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A FACILE PREPARATION OF 2-ARYLPROPIONALDEHYDE FROM 1-ARYL-1-PROPENE

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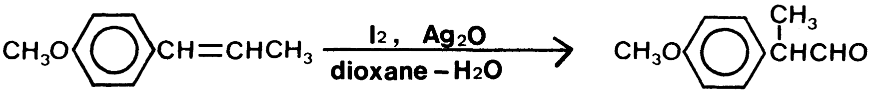
1-Aryl-1-propenes were converted into the corresponding 2-arylpropionaldehydes in high yields by treatment with iodine and silver(I)oxide in aqueous dioxane at room temperature.

Although conversion of olefin to aldehyde is commonly accomplished with ozonolysis, oxosynthesis,[1)] Wacker oxidation[2)] and rearrangement by using reagents such as mercuric sulfate[3)] and thallium(III)nitrate,[4)] a oxidative rearrangement of olefin to aldehyde under mild reaction conditions has never been known yet.

We wish to report here a synthetically useful method for conversion of 1-aryl-1-propene to 2-arylpropionaldehyde by treatment with iodine in the presence of silver(I)oxide in aqueous solution. The 2-arylpropionaldehyde thus obtained is an important precursor of 2-arylpropionic acid, such as 2-(4-isobutylphenyl)-propionic acid and 2-(6-methoxy-2-naphthyl)propionic acid, which have potent anti-inflammatory activity.

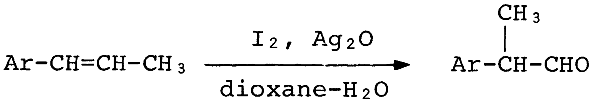
We tried to convert 1-aryl-1-propene into 1-aryl-1,2-epoxypropane by some known procedures. However, satisfactory result was not obtained. Parrilli[5)] has reported that the reaction of an steroidal olefin with iodine and silver(I)oxide in aqueous dioxane affords an epoxide in good yield. When 1-(4-methoxyphenyl)-1-propene was treated according to the method, the expected product, 1-(4-methoxyphenyl)-1,2-epoxypropane was little obtained, but 2-(4-methoxyphenyl)-propionaldehyde was produced in an excellent yield via unique rearrangement (Eq.1).



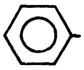
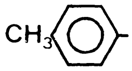
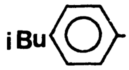
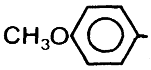
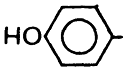
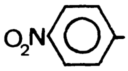
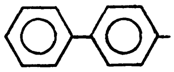
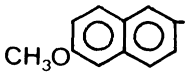
(1)

As shown in Table 1, the rearrangement is generally realized for 1-aryl-1-propenes, especially which have electron-donating groups.

Table 1. Oxidative rearrangement of 1-aryl-1-propene[a]

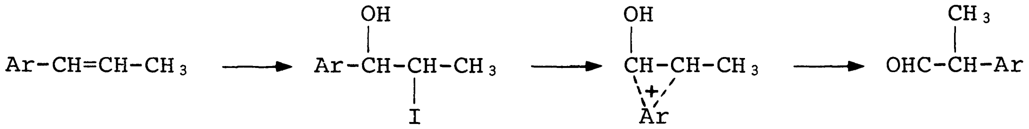


$$\text{Ar-CH=CH-CH}_3 \xrightarrow[\text{dioxane-H}_2\text{O}]{\text{I}_2,\ \text{Ag}_2\text{O}} \text{Ar-}\overset{\text{CH}_3}{\overset{|}{\text{CH}}}\text{-CHO}$$

Entry	Ar	Reaction time/h	Yield of aldehyde/%[b]
1		7	61
2		3	92
3		12	91
4		4	95
5		4	95
6		4	0
7		7	74
8		24	66[6]

a) All reactions were performed in the general procedure (vide infra).
b) Isolated yield. All these products gave satisfactory spectral data.[7]

This rearrangement may be accounted for by the 1,2-sift of aryl group through a bridged phenonium ion in the iodohydrine intermediate[8] (Eq.2). The introduction of electron-withdrawing group such as chloro, fluoro or nitro in the para-position of phenyl group extremely reduced the yields of the corresponding aldehydes, which support the mechanism.



$$\text{Ar-CH=CH-CH}_3 \longrightarrow \text{Ar-}\overset{\text{OH}}{\overset{|}{\text{CH}}}\text{-}\underset{\text{I}}{\underset{|}{\text{CH}}}\text{-CH}_3 \longrightarrow \overset{\text{OH}}{\overset{|}{\text{CH}}}\text{-CH-CH}_3 \ (\overset{+}{\text{Ar}}\ \text{bridged}) \longrightarrow \text{OHC-}\overset{\text{CH}_3}{\overset{|}{\text{CH}}}\text{-Ar} \qquad (2)$$

In order to search optimal condition, reaction of 1-(4-methoxyphenyl)-1-propene with several bases was investigated (Table 2).

Table 2. Effect of bases on the oxidative rearrangement of 1-(4-methoxyphenyl)-1-propene[a)]

Bases	Temp	Time/h	Yield/%[b)] Aldehyde	Epoxide
NaOH	reflux	2	trace	10
$Ca(OH)_2$	reflux	2	trace	5
Na_2CO_3	reflux	2	31	trace
K_2CO_3	reflux	2	22	trace
$CaCO_3$	reflux	2	85	trace
$BaCO_3$	reflux	2	75	0
Ag_2CO_3	r.t.	1	91	0
$AgNO_3$	r.t.	1	95	0
CuO	reflux	2	95	0
Cu_2O	reflux	2	86	0
MgO	reflux	2	29	2

a) Reaction conditions : olefin (1.35 mmol), Iodine (2.05 mmol), Base (4.20 mmol) in 5 : 1 dioxane-water.
b) Yield was determined by GLC (OV-101).

The silver compound such as silver carbonate or silver nitrate was found most effective. Copper oxides (I and II) showed the same effect as silver compounds.

Moreover, we examined the solvent effect on the rearrangement (Table 3). In polar solvents composed of N,N-dimethyl formamide and dimethylsulfoxide, the rearrangement also proceeded in high yields.

The general procedure is as follows. A sample of 1-aryl-1-propene (5.0 mmol) was treated with I_2 (7.8 mmol) and Ag_2O (7.8 mmol) in 5 : 1 dioxane-water (30 ml) at room temperature for several hours. The reaction mixture was filtered, and the filtrate was extracted with ether. The organic layer was washed with water (20 ml x 2), brine (20 ml x 1), and dried on magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica-gel to give the corresponding pure aldehyde.

Table 3. Effect of solvent on the rearrangement of 1-(4-methoxyphenyl)-1-propene to aldehyde[a)]

Solvent	Reaction time/h	Yield of aldehyde/%[b)]
Dioxane-H_2O (5 : 1)[c)]	3	98
DMF-H_2O (5 : 1)	3	92
DMSO-H_2O (5 : 1)	2	78
CH_3OH-H_2O (5 : 1)	3	48

a) All reaction were performed in the general procedure.
b) Yield was determined by GLC (OV-101). c) Volume ratio.

In our opinion, because of the satisfactory yield obtained and mild conditions employed, the present procedure provides a convenient one-pot synthesis of 2-arylpropionaldehyde from 1-aryl-1-propenes.

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References

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5) M. Parrilli, G. Barone, M. Adinolfi, and L. Mangoni, Tetrahedron Lett., 1976, 207.
6) This aldehyde was oxidized by chromic acid to give 2-(6-methoxy-2-naphthyl)-propionic acid in 60% overall yield from olefin. It is noteworthy that the reaction of 1-(6-methoxy-2-naphthyl)-1-propene with Tl(NO$_3$)$_3$·3H$_2$O/HClO$_4$ followed by chromic acid oxidation has been reported to give 2-(6-methoxy-2-naphthyl)-propionic acid in 30% yield.
7) Selected data for 3, 4, and 7 are as follow : 3: 'H-NMR (CDCl$_3$) : 0.90 (6H, d, J=7 Hz), 1.40 (3H, d, J=7 Hz), 1.50-2.25 (1H, m), 2.47 (2H, d, J=7 Hz), 3.60 (1H, dq, J=7 Hz, J=2 Hz), 7.10 (4H, S), 9.64 (1H, d, J=2 Hz). IR (neat) : 3420, 2960, 1735, 1525, 1475, 1030, 810 cm^{-1}. Mass (m/e) : 190, 177, 161, 119, 91. 4: 'H-NMR (CDCl$_3$) : 1.38 (3H, d, J=7 Hz), 3.53 (1H, dq, J=7 Hz, J=2 Hz), 3.74 (3H, S), 6.70-7.20 (4H, m), 9.50 (1H, d, J=2 Hz). IR (neat) : 3470, 3030, 1730, 1625, 1530, 1265, 1040, 845 cm^{-1}. Mass (m/e) : 164, 136, 105, 91, 77. 7: 'H-NMR (CDCl$_3$) : 1.47 (3H, d, J=7 Hz), 3.70 (1H, dq, J=7 Hz, J=2 Hz), 3.86 (3H, S), 6.95-7.77 (6H, m), 9.65 (1H, d, J=2 Hz). IR (KBr) : 3430, 2950, 1720, 1610, 1270, 1035, 855 cm^{-1}. Mass (m/e) : 214, 185, 141, 115. Mp 60-62 °C.
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