Thermal Isomerisation of 2-Alkyl-3-bromotetrahydrofurans and 2-Alkyl-3-bromotetrahydropyrans

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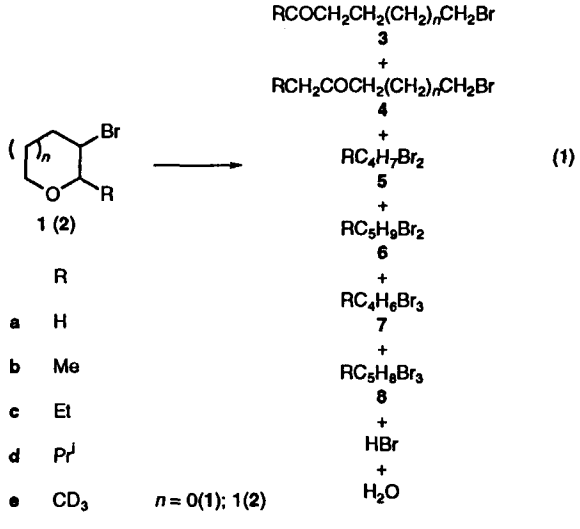
Thermal isomerisation of 2-alkyl-3-bromotetrahydrofurans and 2-alkyl-3-bromotetrahydropyrans gives γ-bromoketones.

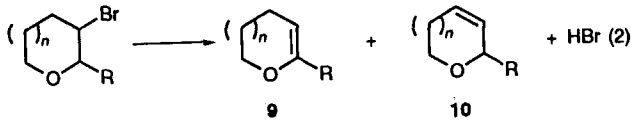
2-Alkyl-3-bromotetrahydrofurans **1** and 2-alkyl-3-bromotetrahydropyrans **2** are known to be the initial substances in the synthesis of various types of organic compounds.[1] The thermal behaviour of **1** and **2** has not yet been investigated.

Exposure of **1** at 190 °C and **2** at 200 °C in a sealed vessel in a controlled atmosphere is accompanied by isomerisation into the corresponding γ-bromoketones **3** and **4**, reaction (1).



In addition, saturated dibromides **5** and **6**, as well as tribromides **7** and **8** (in the case of **1b–d** and **2b–d**), each of which exists as an isomeric mixture, was also formed. For compounds **1a** and **1b** without alkyl substituents in the α-position, the main products appeared to be compounds **5–8**, ketones **4** being formed in small amounts. Compounds **3–8** were isolated using TLC and were identified using mass spectrometry and NMR (^1H and ^{13}C) spectroscopy.

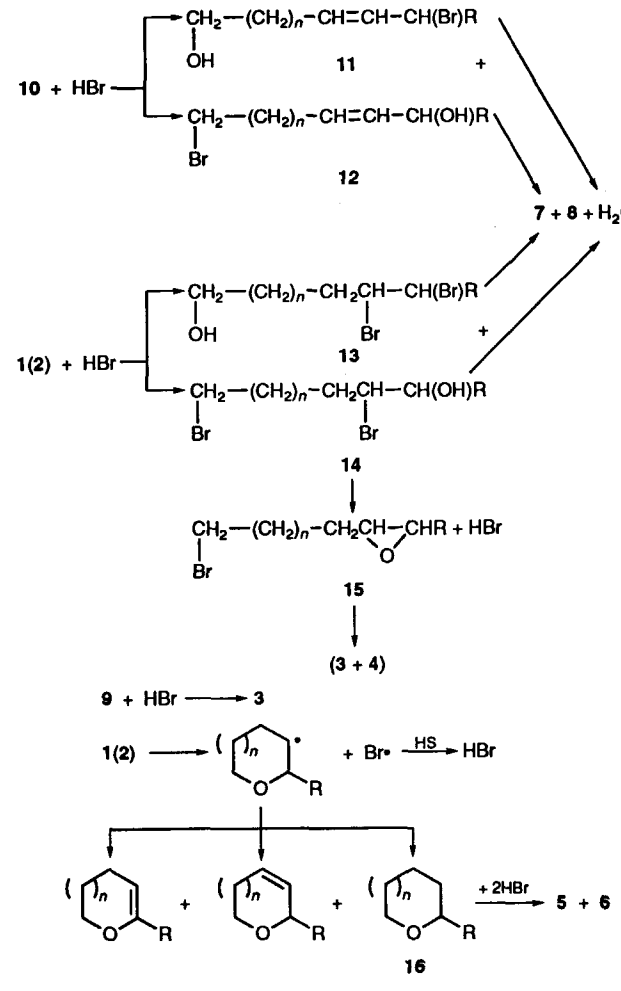
Taking into account the fact that a great amount of HBr is present among the isomerisation products we suggest that the first stage of reaction involves a dehydrobromination stage to give isomeric dihydrofurans and dihydropyrans **9** and **10**, reaction (2).



In fact, 2-isopropyl-4,5-dihydrofuran **9** and 2-isopropyl-2,5-dihydrofuran **10** were identified among the reaction products from **1d** by GC/MS.

Thus, we propose that the processes leading to the main products can be summarised in Scheme 1.

The ring in compound **10** may be split by two alternative routes, depending on the site of bromine atom attack on the heterocycle: the second and fifth positions (for **1**) or the second and sixth (for **2**) to form compounds **11** and **12**. Using GC/MS, we showed that the consecutive, unselective addition of HBr on the double bond of compounds **11** and **12** and substitution of OH group by a bromine atom leads to a mixture of diastereomeric tribromides **7** and **8** and H_2O for **1** and **2**, respectively.



Scheme 1

The initial compounds **1** and **2** may be cleaved under action of HBr also *via* two routes. In this case, compound **13** transforms into tribromides **7** and **8**, hydroxydibromide **14** (together with compounds **7** and **8**) being turned into oxirane **15**. (In the case of **1d** and **2c** the appropriate diastereomeric oxiranes formed in the reaction mixture were identified by GC/MS together with **12**).

The formation of **5** (or **6**) from **1** (or **2**) may be explained by initial debromination[3] followed by splitting of the saturated furan ring of **16** under the action of HBr.

Compounds **11** and **12**, and also dibromide **6**, were identified using GC/MS in the case of **2c**.

Table 1 Product yields for thermolysis of compounds **1a–d** and **2a–d**.

n	R	**3**	**4**	**5**	**6**	**7**	**8**
1	H	—	3	—	41	—	32
1	Me	5	57	*a*	*a*	*a*	*a*
1	Et	11	62	*a*	*a*	*a*	*a*
1	Pr^i	5	53	*a*	*a*	*a*	*a*
0	H	—	2	39	—	54	—
0	Me	71	4	*a*	*a*	*a*	*a*
0	Et	59	3	*a*	*a*	*a*	*a*
0	Pr^i	67	2	*a*	*a*	*a*	*a*

[a] In trace amounts.

At high temperatures and under the action of HBr compound **15** may isomerise into a mixture of two ketones **3** and **4**. Compound **9**, however, can also be transformed into ketone **3** after HBr action.[2]

The substitution of a methyl group by a trideuteromethyl group in **1b** and **2b** leads to the retention of label in the initial position. This is corroborated by the presence in the mass spectrum of characteristic ion peaks for **4e**: $[M]^{+\cdot}$, $[M-CD_3]^+$, $[M-CH_2CD_3]^+$, $[CD_3CH_3C(OH)=CH_2]^{+\cdot}$, and $[CD_3CH_2CO]^+$.

In conclusion, we would like to underline the fact that at high temperatures 2-alkyl-3-bromo substituted tetrahydrofurans isomerise mainly into γ-bromoketones $RCOCH_2CH_2CH_2Br$ and 2-alkyl-3-bromotetrahydropyrans into γ-bromoketones $RCH_2COCH_2CH_2CH_2Br$. This fact is of potential interest for synthetic purposes.

References

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Received: Moscow, 23rd June 1993
Cambridge, 20th October 1993; Com. 3/03699E