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 $C_4H_7NO_4$: 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 $C_{10}H_{20}N_2O_6$: 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 $C_{10}H_{20}N_2O_6$: 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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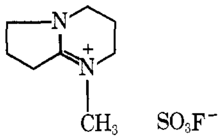
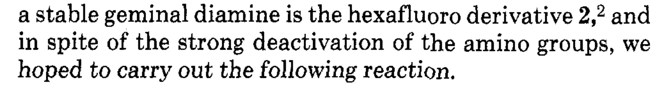
Although quite a few organic compounds are satisfactory for use as laser dyes in the visible and infrared regions of the spectrum,[1] no compounds of comparably high efficiency are known for the ultraviolet region. It occurred to us that since many laser dyes are cyanine or merocyanine dyes with rigid 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 fluorescence. 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.



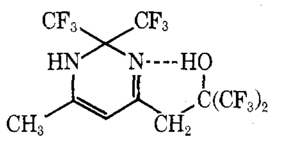
1



2

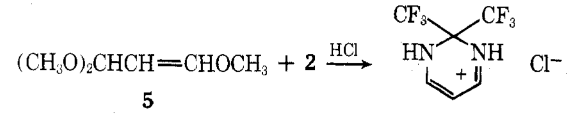
3

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 by-product, 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**.



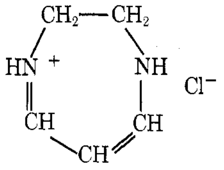
4

The dihydropyrimidine derivative **6** was prepared from **5** and **2**. This condensation worked well in benzene and hydrogen chloride in contrast to the reaction with acetylacetone, which gave a product that was difficult to purify.



5 6

Compounds **3** and **6** showed violet fluorescence in water and had only one absorption peak at 347 nm (ϵ 5000) and 355 (5000), respectively, in water. They fluoresce blue-violet in water, ethanol, and hexafluoro-2-propranol. The fluorescence maximum of **3** is at 398 nm in ethanol. On excitation with the second harmonic of a Q-switched ruby laser (λ 347 nm), **3** lases efficiently at 408 nm in water. The fluorescence of **3** and **6** is in direct contrast to the behavior of **7**, which shows no fluorescence in water or other solvents. The nonfluorescence of **7** probably is due to the nonplanarity of the molecule.



7

Attempts to prepare the *N,N'*-dimethyl derivative of **3**, either by methylation of a neutralized solution of **3** with methyl fluorosulfonate or by the condensation of acetylacetone and the *N,N'*-dimethyl derivative of **2**, were unsuccessful.

Experimental Section

Melting points were determined in a Mel-Temp apparatus and are uncorrected. Ultraviolet spectra were recorded on a Cary 14 spectrometer. Proton spectra were recorded with a Bruker HX-90 instrument and ^{13}C NMR spectra were recorded on a Bruker HX-90 equipped with a Digilab data system at 22.63 MHz. The NMR spectra were run in Me_2SO vs. Me_4Si.

4,6-Dimethyl-2,2-bis(trifluoromethyl)-1,2-dihydropyrimidinium Perchlorate (3). To a solution of 5 g (0.0274 mol) of **2** and 2.74 g (0.0274 mol) of acetylacetone in 25 ml of tetrahydrofuran was added 3.56 g (0.0274 mol) of 70% perchloric acid. The solution was allowed to stand in a 50-ml Erlenmeyer flask until the solvent had evaporated (about 2 weeks). The residue was extracted with 100 ml of hot isopropyl alcohol and filtered hot. The insoluble material (1.5 g) had an ir absorption curve that was identical with that of the perchlorate salt of the diamine **2**. The alcohol solution was evaporated to dryness and the residue was stirred with ether. The white, insoluble crystals of **3** were collected and recrystallized from 1,2,3-trichloropropane: yield 2.9 g; mp 198–200 °C. The ^1H NMR spectrum showed CH_3 (s, 6 H) at δ 2.18, CH (s, 1 H) at δ 5.4, and NH broad at δ 7.2 ppm.

Anal. Calcd for $C_8H_9ClF_6N_2O_4$: C, 27.7; H, 2.6; N, 8.1. Found: C, 27.5; H, 2.5; N, 8.2.

The ether filtrate was evaporated to dryness and the residue was recrystallized from heptane giving 3.2 g of **4**, mp 93–94 °C. The ^1H NMR spectrum showed CH_3 (s, 3 H) at δ 2.18, CH_2 (s, 2 H) at δ 2.98, CH (s, 1 H) at δ 5.05, and NH and OH broad at δ 5.0 and 8.1 ppm. The ^{13}C NMR spectrum showed C_4, 169; C_6, 155.4; CF_3 as two quartets centered at 123.5 and 121.5; C_5, 92.1, COH and C_2, multiplet centered at 76.7; CH_2, 34.0; and CH_3, 18.7 ppm.

Anal. Calcd for $C_{11}H_8F_{12}N_2O$: C, 32.1; H, 1.7; N, 6.8. Found: C, 31.9; H, 1.9; N, 6.8.

2,2-Bis(trifluoromethyl)-1,2-dihydropyrimidinium Chloride (6). Hydrogen chloride was passed through a solution of 5 g of **2** and 3.7 g of 1,3,3-trimethoxy-1-propene in 500 ml of dry benzene for 5 min. After the mixture had stood overnight, the solid was collected and washed with ether: yield 4 g; mp 185 °C dec. The ^{13}C NMR showed C_4 and C_6, 156; CF_3 as a quartet centered at 121; C_5, 91.8; and C_2, as a multiplet at 74.6 ppm.

Anal. Calcd for $C_6H_5ClF_6N_2$: C, 28.3; H, 2.0; N, 11.0. Found: C, 28.6; H, 2.3; N, 11.4.

Acknowledgment. We are grateful for the assistance of Dr. P. M. Henrichs, who interpreted the ^{13}C spectrum of **4** and suggested this structure.

Registry No.—**2**, 1737-80-0; **3**, 59389-77-4; **4**, 59389-78-5; **5**, 17576-35-1; **6**, 59389-79-6; acetylacetone, 123-54-6.

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Photochemical Transformation of 7-Benzoyl-7,8-epoxydibenzobicyclo[2.2.2]octa-2,5-diene

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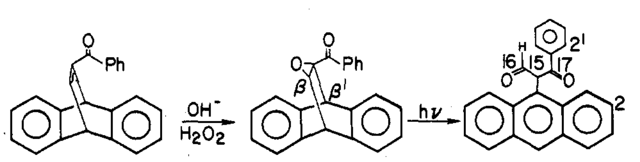
Investigations of a number of α,β-epoxy ketones have demonstrated that these species are exceptionally reactive under the influence of ultraviolet light. It has been shown that irradiation of these compounds may lead to geometrical isomerization, internal hydrogen abstraction, and rearrangement.[1] We have observed a novel, unanticipated photoisomerization of the title compound (**1**) which represents a new diversion in α,β-epoxy ketone rearrangement.

Base-catalyzed epoxidation of 7-benzoyldibenzobicyclo[2.2.2]octatriene[2] with hydrogen peroxide gave the title epoxy ketone (**1**), mp 191–192 °C. Irradiation of a 2% solution of the epoxy ketone **1** in dry benzene in a quartz reactor with unfiltered light from a medium-pressure lamp in a nitrogen atmosphere for 14 h yielded an isomeric (M^+ 324), golden yellow compound, mp 163–165 °C, in about 70% yield.



1 2

A complex absorption pattern at 1600 cm^{-1} in the infrared indicated an enolizable 1,3-dicarbonyl functionality in the photoproduct.[3] A broad band at 2850 cm^{-1} was suggestive of a possible C–H stretch of an aldehyde group. The electronic spectrum of the photoproduct was very similar to that of a 9-substituted anthracene.[4]

These data led to a tentative formulation of the product as **2**. This was further confirmed by a study of its ^1H and ^{13}C NMR spectra, which were as follows. ^1H NMR (220 MHz, $CDCl_3$) δ 8.64, d, 1 H, $C_{16}H$; 8.40, s, 1 H, $C_{15}H$; 7.45, m, 4 H, H at C_1, C_8, $C_{2'}$, and $C_{6'}$; 7.36, m, 4 H, H at C_{10}, $C_{3'}$, $C_{4'}$, and $C_{5'}$; 7.16, d, 2 H, C_4 H and C_5 H; 7.0, t, 2 H, C_2 H and C_7 H; 6.82, t,