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# TRIFLUOROMETHYLMALEIC ANHYDRIDE

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## SUMMARY

α-Trifluoromethylmaleic anhydride has been prepared by an unusual reaction of hexafluoropropene epoxide (HFPO) with acetic anhydride. It reacted as a dienophile with butadiene, cyclopentadiene, furan, and anthracene.

## INTRODUCTION

The known [1] compound α-trifluoromethylmaleic anhydride was an unexpected product obtained in moderate yield from the reaction of HFPO with acetic anhydride. Its formation can be explained on the basis of some known chemistry of HFPO.

## RESULTS AND DISCUSSION

When heated in sealed vessels above 100°, HFPO reacts with acetic anhydride. Three products have been characterized: acetyl fluoride, α-acetyl-α-trifluoromethylsuccinic anhydride 3, and α-trifluoromethylmaleic anhydride 4. 3 is a precursor to 4 since longer heating gave only 4, and 3 has been shown to lose acetic acid on heating to give 4. The formation of these products can be explained by the following mechanism.

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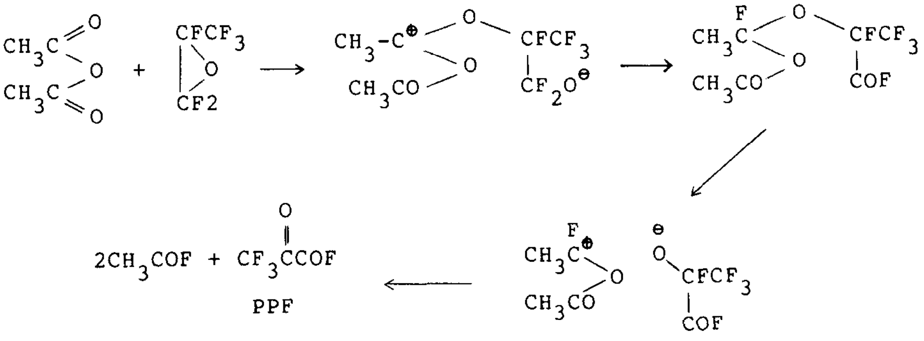
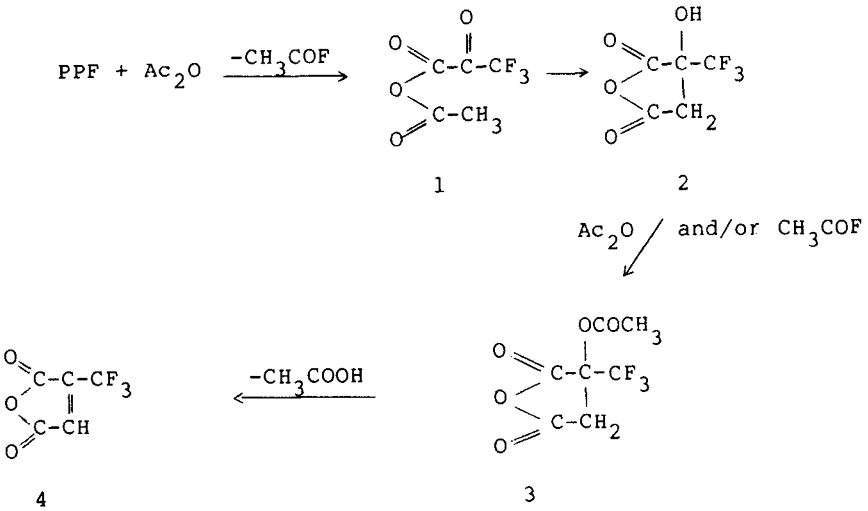
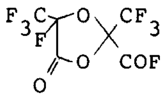




HFPO is known to react with certain carbonyl compounds, in effect exchanging two fluorine atoms for oxygen to form perfluoropyruvyl fluoride (PPF) isolated as monomer or dimer. If benzophenone is used [2], the second product is diphenyldifluoromethane. When dimethylformamide is used [3], difluoromethyldimethylamine is formed along with PPF. Assuming that acetic anhydride is another carbonyl compound that reacts in this manner with HFPO, the products are PPF and acetyl fluoride.

The latter is isolated from the reaction. PPF may form the mixed anhydride 1 with acetic anhydride and undergo an intramolecular condensation to the hydroxyanhydride 2 which is acetylated to 3. In many runs 3 has been the major product isolated pure by distillation along with impure 4. Pure 4 is best prepared by pyrolysis of 3.

In support of the mechanism, 3 was obtained when PPF (as dimer 5) was used in place of HFPO for reaction with acetic anhydride. When isobutyric acid anhydride was reacted with HFPO, the expected isobutyryl ester 6 was isolated.



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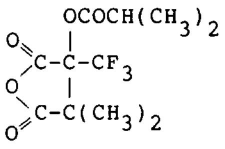

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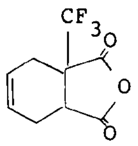

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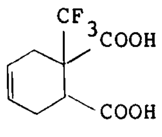

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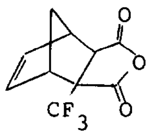
Trifluoromethylmaleic anhydride reacted exothermally with butadiene, and on work-up an 86% yield of the Diels Alder adduct 7 was isolated along with a small amount of the hydrolysis product 8. Similarly, Diels-Alder adducts 9, 10 and 11 were isolated in good yield from cyclopentadiene, furan, and anthracene respectively.



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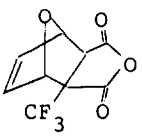

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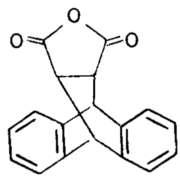

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## EXPERIMENTAL

Melting points and boiling points are uncorrected. PMR spectra were obtained with a Varian A-60 spectrometer operating at 60 MHz; chemical shifts are reported in ppm from tetramethylsilane as external standard with the downfield direction taken as positive. $^{19}F$ NMR spectra were obtained with a Varian A56/60 spectrometer operating at 56.4 MHz using $CFCl_3$ as internal standard. Upfield shifts are reported as negative values.

### Reaction of HFPO with Acetic Anhydride. α-Acetyl-α-trifluoromethylsuccinic Anhydride (3) (nc) and α-Trifluoromethylmaleic Anhydride (4)

A 1 liter Hastelloy bomb was charged with 306 g (3 m) of acetic anhydride and 335 g (2 m) of HFPO. After heating to 125° for 8 hr, it was cooled in wet ice and vented (much acetyl fluoride, bp 18°, was formed). The liquid was distilled to give 49.5 (22%) of 3, bp 78°/0.8 mm, mp (from $CCl_4$) 53-56°. A similar charge using 306 g (3 m) acetic anhydride and 250 g (1.5 m) HFPO was run at 125° for 12 hr and gave 50 g (30%) of the anhydride 4, bp 93°/65 mm.

For 3: IR: 5.30μm, 5.50μm, 5.65μm (C = O). PMR: (20% in $CDCl_3$); 2.22 (singlet, 3H) and 3.35 (quartet, J = 0.67 Hz, 2H). FMR: -78.3 ppm (triplet, J = 0.67 Hz, 3F). Mass spec 166 (parent - $CH_3COOH$), 122 ($-CO_2$), 94 (-CO).

*Anal*. Calcd. for $C_7H_5F_3O_5$: C, 37.20; H, 2.23; F, 25.22.

Found: C, 37.28; H, 2.30; F, 25.56.

For 4 [1]: IR: 5.6μm (broad). PMR: 7.11 (quartet, J = 1.58 Hz). FMR: -66.1 ppm (doublet, J = 1.58 Hz).

### Pyrolysis of 3 to 4

The acetate 3 (20 g), melted in a dropping funnel, was added dropwise to a vertically mounted quartz tube (22 in. x 1 in.) packed with 1/4 in. sections of 8 mm quartz tubing. The hottest spot in the furnace was 555°, and the pressure in the tube was 0.8 mm. Products were condensed in a liquid nitrogen-cooled trap and distilled to give acetic acid (5 g) and trifluoromethylmaleic anhydride 4 (11.8 g, 80%).

### Reaction of Perfluoropyruvoyl Fluoride Dimer (5) with Acetic Anhydride

Perfluoropyruvyl fluoride dimer 5 (15 g, 0.1 m) and 21 g (0.2 m) acetic anhydride were heated together in a sealed tube to 125° for 8 hr. Distillation of the product mixture gave one fraction (1.5 g), bp 77°/9 mm, which crystallized on cooling, and there was obtained 0.3 g of 3, mp 56-58° after two recrystallizations from carbon tetrachloride. By mixed mp and infrared analysis, the material was shown to be identical to that obtained above .

### Reaction of HFPO with Isobutyric Acid Anhydride. α-Isobutyroyl-α-Trifluoromethyl-β,β-Dimethylsuccinic Anhydride (6) (nc)

A mixture of 300 g (0.1 m) isobutyric acid anhydride and 166 g (1.0 m) HFPO was heated in a Hastelloy bomb to 125° for 8 hr. There was recovered 162 g of isobutyryl fluoride, bp 56°, 100 g isobutyric acid anhydride, and about 75 g of an uncharacterized mixture. One cut, 3.5 g, bp >85°/4 mm, partly crystallized, and from it by two recrystallizations from petroleum ether was obtained 1.1 g of 6, mp 34-37°.

For 6: IR: 5.35μm, 5.55μm, and 5.67μm (C = O). PMR: 1.19 (doublet, J = 7.0 Hz, 6H), 1.31 (singlet, 3H), 1.58 (quartet, J = 2.4 Hz, 3H), and 2.75 (septet, J = 7.0 Hz, 1H). FMR: -70.9 ppm (quartet, J = 2.4 Hz).

Anal. Calcd. for $C_{11}H_{13}F_3O_5$: C, 46.85; H, 4.65; F, 20.21.

Found: C, 47.09; H, 4.69; F, 20.32.

For $(CH_3)_2CHCOF$: IR: 5.40μm (C = O). PMR: 0.77 (doublet, J = 7.0 Hz, 6H) and 2.30 (septet, J = 7.0 Hz, 1H). FMR: +32.6 ppm (singlet).

The amount of 6 isolated accounts for only a small part of the isobutyryl fluoride formed, but other products were not characterized.

### Reaction of 4 with Butadiene. 3a-(Trifluoromethyl)-3a,4,7,7a-tetrahydro-1,3-isobenzofurandione (7) (nc) and 1-(Trifluoromethyl)-4-cyclohexene-1,2-dicarboxylic Acid (8) (nc)

A mixture of 16.6 g (0.1 m) trifluoromethylmaleic anhydride (4) and 6 g (0.11 m) butadiene was sealed in a Carius tube at liquid-nitrogen temperature. On thawing and mixing a very exothermic reaction occurred. There was distilled 18.5 g (85%) of the anhydride 7, bp 125°/30 mm, $n_D^{25}$ 1.4329. Some crystals separated from the last 2 g distilled. They were separated and recrystallized from nitromethane to give 0.8 g of the dibasic acid 8, mp 140-142°.

For 7: IR: 5.30μm, 5.48μm (C = O, C = C). PMR: 2.43 (multiplet, 4H), 3.50 (multiplet, 1H), and 5.83 (multiplet, 2H). FMR: -74.3 ppm (singlet).

Anal. Calcd. for $C_9H_7F_3O_3$: C, 49.13; H, 3.21; F, 25.91.

Found: C, 49.19; H, 2.21; F, 26.12.

For 8: IR: 5.73μm and 5.85μm (CO + C = C). PMR: (20% acetone $d_6$) 0.7 to 2.2 (multiplets, 5H), 4.2 (multiplet, 2H), and 7.96 (singlet, 2H). FMR: -72.1 ppm (multiplet).

Anal. Calcd. for $C_9H_9F_3O_4$: C, 45.42; H, 3.81; F, 23.95.

Found: C, 45.81; H, 3.96; F, 23.83.

### Reaction of 4 with Cyclopentadiene. 3a-(Trifluoromethyl)-3a,4,7,7a-tetrahydro-4,7-methanoisobenzofuran-1,3-dione (9) (nc)

A mixture of 17 g (0.1 m) trifluoromethylmaleic anhydride (4) and 7 g (0.1 m) cyclopentadiene frozen in a Carius tube reacted very exothermally on thawing, and some polymer formed before all of the dienophile had melted. After standing overnight there was distilled 4 g of recovered 4 and 12.3 g (57%) of 9, bp 135°/30 mm, which solidified to waxy crystals. The recovered 4 was added to 2 g cyclopentadiene in 25 ml of methylene chloride. A yellow pi complex formed which rapidly faded with an exothermic reaction. An additional 5 g (90%) of 9 was obtained from this reaction. The product was a mixture of isomers.

IR: 5.30μm, 5.52μm (C = O, C = C). PMR: 1.93 (multiplet, 2H), 3.60 (multiplet, 3H), and 6.40 (multiplet, 2H). FMR: -65.8 ppm (multiplet, 26%) and -67.3 ppm (multiplet, 74%).

Anal. Calcd. for $C_{10}H_7F_3O_3$: C, 51.77; H, 3.04; F, 24.57.

Found: C, 51.95; H, 3.17; F, 24.32.

### Reaction of 4 with Furan, 3a-(Trifluoromethyl)-3a,4,7,7a-tetrahydra-4,7-epoxyisobenzofuran-1,3-dione (10) (nc)

A mixture of 17 g (0.1 m) trifluoromethylmaleic anhydride (4) and 8 g (0.12 m) freshly distilled furan was frozen in a Carius tube at liquid-nitrogen temperature. On melting the mixture became deep yellow and then faded to nearly colorless at room temperature when it crystallized exothermally. Recrystallization from carbon tetrachloride gave 20 g (85%) of 10 mp 51-54°. Another recrystallization changed the mp to 53-63°. It was a mixture of isomers. IR: 5.31µm, 5.57µm (C = O and C = C). PMR: (20% in acetone $d_6$). Isomer peaks at 5.05, 5.83, 6.10, 6.20, 6.32, 6.43, 6.93, and 7.40. FMR: -65.6 (doublet, J = 1.62 Hz, 70% of total) and -66.5 (doublet, J = 1.44 Hz, 30% of total).

Anal. Calcd. for $C_9H_5F_3O_4$: C, 46.19; H, 2.15; F, 24.36.

Found: C, 45.38; H, 2.27; F, 25.58.

Reaction of 4 with Anthracene. 3a-(Trifluoromethyl)-3a,4,9,9a-tetrahydro-4,9[1',2']-benzenonaphtho[2,3-c]foran-1,3-dione (11) (nc)

A mixture of 9 g (0.054 m) trifluoromethylmaleic anhydride (4) and 9.7 g (0.054 m) anthracene was warmed to give a deep red melt which changed to light yellow and cooled to a glass which crystallized overnight. It recrystallized slowly from carbon tetrachloride to give 14.3 g (77%) of 11, mp 110-118°. Recrystallization gave 11.5 g, mp 118-121°.
IR: 5.35µm and 5.57µm (C = O). PMR: 3.57, 3.63, 4.85, and 4.92 (AB pattern, 2H), 5.01 (singlet, 1H) and 7.30 (multiplet, 8H). FMR: -67.8 ppm (singlet).

Anal. Calcd. for $C_{19}H_{11}F_3O_3$: C, 66.33; H, 3.22; F, 16.57.

Found: C, 66.22; H, 3.15; F, 16.97.

## ACKNOWLEDGEMENT

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