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CYCLOPROPYLCARBINYL COMPOUNDS FROM HOMOALLYLIC IODIDES

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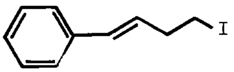
Abstract. A simple synthesis of cyclopropylcarbinyl compounds based on the reaction of homoallylic iodides with silver salts in anhydrous medium is described.

The rearrangement of homoallylic compounds into cyclopropylcarbinyl derivatives is a well known reaction which has received attention mainly in connection with the study of the homoallylic carbonium ion intermediate[1,2]. From a synthetic point of view such a reaction has found poor application probably because of the limitation due to the solvolytic procedures involved which generally require drastic conditions and give mixtures of products[3,4].

Now we wish to describe the use of silver acetate in anhydrous medium to effect this transformation in good yield. In a standard procedure the homoallylic iodide 1 (10 mM) dissolved in dry benzene (5 ml) was stirred with silver acetate (12 mM) at 25° for 30' in the dark. Silver iodide was filtered off and the solution was washed with water. Removal of benzene *in vacuo* gave cyclopropylcarbinyl acetate 2 (X = OAc) quantitatively.



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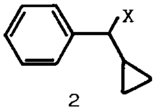
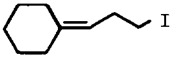
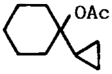
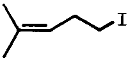
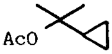
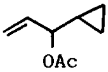
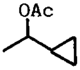
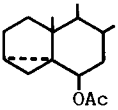
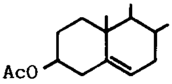
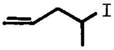


2

As exemplified in the table, γ-disubstituted or conjugated homoallylic iodides are particularly reactive and rearrange to cyclopropylcarbinyl acetates quantitatively; γ-monosubstituted compounds give mixtures of cyclopropylcarbinyl and allylcarbinyl derivatives in a 1:1 ratio whereas allylcarbinyl iodide itself eliminates to the corresponding conjugated diene.

The different degree of substitution at the γ-carbon can very reasonably be invoked to account for these results: with γ-monosubstituted compounds allylcarbinyl acetates formed may arise from a competitive SN-1 like process or alternatively, even if a cyclopropylcarbinyl cation is the only intermediate, the charge density is not sufficient to favour the nucleophilic addition only at the γ-position. With unsubstituted γ-carbon compounds a cyclic intermediate is not favoured and a direct elimination from a homoallylic cation may be expected.

The usefulness of such a reaction to obtain other cyclopropylcarbinyl derivatives was tested by treating the homoallylic iodide 1 with a variety of silver salts: the reaction was quantitative with silver acetate or benzoate; afforded cyclopropyl derivatives with

Reagents	Reac.time	Products (yields)[5]
	1.5 hr	 (98)
	1.5 hr	 (97)
	1.0 hr	 (97)
	8.0 hr	 (50)  (47)
3β-iodo-cholest-5-ene	2.0 hr	 (50)  (47)
	18.0 hr	 (92)
	18.0 hr	 (89)

a 40% of conversion with nitrate or carbonate whereas with silver methoxide gave only the conjugated diene.

It is noteworthy that by adding water (2 mol excess) to a suspension of 1 and silver nitrate in benzene, cyclopropylcarbinol could be obtained quantitatively after 3 hr: in such a case water acts as a better nucleophile than nitrate. The action of other nucleophiles onto the homoallylic iodide 1 in the presence of silver nitrate was then tested and the results are reported in the table:

	Reagents	Reac.time	Products	Yields[5]
1	H_2O	3 hr	2 (X = OH)	98
1	MeOH	3 hr	2 (X = OMe)	97
1	EtOH	3 hr	2 (X = OEt)	96
1	C_2H_5COOH	4 hr	2 (X = $OCOC_2H_5$)	97
1	C_6H_5COOH	4 hr	2 (X = $OCOC_6H_5$)	95
1	piperidine	2 hr	2 (X = piperidinyl)	80

Such a modified procedure so represents a simple route to some cyclopropylcarbinyl compounds as ethers, esters and amines which are otherwise obtainable with difficulty[6].

REFERENCES AND NOTES

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