group at C-4 to the resonance system of this general class of compounds will depend upon the polarization of the rest of the conjugated system which in turn is reflected in the long wavelength absorption maximum of the parent compound. Hence a more accurate estimation of the *D* values for electron donating groups at C-4 is given by the equation

$$D^1 = \frac{\lambda^1 \text{ parent}}{\lambda \text{ parent}} \times D$$

where λ^1 parent is the absorption maximum of the unsubstituted compound in the given series and λ parent is that from which the *D* value was derived. The *D* value for the 4-acetamido group is a case in point (Table I). Using the 4-acetamidobenzalmalononitrile as reference, the D^1 values so obtained for the C_4-acetamido group provides an absorption maximum in agreement with the observed value for 4-acetamido-3-benzal-2,4-pentanedione while that calculated for 4-acetamido-α-cyano-*trans*-benzalacetophenone is 8.5 mμ too high.

The spectra of the ethanolic solutions of these compounds were recorded on a model 15 Cary spectrophotometer. Calculated and observed maxima, and extinction coefficients are listed in Table I.

All of these compounds were prepared by the method of Horning *et al.* (4) with the exception of 4-acetamidobenzalmalononitrile which was prepared by the method of Corson and Stoughton (5) and the α-cyano-*trans*-benzalacetophenones which were prepared by the method of Kauffmann (3). Melting and boiling points and analytical figures for these compounds are listed in Table I.

Acknowledgments

The assistance of Mr. R. F. Silver in the synthesis of these compounds and of Mr. C. E. Lough in recording their ultraviolet absorption spectra is gratefully acknowledged. Microanalyses were done by Mr. R. P. Hicken.

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Reaction of 6,7-dimethoxy-3-isochromanone with hydrazine

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The reaction of the title compound with hydrazine resulted in the formation of the hydroxy hydrazide **5**. Alkylation of **5** took place on both oxygen and nitrogen. Compound **5** can be reconverted to the title compound or to the corresponding isoquinolone.

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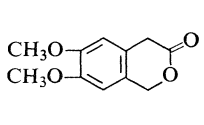
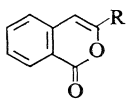
Recently Finkelstein and Brossi (1) reported the synthesis of 6,7-dimethoxy-3-isochromanone (**1**). In view of the reported[1] conversion of compounds of the types **2** and **3** to diazepines on reaction with hydrazine, it was felt that **1** might be an attractive intermediate for the synthesis of 2,3-benzodiazepines of the type **4**.

Reaction of **1** with hydrazine in ethanol gave a compound, $C_{11}H_{16}N_2O_4$, whose analysis would suggest the formation of a hydrate of the desired



1



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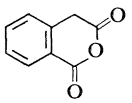

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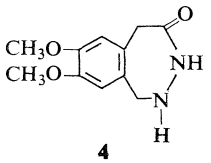
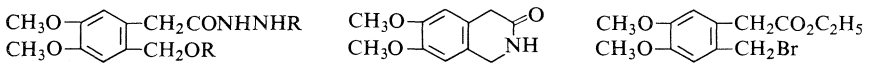


4

[1]See ref. 2 for references to this type of conversion.



5, R = H
6, R = alkyl

7

8

diazepine **4**. Examination of the infrared (i.r.) and nuclear magnetic resonance (n.m.r.) spectra and reactions of this product, however, indicates that rather it is the hydroxy hydrazide **5**. This type of product is similar to those observed (1) from the reaction of **1** with amines. When the reaction with hydrazine was carried out in ethanol containing a trace of acetic acid, **5** was still the major product; however, the reaction of **1** with hydrazine in acetic acid (hot or cold) gave only **1**. It was noted that **5** can be converted to **1** on heating in glacial acetic acid.

Alkylation of **5**, with alkyl halides and sodium hydride in dimethyl formamide, occurred both at nitrogen and oxygen to give compounds of the type **6** as indicated in Table I. Treatment of **5** with 10% hydrochloric acid gave a 76% yield of 6,7-dimethoxy-1,4-dihydro-3(2*H*)isoquinolone (**7**) together with 5% of **1**; with formic acid, **1** was the major product, and as noted above with acetic acid, **1** was the exclusive product.

In a further attempt to convert **1** to **4**, compound **1** was converted to **8** (1) and without isolation the crude **8** was reacted with hydrazine. This reaction gave **7** as the only pure product isolated.

Experimental

Reaction of 6,7-Dimethoxy-3-isochromanone with Hydrazine

To 1 g (0.0048 mole) of **1** dissolved in 20 ml of ethanol was added, slowly, 0.154 g (0.0048 mole) of hydrazine. After 6 h of reflux, the mixture was evaporated to one-half volume and cooled to give 0.945 g (82%) of a white solid (**5**), m.p. 163–165° from ethanol. Infrared (KBr): 3300, 3100, 3000, 1680, 1610 cm^{-1}.

Anal. Calcd. for $C_{11}H_{16}N_2O_4$: C, 54.99; H, 6.71; N, 11.66. Found: C, 54.71; H, 6.64; N, 11.66.

Addition of a trace of acetic acid to the ethanol in the above sequence gave a 68% yield of **5**. Replacement of the ethanol by glacial acetic acid in the above sequence gave a 74% recovery of **1** when the reaction was run in the cold and a 78% recovery of **1** when the reaction was run on the steam bath (in these cases the reaction mixture was poured on ice and the product extracted with methylene chloride).

*Preparation of **6** by Alkylation of **5***

To 0.75 g (0.00312 mole) of **5** dissolved in 15 ml of dimethyl formamide was added at room temperature with stirring 0.25 g (0.00312 mole) of 30% sodium hydride. To the resulting yellow solution was added an excess of the alkyl iodide (or benzyl chloride). After stirring for 1 h, the solution was poured on ice and extracted with chloroform. Evaporation of the dried ($MgSO_4$) extract gave an oil, infrared: 1650 cm^{-1}, which was converted to the picrate as recorded in Table I. (The benzyl product was obtained as a solid.)

*Reaction of **5** with Acid*

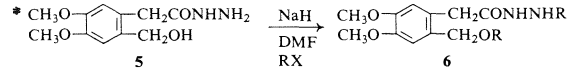
To 1 g (0.00415 mole) of **5** were added 20 ml of 10% hydrochloric acid and the solution was refluxed for 2 h. Upon cooling and the addition of water, 0.65 g (76%) of **7**, m.p. 227–228° (from ethanol), was obtained. Infrared (KBr): 3400 and 1660 cm^{-1}; n.m.r. (DMSO-d_6): 2.7 (Ar), 4.9 (NH), 5.9 (CH_3O), 6.45 (CH_2), and 7.8 τ (CH_2).

Anal. Calcd. for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.53; H, 5.96; N, 6.62.

Extraction of the remaining solution with methylene chloride gave a 5% yield of **1**.

TABLE I
Alkylation of **5***

R	Yield (%)	Melting point† (°C)	Analyses† Calculated C	H	N	Found C	H	N
CH_3	25	149–150	45.88	4.66	14.08	45.41	4.86	13.89
C_2H_5	80	134–135	48.00	5.18	13.33	48.04	4.99	13.39
n-C_3H_7	45	155–158	49.90	5.65	12.65	49.91	5.58	12.56
n-C_4H_9	53	134–135	51.63	6.07	12.04	51.59	5.99	12.06
$C_6H_5CH_2$	42	144–145‡	71.40‡	6.71	6.66	71.34‡	6.71	6.60

* 

5 **6**

†Melting points and analyses of picrates unless otherwise noted.
‡Melting point and analysis of free base.

Replacement of the hydrochloric acid by acetic acid gave a 74.5% yield of **1** and no **7**, while replacement of the hydrochloric acid by formic acid gave a 67% yield of **1** and a 5% yield of **7**.

Acknowledgment

We should like to thank Finkelstein and Brossi (1) for making the details of the procedure for the synthesis of **1** available to us before publication.

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cis-Crotonaldehyde and related compounds

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cis-Crotonaldehyde (**1**) has been prepared as a mixture with *trans*-crotonaldehyde (**2**) by irradiation of **2** with 3000 Å light. The thermodynamic equilibrium value for **1** to **2** was determined to be 1:50. Conditions for attaining this equilibrium and the structural factors contributing to its position are discussed.

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In one reported attempt to prepare *cis*-crotonaldehyde (**1**) by irradiation of an acid solution of *trans*-crotonaldehyde (**2**) no evidence could be found for the formation of **1** (1). The photodecomposition (2–6) and photooxidation (7) of **2** has been studied without reports of the formation of **1**. On the other hand irradiation of *trans*-α,β-unsaturated ketones readily leads to the *cis*-isomers (5, 8, 9). As part of a general study on the chemistry of α,β-unsaturated carbonyl compounds we have investigated the conversion of **2** to **1**.

Irradiation at room temperature of **2** sealed in a 4 mm tube in a Rayonet Srinivasan-Griffin reactor using 16 RPR-3000 Å lamps gave after 4 days a mixture of **1** and **2** in the ratio of 29:71. Further irradiation did not increase the proportion of **1**. Detection of **1** in **2** was possible by nuclear magnetic resonance (n.m.r.) and the spectra of **1** and **2** are given in Table I.[1]

cis-Crotonaldehyde (**1**) was found to be particularly sensitive to acids being converted rapidly with a trace of acid to **2**. The separation of **1** from **2** has as yet been unsuccessful by distillation or vapor-phase chromatography with a variety of columns including DIDP, DNP, Ucon P, silver nitrate-glycerol, DEGS and Poropak Q. Samples collected from the chromatograph (Varian Aerograph A-90P) remained unchanged. Heating samples of **1** and **2** indicated **1** to be also thermally labile with half-life of 2 h at 160°. This value however is a minimum due to the sensitivity of **1** to acid.

The thermodynamic equilibrium of **1** and **2**, attained at room temperature with a trace of dry hydrochloric acid or by heating mixtures to 200 °C for 5 h, contains 2.0% of **1**. No evidence was found for the presence of 3-butenal which would be expected to be less than 0.5% based on the results of Sifniades (11) who found 0.35% of 3-butenal in equilibrium with crotonaldehyde when **1** was heated in the gas phase at 150° and 1% at 210°. For comparison we have determined the acid-catalyzed equilibrium of angelaldehyde with tiglaldehyde to be 1:100 and of *cis*-3-methyl-3-penten-2-one with *trans*-3-methyl-3-pentene-2-one to be 1.5:100.

The marked stability of the *trans*-conjugated forms of these compounds implies a high resonance stabilization in this form. This stabilization apparently is reduced in the *cis* form by distortion from planarity of the carbonyl group of the conjugated system. The importance of this destabilizing interaction is emphasized in angelaldehyde and *cis*-3-methyl-3-pentenoate where the stable isomer involves a *cis* arrangement of two methyl groups rather than a *cis* arrangement of a methyl and the smaller formyl or acetyl groups (the conformational free energy difference $-\Delta G$ for the formyl group on a cyclohexane ring is 1.35 (12) compared to 1.7 for methyl (13)).

The conjugative stabilization in esters is expected to be less than that for ketones and aldehydes and this is supported by the fact that the

[1]The spectrum of **2** is reported in ref. 10.