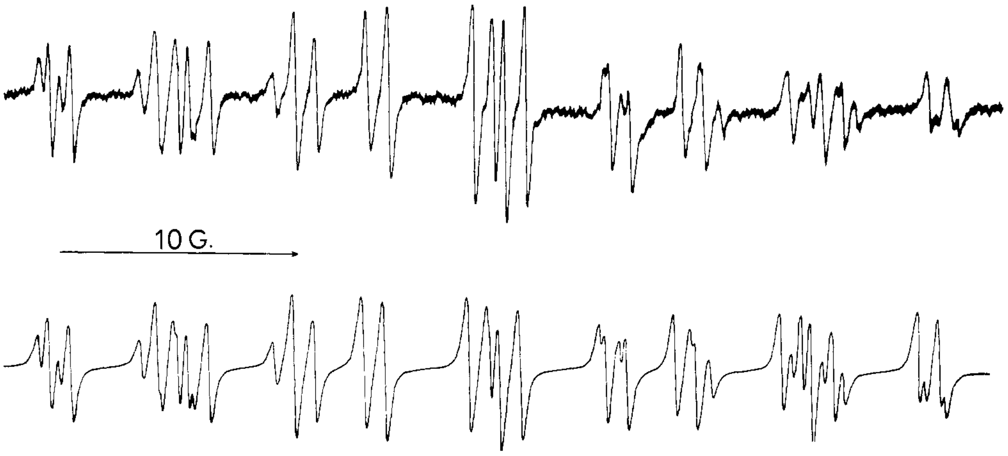
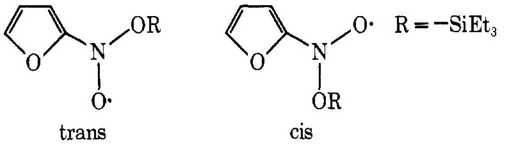


Figure 1. Experimental (upper) and computed esr spectrum of III at −60° showing the existence of two rotational isomers. The hyperfine splitting constants are given in Table I, the intensity ratio of the two species is 7:3, the line width is 0.23 G, and the difference between the two centers of the spectra is 0.10 G.

nitrofuran anion (I) (*i.e.*, one a_N and three a_H couplings) was observed. By lowering the temperature, however, a line width broadening effect was observed and at −60° two well-resolved spectra, corresponding to two different radicals, were detected, their relative intensity being 7:3 (Figure 1).

As the phenomenon appears to be reversible, the two groups of signals were attributed to rotational isomers having respectively the -OR group trans or cis with respect to the heterocyclic oxygen.



The two rotamers have rather similar proton splittings and *g* values, the more stable having the center of its spectrum shifted downfield with respect to that of the less stable by only 0.10 G. As the a_H values are not too different from those of the nitro anion (I), the assignment to the various positions has been made assuming af analogous trend.

It is clear that a restricted rotation exists in aromatic alkoxy nitroxides, as already observed in phenyl nitroxide,[7] and that most likely the same can be inferred for the radical anions of nitro aromatics.

The study is being pursued on the more stable thiophene analog which give the same effect.[8]

Acknowledgment. One of the authors (L. L.) thanks Dr. K. U. Ingold (National Research Council of Canada) for helpful comments.

Registry No.—I, 34480-16-5; II, 34480-15-4; III, 51108-28-2.

References and Notes

(1) R. A. Gavar, J. P. Stradins, and S. A. Giller, *Dokl. Akad. Nauk SSSR*, **157**, 1424 (1964).
(2) J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, **5**, 31, 497 (1962).
(3) L. Lunazzi, A. Mangini, G. F. Pedulli, and M. Tiecco, *Gazz. Chim. Ital.*, **101**, 10 (1971).
(4) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Calculations," McGraw-Hill, New York, N. Y., 1970.
(5) D. J. Cowley and L. H. Sutcliffe, *J. Chem. Soc. B*, 569 (1970); R. B. Sleight and L. H. Sutcliffe, *Trans. Faraday Soc.*, **67**, 2195 (1971).
(6) S. K. Wong and J. K. S. Wan, *Can. J. Chem.*, **51**, 753 (1973).
(7) T. A. J. W. Wajer, A. Mackor, T. J. de Boer, and J. D. W. van Voerst, *Tetrahedron Lett.*, 1841 (1967).
(8) C. M. Camaggi, L. Lunazzi, G. F. Pedulli, G. Placucci, and M. Tiecco, *J. Chem. Soc., Perkin Trans. 2*, in press.

Vapor-Phase Introduction of Vinyl Ketones in Michael Additions

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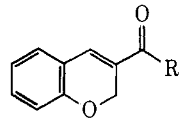
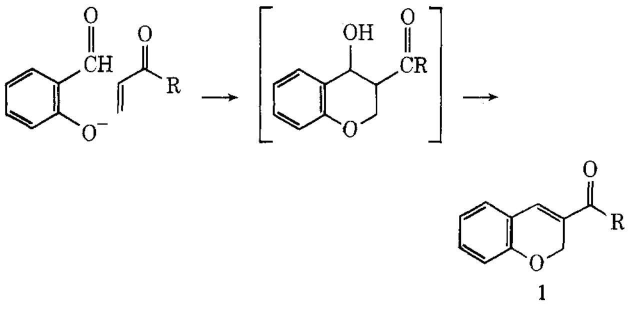
In a study of the photochemistry of some structurally related, unsaturated ketones,[1] the chromenes 1 were needed.



1a, R = H
b, R = CH_3
c, R = Ph
d, R = OH
e, R = OCH_3

Although chromenes **1d** and **1e** have been prepared[2] by the slow addition of sodium hydroxide to a refluxing mixture of salicylaldehyde and acrylonitrile (followed by hydrolysis), **1a–c** have never been reported. Attempts to prepare **1a–c** by the method of Taylor and Tomlinson[2] gave only polymeric mixtures. Attempts to convert **1d** to **1a**, **1b**, or **1c** by conventional reactions (Friedel-Crafts, Grignard, reduction, etc.) also failed, or at best gave poor yields with many side-products. It was then discovered that **1a** and **1b** can be prepared in good yield by stirring a mixture of salicylaldehyde and water with 0.1 equiv of base and introducing 1 equiv of the vinyl ketone (acrolein or methyl vinyl ketone) in the vapor phase in a stream of nitrogen. Apparently this dilution method of adding vinyl ketone prevents polymerization. The chromene is then isolated by simple crystallization or vacuum distillation.



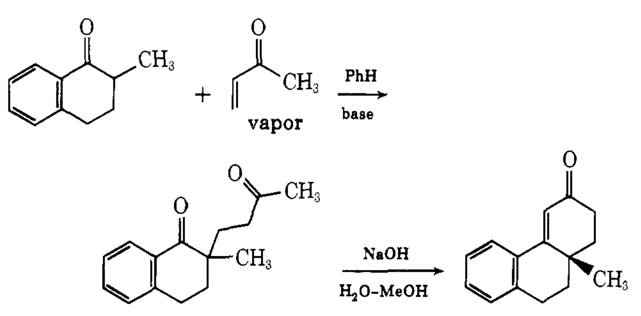
1

The 5-chloro- and 5-bromosalicylaldehydes have also been used successfully in this preparation, but 5-nitrosalicylaldehyde and 2,4-dihydroxybenzaldehyde failed to give isolable products. Use of *o*-hydroxyacetophenone with methyl vinyl ketone did not give an isolable amount of product, but silica gel thin layer chromatography showed a spot having the highly characteristic green fluorescence of the 3-ketobenzopyran system, so it is possible that a trace of the product, 3-acetyl-4-methyl-5,6-benzopyran, may have been formed.

The vapor-phase introduction of vinyl ketones is useful in C-Michael as well as O-Michael additions. For example, a considerably higher yield of 3-phenylcyclohexenone can be obtained from ethyl benzoylacetate and methyl vinyl ketone if the vinyl ketone is introduced as a vapor rather than as a liquid.[3]

This method of introducing a vinyl ketone to a reaction mixture in a dilute form offers an alternative to the widely used Robinson method using the Mannich base methiodide and 1 equiv of base.[4]

Although the Robinson method gives excellent results, the vapor-phase method, when applicable, may be a simpler and easier procedure. For example, the condensation of 2-methyl-1-tetralone with methyl vinyl ketone was carried out by bubbling a stream of nitrogen saturated with methyl vinyl ketone into a benzene solution of 2-methyl-1-tetralone with diazabicyclononene as the base. Cyclization with 2% NaOH in methanol-water then gave the tricyclic compound in good yield.[5]



70% 2 (85%)

Experimental Section

Preparation of 5,6-Benzopyran-3-carboxaldehyde. Salicylaldehyde (122 g, practical grade, Eastman No. P225) was stirred with 850 ml of water and 4 g of sodium hydroxide. A stream of nitrogen (about 50 ml/min) was bubbled through 67 g of acrolein (Eastman No. 2037) and then into the salicylaldehyde-water mixture through a fritted disk. This assembly was left overnight, and by morning all the acrolein had evaporated into the reaction mixture. The mixture was acidified with 25 ml of concentrated HCl and the lower layer was separated, washing the water layer with CH_2Cl_2. The organic layer was dried and distilled under vacuum. At ~1 Torr, the first cut was 42.5 g of salicylaldehyde, bp 58-62°, followed by 88.2 g of **1a**, bp 128-135°. The bright yellow product solidified when a seed crystal was introduced. The yield was 85%, based on salicylaldehyde consumed.

Preparation of 3-Acetyl-5,6-benzopyran. Salicylaldehyde (122 g, Eastman No. 225), was stirred with 1700 ml of water, and 4 g of sodium hydroxide dissolved in 15 ml water was added. A stream of nitrogen was bubbled through 82 g of methyl vinyl ketone (Aldrich No. M8, 750-9, used without purification after 2 years of storage), and then into the salicylaldehyde-water mixture through a coarse fritted disk. When the ketone had evaporated into the mixture, 25 ml of concentrated HCl was added and the organic material was extracted with CH_2Cl_2. Distillation gave 37 g of salicylaldehyde, bp 58-62°, followed by 87 g of **1b**, bp 130-135°, mp 50-53°. The yield was 72% based on salicylaldehyde consumed.

Preparation of 3-Benzoyl-5,6-benzopyran. Salicylaldehyde (122 g), 1000 ml of 50:50 ethanol-water, and 8 g of sodium hydroxide were stirred while 132 g of phenyl vinyl ketone in 400 ml of ethanol was slowly dripped into a 2000-ml vessel at a temperature of 25°. Then a seed crystal was formed and when the product, 3-benzoyl-5,6-benzopyran, had crystallized it was collected and recrystallized from methanol, mp 60-61°.

Preparation of 3-Phenylcyclohexen-1-one. Ethyl benzoylacetate (40 g, Eastman No. 2731) was stirred with 2 g of sodium hydroxide and 300 ml of methanol while 15 g of methyl vinyl ketone was evaporated into the solution in a stream of nitrogen. In the morning, the mixture was solid. The solid was filtered, washed with methanol, and recrystallized from alcohol, mp 148-149°, yield 41 g (82%) of the methyl ester of 3-phenyl-3-hydroxycyclohexanone-4-carboxylic acid. This was converted to the enone by refluxing in aqueous sodium hydroxide.

Preparation of 2. A stream of nitrogen saturated with methyl vinyl ketone was bubbled through a solution of 2-methyl-1-tetralone (10 g, Aldrich No. 16,322-8), 20 ml of benzene, and 2 ml of 1,5-diazabicyclo[4.3.0]non-5-ene (Aldrich No. 13,656-1) until gas chromatographic analysis showed that the tetralone was 95% reacted. The mixture was diluted with 1% HCl and extracted with methylene chloride, the organic layer was dried and evaporated, and the residue was distilled under vacuum, bp 157° (~1 Torr), to give 10.1 g of the Michael adduct, which was cyclized by refluxing with 2% NaOH in 400 ml of 50:50 water-methanol for 3 hr. The product was extracted with CH_2Cl_2, filtered through 2 in. of alumina, and crystallized from 50 ml of hexane, yield 8.0 g (60% overall), mp 54°.

Registry No.—**1a**, 51593-69-2; **1b**, 51593-70-5; **1c**, 51593-71-6; **2**, 51593-72-7; salicylaldehyde, 90-02-8; acrolein, 107-02-8; methyl vinyl ketone, 78-94-4; phenyl vinyl ketone, 768-03-6; 3-phenylcyclohexen-1-one, 10345-87-6; ethyl benzoylacetate, 94-02-0; methyl 3-phenyl-3-hydroxycyclohexanone-4-carboxylate, 51593-73-8; 2-methyl-1-tetralone, 1590-08-5.

References and Notes

(1) The details of the photochemistry will be reported at a later time.

(2) H. V. Taylor and M. L. Tomlinson, *J. Chem. Soc. C*, **50**, 2724 (1950).
(3) G. N. Walker, *J. Amer. Chem. Soc.*, **77**, 3664 (1955).
(4) W. S. Johnson, *et al.*, *J. Amer. Chem. Soc.*, **78**, 6285 (1956).
(5) G. Stork, H. J. E. Loewenthal, and P. C. Mukharji, *J. Amer. Chem. Soc.*, **78**, 501 (1956), describe the preparation of the methoxy-substituted derivative.

Acid-Catalyzed Ketone Rearrangements. Synthesis of Decalins and Spiro[4.5]decanes

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As part of a project to develop new routes to hydroazulenic sesquiterpenoids, we examined the photochemical and acid-catalyzed behavior of the β,γ-unsaturated ketone **1**. As the photochemical properties of **1** have recently been reported by other workers,[1] we would like to communicate our acid-catalyzed rearrangement studies which, surprisingly, led to compounds having a decalin or spirodecane skeleton.

Treatment of enone **1**[1] for 3 hr with boron trifluoride etherate in refluxing benzene resulted in the preparation of the tetrahydronaphthalene[2] **6** and octalone **4** in 46 and 51% yields, respectively. The structure of hydrocarbon **6** was apparent from its spectra and the facile aromatization to 1-methylnaphthalene,[3] while the enone[4] **4** was compared with an authentic sample.[3]

Partially reacted mixtures allowed the isolation of an intermediate **3** whose structure is supported by the spectral data, but different from that reported for the same compound.[5] Confirmation of the assigned structure came from chemical correlation *via* the Kochi decarboxylation[6] of spiro acid **7**[7] in the presence of lead tetraacetate or *via* the thermal decomposition of the corresponding *tert*-butyl