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SHORT COMMUNICATIONS

New Preparative Opportunities Provided by Iodosobenzene Diacetate in Reactions with Alkenes*

M. S. Yusubov[1,2] and G. A. Zholobova[2]

[1]*Siberian State Medical University, Tomsk, 634050 Russia*
[2]*Tomsk Polytechnic University, Tomsk, 634050 Russia*

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The great interest in compounds of polyvalent iodine is due to their versatile synthetic properties. Within last three decades quite a number of reviews and several monographs were published concerning unique transformations involving these substances [1–5]. The reactions of organic derivatives of iodine(III) with alkenes are among the most extensively investigated; depending on the reaction conditions they afford products of addition, oxidation, or rearrangement [1–7]. The iodosobenzene diacetate in contrast to the majority of related compounds is low-electeophilic substance and under common conditions does not react with alkenes.

We found that the reaction of iodosobenzene diacetate (**I**) in methanol or acetonitrile in the presence of sulfuric acid with styrene (**II**), 1,1-diphenylethylene (**III**), chalcone (**IV**), and cyclohexene (**V**) gave rise to oxidative rearrangement resulting in carbonyl compounds or their acetals **VI**–**X** (see table).

The oxidative rearrangement occurred with compounds **II**–**IV** under mild conditions (in −15 ÷ 25°C range) affording in high preparative yields (80–94%) compounds **VI**–**X**. The oxidation of cyclohexene **V** is accompanied with cycle contraction yielding aldehyde **X** as the main reaction product. Using GC-MS method we detected 1,2-dimethoxycyclohexane and 1-methoxy-1-cyclohexene as side products.

These oxidative rearrangements of compounds **II**–**V** were previously performed by treating with

Reaction conditions, yields and characteristics of reaction products obtained from iodosobenzene diacetate and alkenes **II**–**V**, **XI**, **XIII**

Substrate	Reaction product	Time, min	Temperature, °C	Yield, %	bp or mp, °C
II	VI	20	–20	87[a]	217–220 (750 mm Hg) {219–221 (754 mm Hg) [7]}
II	**VII**	20	–15	80[b,c]	–
III	**VIII**	30	–15[d]	94	59–60 (60 [8])
IV	**IX**	320	25	90	97–98 (94 [7])
V	**X**	140	–15[e]	42[e]	–
XI	**XII**	320	–15[g]	59	48–50 ($MeOH–H_2O$)
XIII	**XIV**	300	25	32[h]	–

[a] Isolated by column chromatography on Al_2O_3.
[b] In acetonitrile with the use of 50% aqueous H_2SO_4.
[c] Isolated in the form of 2,4-dinitrophenylhydrazone, mp 120–121°C (120°C [8]).
[d] The reaction temperature was gradually raised to 0°C.
[e] Stirred for 20 min at –15°C, then at 20°C.
[f] Isolated in the form of 2,4-dinitrophenylhydrazone, mp 154–156°C (156–157°C [9]).
[g] Stirred for 20 min at –15°C, then at 20°C.
[h] Isolated in the form of 2,4-dinitrophenylhydrazone, mp 236–238°C (236–237°C [8]).

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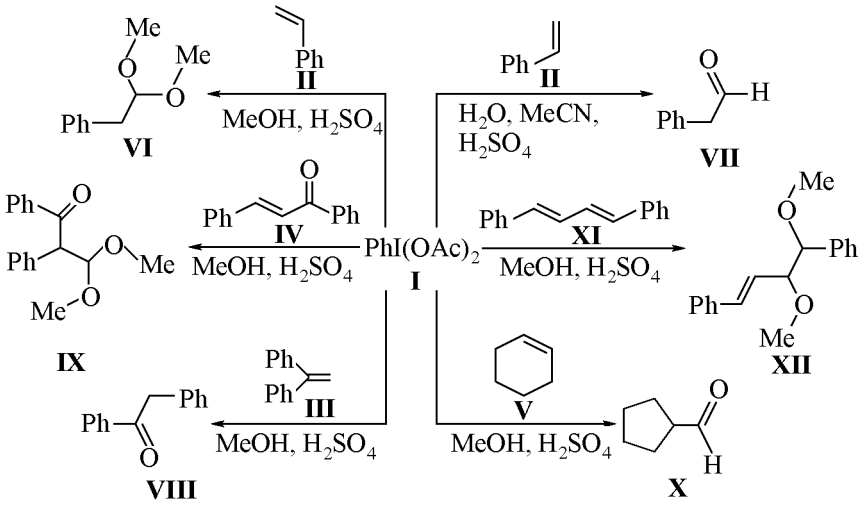

C_6H_5IO in methanol in the presence of acids (CF_3SO_3H, FSO_3H, BF_3–Et_2O), $C_6H_5I(OH)OTs$, phenyl iodosulfate and iodobenzene bis(trifluoroacetate), but the yields of the reaction products were considerably lower (20–60%) [6, 7, 10, 11].

It is important that with (*E*,*E*)-1,4-diphenylbutadiene (**XI**) the oxidative rearrangement did not occur but in 59% yield was obtained 1,2-dimethoxylation product, 3,4-dimethoxy-1,4-diphenyl-1-butene (**XII**). In earlier publications [2, 12] was reported only on reactions of $C_6H_5I(OH)OTs$ with conjugated dienes (1,3-butadiene, isoprene, 2,4-hexadiene, and cyclohexadiene) furnishing only 1,4-addition products in low yield. In [12] the reaction of 1,3-butadiene with Zefirov reagent [μ-oxo-bis(trifluoromethanesulfonyloxy)iodobenzene] gave rise to intractable mixture of 1,2- and 1,4-addition products in 11 : 89 ratio [12].

We failed to perform selectively the oxidative rearrangement of (*E*)-stilbene (**XIII**) under the action of iodosobenzene diacetate. In all cases in the reaction products prevailed benzophenone (**XIV**), and by GC-MS method were detected diphenylacetaldehyde, diphenylacetic acid, epoxystilbene, deoxybenzoin, and benzyl. The nonselectivity of the process is apparently due to the low solubility of (*E*)-stilbene under the reaction conditions.

Thus the results obtained show in general new preparative opportunities opened for iodosobenzene diacetate, the most accessible compound of the polyvalent iodine, and call for wider use of the substance in the organic synthesis.

Oxo compounds and acetals VI, VII–X, XII. To a solution of 2 mmol of alkene in 6–8 ml of methanol cooled to the temperature indicated in the table was added 2.02 mmol of iodosobenzene diacetate (**I**), and dropwise while stirring was added 0.45–0.5 ml of 50% solution of H_2SO_4 in methanol. The mixture was kept at the indicated temperature for the time interval mentioned in the table, then poured into 30 ml of water, extracted with ethyl ether (2×30 ml), washed with saturated aqueous NaCl solution, and dried on Na_2SO_4. The ether was distilled off, the residue was dissolved in benzene and subjected to chromatography on a column packed with silica gel (eluent hexane, then hexane–benzene, 4 : 1). 3,4-Dimethoxy-1,4-diphenyl-1-butene (**XII**). IR spectrum (CCl_4), ν, cm^{-1}: 1140 (C–O–C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.24 s (3H, OMe), 3.26 s (3H, OMe), 3.78 d.d (1H, =CHC<u>H</u>OMe, *J* 4.9, 7.7 Hz), 4.24 d (1H, PhC<u>H</u>OMe, *J* 4.9 Hz), 6.15 d.d (1H, PhHC=C<u>H</u>, *J* 7.7, 16.1 Hz), 6.40 d (1H, Ph<u>H</u>C=CH, *J* 16.1 Hz), 7.20–7.37 m (10H arom). Found, %: C 80.45; H 7.50. $C_{18}H_{20}O_2$. Calculated, %: C 80.56; H 7.51.

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