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ONE POT SYNTHESIS OF α-BROMO AND α-IODO KETONES FROM EPOXIDES

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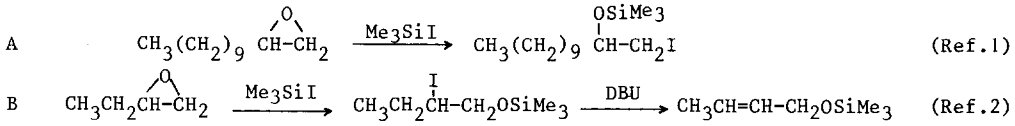
α-bromo and α-iodo ketones are obtained in good yield and in one pot by reaction of terminal and disubstituted epoxides with trimethylsilyl halides and further oxidation (CrO_3/H_2SO_4).

We have recently described [1] that disubstituted epoxides are transformed to olefins when reacted with two equivalents of iodotrimethylsilane in the presence of triethylamine. We observed [1] the intermediary formation of β-silyloxyalkyliodides when only one equivalent of trimethylsilyl iodide was used. We also showed [1] that 1-iodo-2-trimethylsilyloxydodecane was regioselectively obtained in 82% isolated yield when 1,2-oxidododecene was reacted under similar conditions [Me_3SiI : (2.2 eq), triethylamine (3 eq), CCl_4, 0°, 0.5 hr] (Scheme I.A).

Several papers [2,3] presenting the same reaction under conditions close to ours have appeared since that time. One of the authors [2] attributes a reversed ring opening in the case of terminal epoxides (Scheme I.B).

SCHEME I

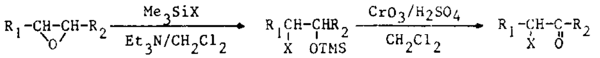


This paper discloses our results concerning the reaction of iodotrimethylsilane [Me_3SiI (1.5 eq), Et_3N (1.65 eq), CH_2Cl_2, 0°, 0.5 hr] and bromotrimethylsilane [Me_3SiBr (1.5 eq), Et_3N (1.65 eq), CH_2Cl_2, 50-55°, 2.5-3 hr] with several terminal and disubstituted epoxides 1. The resulting β-silyloxyalkylhalides 2 were on the one hand isolated and the ratio of the regioisomers carefully determined by |GC|[2] (capillary column OV1, HL, 50m, 0.5mm). On the other hand, the crude mixtures were further directly subjected to an oxidation reaction using 4 fold excess of Jones reagent [CrO_3/H_2SO_4 (4 eq), CH_2Cl_2, 0°, 0.75 hr] leading to α-halo carbonyl compounds 3 in high yield (see experimental part). Decreased yields in α-halo ketone are observed if lower amount of Jones reagent is used . This one pot procedure should be valuable for the synthesis of such derivatives.

The high yield formation of α-halo ketones instead of α-haloacids support our previous structure assignment [1].

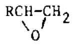
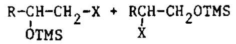
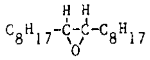
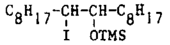
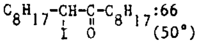
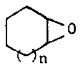
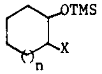
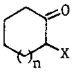
The α-bromoacid resulting from the oxidation of the minor isomer 2b has been in one instance isolated from the oxidation of the crude mixture (see the table, entry 5)[6]. Its percentage compared to the one of the α-bromo ketone reflects the ratio of the starting β-silyloxyalkylbromides. We were, however, unable to get the iodoacid from the reaction performed with

SCHEME II



1 2 3

X = Br,I
TMS = $SiMe_3$

Entry	Epoxide 1	2 ratio of regioisomers before TLC purification				Overall yield in 2	3 overall yield from 1 % (mp)
	 $RCH\text{-}CH_2$	 $R\text{-}\underset{OTMS}{CH}\text{-}CH_2\text{-}X + R\underset{X}{CH}\text{-}CH_2OTMS$					
		X	R	2a	2b		3
1		I	C_2H_5	(84)	(16)	82	63
2		I	C_4H_9	(81)	(19)	86	64
3		I	C_6H_{13}	(80)	(20)	81	71
4		I	$C_{10}H_{21}$	(80)	(20)	77	73 (50°)
5		Br	C_6H_{13}	(74)	(26)	77	72[6]
6		Br	$C_{10}H_{21}$	(80)	(20)	68	58 (40-41°)
7	 $C_8H_{17}\text{-}\overset{H}{C}\text{-}\overset{H}{C}\text{-}C_8H_{17}$ erythro	 $C_8H_{17}\text{-}\underset{I}{CH}\text{-}\underset{OTMS}{CH}\text{-}C_8H_{17}$				93	 $C_8H_{17}\text{-}\underset{I}{CH}\text{-}\underset{O}{\overset{\Vert}{C}}\text{-}C_8H_{17}$: 66 (50°)
							
	n	n	X				n X
8	1	1	I			91	1 I : 56
9	7	7	I			92	7 I : 57
10	3	3	Br			88	3 Br : 91

iodotrimethylsilane[4].

We have repeated the reaction described by Sakurai[2] under his conditions [1,2-oxidobutene (1 mmol), Me_3SiI (1 mmol), Toluene,-78°, 0.5 hr ; 20°, 1 hr]. The percentage of the regioisomers is close to the one observed when the reaction is performed under our conditions. Moreover if the reaction mixture is treated[2] with DBU, only the minor isomer, to which we have attributed the structure 2b (Table) disappears and is transformed to the silylated 2-butene-1-ol. (schemeIB).

These results and the ones disclosed above, unambiguously confirm our regiochemical assignements for 2.

References and notes

1. J.N. Denis, R. Magnane, M. Van Eenoo and A. Krief, Nouveau J. Chim., 3, 705 (1979).
2. H. Sakurai, K. Sasaki and A. Hosomi, Tet. Lett., 2329 (1980).
3. G.A. Krauss and K. Fraser, J. Org. Chem., 45, 2579 (1980).
4. A 83/17 mixture of 1-iodo-2-butanol a and 2-iodo-1-butanol b have been prepared[5] from 1,2-oxydobutene (81% yield). After purification a and b have been subjected to Jones oxidation. The β-iodo ketone was obtained in 88% yield from a. We were however unable to isolate the β-iodoacid from the other regioisomer.
5. J.W. Cornforth and D.T. Green, J.C.S. Chem. Comm. (C), 846 (1970).
6. 13% of the α-bromoacid was isolated as his ester : $nC_6H_{13}CHBrCOOCH_3$.

Experimental. *Oxidocyclooctene (Aldrich, 504 mg, 4 mmol) in CH_2Cl_2 (4 ml) is added at 20° to a solution of bromotrimethylsilane (920 mg, 6 mmol) and triethylamine (660 mg, 6.6 mmol) in CH_2Cl_2 (8 ml). The solution is heated at 55° for 2.5 hr then cooled down to 0°. Jones reagent [CrO_3 (1,6g, 16 mmol). H_2SO_4c (1.4 ml) in water (4.5 ml)] is then added and the mixture stirred for a further 0.75 hr at this temperature. After quenching with water/thiosulfate solution and usual work-up, the crude mixture is purified by TLC (SiO_2, pH-7, ether/pentane: 10/90). 2-bromo cyclooctanone 745 mg (rf : 0.42) is isolated in 91% yield.*

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