

INVESTIGATION OF THE PREPARATION OF 2,4,6-TRIARYL-PYRYLIUM FLUOROBORATES FROM AROMATIC ALDEHYDES AND ARYL METHYL KETONES

I. THIN LAYER CHROMATOGRAPHY TESTING OF THE REACTION

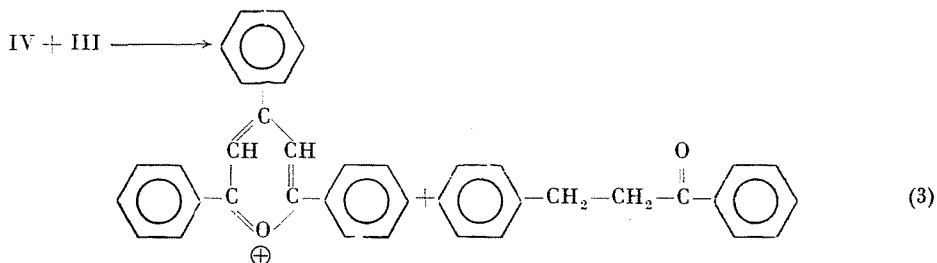
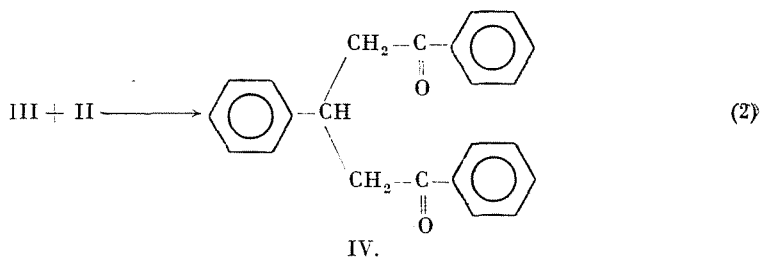
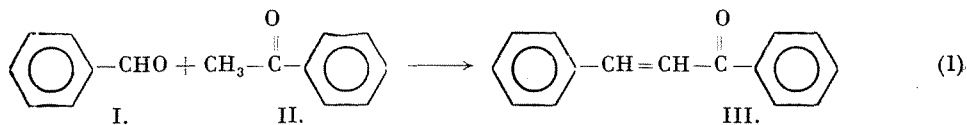
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The preparation of 2,4,6-triaryl-pyrylium salts from acetophenone and benzaldehyde or its derivatives is known since long [1]. The reaction is catalyzed by mineral acids or Lewis acids [2, 3], and proceeds in several steps. First, a condensation of Claisen—Schmidt type occurs between the aryl methyl ketone and the aromatic aldehyde, during which benzylidene-acetophenone (chalcone) or the corresponding substituted derivative is formed (1). Subsequently, this reacts with a further mole of ketone in an addition reaction of Michael type (2), and benzylidene-bisacetophenone thus formed is converted under ring closure into the corresponding pyrylium salt (3). In the latter step, chalcone performs the acceptor role of the hydride ions.



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It was established earlier [4] that the condensation of acetophenone and benzaldehyde, producing chalcone, can be realized with a good yield in abs. acetic acid medium, catalyzed by boron trifluoride. Under the conditions used here, we tried to extend the reaction to the preparation of triaryl-pyrylium fluoroborates, since this reaction has not yet been investigated in abs. acetic acid medium and catalysis with boron trifluoride. The reaction could be realized with a good yield. (Details are reported in communication II of this series.) It seemed therefore expedient to develop a method suitable for the detailed study of the reaction. The formed substances cannot be isolated by preparative methods. Separation by thin layer chromatography (TLC) seemed to be most promising, so that this method was used for the investigation of the reaction.

For the study of the reactions of pyrylium salts, the developing solvent giving the best separation for all the reaction components included in the reaction schemes 1—3 had to be found. The chromatograms were run on Kieselgel G (Merck) layer, and the results are compiled in Table I.

As will be seen, among the various developing solvent benzene and the benzene—methanol mixtures (100 + 2) gave the best separation. Therefore, the latter was used for our investigations. The indicator was vanillin sulphuric acid, first used for this purpose with compounds of this type. As compared to other indicators (e.g. dinitrophenyl hydrazine), this one has the advantage of developing each compound in a different colour, so that even substances with very similar R_f values can sharply be distinguished. Only benzaldehyde is not developed by this reagent, this is, however, no disadvantage, since benzaldehyde is a starting component, and therefore, its presence has not to

Table I

R_f values of the test substances run with various solvents

Developing solvent	$R_f \times 100$						
	Benzaldehyde	Acetophenone	Chalcone	Benzylidene-bisacetophenone	Pyrylium fluoroborate	β -Phenylpropionophenone	Dypnone
Benzene	58	45	38	21	0	43	—
Benzene-methanol 99.5 + 0.5	53	48	51	46	0	57	—
Benzene-methanol 99 + 1	51	47	54	51	0	61	—
Benzene-methanol 100 + 2	29	20	28	15	0	39	44
Benzene-methanol 100 + 2 run twice	45	31	43	25	0	52	50
Benzene-methanol 90 + 10	68	67	73	68	0	74	—
Benzene-ethylacetate 50 : 50	69	67	73	72	0	73	—
Benzene-ethylacetate-acetic acid 90 + 5 + 5	71	56	57	68	0	63	—
Methanol-water 70 : 30	74	79	72	72	0	72	—
Methanol-water 90 : 10	68	68	75	69	0	68	—
Chloroform	65	61	66	66	0	69	—
Ethylacetate-acetone-water 50 + 50 + 10		75	79	82	55	80	—

be proved in the reaction mixture. On the other hand, the disadvantage of running to almost the same distance as chalcone, is thereby eliminated.

In our further work, three reaction mixtures of different initial molar ratios have been investigated. The benzaldehyde: acetophenone molar ratios studied were 1 : 1, 2 : 1 and 1 : 2.

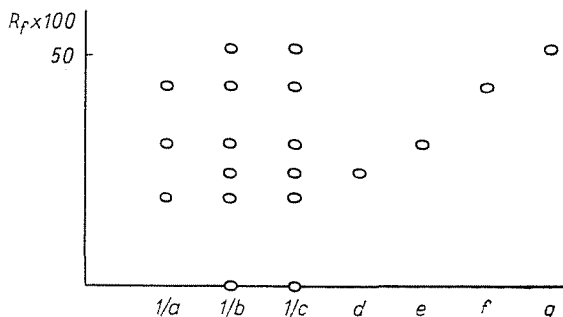
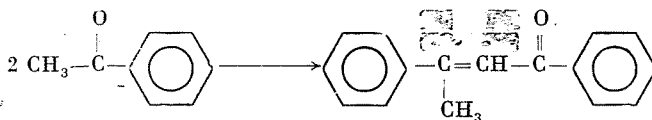


Fig. 1. TLC patterns of a reaction-mixture with different initial compositions; 1a, 1b, 1c reaction mixtures, d) benzylidene bisacetophenone, e) acetophenone, f) chalcone, g) β -phenyl-propiophenone

When benzaldehyde was used in excess (Fig. 1a), only the first step, the Claisen—Schmidt condensation occurred, that is to say, only chalcone formed. Besides the spots of the starting compounds and of chalcone, the chromatogram exhibited several spots different from those of the test substances. It was assumed that these arose from adducts of yet unclear structure, formed by the protonation of benzaldehyde. These adducts presumably formed already at the moment of the preparation of the reaction mixture, and their quantity diminished alongside the reaction.

In the reaction mixture containing acetophenone in excess (Fig. 1b), all the substances indicated in the reaction schemes are present, that is to say, the reaction proceeds according to the quoted equations. In samples taken after a time from the reaction mixture, dypnone formed by the self-condensation of acetophenone as a side reaction, can also be detected:



When benzaldehyde and acetophenone are reacted in a molar ratio of 1 : 1 (Fig. 1c), the principal product is chalcone, to a low proportion, however, all the other substances formed in the reaction with acetophenone in excess are present, thus, the pyrylium salt is formed also in this case, though in a very low quantity.

The experiments were carried out under the same reaction conditions, but using sulphuric acid as catalyst. The chromatographic pattern of the single reactions was the same as that of the reactions catalysed with boron trifluoride. It is remarkable that NOYCE and co-workers [5], in their investigations into the kinetics of chalcone formation, though using an excess of acetophenone, did not take into consideration all the possible reactions, which must have been manifest in their results.

The formation of the pyrylium salt was investigated also in the case where the starting materials were not benzaldehyde and acetophenone, but their intermediate products formed in the reaction sequence discussed. Thus, the reaction has been studied with chalcone and acetophenone or with chalcone and benzylidene-bisacetophenone as starting materials. The chromatograms were the same in both cases as that shown in Fig. 1b, with the difference that no acetophenone could be detected on the ring closure of the 1,5-diketone.

Experimental

Benzylidene-acetophenone [6] and benzylidene-bisacetophenone [7] were prepared by the reaction of benzaldehyde and acetophenone catalysed with alcoholic sodium hydroxide. The acetic acid complex of boron trifluoride was prepared by vacuum fractionation of the commercial product (BDH). Composition of the reaction mixtures investigated by TLC: 0.01 mole of benzaldehyde and 0.01 mole of acetophenone were dissolved in 10 ml of abs. acetic acid, and 0.04 mole of boron trifluoride complex was added. The reaction was carried out at room temperature.

Summary

The preparation of 2,4,6-triphenyl-pyrylium fluoroborate from acetophenone and benzaldehyde in abs. acetic acid and catalysed by boron trifluoride has been investigated by thin layer chromatography. It was established that the reaction stops at different stages, in dependence on the initial molar ratio. The results were compared with those obtained when using sulphuric acid as catalyst.

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