to be *m*-trifluoromethylazoxybenzene. The true *m*-trifluoromethylnitrosobenzene gives no sign of dimer formation in solution. Spectrophotometric study of the monomer–dimer equilibrium in benzene of a series of 2,6-dichloro-4-X-nitrosobenzenes is reported. *para* substituents X were COOEt, H, CH_3, Cl, Br, and OCH_3. Electron-releasing substituents, including the halogens, favor dissociation to monomer. The change in $\Delta F°$ is proportional to the "resonance effect" of X. A comparison is made with benzaldehyde cyanohydrin equilibria and it is concluded that the "resonance effect" of *para*-X is nearly the same in nitrosobenzene as in benzaldehyde, with which it is isoelectronic.

It is well known that most C-nitroso compounds crystallize as colorless dimers, although the monomers, present in solution, are blue or green.[3-12] Both aromatic[9,10] and aliphatic[11,12] dimers have been shown by X-ray crystallography to have the azo dioxide structure A.[13]



A

It is also known[3-8] that substitution of groups larger than hydrogen in the *ortho* position of nitrosobenzene (particularly when both *ortho* positions are substituted) favors dimerization, and it has been shown[1] that the *ortho* effect is due to steric inhibition of resonance in the monomers.

---

(1) Part I: R. R. Holmes, *J. Org. Chem.*, **29**, 3076 (1964).

(2) To whom correspondence should be sent.

(3) C. K. Ingold and H. A. Piggott, *J. Chem. Soc.*, **125**, 169 (1924).

(4) D. L. Hammick, *ibid.*, 3105 (1931).

(5) V. Keussler and W. Luttke, *Z. Elektrochem.*, **63**, 614 (1959).

(6) K. Nakamoto and R. E. Rundle, *J. Am. Chem. Soc.*, **78**, 1113 (1956).

(7) W. J. Mijs, S. E. Hoekstra, R. M. Ullmann, and E. Havinga, *Rec. trav. chim.*, **77**, 746 (1958).

(8) W. Luttke and B. G. Gowenlock, *Quart. Rev.* (London), **12**, 321 (1958).

(9) C. Darwin and D. Hodgkin, *Nature*, **166**, 827 (1950).

(10) C. P. Fenimore, *J. Am. Chem. Soc.*, **72**, 3226 (1950).

(11) M. Van Meersche and G. Germain, *Bull. soc. chim. Belges*, **68**, 244 (1959).

(12) H. Dietrich and D. C. Hodgkin, *J. Chem. Soc.*, 3686 (1961).

(13) Most dimers have the *trans* azo dioxide structure pictured, but some can also be prepared in a less stable form which is presumably the *cis* azo dioxide.