# ETHERS AND PRIMARY ALIPHATIC ALCOHOLS AS TRANSFER AGENTS FOR ACIDS IN IONIC HYDROGENATION.

## COMMUNICATION 2. TRANSFER OF PERCHLORIC ACID

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UDC 541.124:542.941.7-128

Recently, we have shown that ethers and primary alcohols with sufficient length of alkyl chains can be used as transfer agents of $H_2SO_4$ from the aqueous to the organic phase [1]. Such transfers make it possible to use the $H_2SO_4:CH_2Cl_2$ system (1:1 by volume) in the presence of $R_2O$ or ROH (1 M solutions) for ionic hydrogenation of olefins by the action of organohydrosilanes. It could be expected that replacing the $H_2SO_4$ by $HClO_4$ would make the system more effective, inasmuch as the presence of $ClO_4^-$, as a rule, speeds up the reaction by the intermediate formation of carbocations [2, 3].

In the present work we have studied the transfers of $HClO_4$ into the organic phase by ethers with alkyl radicals of different lengths in the two-phase system 65.5% $HClO_4$:octane. Parallel to this same system is the ionic hydrogenation of several unsaturated compounds (Table 1). Hydrogenation is significantly speeded in the presence of all ethers studied except $Et_2O$. In this connection only the ethers with long alkyl radicals are good transfer agents, but those containing four to eight carbons do not facilitate transfer of acid into the organic phase.

It is known that the rate of ionic hydrogenation in homogeneous systems increases with increase of concentration of acids [4]. The absence of a symbatic dependence between the yields of methylcyclohexane and the amount of acid transferred to the organic phase caused us to investigate the course of the ionic hydrogenation in each phase separately. With this in mind the solution of the ether in octane was stirred with 65% $HClO_4$, let stand 1 h, the layers separated, and a mixture of reagents introduced into each layer, i.e., 1-methylcyclohexene and $Ph_2SiH_2$ (see Table 1). It seems that in the case of lower ethers transfer of acid to the organic phase is not facilitated and the ionic hydrogenation does not take place in this phase but occurs to a significant extent in the acid phase (expts. 3 and 4).† This is evidently associated with the fact that dipropyl and dibutyl ethers are partially soluble in the acid phase, which brings about an increased solubility of the silane but the olefin in this layer [5] and an increase in the yield of alkane. In contrast, in the case of ethers of sufficient length of alkane chains the reaction takes place in the organic phase. Methyl dodecyl ether transfers an amount of acid which is adequate for hydrogenation of all olefins initially present in that layer and the reaction in the organic phase goes practically to completion (expt. 7). Dioctyl and butyl dodecyl ethers are less effective as transfer agents of acids into the organic phase since their concentrations in this layer are less and the ionic hydrogenation proceeds more slowly in the organic phase. Establishment of the yield of methylcyclohexane in the two-phase system shows that during the time of the reaction in the two-phase system the transfer agent evidently sometimes succeeds in crossing over the boundary of the separate phase with a new portion of acid according to the scheme

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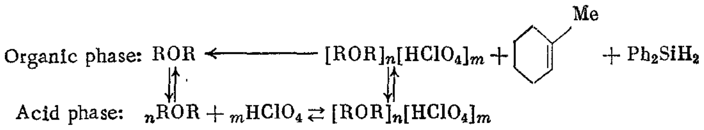
*Deceased.

†The increase in yields of the alkane from 6% to 30% on going over from a two-phase system to the acid phase in the absence of a transfer agent is explained by the increased concentration of reagents. In the case of methyl dodecyl ether, there is a transfer of a large quantity of acid into the organic layer, the concentration of acid in the aqueous layer falls to 63.8%, and the yield of alkane decreases to 8%.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 352-356, February, 1985. Original article submitted November 30, 1983.



Dibutyl ether is of particular interest inasmuch as in the system 65.5% $HClO_4$:$Bu_2O$:octane, besides the organic and acid phases a third phase is formed located between the first two. Carrying out the ionic hydrogenation in this third phase leads to the formation of the products in quantitative yields. Titration of the third phase and GLC analysis showed that this phase is a mixture of perchloric acid and dibutyl ether in the mole ratio 1.5:1 (1:1 by volume) with a small amount of octane (~2-5%). Consequently, it could be expected that the system 65% $HClO_4$:$Bu_2O$ = 1:1 (by volume) would be effective for ionic hydrogenation. Actually, reacting 1-methylcyclohexene with $Ph_2SiH_2$ in a mixture of $HClO_4$:$Bu_2O$ = 1:1 (by volume) proceeds with quantitative yield after 30 min at ~20°C.

The new system found for ionic hydrogenation, i.e., $HClO_4$:$HSiR_3$:octane:ROR seems effective in the case of other substrates (Table 2). Here unbranched olefins such as cyclohexene are not hydrogenated under the conditions studied, but acetophenone is hydrogenated to ethylbenzene. This is evidence for the maintenance of specific selectivity in ionic hydrogenation.

It is necessary to point out the experiments using less concentrated $HClO_4$ appeared unsuccessful: for concentrations of $HClO_4$ lower than 60%, ionic hydrogenation did not proceed under the conditions of the experiment. Thus, we have the stepwise dependence on the $HClO_4$ concentrations observed in [6], where it was

TABLE 1. Hydrogenation of 1-Methylcyclohexene by the System $HClO_4$:$Ph_2SiH_2$:ROR:Octane (0.5 mmole substrate, 0.5 mmole $Ph_2SiH_2$, 1 ml 65.5% $HClO_4$, 1 ml of a 1 M solution of the ether in octane, 30 min, 20-22°C)

| Expt. No. | Ether | No. of C atoms | Concn. of acid in organic phase, mole/liter | Yield of methylcyclohexane, % | | |
|---|---|---|---|---|---|---|
| | | | | in the two-phase system* | in the organic phase | in the acid phase |
| 1 | — | 0 | 0,01 | 6 | 0 | 31 |
| 2 | Diethyl | 4 | 0,025 | 8 | 0 | 34 |
| 3 | Dipropyl | 6 | 0,025 | 70 | 0 | 67 |
| 4 | Dibutyl† | 8 | 0,025 | 98 | 0 | 52 |
| 5 | Dioctyl | 16 | 0,260 | 65 | 22 | 34 |
| 6 | Butyl dodecyl | 16 | 0,360 | 74 | 46 | 33 |
| 7 | Methyl dodecyl | 13 | 0,800 | 87 | 85 | 8 |

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*Organic phase/acid phase = 1:1 (by volume).

†Intermediate phase is formed, yield of methylcyclohexane is 100% in it.

TABLE 2. Ionic Hydrogenation of Unsaturated Compounds by the System $HClO_4$:$HSiR_3$:ROR:Octane*

| Substrate | Ether | Hydrogenation product | Yield, % |
|---|---|---|---|
| 2,3-Dimethyl-2-butene | — | 2,3-Dimethylbutane | 4 |
| » | Dipropyl | » | 54 |
| » | Methyl dodecyl | » | 60 |
| 2-Methyl-2-decene | — | 2-Methyldecane | 2 |
| » | Dipropyl | » | 12 |
| » | Methyl dodecyl | » | 69 |
| Acetophenone | — | Ethylbenzene | 1 |
| » | Diethyl | » | 0 |
| » | Dibutyl | » | 75 |
| » | Methyl dodecyl | » | 91 |
| Cyclohexene | — | Cyclohexane | 0 |
| » | Dioctyl | » | 0 |
| » | Dibutyl | » | 0 |

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*For conditions here and later see Table 1.

TABLE 3. Ionic Hydrogenation of 1-Methylcyclohexene by the System $HClO_4:Ph_2SiH_2:ROH:$ Octane

| Alcohol | No. of C atoms | Yield of methylcyclohexane, % | Concentration of acid in the organic phase, moles/liter |
|---|---|---|---|
| — | 0 | 6 | 0,01 |
| Ethyl | 2 | 10 | 0,02 |
| Butyl | 4 | 26 | 0,02 |
| Octyl | 8 | 35 | 0,08 |
| Dodecyl | 12 | 47 | 0,16 |
| Hexadecyl | 16 | 75 | 0,38 |

TABLE 4. Ionic Hydrogenation of Unsaturated Substrates by the System $HClO_4:HSiR_3:ROH:$Octane

| Substrate | Alcohol | Product | Yield, % |
|---|---|---|---|
| 2,3-Dimethyl-2-butene | — | 2,3-Dimethylbutane | 4 |
| » | Ethyl | » | 15 |
| » | Hexadecyl | » | 45 |
| 2-Methyl-2-decene | — | 2-Methyldecane | 1 |
| » | Ethyl | » | 26 |
| » | Hexadecyl | » | 85 |
| Acetophenone | — | Ethylbenzene | 1 |
| » | Ethyl | » | 16 |
| » | Hexadecyl | » | 72 |

TABLE 5. Starting Mixtures for the Ionic Hydrogenation Reaction

| Substrate investigated | Organohydrosilane | Internal standard | Mole ratio substrate:silane: standard |
|---|---|---|---|
| 1-Methylcyclohexene | $Ph_2SiH_2$ | n. Heptane | 1 : 1,5 : 0,35 |
| Cyclohexene | $Ph_2SiH_2$ | n. Hexane | 1 : 1,5 : 0,35 |
| 2-Methyldecene | $Et_3SiH$ | n. Dodecane | 1 : 1,5 : 0,35 |
| 2,3-Dimethyl-2-butene | $Ph_2SiH_2$ | Cyclohexane | 1 : 1,5 : 0,35 |
| Acetophenone | $Et_3SiH$ | o-Xylene | 1 : 1,5 : 0,35 |

found that the rate of hydrolysis of phenyl acetate increases markedly in the region of $HClO_4$ concentrations of 10M(63%), which is explained by the change from a bimolecular to a carbocation reaction mechanism.

We have found that primary aliphatic alcohols also can be transfer agents of $HClO_4$ from the aqueous phase to the organic phase and facilitate speeding up of the ionic hydrogenation (see Tables 3 and 4).

The transfer of $HClO_4$ to the organic phase and the reaction of ionic hydrogenation in the presence of alcohols obeys the same rules as in the presence of ethers, namely: higher alcohols are capable of fulfilling the role of transfer agents of acids and the ionic hydrogenation proceeds in the organic phase. In the case of octyl alcohol, containing eight carbon atoms, a third phase is formed in which hydrogenation proceeds with high yields (just as it does with ionic hydrogenation in the presence of $Bu_2O$). Lowered yields of methylcyclohexane in the presence of alcohols and a lesser amount of transfer of acid in comparison with ethers can be explained by the formation of perchlorates of alcohols.

## EXPERIMENTAL

Diphenylsilane, methyldodecyl ether, and butyl dodecyl ethyl were obtained as in [7, 9], respectively; 65% $HClO_4$ was prepared by distilling technical $HClO_4$ in a stream of Ar at a still temperature not above 150°C.

Ionic hydrogenation in two-phase systems $HClO_4$:octane is carried out according to the following general method. To a previously prepared mixture of substrate, organohydrosilane, and standard compound (for subsequent GLC analysis, Table 5) is added 1 ml of a 1 M solution of the ether or alcohol and 1 ml of 65.5% $HClO_4$. The reaction mixture was stirred 30 min at ~20°C, after which the layers were separated, and the organic layer was neutralized with soda and analyzed by GLC. Results of analysis are shown in Tables 1-3.

The amount of acid transferred into the organic phase was determined by titration. A mixture of 1 ml of 65.5~ $HClO_4$ and 1 ml of a 1 M solution of ether in octane was stirred 30 min at ~20°C, transfered to a separatory funnel, 0.5 ml of the organic layer separated, 7 ml distilled water added, and then it was titrated with KOH to the phenolphthalein end point. For results see Table 1.

$Bu_2O-HClO_4$ System. Mixed vigorously by shaking were 10 ml of 65.5% $HClO_4$ and 10 ml of a 1 M solution of $Bu_2O$ in octane, in which besides organic and acidic layers an intermediate layer of 1.5 ml formed. The normality of the acid in this layer is 2.24. The dibutyl ether and octane contents were determined by the GLC method.

GLC analysis was carried out on Chrom-3 and Chrom-41 instruments using a 10% PEGA on BLK column and a column with 5% Apiezon on Chromosorb. Internal standards are shown in Table 5; n-nonane was used for the quantitative determination of $Bu_2O$.

## CONCLUSIONS

1. Ethers and primary aliphatic alcohols with alkyl groups of adequate length fulfill the role of transfer agents of perchloric acid into the organic phase.

2. Perchloric acid is the active proton donor in ionic hydrogenation in two-phase systems $HClO_4$:n-octane: ROR(ROH):$HSiR_3$.

3. A new effective homogeneous system for ionic hydrogenation has been proposed – $HClO_4$:$Bu_2O$ (1:1 by volume):$HSiR_3$.

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*The journal title was not cited in the Russian original; however, it is probably Dokl. Akad. Nauk SSSR – Publisher.