J = 4.6 Hz). ^{13}C NMR ($CDCl_3$ + CD_3OD), δ: 136.25 (C(11)); 134.59 (C(13)); 126.08 (C(12)); 125.52 (C(18)); 62.47 (C(30)); 62.08 (C(6′)); C(6″)).

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New electrophilic iodochlorinating systems based on iodine(+1)

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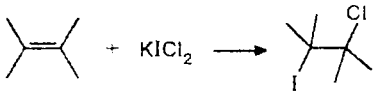
Two new convenient systems for electrophilic iodochlorination of olefins are proposed: KIO_3 + I_2 + HCl (in aqueous solutions) and $KICl_4$ + I_2 (in organic solvents).

Key words: electrophilic addition, iodination, organic iodides.

Previously, we proposed that potassium dichloroiodate(I) would be a convenient reagent for iodochlorination of multiple bonds.[1]

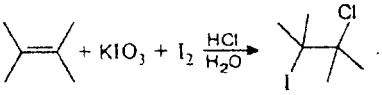


The present work describes two new iodinating systems based on monovalent iodine. Potassium dichloroiodate(I) can be obtained by a three-stage synthesis.[2] The systems proposed make the synthesis simpler because compounds of monovalent iodine are formed *in situ*.

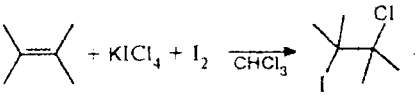
The first system based on KIO_3 + I_2 replaces $KICl_2$ in reactions conducted in aqueous media. It is known that in the presence of HCl the equilibrium

$$IO_3^- + 2I_2 + 6H^+ + 10Cl^- \rightleftharpoons 5ICl_2^- + 3H_2O$$

is shifted to the right.[3] This allows one to obtain acidified $KICl_2$ solutions and to use them as an iodinating system:

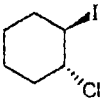


When an organic solvent is used as the medium, a system based on potassium tetrachloroiodate(III) (obtained in one step by chlorination of an aqueous KI solution)[2] and iodine is effective



Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 4, pp. 877—878, April, 1997.

Table 1. Halogenation of olefins

Olefin	Reaction products	Overall yield of halides in the system (%)		
		$KICl_4 + I_2$	$KIO_3 + I_2 + HCl$	$KICl_2$
$PhCH=CH_2$	$PhCHClCH_2I$ (**1**), $PhCHICH_2Cl$ (**2**)	82	77	89 [1]
$PhCH=CHCOOH$	$PhCH(OH)CHICOOH$ (**3**)	—	60	98 [1]
		83	98	100 [1]
$Bu^nCH=CH_2$	$Bu^nCHClCH_2I$ (**4**), Bu^nCHICH_2Cl (**5**)	77	75	82 [1]

The fact that the reaction with $KICl_4$ in the absence of I_2 leads to other results[1] suggests that compounds of monovalent iodine are formed in this system.

The possibilities of the new iodinating systems were illustrated by reactions with four model olefins. As with $KICl_2$, the use of the systems proposed allows one to obtain the main product in high yields for all cases (Table 1). We found that the ratio of the products of the iodochlorination of styrene (**1** : **2** = 5 : 1), which has been determined earlier,[1] is retained when the new systems are used. Equally, the ratio of the isomers of iodochlorohexane (**4** : **5** = 2 : 1), which was found from the high-resolution ^1H NMR spectrum, remains unchanged. As in the case of $KICl_2$,[1] the reaction with cinnamic acid is the exception. This reaction occurs only in an aqueous medium to give iodohydrin (**3**).

$$PhCH=CHCOOH + KIO_3 + I_2 \xrightarrow[H_2O]{HCl} \underset{\mathbf{3}}{PhCH(OH)CHICOOH}$$

Experimental

The physicochemical characteristics of compounds **1**—**3** obtained correspond to those given earlier.[1]

Reactions in aqueous solutions. General procedure. Potassium iodate and iodine (in the molar ratio of 1 : 2) were placed in water, and HCl was added with stirring until a transparent orange-red solution was formed. The solution was cooled to +5 °C, and an olefin was added (in the ratio of 5 mol of the olefin per 1 mol of KIO_3). The reaction mixture was stirred with cooling for 30 min. Then a Na_2SO_3 solution was added until the iodine color disappeared, and the product was extracted with chloroform or ethyl acetate. The extract was dried with $MgSO_4$, and the solvent was evaporated *in vacuo*.

Reactions in chloroform. General procedure. A mixture of $KICl_4$ and I_2 (1 : 1) was grounded in a mortar and poured in $CHCl_3$. An olefin was added with cooling and stirring (in the ratio of 3 mol of the olefin per 1 mol of I_2). Stirring was continued for 30 min, and then the solution was washed with Na_2SO_3 and worked up as above.

Reaction of hex-1-ene with potassium dichloroiodate(I). Hex-1-ene (0.5 g, 0.74 mL, 6 mmol) was added with stirring to a solution of $KICl_2$ (1.42 g, 6 mmol) in 5 mL of chloroform. Isolation was performed similarly to the preceding procedure. A mixture (1.19 g, 82%) of 2-chloro-1-iodohexane (**4**) and 1-chloro-2-iodohexane (**5**) was obtained in the ratio of 2 : 1, n_D^{20} 1.5204. ^1H NMR (400 MHz, $CDCl_3$), δ: **4**: 4.14 (tt, 1 H, HCCl, J_1 = 4.6 Hz, J_2 = 10.4 Hz); 3.96 (dd, 1 H, CH_2I, J_1 = 4.6 Hz, J_2 = 11.2 Hz); 3.74 (dd, 1 H, CH_2I, J_1 = 10.4 Hz, J_2 = 11.2 Hz); **5**: 3.90 (tt, 1 H, HCl, J_1 = 4.6 Hz, J_2 = 8.2 Hz); 3.50 (dd, 1 H, CH_2Cl, J_1 = 4.6 Hz, J_2 = 10.0 Hz); 3.35 (dd, 1 H, CH_2Cl, J_1 = 8.2 Hz, J_2 = 10.0 Hz), 2.05—0.80 (m, 9 H, C_4H_9). Found (%): C, 29.58; H, 4.97. $C_6H_{12}ClI$. Calculated (%): C, 29.24; H, 4.90.

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