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Debromination Reaction of 2-Bromocarboxylic Acids

Yurii N. Polivin,*[a] Robert A. Karakhanov,[a] Bogdan I. Ugrak,[b] Vladimir G. Zaikin,[c] Sergey V. Makarshin,[a] Victor I. Kelarev[a] and Vladimir A. Vinokurov[a]

[a] *I. M. Gubkin State Academy of Oil and Gas, 117919 Moscow, Russian Federation. Fax: +7 095 135 8895*
[b] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russian Federation. Fax: +7 095 135 5328*
[c] *A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 117912 Moscow, Russian Federation. Fax: +7 095 230 2224*

2-Bromo-substituted carboxylic acids (RCHBrCOOH) undergo reductive debromination and form unsubstituted acids RCH_2COOH.

We have found recently[1] that interaction of 2-bromohexanoic acid (BHA) with acetonitrile at high temperatures gives rise to the nitrile of hexanoic acid instead of the nitrile of the initial bromoacid. The reason for such an abnormal transnitrilation has not been explained.

In this connection we thoroughly investigated the thermal behaviour of BHA itself. We showed that BHA transforms into hexanoic acid at 230 °C in 47% yield. Using GC/MS, we identified the following products in the liquid phase: n-hexanoic acid (47%), bromomethane (5%), 1-bromopentane (1%), hydrogen bromide (63%), 3-bromohexanoic acid (2%) as well as CO_2, butane, but-1-ene, pentane, pent-1-ene (ratio 33:37:18:7:5, respectively) in the gas phase, reaction (1).

$$n\text{-}C_4H_9CH(Br)COOH \xrightarrow{230\,^\circ C} CO_2 + HBr + CH_3Br + C_4H_{10} + C_4H_8 + C_5H_{12} + C_5H_{10} + n\text{-}C_5H_{11}COOH + C_3H_7CH(Br)CH_2COOH \quad (1)$$

It was shown earlier[2] that 2-chloropropionic acid thermally transformed into CO, acetaldehyde and HCl, an intimate ion-pair mechanism being proposed for this reaction.

From our point of view, the reductive debromination reaction proceeds *via* a free radical mechanism. In fact, valeraldehyde and CO are absent in the reaction mixture. We consider that the considerable amounts of CO_2 produced are the result of homolysis of BHA, the cleavage proceeding through the generation of two radicals, reaction (2).

$$C_4H_9CH(Br)COOH \longrightarrow C_4H_9\dot{C}HBr + CO_2 + H^\bullet \quad (2)$$

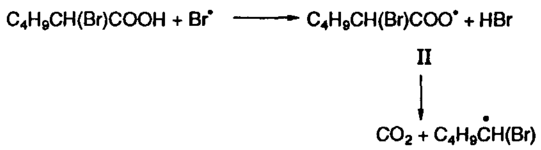
The hydrogen atom formed splits the C–Br σ-bond in the BHA molecule, giving hydrogen bromide and α-carboxypentyl radicals **I**, reaction (3).

$$C_4H_9CH(Br)COOH + H^\bullet \longrightarrow \underset{\mathbf{I}}{C_4H_9\dot{C}HCOOH} + HBr \quad (3)$$

Radical **I** may also form through initial homolysis of the C–Br bond of 2-bromohexanoic acid, reaction (4).

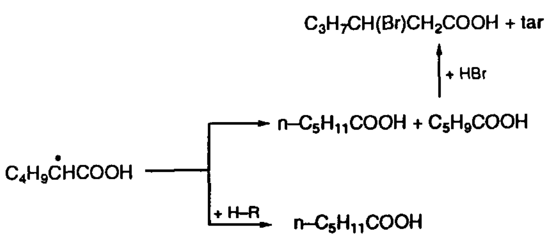
$$C_4H_9CH(Br)COOH \xrightarrow{\text{heat}} \mathbf{I} + Br^\bullet \quad (4)$$

The bromine atom then abstracts an H-atom from the carboxy group of 2-bromohexanoic acid, giving rise to hydrogen bromide and radical **II**, this being further cleaved to CO_2 and bromopentyl radical, Scheme 1.



Scheme 1

The free valency in **I** may collapse *via* two routes typical for free radicals, Scheme 2.



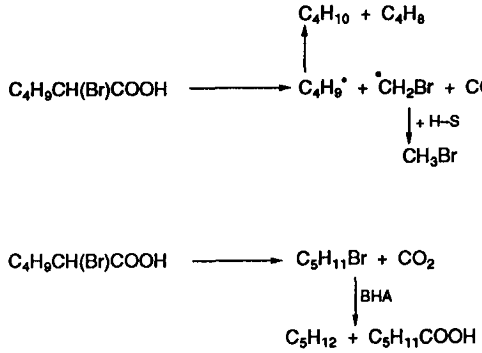
Scheme 2

Hex-2-enoic acid, formed after disproportionation of **I**, polymerises and transforms into tar and 3-bromohexanoic acid under the action of HBr.

Radical **I** can split into CO_2 and pentyl radical; the latter transforms into a pentane–pentene mixture, reaction (5).

$$C_4H_9\dot{C}HCOOH \longrightarrow CO_2 + C_4H_9\dot{C}H_2 \longrightarrow C_5H_{12} + C_5H_{10} \quad (5)$$

The cleavage of BHA probably proceeds *via* an alternative process, Scheme 3, giving rise to methylene dibromide, butane and butene.



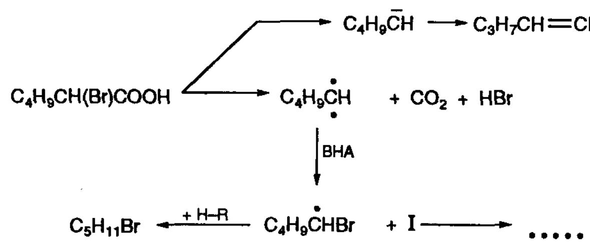
Scheme 3

The low content of pentyl bromide in the reaction mixture is due to the debrominating ability of the initial acid. For example, 1-bromodecane exposed to BHA under the same conditions leads to a considerable amount of n-decane. The hydrogen atoms formed cleave the σ–C–Br bond not only in the acid but also in the alkyl bromide, reaction (6).

$$n\text{-}C_{10}H_{21}Br + n\text{-}C_4H_9CH(Br)COOH \longrightarrow n\text{-}C_{10}H_{22}\ (47\%) + HBr + n\text{-}C_5H_{11}COOH\ (43\%) + C_{20}H_{42} \quad (6)$$

The presence of negligible amounts of eicosane in the reaction mixture indicates the free radical nature of σ–C–Br bond cleavage in the alkyl halogenide.

In addition, reductive debromination may proceed through the intermediate formation of carbenes, Scheme 4.



Scheme 4

The addition of *O*-deuteriated 2-bromohexanoic acid, obtained from the chloroanhydride of 2-bromohexanoic acid, leads to α-deuterohexanoic acid, reaction (7), in 30% yield (not higher due to the high lability of the D label).

$$C_4H_9CH(Br)COCl + D_2O \longrightarrow C_4H_9CH(Br)COOD \xrightarrow{\Delta} C_4H_9CH(H)COOH\ (70\%) + C_4H_9CH(D)COOH \quad (7)$$

The D contents was identified using a correlation of the mass of the ion peaks (*m*/*z*): 60/61.

2-Iodohexanoic acid behaves analogously to BHA, reaction (8).

$$C_4H_9CH(I)COOH \longrightarrow \underset{45\%}{C_5H_{11}COOH} \quad (8)$$

2-Chlorohexanoic acid does not undergo dechlorination under the same conditions. The initial acid regenerates practically completely after exposure at 230 °C. Hex-2-enoic acid forms in trace amounts.

We explored the ability of acids, with a bromine atom connected to a quartenary but not to a tertiary carbon atom, to undergo reductive debromination. With this aim, we exposed 2-bromo-2-methylpropionic acid under similar conditions and found that it appeared to be thermally stable. The dehydrobromination reaction proceeds only to a slight extent, reaction (9).

$$CH_3C(CH_3)BrCOOH \rightarrow CH_3C(=CH_2)COOH + \text{initial } (>90\%) + HBr \quad (9)$$

Thus, the behaviour of aliphatic carboxylic acids qualitatively changes on passing from a tertiary to a quartenary α-carbon atom. The former undergoes debromination, whereas the latter undergoes some dehydrobromination.

On the other hand, 2-bromophenylacetic acid behaves similarly to BHA, thermolysis of the former leading to phenylacetic acid, reaction (10).

$$PhCH(Br)COOH \longrightarrow \underset{47\%}{PhCH_2COOH} + HBr \quad (10)$$

2-Bromobutanoic and 2-bromopentanoic acids also debrominate at high temperatures.

The introduction of a bromine atom into the β- (or a more distant) molecular position does not result in the formation of the reduced dehalogenation product expected, the acids being dehydrohalogenated at a negligible rate. This fact was supported by the example of γ-bromobutanoic and β-bromohexanoic acids.

Thus, it may be concluded that α-bromo(iodo)carboxylic acids with a tertiary α-carbon atom are thermally unstable and undergo reductive debromination at temperatures above 200 °C. BHA may be used as an debromination agent.

References

1 V. A. Vinokurov, E. G. Gaevoi, L. A. Kuznetsova and R. A. Karakhanov, *Zh. Vses. Khim. O-va im. D. I. Mendeleeva*, 1987, **33**, 230 (in Russian).

2 G. Chuchani and S. G. Kotinov, *Int. J. Chem. Kinet.*, 1989, **21**, 367.

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Cambridge, 15th September 1993; Com. 3/04010K