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(20) A less soluble racemate separates during crystallization; however, it is clear that a more extensive racemization occurs in the cyclization reaction.

Formation of Nitrate Esters by the Oxidation of Alkenes and Cyclopropanes with Thallium(III) Nitrate in Pentane[1]

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Nitrate esters are potentially useful synthetic intermediates for which few general methods of preparation are known. The corresponding alcohol may be esterified using nitric acid[2] alone or in a variety of cosolvents.[3-9] The corresponding halide can be metathetically converted to a nitrate ester using silver nitrate under heterogeneous[10-12] or homogeneous conditions.[13,14] More recently nitrates have been formed by mercury assisted solvolysis of alkyl halides.[15]

In our studies of the oxythallation and solvolytic dethallation of olefins by thallium(III) nitrate in methanol, we noted that nitrate esters are formed[16] in addition to the expected methyl ethers and carbonyl products.[17,18] As a result reaction conditions were sought under which the major product would be nitrate esters. Diethyl ether, dimethyl sulfoxide, sulfolane, and dimethylformamide all cause decomposition of the thallium(III) nitrate. Glyme, diglyme, and dioxane dissolve the thallium(III) nitrate to form stable solutions only if 1% nitric acid is added. Despite the fact that thallium(III) nitrate is very insoluble in pentane, the oxidation of the olefin does occur quite readily in this solvent.

In a typical reaction, a solution of the olefin in pentane is added to a stirred heterogeneous pentane–thallium(III) nitrate mixture maintained at room temperature. For most reactions a 10% excess of the oxidizing agent is used. Because of the relative instability of nitrate esters the reaction is terminated when it appears to be complete. The progress of the reaction can be qualitatively monitored by observing the change in the physical state of the thallium reagent.

Oxidation of 1-decene occurs in 1 h to give 1,2-decanediol dinitrate (II) in 85% yield. The remaining product is 2-decanone (III) which arises from a hydride shift in the dethallation

$$C_8H_{17}CH{=}CH_2 \xrightarrow[\text{pentane}]{Tl(NO_3)_3} C_8H_{17}CHCH_2ONO_2 \quad C_8H_{17}CCH_3$$
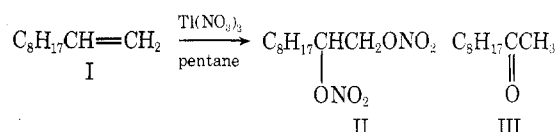
step. Thus a substantial decrease in rearranged product is observed compared to when methanol is the solvent in which yields of 34–40% 2-decanone are obtained.[16]

Reaction of *trans*-stilbene requires 72 h and leads to a mixture of *meso-* and *dl*-1,2-diphenyl-1,2-ethanediol dinitrate. Analysis of the mixture by using NMR resonances described earlier[16] indicates that the meso/*dl* ratio is 2:1. The reaction in methanol was found to be stereospecific.[16] There was no evidence of any rearranged products such as noted in the reaction in methanol.

Oxidation of cyclohexene in pentane occurs in 4 h to give *cis-* and *trans*-1,2-cyclohexanediol dinitrate (85%) and cyclopentanecarboxaldehyde (15%). The trans/cis ratio as determined by NMR is approximately 2/1. The resonance of the cis isomer (δ 5.10–5.55) and the trans isomer (δ 4.82–5.28) overlap somewhat and limit the accuracy of this method. The products contrast strongly with the results obtained in methanol where cyclopentanecarboxaldehyde is the major product.[17]

The *cis-* and *trans*-5-decenes react extremely slowly. After 11 days the cis isomer gave a mixture of *meso-* and *dl*-5,6-decanediol dinitrates in 64% yield with the remainder being 16% unreacted olefin, 9% 5-decanone, and 11% unidentified minor components. The trans isomer reacted more slowly. After 12 days a 38% yield of the *meso-* and *dl*-5,6-decanediol dinitrates was formed. The remaining material was 30% starting olefin, 17% 5-decanone, and 15% unidentified minor components. As the reaction time was increased, decomposition of product occurred with the evolution of NO$_2$. The exact percentages of the two dinitrate products were not determined.

3-Buten-1-ol (IV) reacts in 1 h to form exclusively 3-hydroxytetrahydrofuran nitrate ester (V). The product was isolated in 89% yield. There is no evidence of any open chain product.
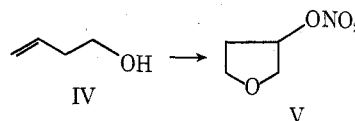
Since we have noted similarities in the reaction of thallium(III) acetate with alkenes[19] and cyclopropanes[20] the oxidative cleavage of a cyclopropane by thallium(III) nitrate was examined. Phenylcyclopropane (VI) reacts in 12 h to give exclusively 1-phenyl-1,3-propanediol dinitrate (VII) which
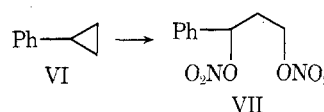
was isolated in 91% yield. There was no evidence of the symmetrically cleaved product, 2-phenyl-1,3-propanediol dinitrate.

The results of this study may be summarized as (1) oxythallation in pentane occurs readily to yield nitrate esters, (2) rearrangement products occur to a lesser extent in pentane than in methanol, and (3) there is a loss of stereospecificity in pentane as solvent.

Experimental Section

General Method for Preparation of Nitrate Esters. Authentic samples of nitrate esters were prepared by slowly adding an acetic acid–water–fuming nitric acid mixture (1.5:1.5:1) to a solution of the proper alcohol in an acetic acid–water mixture (1:1). The reaction mixture was maintained at 0 °C for approximately 1 h. Water was added and the mixture was extracted with ether. The desired nitrate ester was isolated and purified by either distillation or crystallization.

General Procedure for Oxythallations in Pentane. A pentane solution of the olefin was added slowly to a stirred heterogeneous pentane solution, containing a 10% excess of thallium(III) nitrate, maintained at room temperature. Reaction times vary according to the reactivity of the compound. The progress of the reaction is monitored by observing the change in the physical state of the thallium reagent. Upon completion of the reaction, the pentane solution was diluted with ether and the organic layer was washed repeatedly with water. After drying over magnesium sulfate, the solution was filtered and the solvent was removed under reduced pressure. The crude product was then examined by NMR. Purified samples of the products were obtained by elution through silica gel columns.

Preparation of 3-Hydroxytetrahydrofuran Nitrate Ester. Nitration of 3-hydroxytetrahydrofuran was accomplished by the described general method. Distillation afforded 2.9 g (47%) of the ester as a clear liquid: bp 59–61 °C (4 mm); ^{1}H NMR (CCl$_4$) δ 5.36–5.70 m (1), 3.64–4.17 m (4), 1.74–2.67 m (2).

Anal. Calcd for C$_4$H$_7$NO$_4$: C, 36.10; H, 5.30; N, 10.52. Found: C, 35.89; H, 5.25; N, 10.57.

Preparation of *cis*-Cyclohexanediol Dinitrate. Nitration of *cis*-cyclohexanediol by the general method described gave the nitrate ester which was crystallized at 0 °C from petroleum ether: mp 23–24 °C (lit.[21] 24.5–25 °C); ^{1}H NMR (CCl$_4$) δ 5.10–5.55 m (2), 1.33–2.31 m (8).

Preparation of *trans*-Cyclohexanediol Dinitrate. Nitration of *trans*-cyclohexanediol by the general method described gave the nitrate ester which was crystallized at 0 °C from petroleum ether: mp 17–18 °C (lit.[21] 17.5–18 °C); ^{1}H NMR (CCl$_4$) δ 4.82–5.28 m (2), 1.32–2.53 m (8).

Preparation of *dl*-5,6-Decanediol Dinitrate. The title compound was prepared from *dl*-5,6-decanediol by the general method described. Distillation afforded a slightly yellow liquid: bp 112–113 °C (1.4 mm); ^{1}H NMR (CCl$_4$) δ 5.01–5.41 m (2), 1.25–2.04 m (12), 0.70–1.25 m (6).

Anal. Calcd for C$_{10}$H$_{20}$N$_2$O$_6$: C, 45.44; H, 7.63; N, 10.61. Found: C, 45.34; H, 8.18; N, 10.47.

Preparation of *meso*-5,6-Decanediol Dinitrate. *meso*-5,6-Decanediol was nitrated by the general method described. Distillation afforded a slightly yellow liquid: bp 107–108 °C (1.0 mm); ^{1}H NMR (CCl$_4$) δ 5.09–5.46 m (2), 1.29–2.12 m (12), 0.71–1.29 m (6).

Anal. Calcd for C$_{10}$H$_{20}$N$_2$O$_6$: C, 45.44; H, 7.63; N, 10.61. Found: C, 45.23; H, 8.25; N, 10.46.

Registry No.—Thallium(III) nitrate, 13746-98-0; 3-hydroxytetrahydrofuran nitrate, 59331-87-2; 3-hydroxytetrahydrofuran, 453-20-3; *cis*-cyclohexanediol dinitrate, 32342-28-2; *cis*-cyclohexanediol, 1792-81-0; *trans*-cyclohexanediol dinitrate, 32342-29-3; *trans*-cyclohexanediol, 1460-57-7; *dl*-5,6-decanediol dinitrate, 59331-88-3; *dl*-5,6-decanediol, 59367-33-8; *meso*-5,6-decanediol dinitrate, 59331-89-4; *meso*-5,6-decanediol, 58581-15-0; pentane, 109-66-0.

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2,2-Bis(trifluoromethyl)-1,2-dihydropyrimidinium Salts

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Although quite a few organic compounds are satisfactory for use as laser dyes in the visible and infrared regions of the spectrum,[1] no compounds of comparably high efficiency are known for the ultraviolet region. It occurred to us that since many laser dyes are cyanine or merocyanine dyes with rigid structures, compounds of this type with short conjugation might prove interesting as laser dyes. The first short-chain cyanine that we prepared, compound **1**, showed no fluores-

1
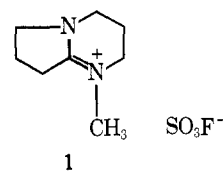
cence. This may be due to quenching by the solvent (alcohol), since the fluorescence would be expected at lower than 300 nm. A simple, higher vinylog of **1** is a 1,2-dihydropyrimidine derivative, and the most direct method for the synthesis of a compound of this type is through the condensation of a 1,3-dicarbonyl derivative with a geminal diamine. An example of a stable geminal diamine is the hexafluoro derivative **2**,[2] and in spite of the strong deactivation of the amino groups, we hoped to carry out the following reaction.
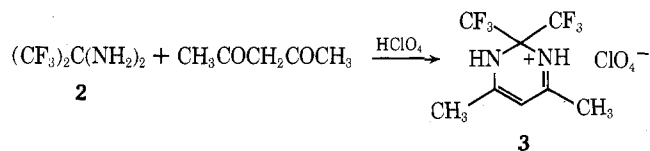
Problems were encountered in obtaining **3**, but a procedure was finally devised that gave **3** in 35% yield along with about a 20% recovery of the perchlorate salt of **2** and 40% of a byproduct, which was shown to have the structure **4**. The latter compound presumably is formed by the condensation of **3** with hexafluoroacetone, which is formed by hydrolysis of **2**.