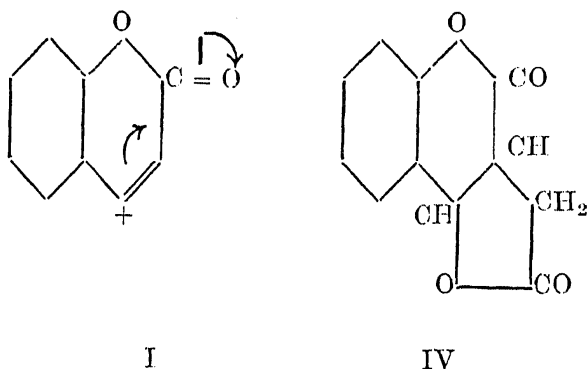
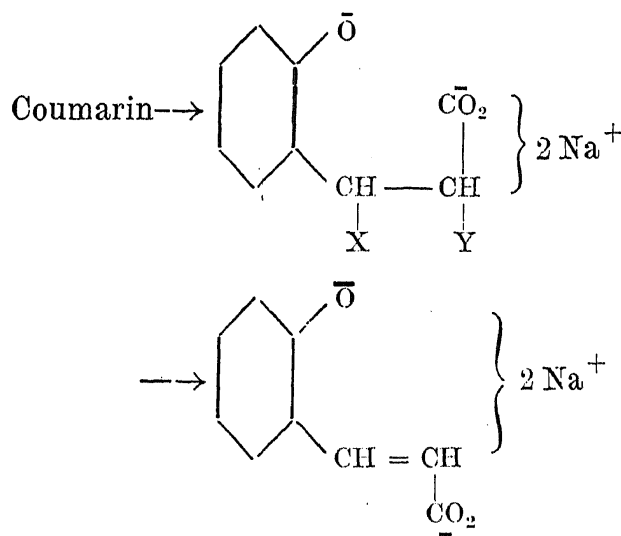


The Mechanism of Geometrical Inversion
in regard to Coumarins and
Coumaric Acids.

THE facility with which geometrical inversion takes place in the acids derived from the coumarins, just as the behaviour of the coumarins in most of their reactions, is controlled by the presence of a Katio-enoid system^{1, 2} producing kationoid reactivity at the carbon atom in position 4. Substituents such as alkyl, hydroxyl and alkoxy groups which act as electron sources tend to reduce the reactivity of the compound especially when they are present in the above-mentioned position.^{3, 4} Again the difference in properties between coumarin 4- (II) and coumarin 3-acetic acids (III) becomes easily intelligible from the above point of view. The possibility of the formation of a lactone IV⁵ may also partly account for the greater stability of III when heated.



Cis to trans inversion.—The change from coumarin to coumaric acid takes place in an alkaline medium only and as an essential preliminary some additive reagent like NaOH, NaOCH₃ or NaHSO₃ has to add on to the double bond, temporarily at least, and thereby facilitate rotation. Several of these addition products have been isolated.^{6, 7, 8} The process can be represented as below:—



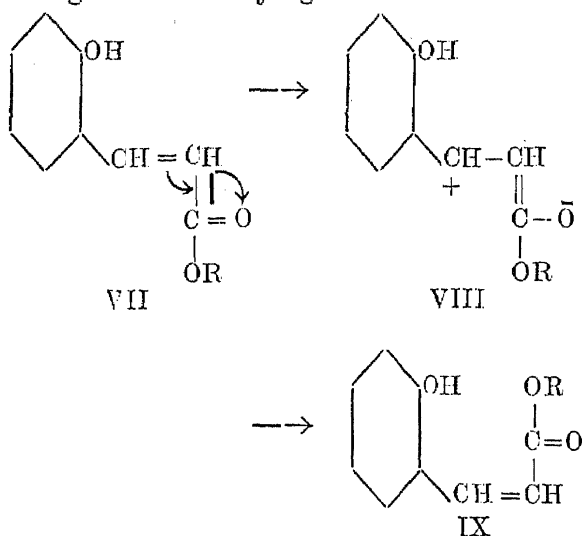
There are, therefore, two factors which control this transformation, *viz.*, (i) addition at the double bond which renders rotation of the groups into the required position possible, and (ii) repulsion between the negatively charged O and CO₂ groups which forms the driving force for the change. The efficiency of the different reagents and the influence of the different substituents are clearly understood when their effects on the above two factors are analysed. In regard to the findings of Sen and Chakravarty⁹ on the use of mercury compounds in producing inversion it should further be remembered that substituents like nitro, chloro and bromo groups inhibit nuclear reactivity of the benzene ring thus preventing mercuriation whereas alkyl, hydroxyl and alkoxy groups have the opposite effect giving rise to mercurated products.

Trans to cis inversion.—Stoermer and his co-workers observed¹⁰ that many coumaric acids and their esters underwent geometrical inversion under the influence of ultra-violet light. Ordinary sunlight has now been found to be equally effective. Very high yields of the coumarins are obtained and in several cases the change is complete within 12 hours. Light supplies the requisite energy for converting the *trans* form into the *cis* having a higher energy content. As for removing the effect of the double bond whereby the rotation of the groups is rendered possible, addition of an addendum seems to be neither possible nor necessary under the circumstances. The following mechanism

¹ Seshadri, *J.C.S.*, 1928, p. 117.
² Robinson, Institute of Chemistry of Great Britain and Ireland, Lecture, 1932, p. 25.
³ Seshadri, *Ibid.*
⁴ Heilborn, *et. al.*, *J.C.S.*, 1927, p. 2005; 1931, p. 1701.
⁵ Linstead, *J.C.S.*, 1932, p. 115.
⁶ Bühmann, *Annalen*, 1912, **388**, 259.
⁷ Dodge, *J. Am. Chem. Soc.*, 1916, p. 446.
⁸ Seshadri, *Ibid.*

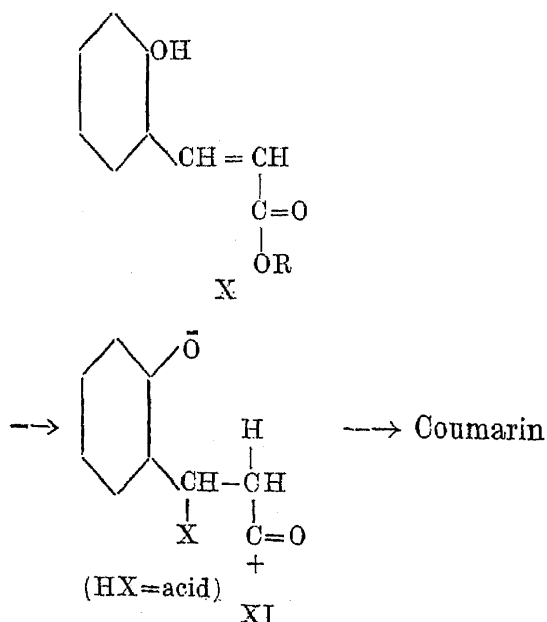
⁹ Sen and Chakravarty, *J. Ind. Chem. Soc.*, 1930, p. 247.
¹⁰ Stoermer, *et. al.*, *Ber.*, 1908, **41**, 335; 1909, **42**, 4865; 1911, **44**, 640; 1912, **45**, 310.

is suggested, the polarisation of the system being facilitated by light:—

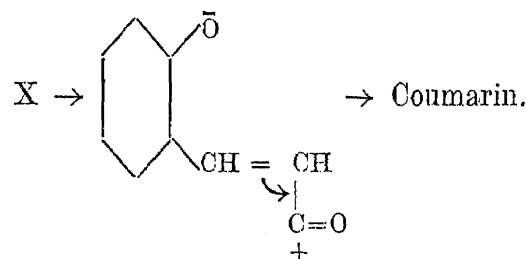


The stage VIII may be formed only momentarily and once the *cis*-phase is produced it is stabilised as coumarin by the ready elimination of alcohol or water. A nitro group in the benzene ring further weakens the double bond by the positive field it creates and hence greatly facilitates the transformation whereas a methoxyl group does the opposite.

In the presence of fuming hydrochloric, hydrobromic and concentrated sulphuric acids, particularly at 100°C. the *trans* acids and their esters undergo easy conversion into the coumarins. The removal of alcohol or water seems to be the first stage in the reaction. The dipole that is formed supplies the necessary energy for the inversion and the rotation of the groups is facilitated by the temporary addition of the acids at the double bond.



The course of the transformation under the influence of heat at the melting points of the substances, seems to belong to a slightly different type. In the case of the esters alcohol is first eliminated and the subsequent inversion may be represented as below:—



Here the combined effect of the carbonyl group and the positive charge on the carbon atom brought about by the removal of OR eliminates the effect of the double bond. Such a process does not obviously take place in the case of the acids partly due to the greater difficulty of the removal of water and partly due to the facility with which the elimination of carbon dioxide takes place producing styrenes. Experimental details will be published elsewhere.

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May 28, 1934.

On a New Method of Synthesis of Bicyclic Terpenes: Synthesis of Ethyl *cyclohexanone* 2:6-dicarboxylate.

THE synthesis of this ester has been attempted in this laboratory by several methods, one of which, *viz.*, the action of sodium ethoxide upon trimethylene dimalonic ester has now yielded the desired product b.p. 140-42°/1-1.5 mm. The formation of the desired *cyclohexane* ring by this method has been definitely established by hydrolysis and decarboxylation of the ester into *cyclohexanone*.

Recourse has also been taken to another method for the preparation of the desired di-ester from *cyclohexanone*-2:2:6:6-tetracarboxylic ester, b.p. 175°/2-3 mm. (pure product 30% yield) obtained by the action of carbonyl bromide upon the disodium derivative of trimethylene dimalonic ester. The tetra ester on being hydrolysed with alcoholic potash gives the corresponding tetra acid m.p. 246°, and is converted into *cyclohexanone* on being boiled with 50 per cent. sulphuric acid during 16 hours. The