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Laser Dye Synthesis — Group C Compounds

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This report describes progress on the syntheses of a number of new potential laser dyes. The goal is to generate new structures allowing the upscaling of flashlamp pumped dye lasers to high energies. These systems ideally should show a lower action threshold, operate with high efficiencies, and exhibit greater photochemical stabilities than do those presently available.

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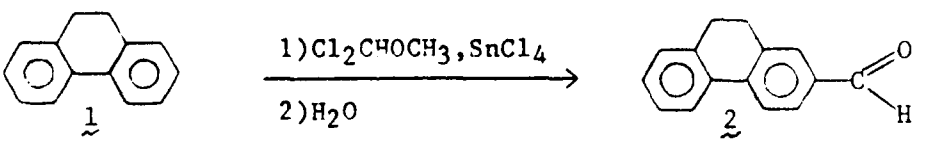
This report describes progress on the syntheses of a number of new potential laser dyes. The goal is to generate new structures allowing the upscaling of flashlamp pumped dye lasers to high energies. These systems ideally should show a lower laser action threshold, operate with high efficiencies, and exhibit greater photochemical stabilities than do those presently available.

Pavlopoulos has proposed (a) that the parent aromatic chromophores be substituted by auxochromic groups such as hydroxy, alkoxy, and dialkylamino and (b) that improvement should result by restricting the chromophore and auxochromic group to coplanarity. This should reduce intersystem crossing and thus improve the quantum fluorescence yield. The potential dye lasers described below are designed to meet these objectives.

I. The Synthesis of 1,2-bis-(9,10-dihydro-2-phenanthryl) ethene (3).

This extended stilbene was prepared by converting dihydrophenanthrene to the aldehyde using dichloromethyl methyl ether and stannic chloride. The general method has been described by Rieche, Gross, and Höft.[1]



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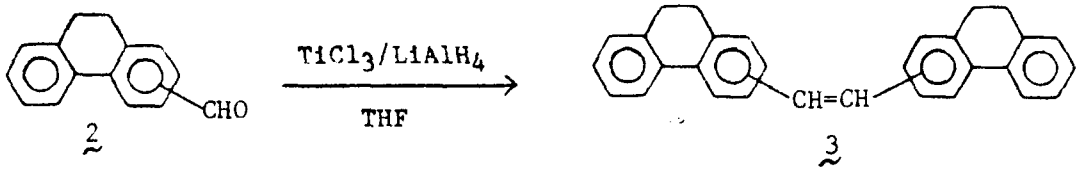
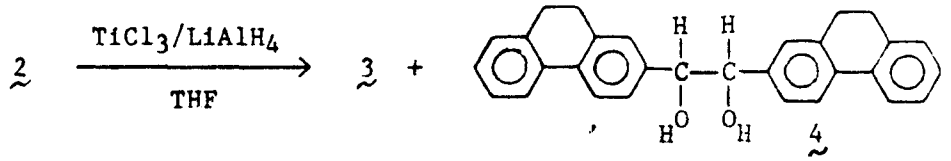
The crude aldehyde was obtained in 85% yield but appears to be a mixture of the 2-carboxaldehyde (shown) and the 3-carboxaldehyde in a ratio of about 3:1. The proton nmr spectrum of this mixture shows the expected aromatic absorptions at δ7.1-7.4 (7-proton multiplet), a four proton multiplet center at δ2.86 and two aldehyde singlets at δ9.86 and δ10.3. The mass spectrum was consistent with the proposed isomeric mixture showing the molecular ion at m/e 208 and fragments corresponding to losses of the aldehydic hydrogen, the aldehyde group (M^+-CHO, parent ion), and the CH_2CH_2 bridge.

The aldehyde mixture was subjected to the McMurry coupling procedure[2] as modified by Geise and coworkers.[3]



2 3

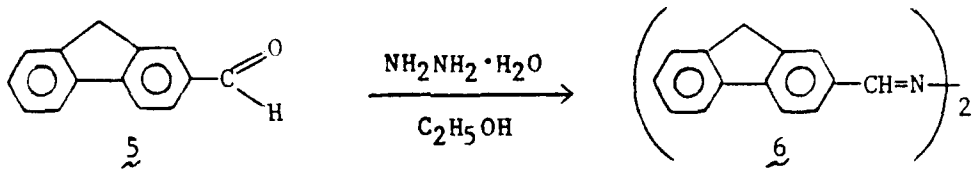
A variety of reagent ratios and reaction times were explored. Relatively low yields (approximately 10-20%) of a highly fluorescent product was obtained as a white solid. After chromatography over florisil and recrystallization from hexane the purified samples still melted over an eleven degree range (239.5-251°C). The proton nmr spectrum and mass spectrum are consistent with the extended stilbene (3) but do not provide quantitative information regarding the distribution of positional and geometric isomers in the mixture. Although future coupling studies employing purified samples of the 9,10-dihydro-2-phenanthrene carboxaldehyde are planned (pending results from laser spectroscopic studies on the delivered samples of 3 mixtures), the McMurry coupling is complicated by formation of substantial quantities of the corresponding diol 4.



II. Attempted Preparation of 1,2-bis-(2-fluorenyl) ethene (7).

A. Thermal Decomposition of Azine

Saint-Ruf and Buu-Hoï[4] have reported the preparation of the bis fluorenyl ethene 7 by thermolysis of the corresponding azine in paraffin oil. Accordingly the azine was prepared in 95% yield by the usual method. However, in our hands several attempts to pyrolyze the azine either in paraffin oils or



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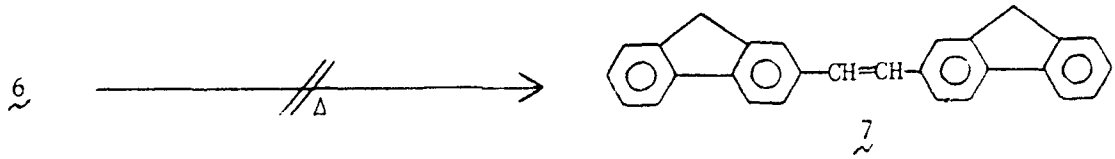
in silicon oil led only to small yields of complex mixtures.



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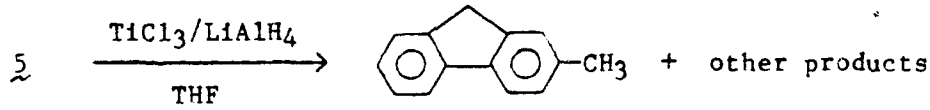
B. McMurry coupling of 2-fluorene carboxaldehyde.

Attempts to obtain 7 using the McMurry coupling procedure[2,3] again led to complex mixtures from which 2-methylfluorene was separated as the only identifiable product.



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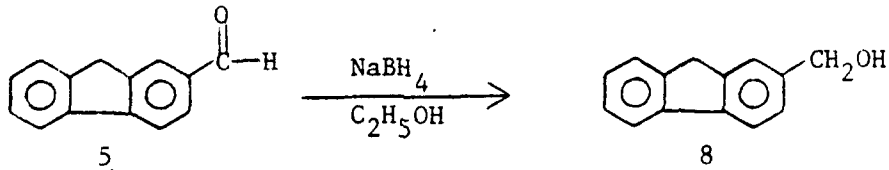
C. Condensation-dehydrobromination of 2-bromomethylfluorene.

Pinck and Hilbert[5] have described the preparation of 1,2-bis(1-fluorenyl) ethene by the treatment of 1-bromomethylfluorene with sodium methoxide in methanol. In hopes of applying this procedure to the 2-bromomethyl isomer, the following transformations were performed. The borohydride reduction of 5



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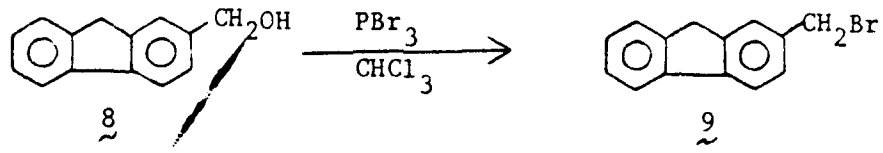
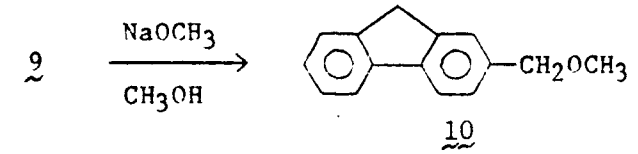


8 9

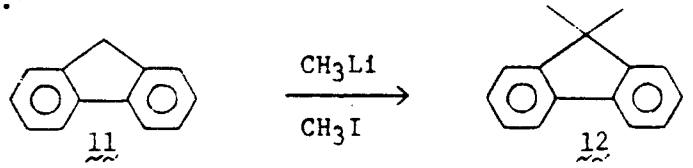
afforded purified 8 in 75% yield. Conversion of the alcohol to the bromide was accomplished using the general procedure of Braun and Engel.[6] However, unlike the behavior of 1-bromomethylfluorene, the treatment of 9 with sodium methoxide afforded the corresponding methyl ether 10 (73%) as the only isolable product. Additional attempts using the condensation-dehydrobromination



route employing potassium t-butoxide or 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) as the base were unsuccessful.

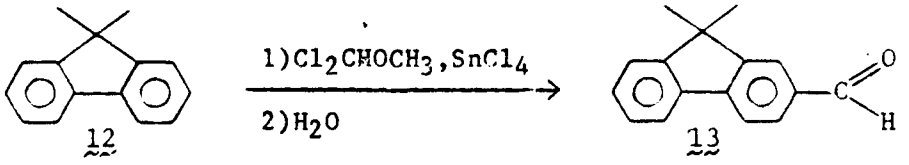
III. Derivatives of 9,9-dimethylfluorene.

To remove complications arising from potential facile removal of protons (or H atoms) from C_9 during the course of various desired trnasformations, fluorene was converted to its 9,9-dimethyl derivative using the procedure described by Bavin.[7]

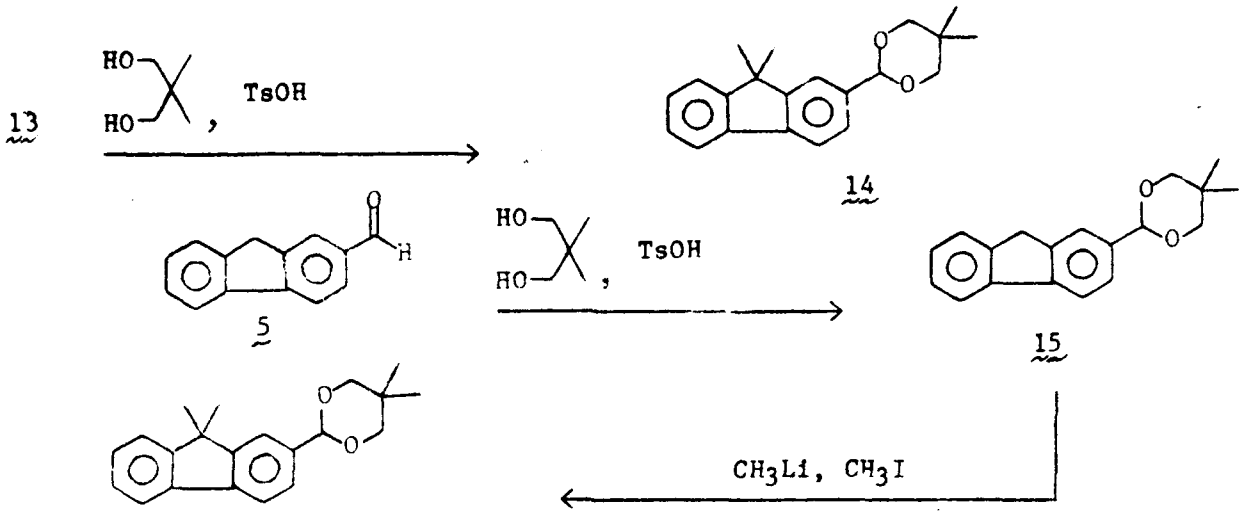


A. 9,9-Dimethyl-2-fluorene carboxyaldehyde (13).

The aldehyde was prepared in yields as high as 89% using the method of Rieche, Gross and Hoft.[1] The spectroscopic properties for 13 were in accord



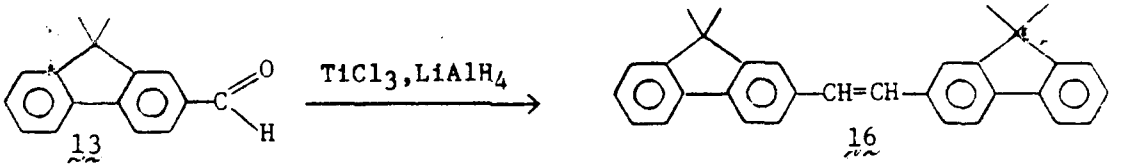
with this proposed structure. Because of the uncertainty regarding the positon of the aldehyde group in 13, the following sequence of transformations was undertaken. The cyclic acetal 14 obtained directly from 13 was shown to be



identical to that obtained starting with an authentic sample of fluorene 2-carboxaldehyde (5).

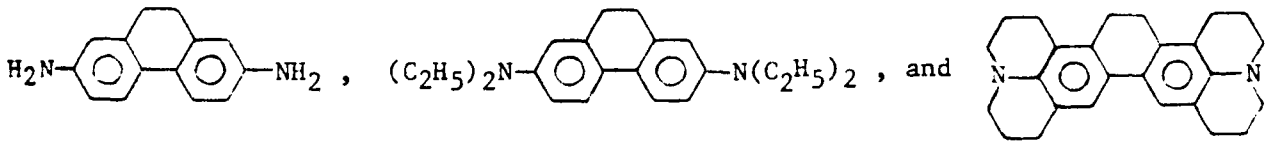
B. 1,2-bis-(9,9-dimethylfluoren-2-yl) ethene (16).

The aldehyde 13 was subjected to the McMurry coupling conditions ($TiCl_3$, $LiAlH_4$). By this procedure the desired alkene was obtained in yields of approximately 10%. The dimethylated bis fluorenylethene



was obtained as a light-yellow highly fluorescent solid.

Samples of 3 and 16 as well as previously prepared samples of



have been delivered for testing.

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