the carbonyl bands fell at 1720 (s) and 1760 cm^{-1} (w) instead of at 1745 and 1780 cm^{-1}. When the reaction was terminated after refluxing for only 22 hr and the total organic extract (after concentration at the water pump) chromatographed on a 20 ft × $\frac{3}{8}$ in. column of 30% SE-30 at 260° and a flow rate of 80 ml/min, there was obtained 0.47 g (24%) of II and 0.54 g (26%) of III. The sample of **2,2,4,4-tetramethyl-5-hydroxy-5-isopropyl-1,3-cyclopentanedione** (III) thus obtained had mp 37.6–38.0°, absorbed in the ir at 1720 (s), 1760 (w), and 3480 cm^{-1} (m), and in the nmr (see text for analysis) at δ 3.03 (singlet, 1 H), 1.67 (septet, J = 7 Hz, 1 H), and 0.7–1.2 (multiplet, 18 H).

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.01; H, 9.68.

Clemmensen Reduction of III.—A 0.230-g sample of III was subjected to the reduction procedure described above for a reaction time of 43 hr. Glpc analysis of the mixture at this time showed approximately 7% unreacted III and 62% II. Separation and purification by preparative glpc gave 0.078 g of II (41% yield), mp 29.4–30.2°, identical in all respects (ir, nmr, and mixture melting point) with the material prepared directly from I.

Registry No.—I, 778-18-7; III, 19165-42-5.

Acknowledgment.—Financial support for this research by the National Science Foundation Grant No. GP-8510 is gratefully acknowledged.

A New Spirocyclohexenedione System

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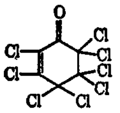
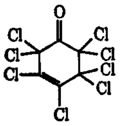
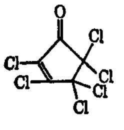
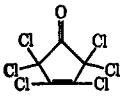
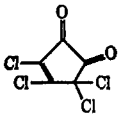
In the course of an investigation on photodecomposition products of pentachlorophenol,(1) a new spirocyclohexenedione compound (1) was found to form from pyrocatechol by the action of chlorine.

According to Zincke and Küster,(2) pyrocatechol reacts with chlorine in acetic acid to produce tetrachloropyrocatechol. However, it was found that further introduction of chlorine at higher temperature produced new light yellow crystals having the composition $C_{12}Cl_8O_4 \cdot H_2O$ (hydrate) in an 80% yield. Chemical and spectral evidence showed that this was spiro[2′,3′,4,5,6,6′,6′,7-octachloro-1,3-benzodioxole-2,1′-[2]-cyclohexene]-4′,5′-dione hydrate (**1**). Mass spectrum of hydrate **1** had a molecular peak at m/e 488 (M^+, 8Cl, as an anhydrous form). Ultraviolet and infrared spectra showed the presence of an α,β-unsaturated ketone group (see Table I) and a phenoxyl nucleus. Dehydration of **1** yielded a yellow colored anhydrous substance, $C_{12}Cl_8O_4$ (**2**), showing spectral bands of an unsaturated 1,2-diketone.(3) The anhydrous substance lost its color in air owing presumably to the conversion of the 1,2-diketone system by the hydration into the ketone system. The infrared spectra of **1** and **2** agreed with this view. When **1** was dissolved in 75% acetic acid and the solution was poured into water, a colorless dihydrate (**3**) was precipitated. The infrared spectrum showed no carbonyl absorption and the ultraviolet spectrum at λ_{max} 234 mμ was compatible with a monoene structure.

Table I

Principal Bands in Ultraviolet and Infrared Spectra of Derivatives

Compd	λ_{max}, mμ (ϵ)	Solvent	ν_{max}, cm^{-1}
1	261 (17,000)	$CHCl_3$	1,730[a]
 [d]	267–268 (10,500)	C_6H_{12}	1,745[b]
 [d]	235–237 (9,000)	C_6H_{12}	1,779[b]
 [e]	259 (10,000)	95% C_2H_5OH	1,739[c]
 [e]	223 (10,000)	95% C_2H_5OH	1,776[c]
 [f]	226 (12,300) 283 (7,840)	C_6H_{14}	1,795 1,748[b]

[a] KBr disk. [b] CCl_4 solution. [c] $CHCl_3$ solution. [d] L. Denivelle and R. Fort, *C. R. Acad. Sci., Paris,* **242,** 2359 (1956). [e] See ref 7. [f] R. M. Scribner, *J. Org. Chem.,* **30,** 3657 (1965).

Reaction of **1** with o-phenylenediamine to form dihydrophenazine **4** confirmed the potential 1,2-diketone system. Acetylation of **1** gave a colorless spiro acetyl ketal (**5**). On reduction, **1** afforded a phenol derivative which gave a triacetate. The reductive acetylation of **1** afforded the same compound. These compounds were identical with a quinol(4) and the acetate(4) derived from 3,4,6-trichloro-5-(2,3,4,5-tetrachloro-6-hydroxyphenoxy)-1,2-benzoquinone, respectively.(1,5) Chlorination of this benzoquinone gave **1** in good yield. Alkaline hydrolysis of **1** yielded a monobasic acid (**6**) which was proved to be a product of the benzylic acid rearrangement (Scheme I). In infrared spectrum, the carbonyl band of **6** was similar to that of 1-hydroxy-2,3,4,4,5,5-hexachloro-2-cyclohexene-1-carboxylic acid.(2)

Hexachloro-3-cyclohexene-1,2-dione (**8**),(2) the anhydrous chlorination product of pyrocatechol, gave, on the benzylic acid rearrangement, 1-hydroxy-2,3,4,4,5,5-hexachloro-2-cyclohexene-1-carboxylic acid which on decarboxylation gave rise to hexachlorocyclopentenone. The Raman spectra(6) as well as physical(7) and chemical(8) properties of this cyclopentenone furnished its assigned structure. The yellow cyclohexenedione (**8**) gave, however, readily a colorless monohydrate (**9**), the

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(1) M. Kuwahara, N. Kato, and K. Munakata, *Agr. Biol. Chem.* (Tokyo), **29,** 880 (1965); **30,** 232, 239 (1966).

(2) T. Zincke and F. Küster, *Ber.,* **21,** 2719 (1888); W. Eller and V. Lorenz, *ibid.,* **58,** 494 (1925).

(3) N. B. Haynes, D. Redmore, and C. J. Timmons, *J. Chem. Soc.,* 2420 (1963).

(4) C. L. Jackson and G. L. Kelley, *Amer. Chem. J.,* **47,** 197 (1912).

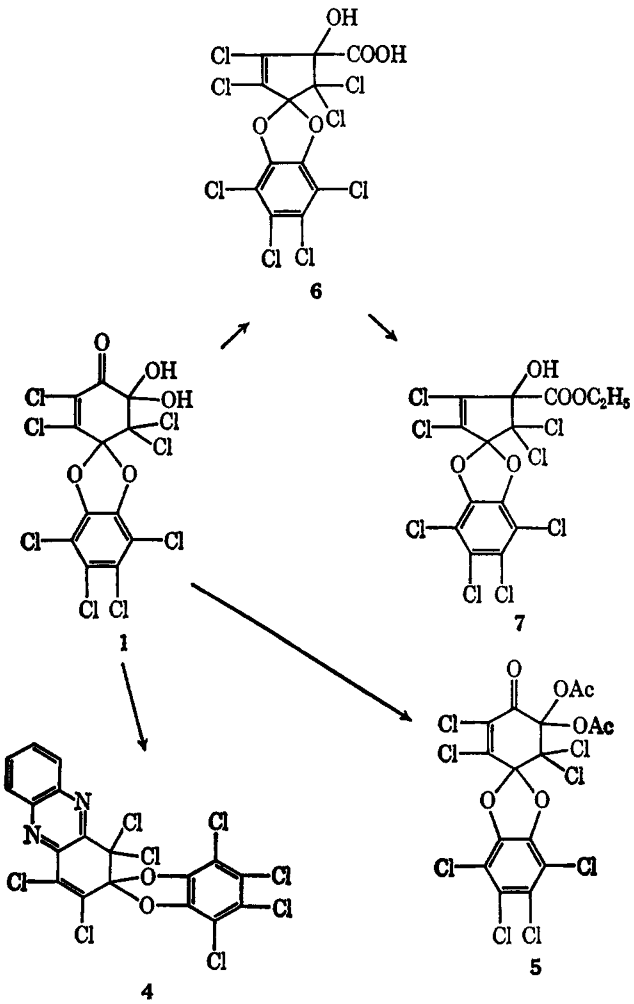
(5) C. L. Jackson and P. W. Carleton, *ibid.,* **39,** 493 (1908).

(6) H. V. Brederode, H. Gerding, and H. J. Prins, *Rec. Trav. Chim. Pays-Bas,* **65,** 174 (1946).

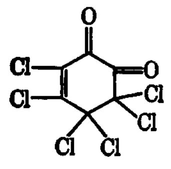
(7) E. T. McBee, D. K. Smith, and H. E. Ungnade, *J. Amer. Chem. Soc.,* **77,** 559 (1955).

(8) J. S. Newcomer and E. T. McBee, *ibid.,* **71,** 946 (1949).

SCHEME I



position of the hydration being untouched. The ultraviolet spectral data satisfied the structures **9** and **8** in accord with the nature of **1** and **2**, respectively.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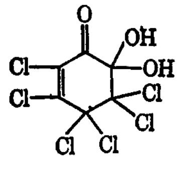
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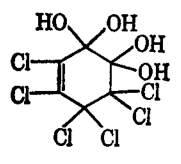
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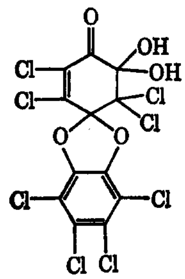
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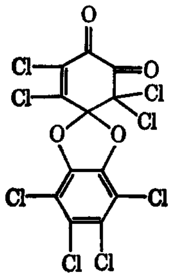
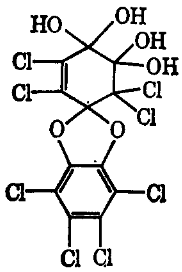

2


3

In a freshly prepared ethanol solution, the ultraviolet spectra of **9** and **1** exhibited each absorption maximum at λ_{max} 262 and 253 mμ characteristic of an α,β-unsaturated ketone (see Table I). These absorption intensities decreased rapidly on standing and new absorption maxima appeared at λ_{max} 222 mμ (ε 9300) and 234 (17,900), respectively. These phenomena might be accounted for by the reversible addition[9] of ethanol forming the hemiketal or the ketal. These data would suggest the conversion of the conjugated ketone systems of **9** and **1** into the monoene systems of **10** and **3** which would appear compatible with shorter wavelength shifts of the absorption maxima by 40 and 19 mμ, respectively. Similar conversion was observed on other 1,2-diketones such as dimeric 3-methoxyl-1,2-benzoquinone[10] and 5-cyclooctene-2,3-dione.[11]

Experimental Section

All melting points were determined on a Yanagimoto melting point apparatus. Infrared spectra were recorded with a Hitachi Model EPI-2 spectrophotometer and ultraviolet spectra with a Hitachi Model EPS-2 spectrophotometer.

Spiro[2′,3′,4,5,6,6′,6′,7-octachloro-1,3-benzodioxole-2,1′-[2]-cyclohexene]-4′,5′-dione Hydrate (1). A.—Chlorine was passed slowly through a solution of pyrocatechol (200 g) in 97% acetic acid (1 l.). The temperature of the mixture was maintained between 20 and 30°. During the reaction, tetrachloropyrocatechol precipitated and the mixture became semisolid. Further introduction of chlorine at 60–70° converted the semisolid mixture into a red solution and then its color turned yellow. The solvent was removed under reduced pressure and the residue (460 g) was recrystallized from chloroform to afford light yellow needles (**1**): mp 209–210°; $\lambda_{max}^{CHCl_3}$ 261, 293, 300 mμ (ε 17,000, 3820, 3160); λ_{max}^{EtOH} 234, 295, 302 mμ (ε 17,900, 2520, 2820); ν_{max}^{KBr} 3350 (OH), 1730 (C=O), 1590 cm^{-1} (C=C); mass spectrum *m/e* (anhydrous form) 488 (M^+, 8Cl), 460 ($M^+ - CO$), 453 ($M^+ - Cl$), 432 ($M^+ - 2CO$), 425 ($M^+ - Cl - CO$), 397 ($M^+ - Cl - 2CO$).

Anal. Calcd for $C_{12}Cl_8O_4 \cdot H_2O$: C, 28.27; H, 0.40; Cl, 55.65. Found: C, 28.22; H, 0.71; Cl, 55.58.

Anhydrous Product.—On drying over phosphorus pentoxide for 5 hr at 120° (0.1 mm), **1** lost 1 mol of water and gave the anhydrous form (**2**): mp 207–210°; ν_{max}^{KBr} 1770, 1720, 1580 cm^{-1}.

Anal. Calcd for $C_{12}Cl_8O_4$: C, 29.30; Cl, 57.67. Found: C, 29.31; Cl, 57.61.

Dihydrate.—Monohydrate **1** was dissolved in 75% aqueous acetic acid and water was added. Precipitated colorless crystals (**3**) were collected, mp 112–114°, solidified and remelted at 207–209°: λ_{max}^{EtOH} 234, 293, 302 mμ (ε 18,500, 2840, 2920); ν_{max}^{KBr} 3350, 1635 cm^{-1}. This compound was converted into **1** in the air or by recrystallization from chloroform or ethanol.

Anal. Calcd for $C_{12}H_4Cl_8O_6$: C, 27.31; H, 0.76; Cl, 53.74. Found: C, 28.05; H, 1.10; Cl, 54.16.

The elemental analysis was not satisfactory presumably because **3** lost water easily in the air to give **1**.

B.—An excess of the chlorine was passed through a solution of 3,4,6-trichloro-5-(2,3,4,5-tetrachloro-6-hydroxyphenoxy)-1,2-benzoquinone[1,5] (3 g) in acetic acid (50 ml) at below 20°. When the solvent was removed under reduced pressure and the resulting crystals were recrystallized from chloroform, there were obtained light yellow needles (1 g), mp 208–209°, identical with spirocyclohexenedione **1** by mixture melting point and infrared spectrum.

Spiro[1,1,3,4,4′,5′,6′,7′-octachloro-1,2-dihydrophenazine-2,2′-[1,3]benzodioxole] (4).—A solution of *o*-phenylenediamine (3 g) in methanol (50 ml) was added with stirring to a solution of **1** (15 g) in a mixture of methanol (80 ml), glacial acetic acid (20 ml) and chloroform (50 ml). When the vigorous exothermic reaction subsided, the mixture was kept at 20° with stirring and allowed to stand in an ice box for 1 day. The yellow solid was collected by filtration, washed with methanol and after drying weighted 14 g. An analytical sample was prepared by crystallization from chloroform as light yellow needles (**4**), mp >300°.

Anal. Calcd for $C_{18}H_4Cl_8N_2O_2$: C, 38.34; H, 0.71; N, 4.97; Cl, 50.30. Found: C, 38.27; H, 0.84; N, 4.97; Cl, 49.97.

Spiro[2′,3′,4,5,6,6′,6′,7-octachloro-5′,5′-diacetoxy-1,3-benzodioxole-2,1′-[2]cyclohexen]-4′-one (5).—Spirocyclohexenedione **1** (10 g) was acetylated with acetic anhydride (100 ml) and sulfuric acid (0.5 ml) by a usual method to give acetate **5**, yield 10 g.

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[9] R. P. Bell, *Advan. Phys. Org. Chem.*, **4**, 1 (1966).

[10] E. Adler, R. Magnusson, B. Berggren, and H. Yhomelius, *Acta Chem. Scand.*, **14**, 515 (1960).

[11] L. Horner and H. Merz, *Ann. Chem.*, **570**, 89 (1950).

Recrystallization from ethanol gave colorless plates: mp 207–208°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 257, 292, 301 mμ (ϵ 16,900, 3130, 3050); $\nu_{\max}^{\mathrm{KBr}}$ 1780 (C=O), 1769 (C=O), 1736 (C=O), 1592 cm^{-1} (C=C); mass spectrum *m/e* 590 (M$^+$, 8Cl), 488 [M$^+$ − $(CH_3CO)_2O$], 460 [M$^+$ − CO − $(CH_3CO)_2O$].

Anal. Calcd for $C_{16}H_6Cl_8O_7$: C, 32.36; H, 1.02; Cl, 47.75. Found: C, 32.37; H, 1.15; Cl, 47.76.

2,3′,4′-Trihydroxy-2′,3,4,5,5′,6,6′-heptachlorodiphenyl Ether.—Zinc dust (10 g) was added with stirring to a solution of **1** (10 g) in acetic acid (100 ml). The mixture was heated for 1 hr and poured into water after removal of the catalyst. The resulting crystals were collected and recrystallized from benzene to give colorless prisms, mp 180° (lit.[4] mp 181–182°), yield 7 g.

2,3′,4′-Triacetoxy-2′,3,4,5,5′,6,6′-heptachlorodiphenyl Ether. A.—Spirocyclohexenedione **1** (10 g) was dissolved in acetic anhydride (100 ml). The mixture was treated with zinc dust until the solution became colorless. After a few drops of sulfuric acid was added, the mixture was heated for 30 min on a water bath. The mixture was poured into water to give colorless prisms (6 g), mp 147–148° (lit.[4] mp 144°).

Anal. Calcd for $C_{18}H_9Cl_7O_7$: C, 36.92; H, 1.55; Cl, 42.39. Found: C, 36.97; H, 1.52; Cl, 42.35.

B.—Acetylation of 2,3′,4′-trihydroxy-2′,3,4,5,5′,6,6′-heptachlorodiphenyl ether (3 g) with acetic anhydride and sulfuric acid gave the colorless triacetate (2 g), mp 147–148°.

Spiro[2′,3′,4,5,5′,5′,6,7-octachloro-4′-hydroxy-1,3-benzodioxole-2,1′-[2]cyclopentene]-4′-carboxylic Acid (6).—Spirocyclohexenedione **1** (10 g) was heated on a water bath with 10% aqueous sodium hydroxide (10 ml) and dioxane (50 ml) for 2 hr. The mixture was poured into water and the resulting crystals were collected by filtration to yield 9 g of the crude material. Recrystallization of this compound from chloroform gave colorless prisms (**6**): mp 188° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3370, 2900 (OH), 1741 (C=O), 1636 cm^{-1} (C=C). Its molecular weight by a potentiometric titration with 0.1 *N* sodium hydroxide was 500.0 (theoretical 527.8) and it was a monobasic acid, pK_a' 3.55 in 10% ethanol solution. The pK_a' value was assumed to be the pH of half-neutralization.

Anal. Calcd for $C_{12}H_2Cl_8O_5 \cdot H_2O$: C, 27.31; H, 0.76; Cl, 53.74. Found: C, 27.54; H, 1.31; Cl, 53.62.

Spiro[2′,3′,4,5,5′,5′,6,7-octachloro-4′-hydroxy-1,3-benzodioxole-2,1′-[2]cyclopentene]-4′-carboxylic Acid Ethyl Ester (7). **A.**—Esterification of **6** (5 g) with ethanol and sulfuric acid gave 2 g of its ester (**7**): mp 176–177°; $\nu_{\max}^{\mathrm{KBr}}$ 3350 (OH), 1740 (C=O), 1638 cm^{-1} (C=C).

B.—To the solution of **1** (5 g) in ethanol (40 ml) was added hydrochloric acid (5 ml). The mixture was heated on a water bath for 2 hr and poured into water. The resulting crystals were collected, dried and recrystallized from ethanol to give colorless prisms, mp 176–177°, yield 2.5 g. This compound was identified as ethyl ester **7** of **6** by mixture melting point and infrared spectrum.

Anal. Calcd for $C_{14}H_6Cl_8O_5$: C, 31.26; H, 1.12; Cl, 52.73. Found: C, 31.07; H, 1.31; Cl, 52.59.

Hexachloro-3-cyclohexene-1,2-dione hydrate (9) was prepared by the method indicated by Zincke and Küster.[2] Chlorine was passed through a solution of pyrocatechol (20 g) in acetic acid (400 ml) under cooling. The reaction mixture was poured into water. The resulting precipitate was collected by filtration and recrystallized from ethanol to obtain colorless prisms (**9**, 39 g): mp 90–92° (lit.[2] mp 93–94°); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 269 mμ (ϵ 8500); $\nu_{\max}^{\mathrm{KBr}}$ 1723 cm^{-1}.

Anhydrous Form (8).—The acetic acid was removed from the above reaction mixture *in vacuo* and the red residue was distilled to give a yellow liquid (**8**): bp 114–116° (0.35 mm) [lit.[2] bp 170° (18 mm)]; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 269 mμ (ϵ 8830); $\nu_{\max}$ 1778, 1720 cm^{-1}.

1-Hydroxy-2,3,4,4,5,5-hexachloro-2-cyclohexene-1-carboxylic acid was produced by the method reported by Prins.[6] A solution of **8** (12.7 g) in acetic acid (25 ml) was added with stirring to a 0.15-mol solution (40 ml) of sodium carbonate. The acid was set free by adding a mixture of acetic acid (25 ml) and hydrochloric acid (12 ml). The mixture was poured into water and the precipitate was filtered to afford colorless plates (8 g): mp 112–113° (lit.[2] mp 111°); $\nu_{\max}^{\mathrm{KBr}}$ 1730 cm^{-1} (C=O).

Registry No.—**1**, 19254-91-2; **2**, 19254-92-3; **3**, 19294-05-4; **4**, 19294-06-5; **5**, 19294-07-6; **6**, 19254-90-1; **7**, 19254-93-4; **8**, 19254-94-5; **9**, 19254-95-6.

The Thermolysis of Bromodifluoroacetic Anhydride

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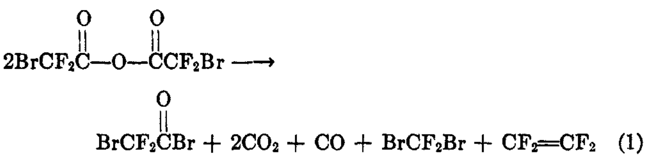
Received May 31, 1968

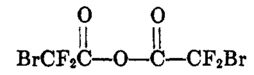
The thermal decomposition of fluorinated carboxylic acid anhydrides has been of interest for several years.[1,2] Kirshenbaum, *et al.*,[2] in a detailed study of the action of heat on the silver salts of perfluorocarboxylic acids, reports qualitative data on the thermolysis of perfluorobutyric anhydride. The reactions were carried out at autogenous pressures at 400–435° for 3 hr. The anhydride in the presence of Ag_2O gave the coupled product, C_6F_{14}. When, however, the thermolysis was attempted using a perfluoroanhydride *without* Ag_2O very little coupled product was realized.

In our studies, we have found that the thermolysis of bromodifluoroacetic anhydride proceeds almost quantitatively in the absence of an added catalyst (*i.e.*, Ag_2O), as represented by eq 1.



$$2BrCF_2C(=O){-}O{-}C(=O)CF_2Br \longrightarrow BrCF_2C(=O)Br + 2CO_2 + CO + BrCF_2Br + CF_2{=}CF_2 \quad (1)$$

The coupled products in Kirshenbaum's work were stable, isolable compounds but, in the case of bromodifluoroacetic anhydride, the coupled product, $BrCF_2CF_2Br$, is unstable at high temperatures (*i.e.*, 300°). An independent experiment has confirmed the presence of Br_2 + polyperfluoroethylene and perhaps $CF_2{=}CF_2$, from the thermolysis of $BrCF_2CF_2Br$ under the same experimental conditions used in the thermolysis of



$$BrCF_2C(=O){-}O{-}C(=O){-}CF_2Br$$

Experimental Section

A. Apparatus.—The thermolysis system consisted of an airtight, heated vertical Vycor tube loosely packed with glass wool. The reactant entered the system through an addition funnel and was flushed down with anhydrous nitrogen. The products from the thermolysis were trapped in cold traps at −70°.

B. Procedure.—In a typical run, the Vycor tube and glass wool was heated to 150° for 2 hr under a stream of nitrogen. The temperature was then increased to 300° and bromodifluoroacetic anhydride (100 g, 0.30 mol) was allowed to enter slowly into the reaction zone.

The material condensing in the traps was then distilled through a 6-in. Vigreux column. Based on eq 1, a 76% yield (25 g) of $BrCF_2Br$, bp 23° (lit.[3] bp 20–25°), and 92% yield (33 g) of $BrCF_2C({=}O)Br$, bp 71°, was isolated. Infrared spectroscopy (CCl_4) shows two absorptions in the carbonyl region at 5.55 (strong) and 5.68 μ (weak) for $BrCF_2C({=}O)Br$. These bands are in accord with the spectra of known acid halides.[4] ^{19}F nmr shows a single at 59.1 ppm (relative to $CFCl_3$) and mass spectrometry gives a fragmentation pattern consistent with

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(1) R. N. Haszeldine, British Patent 747,893 (1956).

(2) A. D. Kirshenbaum, A. G. Streng and M. Hauptschein, *J. Amer. Chem. Soc.*, **75**, 3141 (1953).

(3) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, p 48.

(4) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 45.