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STUDY OF THE NITRATION OF 3,3,3-TRIFLUORO-1,2-EPOXYPROPANE

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PICATINNY ARSENAL
DOVER, NEW JERSEY

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STUDY OF THE NITRATION OF 3,3,3-TRIFLUORO-1,2-EPOXYPROPANE

by

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Feltman Research Laboratories
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Dover, N. J.

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SUMMARY

3,3,3-Trifluoro-1,2-epoxypropane, $CF_3-CH(O)-CH_2$, was nitrated with (1) 98% nitric acid, (2) mixed acid (H_2SO_4:HNO_3, 1:1 by wt), and (3) boron trifluoride-nitric acid complex.

Each nitrating agent afforded the desired 3,3,3-trifluoro-1,2-propane dinitrate, $CF_3-CHONO_2-CH_2ONO_2$ together with variable amounts of the two mononitrates $CF_3-CHOH-CH_2ONO_2$ and $CF_3-CHONO_2-CH_2OH$.

Under the conditions of the experiments, only with the boron trifluoride-nitric acid complex were reasonable yields of the dinitrate obtained.

During this study, it was observed that the dinitrate was partially hydrolyzed (20%) on a silica gel column to the mononitrate $CF_3-CHOH-CH_2ONO_2$.

CONCLUSIONS

The possibility of nitrating 3,3,3-trifluoro-1,2-expoxypropane directly to form 3,3,3-trifluoro-1,2-propane dinitrate has been demonstrated in these experiments. Thus the tedious step of ring opening which was part of the original synthetic scheme is eliminated.

Among the nitrating agents evaluated, only the complex boron trifluoride-nitric acid appears to be of practical value. With the mixed acid or the 98% nitric acid, yields of dinitrate lower than 20% were realized. However, since no attempt was made during this exploratory investigation to find the optimum experimental conditions for these nitrating agents, no firm negative conclusion can be reached as to their potentialities.

The ability of silica gel to hydrolyze the dinitrate $CF_3-CHONO_2-CH_2ONO_2$ to the mononitrate $CF_3-CHOH-CH_2ONO_2$ demonstrates the unstable nature of the nitrate group on the secondary carbon relative to the nitrate group located on the primary carbon. It is consequently possible that the hydroxynitrate $CF_3-CHOH-CH_2ONO_2$, which was consistently detected in the products from all experiments, could have arisen through hydrolysis during the working up procedures rather than from incompleteness of the reaction.

INTRODUCTION

In connection with our research on fluoro-nitroxy compounds, we became interested in the molecule, 3,3,3-trifluoro-1,2-propane dinitrate (CF_3–$CHONO_2$–CH_2ONO_2) which, theoretically, upon combustion should yield products completely balanced in HF and CO_2. Its synthesis has been accomplished in this laboratory (Ref 1) following the scheme shown on p 3.

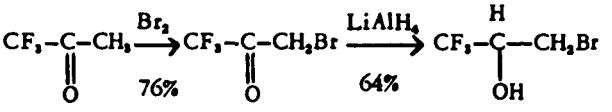
Starting from trifluoroacetone, five steps were required to arrive at the desired product. The overall yield of 3,3,3-trifluoro-1,2-propane dinitrate based on the starting ketone was about 25% of theoretical. As substantial quantities of this compound were needed for evaluation, it became imperative that some efforts be directed towards improving the efficiency of our synthesis. Although it is conceivable that a variety of different synthetic routes could successfully lead to the desired product, we preferred to direct our attention to the sequence given on p 3 as a framework since, from the standpoint of chemistry, this approach offered many possibilities for investigation. We then proceeded to explore the possibility of eliminating some of the steps. Our first objective was to bypass step 4 by nitrating directly the epoxide, 3,3,3-trifluoro-1,2-epoxypropane.

Many references to the nitration of the oxirane ring can be found in the literature. Most often the product isolated is a hydroxynitrate ester. For example, Nichols and coworkers (Ref 2) have reacted unsymmetrical oxides in aqueous solution with nitric acid in the presence of a nitrate salt (sodium nitrate or ammonium nitrate), the temperature being kept in the neighborhood of 30°C. Under these conditions, they have obtained the corresponding nitratoalcohol. As is shown in the equation, when one starts with an unsymmetrical oxide, the two isomers identified below as I and II are susceptible of formation.

$$R\text{–}\underset{\underset{O}{\diagdown\diagup}}{CH}\text{–}CH_2 + NO_3^- + H_3O^+ \rightarrow \underset{\text{I}}{R\text{–}CHOH\text{–}CH_2ONO_2} + \underset{\text{II}}{R\text{–}CHONO_2\text{–}CH_2OH} + H_2O$$

By using proper conditions, the primary nitrate ester I can be formed predominantly. Surprisingly enough, very few records of the nitration of the oxirane ring to form a vicinal dinitrate are reported. An old reference in Beilstein (Ref 3) mentions the preparation of 1,2-propane dinitrate by reacting cold 1,2-propylene oxide with fuming nitric acid and concentrated

SYNTHESIS OF 3,3,3-TRIFLUORO-1,2-PROPANE DINITRATE



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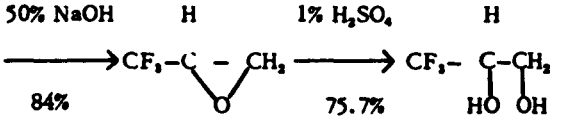

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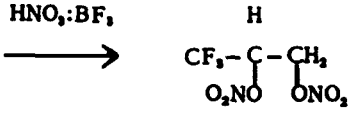

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sulfuric acid. A more recent paper by French workers (Ref 4) reports a similar preparation using 1,2-propylene oxide with a 50/50 mixture of nitric acid and sulfuric acid. But to our knowledge no investigation on the nitration of oxides has been recorded where one of the oxide carbons is flanked by a perfluorocarbon group.

RESULTS AND DISCUSSION

At the outset, we planned to investigate the nitration of 3,3,3-trifluoro-1,2-epoxypropane, $CF_3-CH-CH_2$ (O), using the following nitrating agents:

1. 98% nitric acid
2. Mixed acid (sulfuric/nitric, 1/1 by weight)
3. A complex consisting of boron trifluoride and nitric acid (98%)

Since liberal use was made of infrared spectroscopy[1] for the interpretation of our results, we believe that it would be instructive to incorporate in this discussion all the information and implications obtained with this tool This practice is, we feel, justified by the fact that further work is now in progress based on these infrared interpretations.

It should be mentioned here that the capillary film technique was used throughout this work in the preparation of samples for infrared study. It would also be appropriate before going further to comment on the spectrum of the pure dinitrate (Fig 1, p 20) which had been prepared previously through the sequence of reaction shown on page 3. The band of greatest interest is the strong band in the 6μ (1670 cm^{-1}) region assigned to the asymmetrical $-NO_2$ stretching vibration (Ref 6). We believe that this absorption is susceptible to resolution into two peaks originating from the two nonequivalent nitrate groups in 3,3,3-trifluoro-1,2-propane dinitrate. We further speculate that the high frequency side of the unresolved band arises from vibration of the nitrate group on the secondary carbon (2) while the low frequency side arises from vibration of the nitrate group located on the primary carbon (1),

$$\overset{(2)}{CF_3-CHONO_2}-\overset{(1)}{CH_2ONO_2}$$

III

[1]Perkin Elmer double-beam infrared spectrophotometer, Model 21. Rock salt optics were used and the infrared region covered extended from 2 to 15 microns.

on the ground that the electronegative CF_3 group will exert on an adjacent group (carbon (2) nitrate) an inductive effect which should shift the band to a higher frequency. We intend to verify this in the near future by attempting the resolution of the nitrate absorption band at 6μ (1670 cm^{-1}) and also by preparing mononitrates IV and V.

$CF_3-CHOH-CH_2ONO_2$ $\qquad$ $CF_3-CHONO_2-CH_2OH$

IV $\qquad$ V

Nitration With 98% Nitric Acid

When 3,3,3-trifluoro-1,2-epoxypropane was added slowly to a threefold excess of 98% nitric acid kept at 0°C, there was obtained a yellowish liquid which, upon distillation under vacuum, gave a colorless liquid in a 20% yield (assuming it was the desired dinitrate). The refractive index of the product, $n^{20°}$ 1.387, was close enough to that of the pure dinitrate, $n^{20°}$ 1.389, to suggest that we had obtained the desired dinitrate. The infrared study was, however, more informative.

Infrared Study of Crude Product (Fig 2, p 20)

In the region extending from 6μ (1670 cm^{-1}) to 15μ (670 cm^{-1}) both the pure dinitrate and the crude product from the 98% nitric acid experiment spectra are superimpossible. Both spectra also show strong absorption in the 6μ (1670 cm^{-1}) region with the difference that, in the crude product, this band has lost the symmetry observed in the dinitrate. Another divergence in the profile of both spectra is found in the 3μ (3330 cm^{-1}) region. The pure dinitrate spectrum is almost completely transparent while the crude product shows a broad (half width 400 cm^{-1}) medium symmetrical band, with a maximum at 2.95μ (3400 cm^{-1}).

Infrared Study of Distillate (Fig 3, p 20)

Distillation of the crude product brings about a marked change in the appearance of the 3μ (3330 cm^{-1}) absorption band, which is decreased in height but sensibly broadened, extending from 2.8μ (3580 cm^{-1}) to 3.0μ (3330 cm^{-1}). Also a distinct shoulder appears on the low frequency side of the 8.7μ (1150 cm^{-1}) band.

The nitration of 3,3,3-trifluoro-1,2-epoxypropane with 98% nitric acid could lead to the following products:

$$CF_3-\underset{\diagdown O \diagup}{CH}-CH_2 + HNO_3 \rightarrow \underset{III}{CF_3-CHONO_2-CH_2ONO_2} + \underset{IV}{CF_3-CHOH-CH_2ONO_2} + \underset{V}{CF_3-CHONO_2-CH_2OH} \quad (1)$$

The spectral observations indicate that under the conditions of this experiment the dinitrate III is formed along with a small smount of a hydroxy compound. Distillation has certainly decreased the concentration of the contaminant as shown by the reduced intensity of absorption in the 3μ (3330 cm^{-1}) region following distillation. This is also shown by the closeness of the refractive indexes of the distillate and the reference sample of dinitrate III. The similarity in absorption in the fingerprint region would furthermore forbid the presence of substantial quantities of the mononitrates. The shape of the nitrate band at 6μ (1670 cm^{-1}) in both the crude product and the distillate (in which the high frequency side intensity is decreased) suggests that the contaminant is probably the mononitrate $CF_3-CHOH-CH_2ONO_2$ IV.

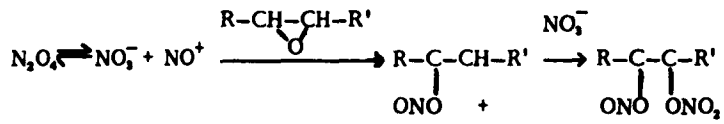
A.M. Pujo and M. J. Boileau (Ref 4) have synthesized nitrite-nitrate esters by the action of dinitrogen tetroxide on propylene oxide. Consequently one could argue that the epoxide under study might similarly lead to the two nitrite-nitrate esters VI and VII upon treatment with nitric acid.

$\underset{VI}{CF_3-CHONO-CH_2ONO_2}$ $\underset{VII}{CF_3-CHONO_2-CHONO}$

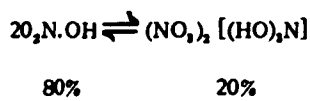
We believe that this course of the reaction is quite improbable for the following reasons. The absence of absorption at 1736 cm^{-1} (5.77μ) is a strong indication that the product is not the nitrite-nitrate ester VI. For it has been reported (Ref 5) that 2,2,2-trifluoroethyl nitrate, $CF_3-CH_2ONO_2$ shows two N=O stretching vibrations, at 1736 cm^{-1} (5.77μ) and at 1695 cm^{-1} (5.90μ). These are attributed to the trans- and cis- forms of the nitrite structure. In VI, which incorporates the trifluoroethyl nitrite group in its structure, the absence of absorption at 1736 cm^{-1} would consequently mean that the nitrite structure exists in the cis- form to the exclusion of the transform and this to us seems very improbable. The infrared spectrum of the product in the 6μ region does not reveal unequivocal features for or

against VII. However, the overall appearance of the spectrum is too close to the spectrum of the pure dinitrate to suggest structures VI or VII for the product. In addition, bands corresponding to combinations of the fundamentals (γ NO + γ N=O) at 2300-2250 cm^{-1} (4.34μ - 4.45μ) and (γ N-O + γ N=O) near 2500 cm^{-1} usually observed in the spectra of nitrite compounds are completely absent in our product.

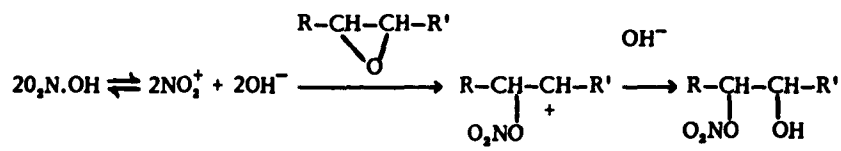
From a mechanistic point of view, the two nitrating agents dinitrogen tetroxide and nitric acid should, upon reaction with an oxirane ring, lead to a nitrite-nitrate ester and a dinitrate ester, respectively. This is shown as follows: According to recently published views (Ref 17), dinitrogen tetroxide is in equilibrium with the species NO_2^- and NO^+, the latter adding first to the electron-rich center.

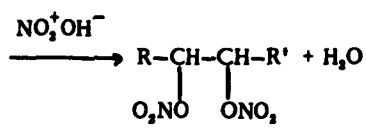


Nitric acid (98%), on the other hand, would consist of an equilibrium mixture of a pseudoacid (80%) and a nitracidium dinitrate (20%):

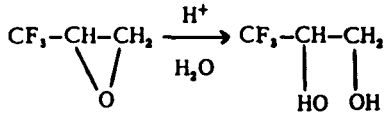


The nitrating properties are ascribed to the pseudoacid which, in the presence of a suitable substrate, would dissociate and react as follows:





We have as yet no explanation for the low yield of dinitrate obtained by this method. Our material balance being markedly below 100%, we suspect that our experimental technique was partly responsible for some losses of the extremely volatile starting epoxide. It is also possible that the following competing reaction might occur appreciably under the experimental conditions. This diol being quite soluble in water, it might have been lost during the working-up process.



Nitration With Mixed Acid (HNO_3/H_2SO_4, 1/1 by weight)

Nitration with the mixed acid was done between -20°C and -10°C. A crude product was obtained which upon distillation under vacuum gave two fractions: fraction (1) was a colorless liquid, $n^{25°}$ 1.387; fraction (2) was also a colorless liquid, $n^{25°}$ 1.389. These refractive indexes are to be compared with that of the reference dinitrate, 1.387 at 25°C.

Infrared Study of Crude Product (Fig 4, p 22)

The crude product shows a strong associated OH absorption at 2.95μ (3400 cm^{-1}). From 7μ (1430 cm^{-1}) to 15μ (670 cm^{-1}) many deviations from the spectrum of the reference dinitrate are apparent. The general profile of this region is also poorly defined.

Infrared Study of Distillates (Figs 5 and 6, p 22)

The spectrum of distillate (1) is very similar to that of the distillate obtained with the 98% nitric acid reaction. In the 3μ region, a broad band is observed with a maximum at 2.95μ (3400 cm^{-1}) flanked by a discrete shoulder (or inflection) at 2.80μ (3580 cm^{-1}). Both associated and free OH groups must consequently coexist in this liquid.

The absorption at 6μ is broad with an observable partial collapse on the high frequency side of the band. These observations give evidence for the presence of some of the hydroxynitrate ester IV, $CF_3-CHOH-CH_2ONO_2$.

A glance at the spectrum of distillate 2 shows that it is responsible for the deviations observed in the fingerprint region of the crude product. Furthermore, there is no sign of strong OH association in this fraction; only one peak is observed at 2.83μ (3520 cm^{-1}).

Of greatest interest is the absorption at 5.95μ (1689 cm^{-1}). To us, this is strong evidence of the presence of the hydroxy-nitrate ester (V) $CF_3-CHONO_2-CH_2OH$ in substantial amount in distillate 2.

The information gathered from the infrared study leads to the conclusion that distillate 1 is probably the expected dinitrate contaminated with the mononitrate IV, while distillate 2 is also the dinitrate III but containing a substantial quantity of the mononitrate V. The refractive indices of distillate 1, $n^{25°}$ 1.387, and distillate 2, $n^{25°}$ 1.389, are on the other hand very close to each other and to the expected dinitrate III. It is possible of course that the refractive indices of pure mononitrates IV and V may be sufficiently close to each other and to the dinitrate III to render this physical property unreliable for identification purposes.

The vapor pressures of the distillates are far enough apart to support the conclusion that distillate 1 and distillate 2 are two different mixtures.

As with the experiments with 98% nitric acid, our yield is very low: 19% based on the dinitrate; 27% based on complete transformation to either mononitrate IV or V.

Nitration With The Complex Boron Trifluoride-Nitric Acid

Boron trifluoride is known to be an effective promoter of nitration (Ref 6). According to the literature, boron trifluoride can add to nitric acid in two different stoichiometries. In one instance, boron trifluoride forms with nitric acid a complex having a 1:1 mole ratio, i.e., $HNO_3:BF_3$ (Refs 7 and 8). From cryoscopic and spectroscopic studies, this complex is believed to be ionic and to have the structure $[BF_3OH]^-\ [NO_2]^+$ (Ref 8). The second stoichiometry possible in the addition of boron trifluoride to nitric acid is in the ratio of two molecules of boron trifluoride to one molecule of nitric acid, i.e., $HNO_3:2BF_3$. A study of the Raman spectrum of this complex (Ref 9) indicates the absence of the nitronium ion, NO_2^+, the band at 1400 cm^{-1} assigned to this ion not being observed.

For our nitration studies, we prepared the complex by bubbling gaseous boron trifluoride into 98% nitric acid until the saturation point was reached. This reaction was exothermic and cooling was necessary to prevent the temperature from rising too high. Three different batches of the complex were prepared, with boron trifluoride/nitric acid molar ratios of 1.17/1, 1.35/1, and 1.75/1. We have also observed that the nitric acid, which is originally reddish-brown, gradually becomes colorless upon the addition of boron trifluoride, the last traces of color fading when the molecular ratio of 0.6 BF_3 to 1.0 HNO_3 is reached.

To determine whether the resulting complex contained a substantial amount of dissolved, free boron trifluoride the complex was heated for two hours at 110°C. No loss in weight was observed, eliminating this possibility.

When 3,3,3-trifluoro-1,2-epoxypropane was added slowly to a saturated solution of the complex cooled to 0°C and the resulting mixture was worked up, a product was obtained whose infrared spectrum differed from the spectrum of the expected dinitrate by the appearance of additional bands at 3.0μ (3330 cm^{-1}) (broad) and at 6.4μ (1560 cm^{-1}). The intensity of absorption at 3.55μ (3000 cm^{-1}) is also markedly increased in the new spectrum (Fig 7, p 23).

The crude product was subsequently distilled under vacuum. Distillate 1 had an infrared spectrum (Fig 8, p 23) very close to that of the pure dinitrate but still absorbed at 3.0μ (3330 cm^{-1}). There was also some vestige of absorption at 6.4μ (1560 cm^{-1}).

Distillate 2 has an infrared spectrum (Fig 9, p 23) which closely resembles that of the pure dinitrate except for a sharp band at 2.75μ (3630 cm^{-1}) and a weak band at 2.90μ (3450 cm^{-1}). Moreover, the refractive index is 1.387 at 25°C, which is similar to that of the dinitrate.

The residue, which would not volatilize under 5 mm vacuum and 230°C, was a very viscous liquid. Inspection of the infrared spectrum (Fig 10, p 23) shows that this fraction is responsible for the irregularities observed in the crude product at 3.34μ (3000 cm^{-1}) and 6.4μ (1560 cm^{-1}).

Only distillate 2, which was obtained in a 19% yield, appears from the infrared spectrum and refractive index to be the desired dinitrate. The low material balance, 55% based on dinitrate, is believed to be due to the loss

of the volatile starting epoxide during the reaction. Boron trifluoride is a well known polymerization catalyst (Ref 9-14). The substantial amount of non-volatile residue is probably the result of such polymerization.

In an attempt to minimize polymerization, the nitration was repeated at a lower temperature, -20°C. Under these conditions, a crude product was obtained in a yield of 51%.

The infrared spectrum of this product (Fig 11, p 24) roughly parallels that of the pure dinitrate, the divergences in the regions of 3.45μ (2900 cm^{-1}), 7.25μ (1380 cm^{-1}), 8.95μ (1120 cm^{-1}), and 9.6μ (1040 cm^{-1}) arising possibly from residual ether from the working-up procedure.

Purification by chromatography was chosen instead of the usual distillation in order to prevent possible decomposition of the crude product by heat. Silica gel, Grade 12, from the Davison Chemical Company was chosen as adsorbent and the crude product was eluted by adding distilled methylene chloride followed by a mixture of methylene chloride-ether, 50:50. This eluting procedure gave us a 95% recovery.

Fractions 2, 3, and 4, which were consecutive in the elution process and which constituted 98% of the original feed to the column, had similar spectra (Fig 13, p 25). Furthermore, these spectra were similar to the spectrum of the pure dinitrate.

On the other hand, fraction 8, constituting only 4% of the total input, showed definite divergence from the spectrum of the dinitrate (Fig 13, p 25). A broad medium band at 2.95μ (3400 cm^{-1}) is observed; the high frequency side of the 6μ band appears eliminated; the broad absorption in the 12μ region has been shifted to higher frequencies (lower wavelength).

These observations lead us to believe that under the conditions of this experiment approximately 80% of the crude product probably consists of the expected dinitrate while about 4% would be the hydroxy-nitrate ester IV: $CR_3-CHOH-CH_2ONO_2$.

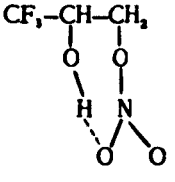
We though it advisable to repeat this last experiment using a different ratio of boron trifluoride to nitric acid in the nitrating agent. We hoped that changing this ratio to less than one part boron trifluoride per part nitric acid would be beneficial since then there would never be an excess of boron trifluoride in the mixture. Such an excess, as we have mentioned earlier, could easily initiate polymerization in the system.

We therefore prepared the nitrating agent BF_3:HNO_3 in the ratio of 0.5:1. With this nitrating agent, the nitration gave us a 78.8% yield of the crude product.

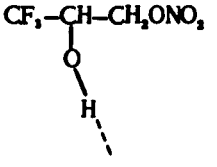
The infrared spectrum of this crude product (Fig 12, p 24) is very similar to the spectrum of the pure dinitrate throughout the entire spectral range except for very weak absorption at 3.05μ (3280 cm^{-1}) and a somewhat too intense absorption in the C-H stretching at 3.35-3.45μ (2900-3000 cm^{-1}), with shoulders at 3.45μ (2900 cm^{-1}) and 3.50μ (2870 cm^{-1}). This again could very well be caused by residual ether in the product.

This crude product was subsequently chromatographed on silica gel as in the previous experiment with a quantitative material recovery. Fractions 3 and 4 from the methylene chloride elution, which constituted 72% of the crude product, have spectra (Fig 14, p 25) which are superimposable on the spectrum of the pure dinitrate. On the other hand, fraction 7, which amounted to more than 25% of the original crude product, has a spectrum (Fig 14) characterized by extensive absorption at 3μ (3330 cm^{-1}) that extends to the C-H stretching region at 3.45μ (2900 cm^{-1}) and also by a strong absorption band at 6.1μ (1640 cm^{-1}).

It is likely, therefore, that fraction 7 consists of the hydroxynitrate ester IV, CF_3–CHOH–CH_2ONO_2. The shift of the absorption band to 6.1μ (1640 cm^{-1}) in conjunction with the strong absorption at 3μ (3330 cm^{-1}) indicates either intermolecular or intramolecular hydrogen bonding.



Intra



Inter

The occurrence of intramolecular hydrogen bonding would be favored in terms of energy by the formation of a seven-membered ring which would stabilize the molecule.

We became suspicious of a reaction occurring between the product and the silica gel adsorbent. We had observed previously that, in the presence of solvents containing oxygen, such as ethyl acetate and ether, silica gel releases a substantial amount of heat with transformation of the gel to what appears to be a crystalline form. It would not be at all surprising then, if a molecule incorporating nitrate groups would interact similarly with the silica gel adsorbent.

This hypothesis was tested by chromatographing the pure dinitrate under the conditions described above. Seven fractions were collected with a quantitative material recovery. Fractions 2 and 3 amounting to 77% of the sample used, had spectra (Fig 15, p 25) similar to the original dinitrate. Fraction 7, amounting to 20% of the original sample, had a spectrum (Fig 15) indicating hydrolysis of the nitrate grouping located on carbon (2) to give the hydroxynitrate ester IV:

$$\underset{\text{III}}{CF_3\overset{(2)}{C}HONO_2\text{–}\overset{(1)}{C}H_2ONO_2} \longrightarrow \underset{\text{IV}}{CF_3\text{–}CHOH\text{–}CHONO_2}$$

An intense absorption band is observed at 3μ (3330 cm^{-1}); the nitrate grouping has its maximum at 6.05μ (1650 cm^{-1}).

It has been previously observed by other investigators that the presence of electron-attracting groups such as NO_2^+ and Cl^- decreases the stability of the nitrate group. These structural effects have been summarized by Phillips in his review on the thermal decomposition of nitrate esters (Ref 16). Our own results are in line with these prior findings. The nitrate group on carbon (2), being adjacent to the strong influence of the electron-attracting group CF_3, is preferentially hydrolyzed on the surface of the absorbent.

EXPERIMENTAL PROCEDURE

Preparation of the Nitric Acid-Boron Trifluoride Complex

25 ml (37.3 g) of 98% nitric acid was transferred into a tared 100-ml 3-neck flask. The flask was subsequently equipped with a thermometer, a calcium chloride drying tube, and a glass tubing whose lower end was drawn to a small opening and immersed in the nitric acid. The upper end of the glass tubing was connected by means of tygon tubing to a trap leading to a cylinder of gaseous boron trifluoride. In some experiments a pipette was used in place of both the trap and the glass tubing. A magnetic stirrer (Kel-F magnetic bar) provided agitation. The temperature was maintained between 10-20°C by means of a salt-ice bath. A slow stream of boron trifluoride was bubbled through the nitric acid until dense white fumes appeared above the surface of the liquid. After the addition of boron trifluoride was complete, the tared flask was weighed. The increase in weight, amounting to 46.8 g, corresponds to a ratio of boron trifluoride to nitric acid of 1.17/1.

On other occasions, the preparation of the complex by the same procedure led to ratios of 1.35/1 and 1.75/1. When it was desired to form a complex with a lower ratio of boron trifluoride to nitric acid, the bubbling of the gas was simply stopped at some time prior to the saturation point.

The original yellow color of the nitric acid disappears gradually during the addition of the boron trifluoride. In one experiment, the solution was weighed when it was judged that the last traces of color had disappeared. It was found that the content of boron trifluoride relative to nitric acid was in a ratio of 0.60:1.

Nitration of 3,3,3-Trifluoro-1, 2-Epoxy Propane Dinitrate with the Complex Boron Trifluoride-Nitric Acid

Experiment 1

80 g of the nitrating complex (boron trifluoride-nitric acid, 1.34:1) was transferred into a 3-neck round-bottom flask equipped with a stirrer, a dropping funnel, and a calcium chloride drying tube. With the temperature kept in the neighborhood of 0°C, 21.5 g (0.192 mole) of 3,3,3-trifluoro-1,2-epoxypropane was added dropwise. The mixture was agitated for an extra

4 hours after the addition was completed and was then poured over cracked ice. The aqueous and oil phases were transferred to a separatory funnel and 300 ml of ether was added.

After separation of the ether layer, the aqueous phase was extracted twice with 100 ml of fresh ether. The combined ether extracts were washed with 300 ml of distilled water followed by a 5% aqueous solution of sodium bicarbonate until neutral. The ether solution was given a final wash with distilled water and was dried over anhydrous sodium sulfate. Removal of the salt by filtration was followed by concentration on the steam bath.

The residue was subjected to vacuum distillation in a semi-micro vigreux column. Two fractions were collected: fraction 1, 5.6 g, passed at 40-44°C (5 mm); fraction 2, 8.2 g, passed at 44°-47°C (5 mm). The residue, which would not volatilize upon heating to 230°C (5 mm), was a viscous liquid amounting to 9.6 g.

Both of these volatile fractions, in addition to the non-volatile residue, were subjected to infrared study.

Experiment 2

To a 50-ml Erlenmayer flask containing 34 g of the nitrating complex (BF_3:HNO_3, 1.35:1) maintained between -30°C and -20°C by means of a dry ice-acetone bath, 5.2 g (0.04 mole) of 3,3,3-trifluoro-1,2-epoxypropane was added slowly with a medicine dropper. The epoxide had been previously kept at 0°C to prevent excessive loss by vaporization.

At this temperature, the reaction mixture attained a viscosity at which the magnetic stirrer was ineffective. The agitation was consequently done manually by means of a glass rod. The reaction mixture was kept between minus 20°C and minus 10°C for an extra one-half hour with intermittent stirring. Following warming to room temperature the mixture was poured into cracked ice and from there on the procedure followed as described above to yield 5.07 g of a crude orange product. This crude product was submitted for infrared study.

A chromatographic column, 25 cm long by 2.5 cm diameter, equipped with a teflon stopcock and a coarse sintered glass bottom, was charged

with 50 g of Grade 12 silica gel, from the Davison Chemical Company, in distilled methylene chloride (absorbent height, 20 cm). The crude product was dissolved in a minimum volume of methylene chloride and transferred to the column. Elution was done with methylene chloride, giving seven 25-ml fractions. This was followed by 100 ml of the mixed solvents, methylene chloride-ether (1:1 vol). Each fraction was concentrated to dryness to yield a weight distribution shown in the table.

Fraction	Eluting Solvent	Residue, g
1	Methylene chloride	0.01
2	Methylene chloride	1.99
3	Methylene chloride	1.91
4	Methylene chloride	0.60
5	Methylene chloride	0.11
6	Methylene chloride	0.02
7	Methylene chloride	0.01
8	Methylene chloride and ether	0.21
	Total	4.86
	recovery	95%+

Fractions 2, 3, 4, and 8 were submitted for infrared study.

Experiment 3

Into a 50-ml Erlenmayer flask containing 22 g of the nitrating complex (BF_3:HNO_3, 0.5:1) maintained between minus 30°C and minus 20°C by means of a dry ice-acetone bath, 4.67 g (0.04 mole) of 3,3,3-trifluoro-1,2-epoxypropane was added slowly with a medicine dropper.

From here on the procedure used in Experiment 2 was followed, and 7.23 g (78.8% yield) of an crude orange product was obtained. This crude product was subjected to infrared study.

Fraction	Eluting Solvent	Residue, g	Refractive Index, 25°C	Density,* 25°C
1	Methylene chloride	0.00		
2	Methylene chloride	0.00		
3	Methylene chloride	3.57	1.380	1.612
4	Methylene chloride	1.65	1.382	1.593
5	Methylene chloride	0.07		
6	Methylene chloride	0.11		
7	Methylene chloride and ether (1:1 by volume)	1.91	1.377	1.469
	Total	7.31		
	Recovery	101.1%		

*The density measurements were done on the Fisher-Davidson Gravitometer using freshly distilled ethylbenzene as the reference liquid.

Chromatography of Pure 3,3,3-Trifluoro-1,2-Propane Dinitrate, CF_3–$CHONO_2$–CH_2ONO_2

3,3,3-Trifluoro-1,2-propane dinitrate, 3.15 g (0.01 mole) was chromatographed on 50 g of silica gel following the procedure described in 2-B.

For the last two fractions, a mixture of two solvents, methylene chloride-methanol, was used instead of methylene chloride-ether.

The distribution of the products if given on p 18.

Fraction	Eluting Solvent	Residue, g	Refractive Index, 25°C.	Density, 25°C
1	Methylene chloride	0.01		
2	Methylene chloride	1.76	1.387	1.603
3	Methylene chloride	0.68	1.387	
4	Methylene chloride	0.04		
5	Methylene chloride	0.05		
6	CH_2Cl_2–CH_3OH (1:1 by volume)	0.01		
7	CH_2Cl_2–CH_3OH (1:3 by volume)	0.62	1.381	
	Total	3.17		
	Recovery	100.6%		

Nitration of 3,3,3-Trifluoro-1,2-Epoxypropane with 98% Nitric Acid

Into a 3-neck round-bottom flask equipped with a stirrer, dropping funnel, and calcium chloride drying tube, 50 g of 98% nitric acid was transferred. While the flask was kept in the neighborhood of 0°C, 15 g (0.13 mole) of 3,3,3-trifluoro-1,2-epoxypropane was added dropwise. The mixture was agitated at this temperature for an extra hour, after which time it was poured onto ice.

The subsequent steps followed the procedure described in Experiment 2 on p 15. 13.1 g of an orange residue was obtained and subjected to infrared study.

The crude product was subsequently subjected to fractional distillation in a semi-micro vigreux column. A colorless liquid, 5.9 g (20% yield) passing at 40° –44°X, (5 mm), $n^{20°}$, 1.387, was collected. This distillate was submitted for infrared study.

Nitration of 3,3,3-Trifluoro-1,2-Epoxypropane with the Mixed Acid (Sulfuric/ Nitric, 1/1 by weight)

Into a 3-neck round-bottom flask equipped with a stirrer, dropping funnel, and calcium chloride drying tube, 50 g of the mixed acid (25 g 98% nitric acid and 25 g 95% sulfuric acid) was transferred. While the flask temperature was kept between minus 20°C and minus 10°C, 15 g (0.13 mole) of

3,3,3-trifluoro–1,2-epoxypropane was added dropwise. The mixture was agitated at this temperature for an extra hour, after which it was poured onto ice.

The subsequent steps followed the procedure described in Experiment 2. A crude product was obtained to the amount of 9.6 g (32% yield). This product was submitted for infrared study.

Upon distillation under vacuum in a semi-micro vigreus column, two fractions were collected: fraction 1, 3.4 g of a colorless liquid, $n^{25°}$, 1.387; fraction 2, 2.3 g of a colorless liquid, $n^{25°}$, 1.389.

These two liquid fractions were subjected to infrared study.

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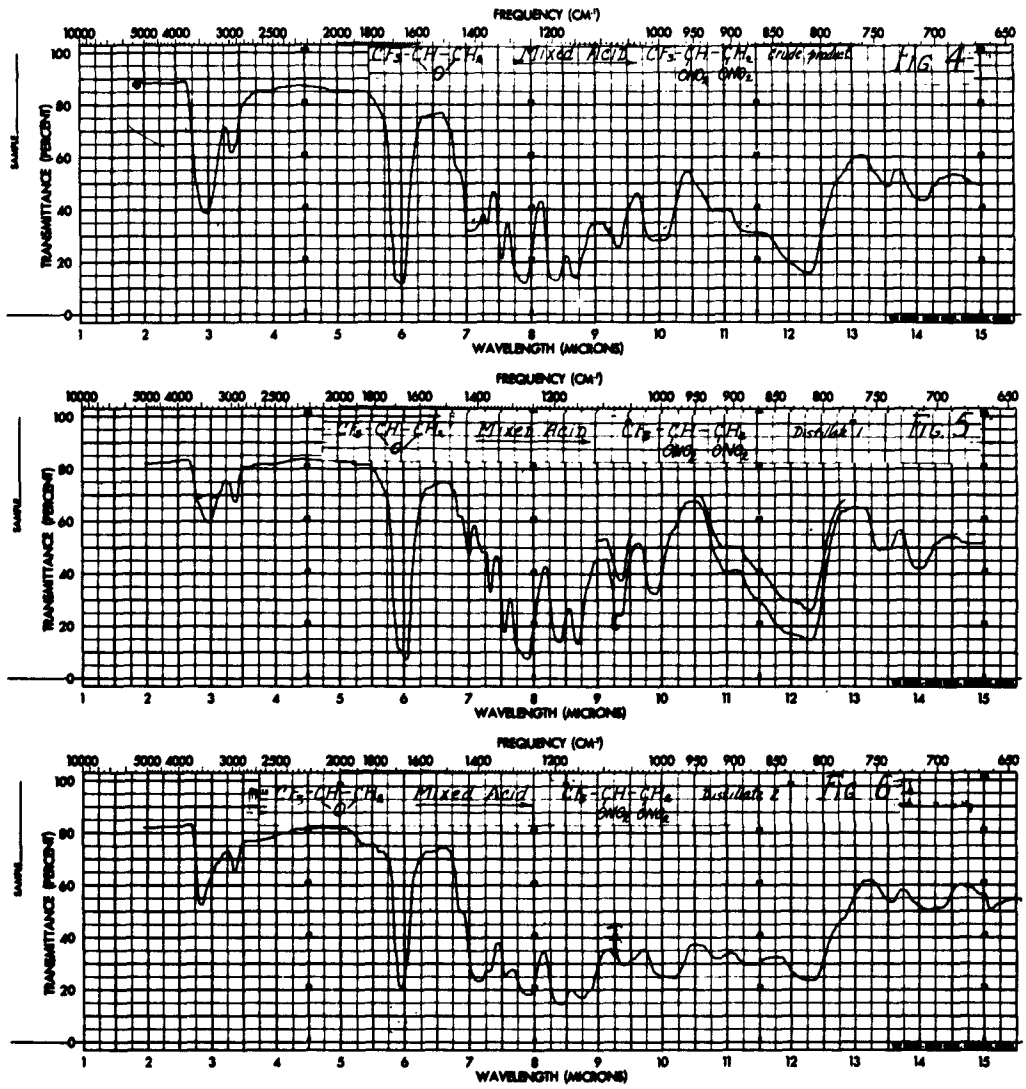
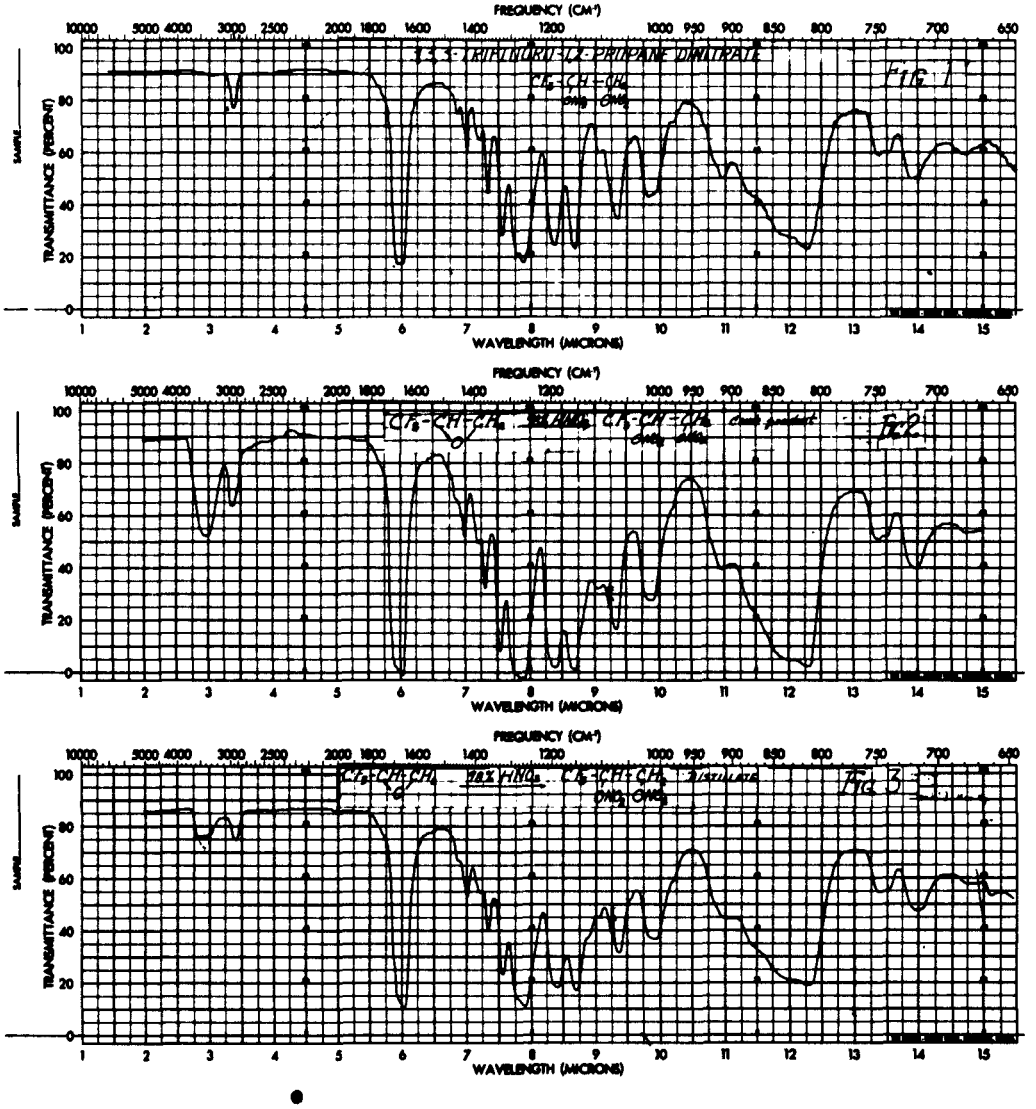
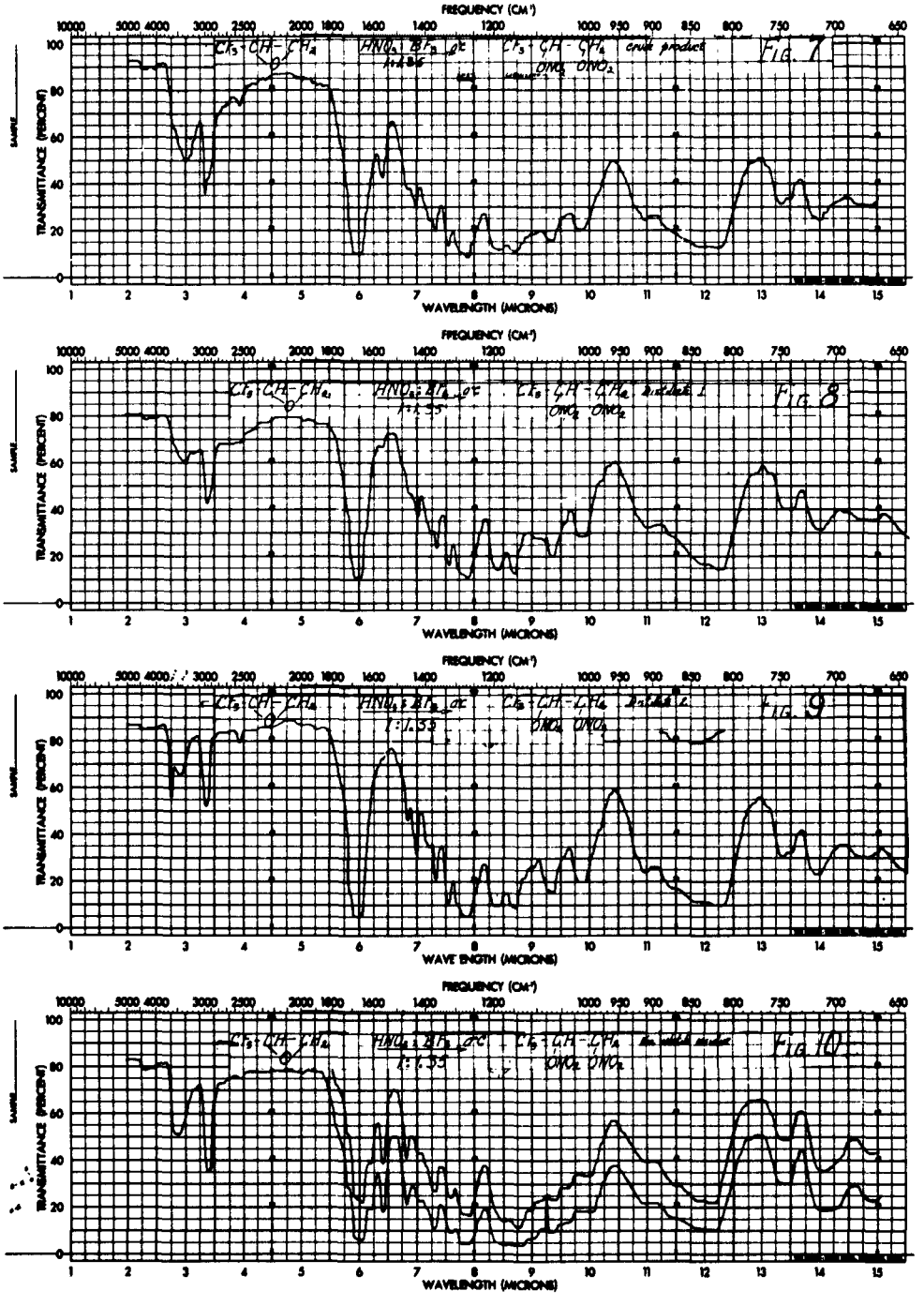


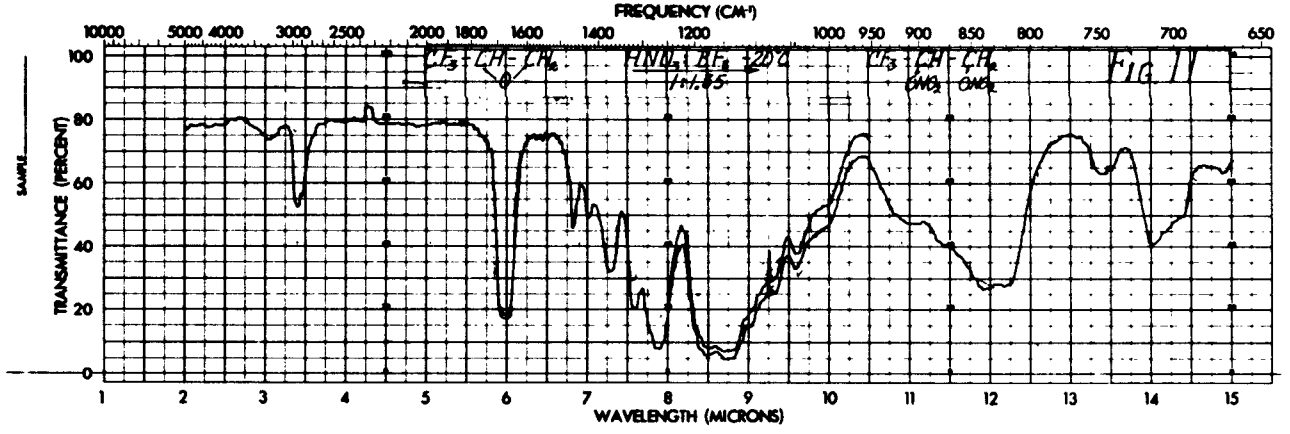
Figs 1 - 3 Infrared Spectra



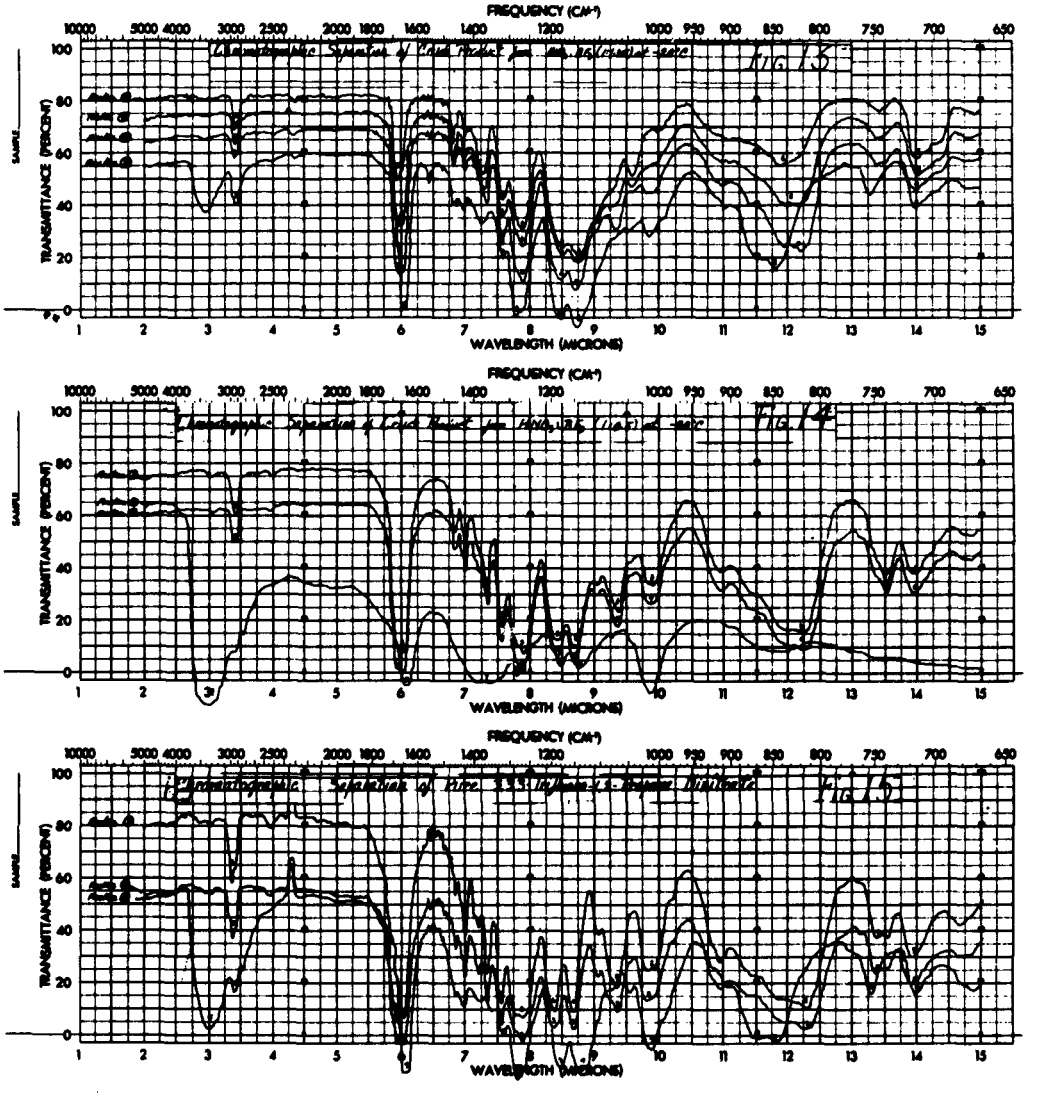
Figs 4 - 6 Infrared Spectra



Figs 7 - 10 Infrared Spectra



Figs 11 - 12 Infrared Spectra



Figs 13 - 15 Infrared Spectra

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STUDY OF THE NITRATION OF 3,3,3-TRIFLUORO-1,2-EPOXYPROPANE

Yvon P. Carignon

Technical Report 3055, April 1963, 26 pp, figures. OMS 5010.11.585, DA Proj 5B17-06-002. Unclassified report.

3,3,3-Trifluoro-1,2-epoxypropane, $CF_3-\underset{O}{\underbrace{CH-CH_2}}$, was nitrated with (1) 98% nitric acid, (2) mixed acid (H_2SO_4: HNO_3, 1:1 by wt), and (3) boron trifluoride-nitric acid complex.

Each nitrating agent afforded the desired 3,3,3-trifluoro-1,2-propane dinitrate, $CF_3-CHONO_2-CH_2ONO_2$, together with variable amounts of the two mononitrates $CF_3-CHOH-CH_2ONO_2$ and $CF_3-CHONO_2-CH_2OH$.

(over)

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2. Trifluoro-1,2-propane dinitrate

I. Carignan, Yvon P.

UNITERMS

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Trifluoro-1,2-propane dinitrate
Nitration
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Under the conditions of the experiments, only with the boron trifluoride-nitric acid complex were reasonable yields of the dinitrate obtained.

During this study, it was observed that the dinitrate was partially hydrolyzed (20%) on a silica gel column to the mononitrate $CF_3-CHOH-CH_2ONO_2$.

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