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Triphenylbismuth Dibromide-Iodine: An Efficient Reagent for the Dehydration of Alcohols

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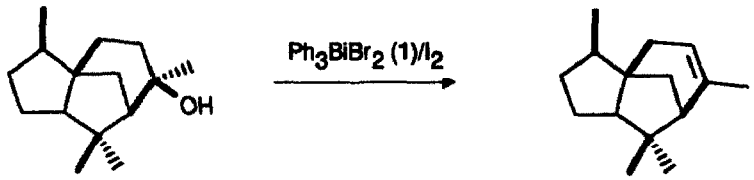
Abstract: *Tertiary and secondary alcohols react under mild conditions with triphenylbismuth dibromide and iodine under an inert atmosphere to give the corresponding most stable alkenes in good yields.*

The oxidizing capability of arylbismuth reagents[1] of the type Ar_3BiX_2 has been known for many years,[2] but the more recent developments in the application of organobismuth derivatives for the oxidation of organic substrates are due to Barton *et al.*[3]

Continuing our program of exploring new oxidizing agents[4] we examined the action of the system triphenylbismuth dibromide (**1**)[5]-iodine on alcoholic substrates to find that the elimination to the corresponding alkenes occurred exclusively (Scheme), the expected hydrogen abstraction,[4a] oxidation or fragmentation reactions[4b,c] not being observed.

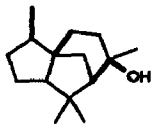
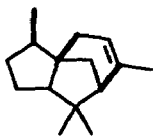
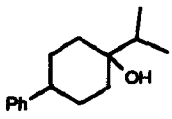
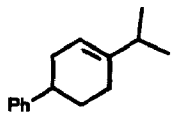
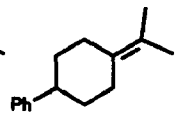
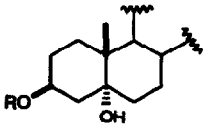
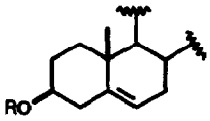
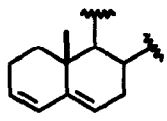
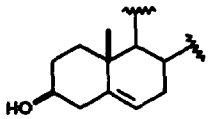
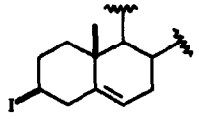
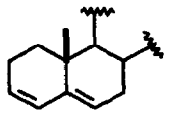
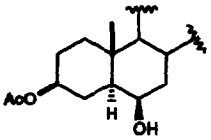
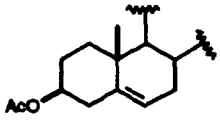
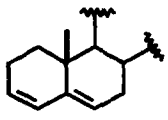
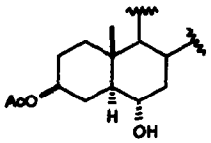


2 **4**

Scheme

Although several methods are available for the conversion of alcohols to olefins,[6] they involve the use of strong acids, high temperatures or transformation to their ester derivatives which, in some cases, preclude them for use with sensitive molecules. Hence, we report this mild and simple novel method for the direct dehydration of tertiary and secondary hydroxy compounds that avoids the two-step sequence: ester derivative formation and subsequent elimination reaction. The procedure consists in the treatment of the alcohols dissolved in cyclohexane with triphenylbismuth dibromide (**1**) and iodine at the temperatures and for the times specified in the Table. After the completion of the reaction (monitored by TLC) the mixture is filtered

Table. Dehydration of alcohols with the Ph_3BiBr_2/I_2 system.

Entry	Substrate	Reagents[a]	(mmol)[b]	Temp.(°C)	Time(h)	Products[c](%)	
							
1	2	I_2	(1.2)	25	48	no reaction	
2	2	Ph_3Bi/I_2	(1.5/1.2)	40	24	"	
3	2	Ph_2BiI (3a)	(1.0)	25	16	"	
4	2	$PhBiI_2$ (3b)	(1.2)	25	24	"	
5	2	Ph_3BiBr_2 (1)	(1.2)	25	96	4 (82)	
6	2	Ph_3BiBr_2/I_2	(1.2/1.0)	25	2	4 (87)	
							
7	5	Ph_3BiBr_2/I_2	(2.4/2.0)	45	3	6 (73)	7 (8)
							
8	8[d] R = Ac	Ph_3BiBr_2/I_2	(1.2/1.0)	45	2.5	10 R = Ac (82)	12 (15)
9	9 R = H	Ph_3BiBr_2/I_2	(1.2/1.0)	45	2.5	11 R = H (80)	12 (8)
							
10	11[d]	Ph_3BiBr_2/I_2	(1.2/1.0)	45	48	13 (22)	12 (44)
							
11	14[d]	Ph_3BiBr_2/I_2	(1.2/1.0)	40	10.5	10 (91)	12 (8)
							
12	15[d]	Ph_3BiBr_2/I_2	(1.2/1.0)	60	48	no reaction	

[a] All reactions were performed in cyclohexane. [b] Per mmol of substrate. [c] All known compounds were identified by comparison with an authentic sample. [d] Cholestane derivative.

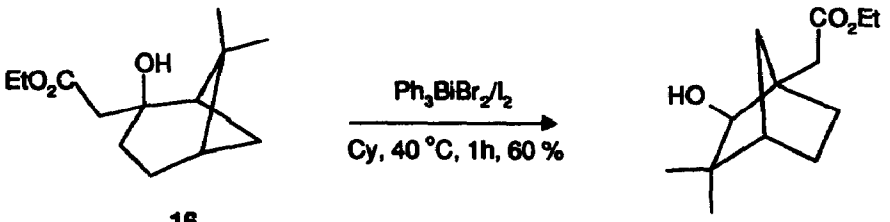
leaving a filtrate which contains the olefins and a precipitate unsoluble in cyclohexane which corresponds to an unstable bismuth derivative.[7]

The results and conditions for the dehydration of several tertiary and secondary alcohols are summarized in the Table. Thus, in examining this reaction on the sesquiterpenic alcohol (2), cedrol (entries 1-6) we determined that triphenylbismuth dibromide (1) is responsible for the alkene formation (entry 5) although the combination with iodine makes the reaction much faster (entry 6). The iodine[8] by itself, a mixture of iodine and triphenylbismuthine, yellow crystalline diphenylbismuth iodide[9] (3a) or red crystalline phenylbismuth diiodide (3b)[9b] are unable to produce any elimination to cedrene (4)[10] (entries 1-4).

The treatment of 1-isopropyl-4-phenylcyclohexanol (5) with the system Ph_3BiBr_2-iodine afforded the corresponding alkenes (6)[11] and (7) with excellent regiocontrol and in good yield (entry 7), proving to be a convenient method which compares with the BF_3-OEt_2 procedure[12] and other well-known dehydrating agents.[13] The course of this reaction was monitored by ^1H NMR isolating, after chromatography on SiO_2 impregnated in $AgNO_3$, the two alkenes in 81% overall yield in the ratio 90:10, as indicated in the Table.

The dehydration of 3β-acetoxy and 3β-hydroxy-5α-cholestane (8) and (9) afforded the corresponding alkenes (10) and (11), respectively, with similar yields to those published[14] for these tertiary alcohols. Futhermore, in both cases, we observed the formation of a diene compound (12)[15] derived from the dehydroacetylation or dehydration of the 3β-secondary functions. Thus, the secondary homoallylic alcohol (11), cholesterol, was submitted to the reaction conditions obtaining after 48 hours the dienic compound (12) (44%) resulting from the elimination of the hydroxy group, together with an iodo-compound (13) (22%) derived probably from the competitive substitution reaction.[16]

The experiment of dehydration of an *axial* secondary alcohol (14) gave satisfactorily the alkene (10) in excellent yield (91%) and a small amount of the diene (12) (8%). Nevertheless, several attempts to dehydrate the *equatorial* homolog (15) did not result in the elimination product, an *anti* disposition seeming to be required for the dehydration process to take place.



16 17

Finally, the tertiary alcohol (16), which is prone to carbocation rearrangement,[17] gave the fenchol derivative (17)[18] when exposed to the reaction conditions.

Experimental Procedure: To a solution of cedrol (2) (50 mg, 0.23 mmol) in cyclohexane (5 mL) were added triphenylbismuth dibromide (162 mg, 0.27 mmol) and iodine (58 mg, 0.23 mmol) and the mixture was stirred under an argon atmosphere for 2 hours at room temperature. The reaction mixture was then filtered to remove an unstable red precipitate which slowly turned yellow upon standing in the dark for several days, even when stored under an argon atmosphere. The filtrate was poured into aqueous thiosulfate solution and extracted with methylene chloride. Rotative chromatography of the residue with *n*-hexane gave exclusively cedrene (40 mg, 87%).

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