Preparation of Unsaturated Hydrazides by Hydrazinolysis

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In the present paper, a direct method for the preparation of unsaturated hydrazides is reported. Oleic hydrazide has been prepared by hydrazinolysis of methyl oleate in the nitrogen atmosphere.

Darstellung von ungesättigten Hydraziden durch Hydrazinolyse

Die Verfasser berichten über eine direkte Methode zur Herstellung von ungesättigten Hydraziden. Ölsäurehydrazid wurde durch Hydrazinolyse von Methyloleat in Stickstoff-Atmosphäre erhalten.

Fabrication d'hydrazides insaturés par hydrazinolyse

Les auteurs traitent d'une méthode directe pour la fabrication d'hydrazides insaturés. L'hydrazide de l'acide oléique a été obtenu par hydrazinolyse de l'oléate de méthyle en atmosphère d'azote.

Получение ненасыщенных гидразидов гидразинолизом.

Авторы описывают прямой метод получения ненасыщенных гидразидов. Гидразид олеиновой кислоты получается гидразинолизом метилолеата в атмосфере азота.

In the past several attempts were made to prepare oleic hydrazide by direct hydrazinolysis of methyl oleate with hydrazine hydrate[1-3]. In all these studies stearic hydrazide was obtained instead of oleic hydrazide. So much so, it is mentioned in the literature that "apparently unsaturated hydrazides can usually be prepared only via the acid chloride"[4]. *T. Malkin*[5] also in his earlier experiments to synthesize dioleyl cephalin, noticed that the product was invariably contaminated with distearyl cephalin when hydrazine was used to remove phthalyl group.

Recent studies[6-8] on the mechanism of hydrazine reduction has revealed that the actual reductant is an unstable intermediate produced by oxidation of hydrazine and it has also been shown that hydrazine acts as a reducing agent only in presence of oxygen or an oxidizing agent. This finding enabled *T. Malkin*[5] to synthesize dioleyl cephalin by carrying out the reaction in an atmosphere of nitrogen. Therefore it was thought that it might be possible to prepare oleic hydrazide by direct hydrazinolysis in an atmosphere of nitrogen. With this object in view, the present study was undertaken.

Experimental

Oleic acid (*E. Merck*, I. V. 89.5) was converted into methyl ester by usual method. 50 ml of ethanol freed from dissolved oxygen by bubbling nitrogen continuously was taken in a round bottomed flask fitted with a ground glass condenser. Then the calculated quantity of hydrazine hydrate (*E. Merck*, 85 %) was introduced into a flask through a side tube, using a mole ratio of 20 : 1 of hydrazine hydrate to ester, as the lower ratios are found to favour the formation of secondary hydrazides. Methyl oleate dissolved in ethanol, previously freed from dissolved oxygen was added dropwise to the refluxing solution of hydrazine in alcohol. The rate of addition was adjusted in such a way that it favours the formation of mono-acylated hydrazine derivative. Throughout the course of the reaction nitrogen was bubbled through the solution. The reaction was continued till the ester was completely converted into hydrazide which required four hours.

In order to find the complete conversion, the partially hydrazinolysed samples at different intervals were tested on T. L. C. using silica gel G layers on microplates and developing them in a solvent mixture of ethyl acetate and benzene (5 : 95). With this solvent mixture it was noticed that the spot due to hydrazide remained at the origin while the ester migrated along with the solvent front. Sample at the end of four hours gave only one spot at the origin indicating that conversion was complete. The hydrazide was then washed thoroughly with excess water saturated with nitrogen. The product after recrystallization was examined for m. p., nitrogen content by *Kjeldahl* and I. V. by *Wijs*. A portion of the hydrazide was hydrolysed by usual method taking care that atmospheric oxygen was excluded from the reaction zone during hydrolysis. The acid thus obtained was examined for its unsaturation by I. V. The results obtained are recorded in the Table 1.

Table 1

Hydrazinolysis of Methyl Oleate

Mole ratio of hydrazine hydrate to ester 20 : 1

Time [hrs.]	Iodine value		Melting point [°C]	Percentage of nitrogen
	Hydrazides	Acids obtained from hydrazides		
1	119.6	90.0	58.6	7.80
2	121.2	89.6	60.2	7.90
3	120.1	89.7	62.4	7.93
4	138.1	89.5	66—67	8.51
6	135.6	89.4	66—68	8.48

Discussion

Nitrogen content of the hydrazide clearly indicates that the product obtained predominantly consists of a simple mono-acylated derivative of hydrazine and the formation of secondary or diacylated derivative of hydrazine is suppressed. The determined iodine values of hydrazides are erratic and abnormal indicating some interference of the hydrazide with the usual iodine value determination by *Wijs*' method. The iodine value of the acid recovered from the hydrazide by hydrolysis remains almost the same as the iodine value of the original oleic acid. Thus under the experimental conditions reported here the hydrogenation was suppressed as hydrazine is incapable of hydrogenating the ethylenic linkages in the absence of oxygen or an oxidizing agent, although hydrazinolysis proceeds. In conclusion it may be stated that unsaturated hydrazides can be prepared by hydrazinolysis under the experimental conditions described here. Further work on the preparation of hydrazides of other unsaturated fatty acids is in progress.

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