Tetrahedron Letters No. 4, pp 317 - 318, 1972. Pergamon Press. Printed in Great Britain.

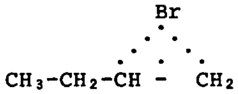
PHOTOBROMINATION OF N-BUTYL BROMIDE LABELLED WITH ^{82}BR. ON THE INTERMEDIACY OF BRIDGED BROMOALKYL RADICALS

Claude RONNEAU, Jean-Philippe SOUMILLION, Pierre DEJAIFVE and Albert BRUYLANTS
Laboratoire de Chimie Générale et Organique,96, rue de Namur,B-3000 LOUVAIN
(Belgium)

(Received in UK 11 November 1971; accepted for publication 28 December 1971)

Several authors emphasized the particular selectivity of the photobromination of bromoalkanes ($^{1-4}$) which mainly leads to the vicinal dibromide.

Two explanations of the observed results have been given. According to the first one, a bridged radical stabilizes the transition state by a delocalisation of the odd electron ($^{1-3,5-7}$).



$$\mathrm{CH_3{-}CH_2{-}CH \overset{Br}{-} CH_2}$$

An alternative explanation is proposed by TANNER et al., who showed that the relative amount of vicinal dibromide increases as the reaction proceeds(^{4}). Taking into account that the first step of the reaction is reversible, the β-bromoalkyl radical should form an olefin that subsequently adds a bromine molecule.

The present work‸tempts to find criteria of choice between the two mentioned mechanisms by using n-butyl bromide labeled with radioactive bromine. The bromination of n-butyl bromide is performed in carbon tetrachloride as a solvent, using essentially the same reaction conditions as have been used by TANNER (^{4}). The inorganic products (H-Br and Br_2) are isolated by trapping on potassium hexacyanoferrate (II) at the head (^{8}) of the chromatographic column. The results of a typical experiments are given below.

The following table is especially significant when the activity of the inorganic species is considered : this fraction only contains 3% of the total activity; this low yield is maintained even when the reaction is allowed to proceed to large extents.

A second series of experiments aimed to determine the location of radioactive

RADIOACTIVITY REGISTERED AFTER PHOTOBROMINATION OF LABELED n-BUTYL BROMIDE

Temperature : 20° C - Reaction mixture : 20 µl $C_4H_9Br^*$ + 5 µl Br_2 + 20 µl CCl_4

	Inorg.species	C_4H_9Br	1,1-dibromo	1,2-	1,3-	Tribromo	(†)
Activity(*)	13563	269064	4295	108164	21736	20169	4491
(%)	3	60	1	25	5	5	1

(†)*Activity of products retained between peaks.* (*) *In counts per minute.*

bromine in the 1,2 dibromobutane obtained. The latter is dehydrobrominated on solid sodium hydroxyde and the activity in the produced 1- and 2- bromobutenes is measured;the activity is distributed as follows:10% as 2-bromo- and 90% as 1-bromobutene.

To conclude ,the particular selectivity of the reaction cannot be justified by the decomposition of the β-bromoalkyl radicals into free olefin and bromine atoms. On the contrary,it is possibly explained by a lowering of the activation energy of the reaction,due to a stabilisation of the transition state by bridging the intermediate radical.However,the bridged radical is not a sufficient explanation: while in agreement with the observed rearrangement and high selectivity,it does not explain the results obtained by TANNER(4).Furthermore,even if the reaction includes a bridged radical,the extent of the rearrangement must be low.However,a recent paper makes it possible to reconcile our findings with a modified mechanism proposed by TANNER(9).

---

(1) P.S.JUNEJA,E.M.HODNETT,J.Am.Chem.Soc.,1967,89,5685.

(2) P.S.SKELL et alii,J.Am.Chem.Soc.,1961,83,504;1963,85,2849,2850;1964,86,3334.

(3) W.THALER,J.Am.Chem.Soc.,1963,85,2607.

(4) D.D.TANNER,D.D.DARWISH,M.W.MOSHER,N.J.BUNCE,J.Am.Chem.Soc.,1969,91,7398.

(5) P.I.ABELL,L.H.PIETTE,J.Am.Chem.Soc.,1962,84,916.

(6)J.G.TRAYNAM,W.G.HINES,J.Am.Chem.Soc.,1968,90,5208.

(7) G.A.RUSSEL et alii,J.Am.Chem.Soc.,1963,85,2983,2988.

(8) C.RONNEAU et alii,Radiochem.Radioanal.Letters,1971,7,1,67.

(9) D.D.TANNER et alii,J.Am.Chem.Soc.,1971,93,4802,5846.