observed in the hydra tentacle regeneration assay when a hydrophilic group was present in the alkyl side chain of certain 6-(substituted)aminopurines.[1]

A slight but definite stimulatory effect on the rate of germination was observed when lettuce seed (Early Curled Simpson) were presoaked in 10 γ/ml. solutions of α-(6-purinylthio)butyric acid and the corresponding valeric acid derivative. The butyric acid analog gave approximately a 250% increase in the number of seeds germinating after 72 hours in the dark at 30°, while the valeric acid derivative gave an 80% increase, as compared with seed presoaked in water alone. These values represent only moderate stimulations of seed germination in comparison with the more active 6-(substituted)purines.[2,8,9] It is interesting to note that the most active 6-alkylthiopurines with respect to stimulation of seed germination were those derivatives containing four to six carbon atoms in the substituent group, and correspondingly, the more active purinylthiocarboxylic acids are those which contain groups of similar size.

EXPERIMENTAL[10]

Biological assay techniques. The assay procedures used were the same as those previously reported in the study of similar 6-(substituted)purine compounds for stimulation of lettuce seed germination,[2] inhibition of hydra tentacle regeneration,[5] and microbiological assays.[7]

α- and β-(6-Purinylthio)carboxylic acids. These compounds were prepared by an alkaline-catalyzed condensation between the appropriate haloacid and 6-mercaptopurine, as indicated in Table I, following a procedure which has previously been reported.[1]

An alternate condensation procedure involved using an excess of triethylamine as the condensing agent and allowing the reaction to proceed at room temperature. The course of these reactions was followed by observing the decrease in ultraviolet absorption at 328 $m\mu$ and the appearance of an absorption band at 282–289 $m\mu$. The former λ_{max} is associated with 6-mercaptopurine, and the latter absorption is indicative of a 6-(substituted)thiopurine.[11] The reaction mixtures were then taken to dryness *in vacuo* to remove the excess amine, and the residues were crystallized as indicated in Table I. Attempts to increase the rate and yield of the reactions by heating in the presence of triethylamine resulted in varying amounts of decomposition products.

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[8] C. G. Skinner, J. R. Claybrook, F. D. Talbert, and W. Shive, *Arch. Biochem. Biophys.*, **65**, 567 (1956).

[9] C. G. Skinner, P. D. Gardner, and W. Shive, *J. Am. Chem. Soc.*, **79**, 2843 (1957).

[10] All melting data were taken on a Fisher-Johns micro hot stage and the temperatures are uncorrected. The ultraviolet absorption spectra were determined on a Beckman model DK-2 recording spectrophotometer using a 10 γ/ml. solution of the appropriate compounds dissolved in 95% ethyl alcohol.

[11] C. G. Skinner, R. G. Ham, O. C. Fitzgerald, Jr., R. E. Eakin, and W. Shive, *J. Org. Chem.*, **21**, 1330 (1956).

Reactions of Nitrate Esters. V.[1] Decomposition of Primary Nitrates in Perfluorinated Acids

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Received February 28, 1958

We wish to report the occurrence of an unusual decomposition reaction of simple primary aliphatic nitrates, which can be achieved by merely dissolving the esters in trifluoroacetic acid (TFA) and allowing the solutions to stand at room temperature for 24 hours or less. The main products obtained from the decomposition are nitric oxide and the carboxylic acid having the same number carbon atoms as the ester. The reaction is catalyzed by ultraviolet light, although it does proceed even in the dark. Atmospheric oxygen appears to have no effect. A similar reaction occurs in other perfluorinated acids but not in 100% acetic or 100% sulfuric acid.

In addition to the main decomposition products, which are produced in yields of the order of 50%, there are obtained traces of solid acidic materials, and significant amounts (*ca.* 50%) of the alkyl trifluoroacetates. The latter are presumably formed either by an ordinary metathesis, or by a complex ionization similar to that reported for solutions of alkyl nitrates in sulfuric acid.[2]

Most of the work thus far has been with *n*-butyl nitrate, and typical procedures are described in the Experimental portion. Ethyl and *n*-propyl nitrates react in the same way with TFA. The butyl nitrate decomposition proceeds in perfluorobutyric or perfluorohexanoic acid in the same manner as in TFA. The reactions of secondary mononitrates with TFA have not been investigated, but 2,3-dinitroxybutane has been found to react readily, giving oxides of nitrogen and diacetyl.

The rate of disappearance of butyl nitrate has been followed polarographically. Attempts to follow the reaction by observing changes in the ultraviolet spectrum led to ambiguous results, due to the fact that ultraviolet light catalyzes the reaction, and to the fact that reaction products absorb in the same spectral region (*ca.* 255 $m\mu$) as does the nitrate ester. The absorbance in this region remains essentially constant for a period of several hours, after which it increases rapidly. The length of this apparent induction period varies with concentration and with the duration of exposure to ultraviolet light in the spectrophotometer. The existence of an apparent induction period seems to be due to a compensating effect of increasing absorbance by reaction products and decreasing absorbance (at the same wave length) by butyl nitrate, since no

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[1] Previous paper: R. T. Merrow, *J. Am. Chem. Soc.*, **78**, 1297 (1956).

[2] L. P. Kuhn, *J. Am. Chem. Soc.*, **69**, 1974 (1947).

induction period was observed when the reaction was followed polarographically.

While the mild conditions and the nature of the solvent suggest an ionic mechanism for this decomposition, the nature of the products and catalysis by ultraviolet light are indicative of a radical process. Thermal[3] and photochemical[4] decompositions are known to proceed *via* an initial homolytic cleavage, *viz:*

$$RCH_2ONO_2 \longrightarrow RCH_2O\cdot + NO_2$$

This is followed by a number of possible reactions leading to the observed products, including nitric oxide, aldehydes, and nitrite esters. Such decompositions of simple mononitrates have never been reported under the mild conditions used in the present work.

Further investigation into the mechanism of this decomposition, and particularly into the role of the fluorinated acids, is in progress.

EXPERIMENTAL

All of the chemicals used were commercially available materials. Melting and boiling points are uncorrected.

Trifluoroacetolysis of n-butyl nitrate. One-tenth mole of *n*-butyl nitrate was dissolved in 40 ml. of ice cold trifluoroacetic acid in an Erlenmeyer flask fitted with a ground glass stopper. The solution was cooled for 6 hr. in an ice water bath, and then allowed to stand at room temperature for another 18 hr. The solution became quite yellow within the first hour, and then became green on standing. On admission of air the color rapidly changed to a yellow-brown, and brown fumes formed above the liquid. The mixture was distilled, yielding 7.0 g. (.04 mole) of *n*-butyl trifluoroacetate, b.p. (713 mm.) 102–103°, $n_D^{26.5}$ 1.3376 (lit.[5] b.p. 102.7–102.8°, n_D^{20} 1.3391) and 5.1 g. (0.058 mole) of butyric acid, b.p. (713 mm.) 158–160°. From the dark tarry residue, traces of a water-soluble white solid acid, m.p. (dec.) 125–130°, were obtained. There was not enough of this material to characterize.

Nitric oxide was determined in a separate experiment, by absorption in sulfuric acid and titration of the nitrosylsulfuric acid with permanganate.[6] This run was carried out under a stream of nitrogen, and proceeded in the same manner as the other experiment, except that no appreciable color developed in the solution. From 20.0 millimoles of butyl nitrate, there was obtained 9.27 millimoles (46%) of nitric oxide.

Ethyl and *n*-propyl nitrates in TFA decomposed to give, qualitatively, the same types of products. The solid material from ethyl nitrate was identified as oxalic acid, m.p. and mixed m.p. 101–102° (dihydrate, recrystallized from water).

Butyl nitrate was recovered quantitatively from solutions in 100% acetic acid after standing 24 hr. at room temperature. Solutions in sulfuric acid gave no oxides of nitrogen, although, as reported previously,[2] the nitrate ester cannot be recovered by drowning the solution in water.

Rate studies. A 0.025*M* solution of butyl nitrate in TFA was prepared. A portion of this was placed in a 1-cm quartz cell and scanned in the ultraviolet region periodically, using a Cary Model 11MS Recording Spectrophotometer. There was essentially no change in the absorbance at the maximum over the first 8 hr. After 24 hr., however, the absorbance was much greater than the range of the instrument. However, the bulk of the solution, which had remained in a glass flask, showed the same absorbance after 24 hr. as it did initially. The absorbance did not increase until sometime between 36 and 48 hr.

Samples of the same solution were polarographed periodically. One-ml. aliquots were added to 5 ml. of 95% ethanol containing 3 drops of methyl red (0.1%). The solutions were brought to the first permanent yellow color with 0.5*N* NaOH solution, and then made up to 10 ml. with 95% ethanol. These solutions were then polarographed from zero to −2.0 volts, using a Sargent Model 21 Recording Polarograph with a sensitivity setting of 0.100. It was found unnecessary to remove dissolved oxygen. A blank correction for oxygen, obtained by treating pure trifluoroacetic acid in the same manner as above, was subtracted from the total wave height obtained in the nitrate determinations. The butyl nitrate concentration was found to decrease steadily, with no "induction period." The half-life at this concentration was about 56 hr. The data for any given run fit a first-order rate law fairly well, but the values of k vary greatly with concentration.

The reaction was found to proceed even in the dark, but it was shown to be catalyzed by ultraviolet light. The apparent induction period (observed spectrophotometrically) was shortened, and the rate of butyl nitrate disappearance (measured polarographically) was increased by exposure of the solution to the unfiltered light of a mercury arc lamp (mostly 2537 A).

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Arenesulfonic Acids as Catalysts in the Alcoholysis of Nitriles to Esters

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Received March 3, 1958

Arenesulfonic acids have been found to be effective catalysts in the alcoholysis of nitriles to esters, and their use eliminates the objectionable features which have characterized this type of reaction when other catalysts were used. Earlier procedures called for the passing of anhydrous hydrogen chloride into a hot reaction mixture of nitrile, alcohol, and water[3] or refluxing a similar mixture with concentrated sulfuric acid.[4] The first of these involves difficulties in handling anhydrous hydrogen chloride at elevated temperatures. The second, in our experience, is often accompanied by more or less extensive charring. Presumably because of these disadvantages this reaction has not been used very extensively, although occasional

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[2] From the Master's thesis of W. H. B.

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