1,3-Iodofunctionalization of Cyclopropanes by Means of the Mercury(II) Salt-Iodine Combination

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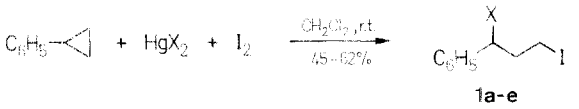
The reaction of phenylcyclopropane with iodine and various mercury(II) salts affords regiospecifically 1,3-bifunctionalized phenylpropanes following the Markownikoff rule; in the case of cyclopropyl phenyl ketone, the reaction with mercury(II) chloride-iodine leads to (3-chloro-1-iodopropyl) phenyl ketone.

Several reagent systems generating electrophilic iodine can be used for the iodofunctionalization of unsaturated compounds.[1] However, the same reaction with cyclopropane derivatives has

been seldom explored. We recently reported that the mercury(II) salt-halogen combination is an adequate reagent for the stereoselective halofunctionalization of alkenes[2] and alkynes.[3] Mercury(II) chloride-iodine has also been used for the regiospecific iodination of carbonyl compounds.[4] We have now studied the behaviour of cyclopropanes toward this combination in order to achieve a homolog of the 1,2-halogenofunctionalization of olefins.

When phenylcyclopropane was allowed to react with iodine and various mercury(II) salts, e.g., chloride, bromide, acetate, trifluoroacetate, and nitrate, in dichloromethane at room temperature 1,3-bifunctionalized phenylpropanes (**1**) were obtained (Table 1 and 2).

The ring opening takes place regiospecifically according to the Markownikoff rule and only the corresponding 1,3-addition was observed. These results contrast with those obtained in the same type of reaction carried out with silver and thallium(I) carboxylates[5] from which mixtures of several products were isolated.



1	a	b	c	d	e
X	Cl	Br	$OCOCH_3$	$OCOCF_3$	ONO_2

Attempts to achieve the bromofunctionalization of phenylcyclopropane failed and only the formation of 4-bromophenylcyclopropane was observed.[6] On the other hand, the reaction of other cyclopropane derivatives such as butylcyclopropane or norcarane with the mercury(II) salt-iodine combination gave mixtures of products. Functionalized cyclopropanes, e.g., cyclopropylmethanol or cyanocyclopropane did not react under the conditions studied by us. On the contrary, treatment of cy-

Table 1. 1,3-Iodofunctionalized Products **1** and **2** Prepared

Product	Reaction Time (h)	Yield[a] (%)	b.p. (°C)/torr	Molecular Formula[b] or Lit. b.p. (°C)/torr	MS (70 eV)[d] *m/e* (rel. int.%)
1a	15	61	92–95/0.1	$C_9H_{10}ClI$ (280.5)	282 (7, $M^+ + 2$); 280 (23, M^+); 245 (7, $M^+ - Cl$); 127 (25); 125 (40); 117 (100); 115 (27); 91 (36)
1b	8	45	110–113/0.1	$C_9H_{10}BrI$ (325.0)	
1c	16	60	128–131/0.1	135°/0.1[5]	[5]
1d	12	58	–[c]	–[5]	358 (24, M^+); 127 (22); 115 (25); 91 (30); 77 (23); 69 (41); 51 (23)
1e	6	62	130–133/0.1	$C_9H_{10}INO_3$ (307.1)	307 (4, M^+); 261 (6, $M^+ - NO_2$); 245 (3, $M^+ - NO_3$); 155 (63); 106 (38); 105 (100); 78 (28); 77 (25); 51 (32)
2	24	53	98–111/0.1	$C_{10}H_{10}ClIO$ (308.5)	272 (1, $M^+ - HCl$); 204 (1, $M^+ - C_6H_5CO$); 181 (2, $M^+ - I$); 105 (100); 77 (36)

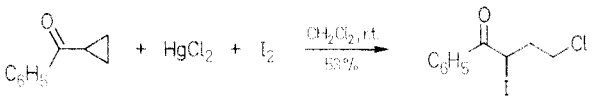
[a] Yield of isolated product, based on iodine. The unreacted cyclopropane can be recovered by distillation or column chromatography.
[b] Satisfactory microanalyses obtained (except for instable **1b**): C ±0.4, H ±0.3.
[c] R_F value: 0.58; Merck silica gel plates, mobile phase: hexane/ether (2:1).
[d] Recorded with a Hewlett-Packard 5987 spectrometer.

Table 2. Spectrometric Data of Compounds **1** and **2**

Product	IR (neat)[a] ν(cm^{-1})	^{1}H-NMR (CCl_4/TMS)[b] δ(ppm)	^{13}C-NMR (CCl_4)[c,d] δ(ppm)[e]
1a	3060, 3030, 1600, 750, 690	2.4 (m, 2H, CH_2CH), 3.1 (m, 2H, CH_2I); 4.95 (t, 1H, J = 7.5 Hz, CHCl); 7.25 (m, $5H_{arom}$)	1.8 (CI); 43.1 (CH_2CH); 62.7 (CCl); 126.8, 128.3, 128.5, 139.8 (C_{arom})
1b	3060, 3020, 1600, 1580, 1490, 750, 690	2.5 (m, 2H, CH_2CH); 3.05 (m, 2H, CH_2I); 4.8 (dd, 1H, J = 11, 9 Hz, CHBr); 7.3 (m, $5H_{arom}$)	4.1 (CI); 42.3 (CH_2CH); 54.85 (CBr); 127.1, 128.3, 128.55, 140.1 (C_{arom})
1c	1700, 1220	2.0 (s, 3H, CH_3); 2.4 (m, 2H, CH_2CH); 3.0 (m, 2H, CH_2I); 5.8 (t, 1H, J = 7.5 Hz, CHO); 7.35 (m, $5H_{arom}$)[5]	1.95 (CI); 22.0 (CH_3); 41.2 (CH_2CH); 76.6 (CHO); 127.5, 129.2, 129.7, 140.5, (C_{arom}); 170.1 (C=O)
1d	1775, 1220	2.35 (m, 2H, CH_2CH); 3.0 (m, 2H, CH_2I); 5.9 (t, 1H, J = 7.5 Hz, CHO); 7.35 (s, $5H_{arom}$)[5]	−0.6 (CI); 39.9 (CH_2CH); 81.3 (CHO); 114.4 (q, J_{CF} = 283.3 Hz, CF_3); 127.2, 129.8, 130.0, 137.6 (C_{arom}); 156.4 (q, J_{CCF} = 41.5 Hz, C=O)
1e	1625, 1225, 850	2.25 (m, 2H, CH_2CH); 3.0 (m, 2H, CH_2I); 5.85 (t, 1H, J = 7.5 Hz, CHO); 7.3 (m, $5H_{arom}$)	0.9 (CI); 38.7 (CH_2CH); 86.0 (CHO); 127.5, 130.0, 130.3, 137.6 (C_{arom})
2	1680[f]	2.5 (t, 2H, J = 7.5 Hz, CH_2CH); 3.65 (t, 2H, J = 7.5 Hz, CH_2Cl); 5.6 (t, 1H, J = 7.5 Hz, CH); 7.5, 8.0 (2m, $5H_{arom}$)	23.4 (CI); 38.1 (CH_2CH); 45.2 (CCl); 129.0, 129.4, 129.7, 134.5 (C_{arom}); 193.9 (C=O)

[a] Recorded with a Perkin-Elmer 577 spectrophotometer.
[b] Recorded on a Varian EM-390 spectrometer.
[c] Recorded on a Varian FT-80 spectrometer with a D_2O capillary.
[d] Assignment based on undecoupled NMR experiment.
[e] Refered to the solvent CCl_4.
[f] In CCl_4.

clopropyl phenyl ketone with mercury(II) chloride and iodine in dichloromethane yielded (3-chloro-1-iodopropyl) phenyl ketone **(2)** (Table 1 and 2).



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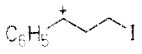
A probable mechanism for the mercury(II) salt-iodine promoted 1,3-bifunctionalization of cyclopropanes may involve an interaction between the cyclopropane ring and the activated iodine molecule ($^{\delta+}I...I...^{\delta-}HgX_2$) followed by generation of the more stable carbenium ion **3**



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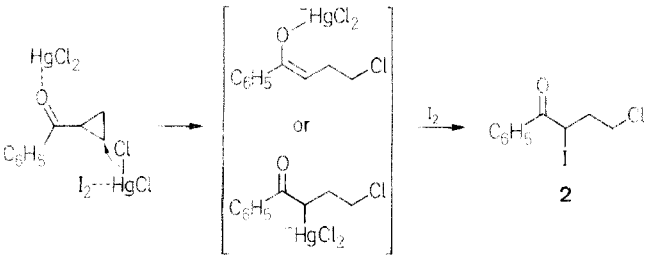
and further attack of the mercury(II) salt anion.[7] The formation of compound **2** could be explained by the following pathway:[8]



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Iodofunctionalization of Cyclopropanes; General Procedure:
To a suspension of the cyclopropane derivative (5 mmol) and the mercury(II) salt (5 mmol) in dichloromethane (20 ml) is added iodine (1.27 g, 5 mmol). The mixture is stirred (see Table 1) until no more precipitation of mercury(II) iodide is observed. The precipitate is filtered off and the filtrate washed with aqueous 0.1 molar sodium thiosulfate (10 ml) and a saturated aqueous solution of potassium iodide (10 ml). The organic layer is dried with sodium sulfate, the solvent is evaporated under reduced pressure (15 torr), and the residue is purified by distillation or by column chromatography on silica gel (see Table 1) to give compound **1** or **2**.

Dedicated to Prof. R. Usón on his 60th birthday.

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(7) This mechanism is essentially the same as those proposed for the iodofunctionalization of olefins (Lit.[2]).
(8) We thank one of the referees for the suggestion of this possible mechanism.