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# Chemistry

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## Abstract

## Full Text

## Chemistry

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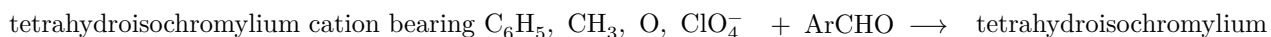
# ON THE CONDENSATION OF 1-METHYL-3-PHENYL-5,6,7,8-TETRAHYDROISOCROMYLIUM PERCHLORATE WITH AROMATIC ALDEHYDES

*(Presented by Academician M. M. Shemyakin, October 21, 1963)*

It is known<sup>(1-5)</sup> that the hydrogen atoms of the  $\alpha$ - and  $\gamma$ -methyl groups in pyrylium salts possess increased reactivity. In order to obtain intensely colored styryl derivatives in the series of pyrylium salts, Heilbron<sup>(1,2)</sup>, Vissinger<sup>(3)</sup>, and Khromov-Borisov and co-workers<sup>(4,5)</sup> studied the condensation of readily accessible salts of 2-methyl-4,6-diphenyl- and 4-methyl-2,6-diphenylpyrylium with certain aldehydes of the aromatic series.

We have studied the condensation of 1-methyl-3-phenyl-5,6,7,8-tetrahydroisochromylium perchlorate, synthesized by the procedure proposed by one of us and Dulenko<sup>(6,7)</sup>, with aromatic aldehydes (benzaldehyde, *p*- and *m*-nitrobenzaldehyde, *p*-dimethylaminobenzaldehyde, cinnamic and veratric aldehydes).

The condensation of the indicated salts with aromatic aldehydes proceeds according to the following scheme:



The reaction was carried out by boiling the reaction mixture at a ratio of pyrylium salt to aldehyde of 1 : 1.4 in acetic acid solution for 15–120 min, depending on the reactivity of the aldehyde. To the reaction mixture were added 1–2 drops of 67% hydrochloric acid to prevent opening of the pyrylium ring.

On dilution of the cooled reaction mixture with ether, the condensation product separates as a crystalline precipitate.

The condensation of 1-methyl-3-phenyl-5,6,7,8-tetrahydroisochromylum perchlorate with aromatic aldehydes proceeds very readily, with formation of 1-styryl-3-phenyl-5,6,7,8-tetrahydroisochromylum perchlorate in 73-93% yield.

Data on the yields of the condensation products and their properties are given in Table 1.

With *p*-dimethylaminobenzaldehyde the reaction proceeds most readily and rapidly, without addition of hydrochloric acid.

It should be noted that introduction of electron-donor substituents into the styryl residue of the condensation products gives a deepening of the color (a bathochromic effect), whereas introduction of electron-acceptor substituents leads to a hypsochromic effect.

Polarization of the aldehyde group with increasing negative charge on oxygen promotes an easier course of the reaction. Thus, with *p*-dimethylaminobenzaldehyde the reaction is complete within 15 min, whereas with *p*-nitrobenzaldehyde heating for two hours is necessary.

The condensation product of the pyrylium salt with benzaldehyde was obtained in low yield by a reverse synthesis through acylation of cyclohex-

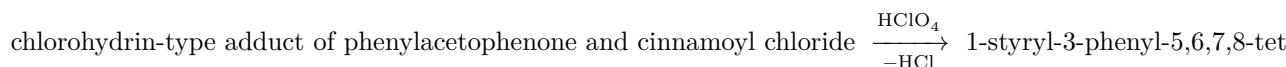
**Table 1\***

Perchlorates of  $\left[ \begin{array}{c} \text{1-styryl-3-phenyl-5,6,7,8-tetrahydroisochromylum derivatives} \\ R = \text{substituent in } -\text{CH}=\text{CHR} \end{array} \right] \text{ClO}_4^-$

R	Color of solution	Reaction duration, min	Yield, %	m.p., °C	Found, % C	Found, % H	Empirical formula	Calculated, % C	Calculated, % H
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Yellow	120	73.5	208	60.96	5.01	C <sub>23</sub> H <sub>20</sub> ONCl	60.96	4.62
<i>o</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Yellow	40	73	214	60.90	4.96	C <sub>23</sub> H <sub>20</sub> ONCl	60.96	4.62
C <sub>6</sub> H <sub>5</sub>	Red	100	84	195	66.59	5.35	C <sub>23</sub> H <sub>21</sub> ONCl	66.89	5.13
CH=C(CH <sub>3</sub> ) <sub>2</sub>	Red	15	79	184	68.68	5.83	C <sub>25</sub> H <sub>23</sub> ONCl	68.46	5.29
dimethylphenyl	Yellow	15	75	180	63.56	5.49	C <sub>25</sub> H <sub>25</sub> ONCl	63.32	5.34
<i>p</i> -N(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Blue	15	93	178	65.59	5.92	C <sub>25</sub> H <sub>26</sub> ONCl	65.87	5.75

\* All products were recrystallized from acetic acid.

...phenylacetophenone with cinnamic acid chloride in the presence of perchloric acid according to the scheme:



The synthesized product, as well as the 1-styryl-3-phenyl-5,6,7,8-tetrahydroisoquinoline obtained from it, proved to be identical with the condensation product and the corresponding isoquinoline. This confirms that the condensation of 1-methyl-3-phenyl-5,6,7,8-tetrahydroisochromylum perchlorate with aldehydes proceeds at the methyl group of the pyrylium ring.

On interaction of the pyrylium salts obtained with a concentrated solution of ammonia, the corresponding 1-styryl-3-phenyl-5,6,7,8-tetrahydroisoquinolines were obtained:



Ar = aromatic substituent

The reaction proceeds well when the suspension of the salt is allowed to stand in an ammonia solution for 1-3 days with periodic stirring. 1-(4-Phenylbutadienyl)-, 1-(3,4-dimethoxystyryl)-, and 1-(p-nitrostyryl)-3-phenyl-5,6,7,8-tetrahydroisoquinolines crystallize well from alcohol and benzene, while the remaining isoquinolines were isolated by chromatography on an alumina column in quantitative yield.

Thin-layer chromatography on alumina showed that all the isoquinolines are individual substances. The isoquinolines obtained were characterized as picrates. Data on the properties of the isoquinolines and their picrates are given in Table 2.

### Table 2\*

General structure: 3-phenyl-5,6,7,8-tetrahydroisoquinoline derivative with substituent  $-\text{CH}=\text{CHR}$  at position 1.

<i>R</i>	M.p., °C	<i>R<sub>f</sub></i>	Found N, %	Calculated N, %	M.p. of picrates, °C
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	220	0,88	7,46	7,86	226–228
<i>o</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	70	0,95	7,46	7,86	173
–CH=CH–C <sub>6</sub> H <sub>4</sub>	135	0,9	3,91	4,13	243
C <sub>6</sub> H <sub>3</sub> (OCH <sub>3</sub> ) <sub>2</sub>	180	0,81	3,48	3,76	193–195
<i>p</i> -N(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	142	0,86	7,70	7,90	195–198
C <sub>6</sub> H <sub>5</sub>	oil	0,92	4,52	4,50	234

\* Thin-layer chromatography on alumina; solvent benzene : chloroform (2:3).

Some of the synthesized isochromylium salts and sulfuric-acid salts of isoquinolines were subjected to microbiological investigation in the microbiology laboratory of the Biological Institute of Rostov State University under the direction of V. G. Akimenko. It was established that they are active against groups of Gram-positive bacilli, pigmented actinomycetes, and sarcinae. The results of microbiological investigations of the pyrylium salts and substituted 5,6,7,8-tetrahydroisoquinolines will be published in a separate paper.

## Experimental Part

**1-(4-Phenylbutadienyl)-3-phenyl-5,6,7,8-tetrahydroisochromylium perchlorate.** To 3 g of 1-methyl-3-phenyl-5,6,7,8-tetrahydroisochromylium perchlorate are added 1.83 g of cinnamaldehyde, 15 ml of glacial acetic acid, and 2 drops of 67% perchloric acid. The reaction mixture is boiled for 15 min. On cooling, brown crystals separate. The reaction product is obtained by precipitating the reaction mixture with 40 ml of ether. Weight of precipitate 3.2 g (79%).

**1-(4-Phenylbutadienyl)-3-phenyl-5,6,7,8-tetrahydroisoquinoline.** To 2 g of 1-(4-phenylbutadienyl)-3-phenyl-

20 ml of concentrated ammonia solution is added to the 5,6,7,8-tetrahydroisochromylium salt. The suspension of the salt is periodically stirred while the substance is allowed to stand for three days. The light-brown precipitate is filtered off, washed with water, and dried. The product is recrystallized from benzene. On chromatography of the resulting isochinoline in a thin layer of alumina,  $R_f = 0.90$  (solvent chloroform : benzene 3 : 2).

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*Note: Figure translations are in progress. See original paper for figures.*

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