CHEMISTRY LETTERS, pp. 733-736, 1990.

Iodohydrin Synthesis from Simple and Functionalised Olefins on Treatment with Periodic Acid and Sodium Bisulfite

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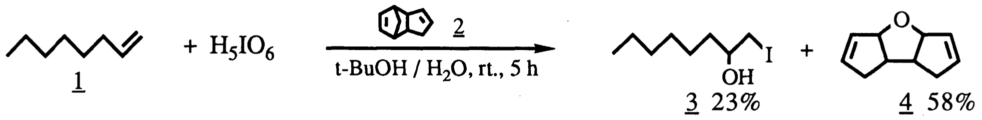
Periodic acid (H_5IO_6) in combination with sodium bisulfite was found to be a prominent reagent to convert simple and functionalised olefins into the corresponding iodohydrins in fair to good yields under mild conditions. Allylic alcohols gave iodohydrins whose orientation obeyed anti-Markovnikov rule in contrast to olefins which gave Markovnikov products.

Periodic acid, $HIO_4 \cdot 2H_2O$ (abbreviate to H_5IO_6), or periodates such as $NaIO_4$ and KIO_4 are often used as oxidants of various organic substrates, i.e., glycols, polycyclic aromatic hydrocarbons, steroids, amines, and phenols.[1)] For the purpose of olefin oxidations, however, these reagents are employed as a secondary oxidant with a wide variety of metal oxides (e.g., permanganate,[2)] osmium tetraoxide,[3)] and ruthenium tetraoxide[4)]), since olefins are not oxidized by periodic acid or periodates alone. In the previous paper,[5)] we showed that 1-octene (1) on treatment with H_5IO_6 in the presence of dicyclopentadiene (2) in aqueous tert-butyl alcohol affords 1-iodo-2-octanol (3) together with furan derivative 4 which appears to be formed via rearrangement of iodohydrin of 2(Eq. 1).



(1)

In this reaction, 2 seemingly functions as a reducing agent to be generated in situ hypoiodous acid, IOH, from H_5IO_6. Our attention has been directed toward the direct preparation of iodohydrins from various substrates by using H_5IO_6 and an appropriate reducing agent in place of 2.

Usually, iodohydrins are prepared either by the reaction of epoxides with hydriodic acid or with metal iodides,[6)] or by the exchange of chlorohydrins or bromohydrins with sodium iodide,[7)] but the direct synthesis of iodohydrins from olefins is scarcely published.[8,9)]

This paper describes a versatile iodohydrin synthesis by the use of H_5IO_6 in combination with $NaHSO_3$ under mild conditions.

The conversion of 1 to 3 was chosen as a model reaction and carried out under various reaction conditions. Table 1 shows the results on the reaction of 1 with H_5IO_6 under the influence of several reducing agents.

A typical reaction procedure is as follows: To a solution of 1 (10 mmol) in CH_3CN (20 ml) was added H_5IO_6 (12 mmol) in water (6 ml), and then $NaHSO_3$(24 mmol) in water (24 ml) for a period of 10 min under stirring. The solution was allowed to react for an additional 2 h at room temperature. The reactant was extracted with ether, and the ether layer was washed with 20% $Na_2S_2O_3$. The extracts were dried over $MgSO_4$, filtered and evaporated to give almost pure 3 (85% yield).

Table 1. Conversion of 1-Octene(1) to 1-Iodo-2-Octanol(3) with H_5IO_6 in the Presence of Various Reducing Agents [a)]

Run	Reductant (equiv.)		Conversion/% [b)]	Selectivity/% [b)]
1	$NaHSO_3$	(1.0)	74	45
2	$NaHSO_3$	(2.0)	95	90
3	$NaHSO_3$	(3.0)	>98	61
4 [c)]	$NaHSO_3$	(2.0)	95	40
5	Na_2SO_3	(2.0)	62	37
6	$Na_2S_2O_3$	(2.0)	50	40
7	Na_2HPO_3	(2.0)	no reaction	
8	$FeSO_4$	(2.0)	no reaction	
9	$H_2C_2O_4$	(2.0)	no reaction	
10 [d)]	$NaHSO_3$	(2.0)	no reaction	
11 [d,e)]	$NaHSO_3$	(2.0)	95	90

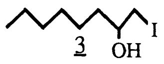
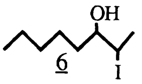
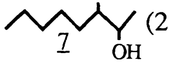
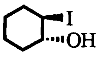
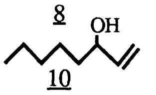
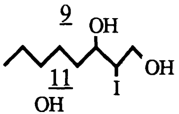
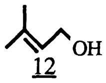
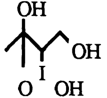
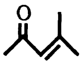
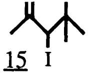
a) To a mixture of 1 (10 mmol) and H_5IO_6 (12 mmol) in aqueous CH_3CN(26 ml, 77 v/v %) was added reductant (24 mmol) in water (24 ml) and stirred at room temperature for an additional 2 h. b) Determined by VPC.
c) Aqueous $NaHSO_3$ was added all at once to the reaction system. d) $NaIO_4$ was used in place of H_5IO_6. e) Medium was acidified at pH 1 by 2M-H_2SO_4.

H_5IO_6-$NaHSO_3$ system was found to be the best combination for the conversion of 1 to 3. To achieve the reaction with satisfactory yields, two equivalents of $NaHSO_3$ to H_5IO_6 must be used (Run 2). However, two molar excess of $NaHSO_3$ resulted in a lowering of the selectivity. When the reductant was added all at once to the medium, the yield of 3 decreased to 40% (Run 4). The combination of H_5IO_6 with Na_2SO_3 or $Na_2S_2O_3$ was less efficient than that with $NaHSO_3$, and 3 was formed in moderate yields (Runs 5 and 6). Na_2HPO_3, $FeSO_4$, and oxalic acid were inadequate for this purpose (Runs 7-9). Sodium periodate, $NaIO_4$, was also used as the oxidant in place of H_5IO_6 under acidic medium (pH 1), but no reaction took place in a neutral solution (Runs 10 and 11).

On the basis of these results, it seems that H_5IO_6 is reduced by $NaHSO_3$ to form apparently hypoiodous acid, IOH, as an active species, although the detailed reaction path is uncertain.

Iodohydrins were prepared from various substrates using H_5IO_6-$NaHSO_3$ system (Table 2).

Table 2. Iodohydrin Synthesis from Simple and Functionalised Olefins by H_5IO_6-$NaHSO_3$ System a)

Run	Substrate	Conv./ % b)	Product (Selec./ %) b)
1	1	95	 3 (90)
2	 5	98	 6 (53)  7 (26)
3	 8	87	 9 (80)
4c)	 10	80	 11 (80)
5	 12	-	 13 [60] d)
6	 14	-	 15 [81] d)

a) Reactions were carried out in the same method as Table 1.

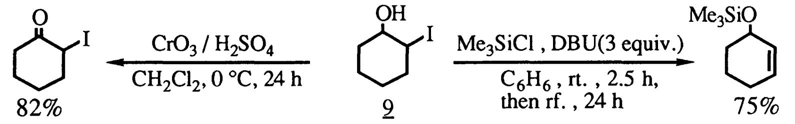
b) Determined by ^1H-NMR and VPC measurements. c) $NaHSO_3$(24 mmol) in water (5 ml) was added to the reaction system. d) Isolated yields.

The orientation of the reaction for the terminal olefin 1 obeyed Markovnikov rule to produce 3 in which iodine is bonded to the terminal carbon. However, internal olefin such as 2-octene (5) afforded a regioisomeric mixture of iodohydrins, 6 and 7, whose ratio was about a 2:1. The preferential formation of 6 to 7 may be due to the easy attack of water (or OH^-) to the C-3 cation resulted from the iodonium ion intermediate derived from the addition of I^+ to 5. Cyclic olefin, cyclohexene (8), gave trans-2-iodo-1-cyclohexanol (9) in 70% yield.

The addition of IOH to 1-octen-3-ol (10) took place regioselectively, but not stereoselectively, to yield 2-iodo-1,3-octanediol (11) in high selectivity. It is attractive that the reaction followed anti-Markovnikov rule in contrast to the case of simple olefins which gave Markovnikov products. This is believed to be due to the difficulty of the attack of water from the C-2 side owing to the electrostatic repulsion by the neighboring hydroxy group. Likely 10, 3-methyl-2-buten-1-ol (12) gave anti-Markovnikov product, 2-iodo-3-methyl-1,3-diol (13) in

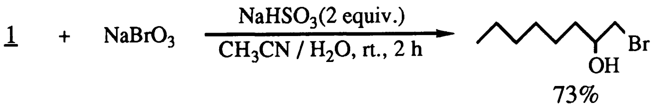
60% yield. The reaction of α,β-unsaturated ketone, 4-methyl-3-penten-2-one (14), took place regioselectively, leading to 4-hydroxy-3-iodo-4-methylpenten-2-one (15) in 81% yield.

In order to utilize the resulting iodohydrins, 2-iodo-1-cyclohexanol 9 was allowed to react with chlorotrimethylsilane in the presence of DBU at ambient temperature followed by refluxing temperature to give allylic alcohol protected by trimethylsilyl group in 75% yield. Furthermore, the oxidation of 9 by Jones reagent produced 2-iodo-1-cyclohexanone in good yield (Eq. 2).



(2)

Meanwhile, this method was extended to the preparation of bromohydrins by the use of $NaBrO_3$ in place of $NaIO_4$ under the same reaction conditions (Eq. 3).



(3)

In conclusion, H_5IO_6 in combined with $NaHSO_3$ was found to be a prominent reagent which provides a facile iodohydrin synthesis from simple and functionalised olefins in aqueous acetonitrile under mild conditions.

References

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(Received February 28, 1990)