

Benzylidene-Flavanones of the type (I) which contain the group $-\text{CO}-\overset{\cdot}{\text{C}}:\text{CH}-$ present in chalcones also undergo the above types of reactions, (II) and (III) being obtained by the condensation of the corresponding benzylidene-flavanones with acetoacetic ester and desoxy-

benzoin respectively. The oxides (IV) and (V) analogous to chalcone oxides have also been prepared. Similar compounds have been obtained from other arylidene-flavanones.

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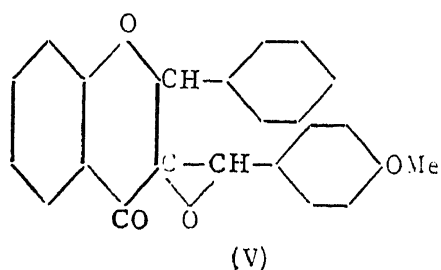
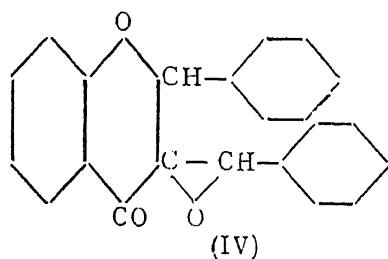
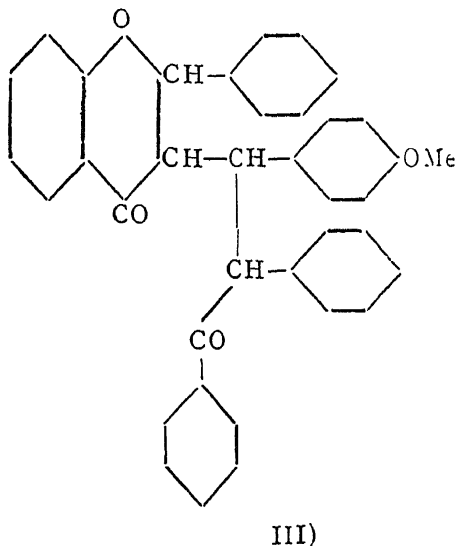
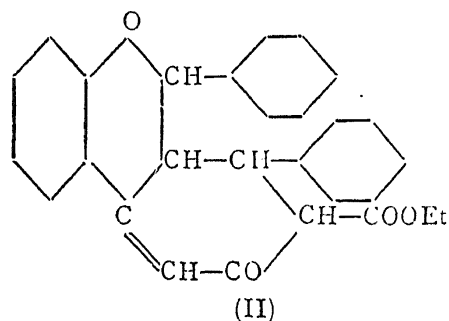
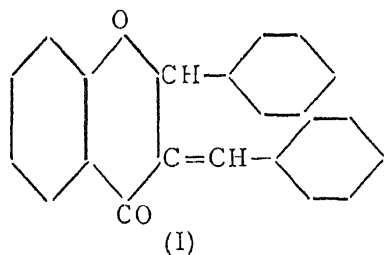
May 4, 1939.

¹*Curr. Sci.*, 1938, 7, 181.

A New Synthesis of 3-Aminocoumarin

ERLENMEYER, JUN. AND BADE¹ state that salicylaldehyde does not condense with glycine to give α -amino- β -hydroxy acids by the method associated with the name of Erlenmeyer. Linch² has published a paper on 3-aminocoumarin; he found that salicylaldehyde and glycine did combine, in the presence of sodium acetate and acetic anhydride by Perkin's method, to give 3-acetyl-aminocoumarin, which on hydrolysis gave 3-aminocoumarin, but that the yield of the former was very unsatisfactory, being 25-30 per cent. at best. He has therefore followed a roundabout method of condensing salicylaldehyde with ethylacetoacetate (Knoevenagel) to obtain 3-acetylcoumarin, the oxime of which on undergoing the Beckman transformation, gave 3-acetylaminocoumarin and this on careful hydrolysis gave the base. The exact yield calculated on the first starting materials is not stated, but the method is said to be advantageous.³

We now find that salicylaldehyde and glycine, when heated directly together at 130-140° for five hours, give the 3-aminocoumarin in about 23 per cent. yield, and that yield can be further augmented by the use of a trace of pyridine. The ultimate yields obtained by suitable modifications, are exceedingly good. In two experiments the yields were 80 per cent. and the condensation of salicylaldehyde and glycine proceeded very well. Salicylaldehyde (1.5 mol.), glycine (1 mol.) and a trace of pyridine were heated together for five hours at 130-140°. The product crystallised from water melted at



130° and was identical with the 3-aminocoumarin obtained by the method of Linch.

Yield 80 per cent. of theory.

Other aldehydes are being investigated.

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¹ *Annal.*, 1904, **337**, 222-35; *C.A.*, 1905, **1**, 131.

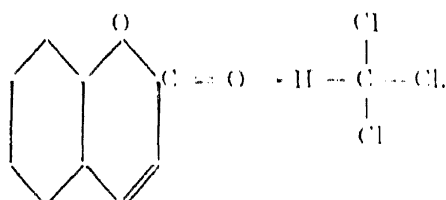
² Linch, *J.C.S.*, 1912, T., 1758.

³ Linch, *loc. cit.*

Molecular Complexes in Chloroform Solution

THAT polar solvents are capable of forming complexes with suitable solutes has been fairly well recognised and various methods have been used for detecting their formation.¹ Chloroform is said to undergo these combinations through a co-ordinate bond involving its H atom.²

It was recently shown by us³ that the Raman line for the C = O group of coumarin in chloroform solution undergoes a marked shift towards the exciting line as compared with a carbon tetrachloride solution which was taken as the standard. The phenomenon was explained as due to the formation of hydrogen bond as below:—



As a result of this complex formation, in which the oxygen atom of the C = O is the donor and the hydrogen of chloroform the acceptor, the C = O bond is diminished in strength and the frequency is reduced. In the course of the extension of this work a large number of carbonyl compounds have been studied in carbon-tetrachloride and chloroform solutions. In the case of saturated ketones, acids or esters no

difference between the two solvents was noticed. Obviously with these substances complex formation, if it took place at all, could not produce sufficient change to be exhibited in the Raman spectra. On the other hand, in unsaturated carbonyl compounds such as those given in the table below there was appreciable effect which could be noticed by a definite broadening of the line and a shift towards lower frequencies.

TABLE I

The C = O frequencies are given in $\Delta\bar{\nu}$

| Substance | Pure state | Chloroform solutions | Carbon tetrachloride solutions |
|---------------------|------------|---|--------------------------------|
| Benzylidene acetone | 1668 | 1653 | 1670 |
| Methyl cinnamate | 1712 | Diffuse towards shorter wave-lengths | 1712 |
| Ethyl cinnamate .. | 1712 | Do. | .. |
| Phenyl cinnamate | 1740 | 1722 | 1740 |
| Coumarin .. | 1708, 1731 | 1720 | 1742 |

Further work in regard to the detailed study of these is in progress. The close resemblance between coumarin and phenyl cinnamate in this respect is noteworthy and finds an easy explanation in the similarity of their structures.

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¹ Macleod, *Trans. Farad. Soc.*, 1934, **30**, 482; Macleod and Wilson, *ibid.*, 1935, **31**, 596; Glasstone, *ibid.*, 1936, **31**, 200; Bramley, *J.C.S.*, 1916, **109**, 11-14 and 343-519; Smith and Berkman, *Proc. Roy. Acad. Sci., Amsterdam*, 1918, **401**, 21; Dolezalek, *Z. Physik. Chem.*, 1910, **71**, 191.

² Walter Gordy, *Nature*, 1938, **142**, 831.

³ Murli and Seshadri, *Proc. Ind. Acad. Sci.*, 1938, **8**, 519.