

EFFECT OF SUBSTITUENTS ON THE IONIC
HYDROGENATION REACTION OF OLEFINSZ. N. Parnes, G. I. Bolestova,
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Previously it was shown that only those olefins, which as the result of adding a proton are capable of forming a tertiary carbonium ion, or a secondary ion that is stabilized by conjugation with either a benzene or a cyclopropane nucleus, enter into the ionic hydrogenation reaction (under the influence of CF_3COOH and triethylsilane) under mild conditions. In general, less stable carbonium ions are not formed under the reaction conditions [1-3].

In the present paper we studied the effect of some other electron-donor substituents, found in the α -position to the $\text{C}=\text{C}$ bond, and specifically $-\text{OR}$, $-\text{OCOR}$, and $-\text{SR}$, on the ionic hydrogenation reaction. From the obtained data (Table 1) it can be seen that all of the investigated compounds, except vinyl trifluoroacetate, enter into the ionic hydrogenation reaction. This is obviously associated with the fact that conjugation with the unshared electron pair of oxygen or sulfur makes the secondary carbonium ion sufficiently stable so that it can exist under the reaction conditions. A difference in the ease with which ethers and esters are hydrogenated is explained by the fact that the alkoxy group is a much stronger electron-donor substituent than the acyl moiety.

Vinyl trifluoroacetate does not enter into the ionic hydrogenation reaction, which is probably explained by the strong electron-acceptor properties of the CF_3 group. It should be mentioned that the hydrogenation of vinyl acetate gives, together with ethyl acetate, also transesterification products, and specifically ethyl trifluoroacetate and vinyl trifluoroacetate. The ability of the vinyl and ethyl acetates to undergo transesterification in CF_3COOH medium was corroborated by special experiments.

At first glance, an unexpected result was obtained in the hydrogenation of butyl vinyl sulfide. It is known that the free electron pair in the sulfide molecule is more labile than that of the oxygen in an ether, and it could be expected that the reaction for the ionic hydrogenation of the sulfide will proceed more easily than in the case of butyl vinyl ether. However, the yield of butyl ethyl sulfide in 20 h at 50°C does not exceed 15%. This phenomenon is possibly explained by the formation of a stable three-membered cyclic

TABLE 1

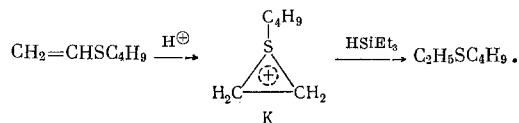
Starting compound	Reaction time, h, at 50°C	Reaction products	Yield, %
$\text{CH}_2=\text{CHOC}_4\text{H}_9$	10	$\text{C}_2\text{H}_5\text{OC}_4\text{H}_9$	80
$\text{CH}_2=\text{CHOCOCH}_3^*$	10	$\text{C}_2\text{H}_5\text{OCOCH}_3$	8
	60 and 75	$\text{C}_2\text{H}_5\text{OCOCF}_3$	3
		$\text{C}_2\text{H}_5\text{OCOCH}_3$	13
$\text{CH}_2=\text{CHOCOCF}_3$	75	$\text{C}_2\text{H}_5\text{OCOCF}_3$	12
$\text{CH}_2=\text{CHSC}_4\text{H}_9$	2	$\text{C}_2\text{H}_5\text{OCOCF}_3$	0
	20	$\text{C}_2\text{H}_5\text{SC}_4\text{H}_9$	5
$(\text{CH}_3)_2\text{C}=\text{CH}-\text{NO}_2$	10	$(\text{CH}_3)_2\text{CHCH}_2\text{NO}_2$	15
	50		0
$(\text{CH}_3)_2\text{C}=\text{CHCOOH}$	12	$(\text{CH}_3)_2\text{CHCH}_2\text{COOH}$	0

* The reaction products contain 5-6% of vinyl trifluoroacetate.

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complex of the K type [4]. If such a complex is formed during the course of the ionic hydrogenation of butyl vinyl sulfide, then it may be assumed that due to its greater stability it will react slowly with triethylsilane and the overall rate of the hydrogenation will decrease



As a continuation of this work we studied the effect of electron-acceptor substituents, attached to an ethylenic carbon, on the ionic hydrogenation reaction. It was natural to assume that the insertion of such substituents in the α -position to the double bond of an olefin, having branching at the ethylenic carbon, will retard the progress of the reaction. Actually, it proved that not only such a strong electron acceptor as the nitro group, but also the less active electron-acceptor carboxyl group, completely suppress the ionic hydrogenation reaction.

From Table 1 it can be seen that neither 1-nitro-2-methyl-1-propene nor β, β' -dimethylacrylic acid are hydrogenated under the conditions studied.

EXPERIMENTAL METHOD

1-Nitro-2-methyl-1-propene was obtained as described in [5]. 1-Nitro-2-methylpropane, needed as a standard for the chromatographic analysis, was synthesized as described in [6]. β, β' -Dimethylacrylic acid was obtained as described in [7].

The GLC analysis was run on a "Khrom-3" instrument; as the stationary phase we used 15% diisodecyl phthalate deposited on Chromosorb W (condition a), 10% poly(ethylene glycol adipate) deposited on Resorb BLK (condition b), or 15% diethylene glycol succinate deposited on Celite 545 (condition c). In the TLC analysis we used "Silufol" plates, and the system petroleum ether : $\text{CHCl}_3 = 3:1$.

Hydrogenation of Butyl Vinyl Ether. A mixture of 0.005 M of butyl vinyl ether, 0.005 M of Et_3SiH and 0.01 M of CF_3COOH was heated at 50° for 10 h, after which it was analyzed by GLC (condition a). The yield of n-butyl ethyl ether was 80%.

Reaction of Vinyl Acetate with CF_3COOH and Triethylsilane. With stirring and cooling in ice, to a mixture of 0.02 M of vinyl acetate and 0.02 M of Et_3SiH was added 0.04 M of CF_3COOH in drops, after which the mixture was allowed to warm up to room temperature and then placed in a thermostat (50°). See Table 1 for the hydrogenation results. The reaction products also contained unreacted vinyl acetate. The reaction products were analyzed by GLC (condition b).

Hydrogenation of Butyl Vinyl Sulfide. The experimental procedure was the same as described above. The yield of butyl vinyl sulfide increased from 5 (50° , 2 h) up to 15% (50° , 20 h). The analysis was performed by the GLC method (condition c).

Attempted Hydrogenation of 1-Nitro-2-methyl-1-propene and β, β' -Dimethylacrylic Acid with CF_3COOH and Et_3SiH . A mixture of 0.01 M of the hydrogenated compound, 0.01 M of Et_3SiH , and 0.02 M of CF_3COOH was heated at 50° . The absence of 1-nitro-2-methylpropane was shown by GLC analysis (condition b). The absence of isovaleric acid was shown by the TLC method.

CONCLUSIONS

Electron-donor substituents ($-\text{OR}$, $-\text{OCOR}$, $-\text{SR}$) attached to an ethylenic carbon facilitate progress of the ionic hydrogenation reaction, while electron-acceptor substituents ($-\text{NO}_2$, $-\text{COOH}$) prevent the progress of this reaction.

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