A NEW METHOD FOR PREPARING N-METHYLIMIDE OF CITRACONIC ACID

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Abstract

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A NEW METHOD FOR PREPARING N-METHYLIMIDE OF CITRACONIC ACID

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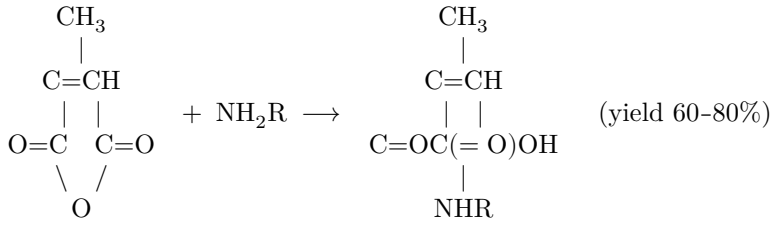
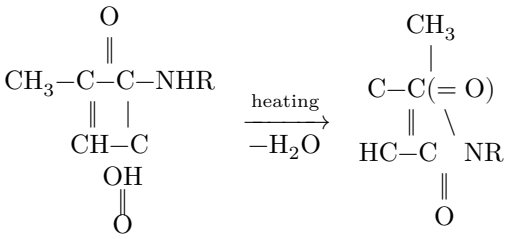
As was shown by one of us ([1]), the synthesis of previously undescribed alkylimides of citraconic acid can be carried out by analogy with the synthesis of alkylimides of maleic acid, developed by Piutti ([2]) as early as the last century.

The reaction proceeds in two stages according to the following scheme:

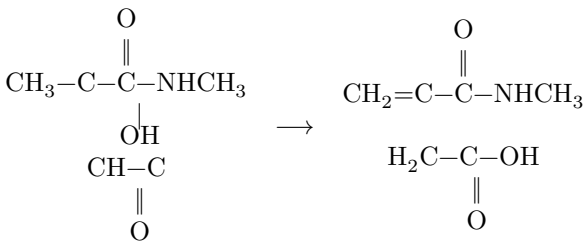




In our first experiments, at a dehydration temperature of 160-200°, i.e., under the conditions selected by Piutti for obtaining alkylmaleimides, the formation of alkylcitraconimides was accompanied by considerable resinification, and the yield of alkylcitraconimides did not exceed 40% of the theoretical amount, calculated on the consumed amido acid, and consequently amounted to 24-32% of the citraconic anhydride. Lowering the reaction temperature to 130-140° made it possible to reduce resinification and to raise the yield of imides to 50-75% based on the amido acid and, correspondingly, to 37-50% based on the anhydride.

We explained the formation of considerable resinification by the isomerization of alkylamides or alkylimides of citraconic acid into the corresponding derivatives

of itaconic acid.



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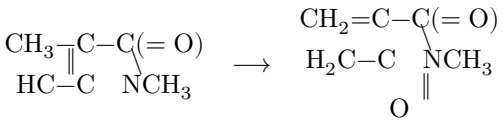
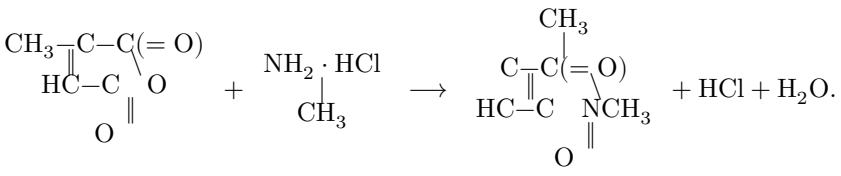


Derivatives of itaconic acid, being asymmetrically substituted ethylene, are prone to polymerization, i.e., resinification.

In 1899, Fittig [3] showed that an alkaline medium promotes the isomerization of citraconic acid into itaconic acid. During dehydration of an alkylamide, an alkaline medium may arise as a result of partial thermal decomposition with the formation of free alkylamines.

In order to eliminate this phenomenon, along with lowering the reaction temperature, experiments were carried out to obtain the methylimide of citraconic acid by the action of methylamine hydrochloride on citraconic anhydride.

The reaction was conducted in one stage, without isolation of the alkylamido acid.



The hydrogen chloride liberated during the reaction promoted dehydration and created an acidic medium in the reaction mixture, which ensured suppression of isomerization. The yield of *N*-methylimide of citraconic acid in this case ranged from 70-80% of the anhydride, instead of 36-50% by the first method.

In order to confirm the stated assumption that, in the above reaction, the acidic medium suppresses the isomerization of citraconic acid derivatives into the corresponding derivatives of itaconic acid, an experiment was carried out to obtain

N-methylimide of itaconic acid by the interaction of methylamine hydrochloride and itaconic anhydride. As a result of the reaction, *N*-methylimide of citraconic acid was isolated in a yield of 40% of the theoretically possible amount; the remaining part of the reaction mixture resinified. *N*-Methylimide of itaconic acid could not be isolated.

Experimental Part

Equimolecular amounts of citraconic anhydride and methylamine hydrochloride were placed in a Wurtz flask with two side tubes. The flask was connected to a descending Liebig condenser and equipped with two thermometers for measuring the temperature of the reaction mixture and of the vapors, as well as with a bubbler for inert gas. Heating was carried out in an oil bath or in Wood' s alloy. The temperature of the reaction mixture was maintained for 8 hr at 130–140°, and for 2 hr at 160–200°, with constant bubbling of CO_2 or nitrogen. In the process, the bulk of the reaction water and HCl was distilled off, and during the last 2 hours, a small amount of imide.

After heating was stopped, the condenser was connected to a receiver attached to a water-jet pump, and the entire reaction mixture was distilled off without fractionation at a residual pressure of 30–40 mm.

Then, after neutralization of the distillate with soda, the imide was extracted with ether. The ether extract was dried over Na_2SO_4. The ether was distilled off, and the imide was distilled under vacuum.

The results of the experiments are summarized in Table 1.

Table 1

Amount of citraconic anhydride	Amount of citraconic anhydride	Amount of $HClNH_2CH_3$	Amount of $HClNH_2CH_3$	Yield	Yield	Refractive index*
g	mol.	g	mol.	g	mol.	%	
22.4	0.2	13.5	0.2	19.05	0.1524	76.2	1.4938
112	1	70	1.03	93.3	0.748	74.8	1.4940
42.4	0.38	25.7	0.38	37.3	0.30	78.8	1.4938
22.4	0.2	13.5	0.2	17.8	0.143	71.5	1.4940

* The refractive index of N-methylimide of citraconic acid, determined by us earlier, is 1.4942.

Under the same conditions, one experiment was carried out to obtain the N-methylimide of itaconic acid.

Starting materials: 5.6 g (0.05 mole) of itaconic anhydride and 3.4 g (0.05 mole) of methylamine hydrochloride.

As a result of the reaction, 2.5 g of a liquid product was obtained with b.p. 84.5-85°/10 mm, specific gravity 1.1530, and refractive index 1.4943.

All the constants of this product correspond to the constants of the N-methylimide of citraconic acid.

Found, %:	C 57.68;	H 5.5;	N 11.5
$C_6H_7NO_2$. Calculated, %:	C 57.60;	H 5.6;	N 11.2

(The reaction is accompanied by considerable resinification.)

Consequently, when itaconic anhydride reacts with methylamine hydrochloride, isomerization takes place with formation of the N-methylimide of citraconic acid, whose yield is 40% of the theoretically possible amount.

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CITED LITERATURE

1. T. V. Sheremeteva, G. N. Larina, *Izv. AN SSSR, OKhN* (in press).
2. A. Piutti, E. Giustiniani, *Gaz. Chim. Ital.*, **26**, parte 1, 431 (1896).
3. R. Fittig, *Lieb. Ann.*, **304**, 155 (1899).

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