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New Synthesis of Coloured Dihydrofurylium Salts

Preliminary Communication

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A new synthesis has been described for coloured dihydrofurylium salts of the hemicyanine type based on the reaction of 2,2,5-trisubstituted 3-benzoylmethylidene-2,3-dihydrofurans with organomagnesium or organolithium compounds, tertiary aromatic amines or 1,1-diarylethylenes.

(Keywords: Dihydrofurylium salts; Dyes; Hemicyanine dyes)

Eine neue Synthese von Dihydrofuryliumfarbsalzen
(Vorläufige Mitteilung)

Es wurde eine neue Synthese für Dihydrofuryliumfarbsalze beschrieben. Die Synthese gründet sich auf die Reaktion von 2,2,5-trisubstituierten 3-Benzoylmethyliden-2,3-dihydrofuranen mit den Magnesium- bzw. Lithiumorganischen Verbindungen, tertiären aromatischen Aminen oder unsymmetrischen Diarylethylenen.

Not long ago we have worked out a simple synthesis of so far undescribed 2,2,5-trisubstituted 3-benzoylmethylidene-2,3-dihydrofurans (3-furylideneacetophenones) **1** based on isomerization of easily accessible diacetylene 1,2-diols[1].

We have found that the unknown styryldihydrofurylium salts of hemicyanine type with substituents in the vinylene group (**2, 3, 4**) which were impossible to obtain by so far known methods[2–6] could be now synthesized basing on furylideneacetophenones (**1**).

Dihydrofurylium salts were so far accessible by cyclization of some monoacetylene diols[2,3] and from unsaturated γ-lactones[4,5] or isomeric 2,3-dihydro-3-furanones[6].

As it comes out from our investigations, the carbonyl group is equally active in 3-furylideneacetophenones as in unsaturated γ-

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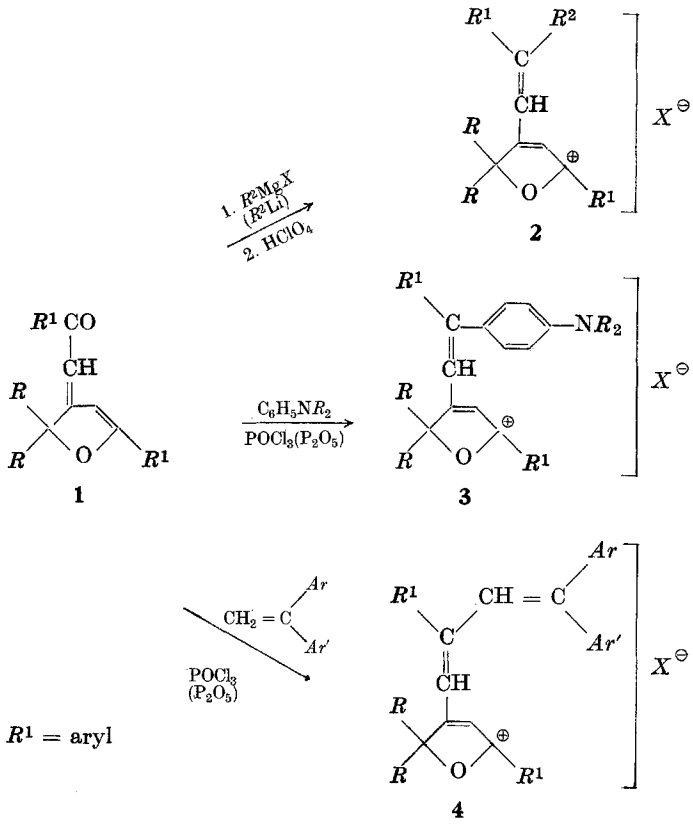
lactones and 2,3-dihydro-3-furanones and in analogous conditions reacts with formation of dihydrofurylium salts **3**, **4** and **2**.

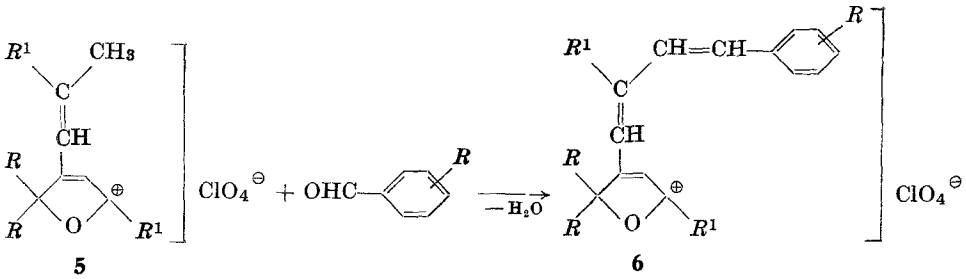


1 **2** **3** **4**

In our investigations the furylideneacetophenones **1** have reacted with organomagnesium and organolithium compounds giving carbinols, which have formed the coloured dihydrofurylium perchlorates **2** ($X = ClO_4$). Thus, e.g. 2,2-dimethyl-5-phenyl-3-furylideneacetophenone (**1**) ($R = CH_3$, $R^1 = C_6H_5$) in reaction with arylmagnesium bromides gives the perchlorates **2** ($R = CH_3$, $R^1 = C_6H_5$, $R^2 = C_6H_5$, p-$C_6H_4CH_3$, p-$C_6H_4OCH_3$) in 50–60% yield. In the case of methyl- and ethylmagnesium bromides ($R^2 = CH_3$, C_2H_5) slighty smaller yields (40%) have been obtained.

2-Phenyl-5,5-dimethyl-4-(β-methylstyryl)dihydrofurylium perchlorate (**5**), obtained with the use of methylmagnesium bromide has in accordance with the vinylogy rule the active methyl group and subjected to condensation with aromatic aldehydes forms the unknown hemicyanine dyes **6**.

3-Furylideneacetophenones **1** heated with tertiary aromatic amines or with unsymmetric diarylethylenes in $POCl_3$ medium (or possibly with addition of P_2O_5) undergo condensation forming coloured dihy-



5 **6**

drofurylium salts **3** and **4**. These salts are easily separable as sparingly soluble perchlorates; purification and identification proceeds with ease. E.g. in reaction of 2,2-dimethyl-5-phenyl-3-furylideneacetophenone (**1**) with *N*,*N*-dimethyl- and *N*,*N*-diethylaniline or *N*,*N*-dimethyl-1-naphtylamine in the $POCl_3$ medium the unknown perchlorates **3** have been obtained in 25–35% yield. Better yields have been obtained in the case of condensation of **1** with 1-phenyl-1-(*p*-methoxyphenyl)ethylene and 1,1-di-(*p*-methoxyphenyl)ethylene (45 and 60%).

Further investigations on application of furylideneacetophenones in synthesis of carbocyanine dyes with a substituent in the polymethine chain are now in progress.

Acknowledgments

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