

PROTONATED CYCLOPROPANE INTERMEDIATES IN THE REACTION OF CYCLOPROPANE
WITH TRITIATED SULFURIC ACID OR WITH TRITIATED LUCAS REAGENT*

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In 1964, Baird and Aboderin (1) reported that solvolysis of cyclopropane in 8.4 M D_2SO_4 gave 1-propanol and 1-propyl hydrogen sulfate and after the hydrolysis of the latter, the combined sample of 1-propanol showed 0.38, 0.17 and 0.46 D atoms, respectively, at the C-1, C-2, and C-3 positions. More recently, however, Deno (2, 3) has reported that reaction of cyclopropane with D_2SO_4 of various concentrations gave 1-propyl hydrogen sulfate with the deuterium atoms equally distributed in all the three carbon positions. As there is considerable current interest in protonated cyclopropanes as reaction intermediates (see, for example, ref. 4), it was thought to be worthwhile to attempt to resolve the discrepancy between the observations of Baird and Deno by reinvestigating the problem using H_2SO_4-t . In addition, the reaction between cyclopropane and tritiated Lucas reagent was studied since this reaction might also proceed via protonated cyclopropane intermediates.

Purified cyclopropane (1) was bubbled through 40 ml. of 9.2 M or 13.8 M H_2SO_4-t for 3 hr. at room temperature. The 1-propanol was then recovered, with the aid of added inactive carrier, either before or after the reaction mixture was heated at $50 \pm 2^\circ C$ for 30 hr. to hydrolyze the 1-propyl hydrogen sulfate (1). The samples of 1-propanol obtained from the various runs were degraded to give the t -distributions by procedures previously described (4). In the present work, however, the radioactivity of the 1-propanol was assayed as its 3,5-dinitrobenzoate (corrected for quenching) instead of the previously used α -naphthylurethan (4) in order to prevent the incorporation of any t -activity from the hydroxyl group into the derivative. The results are summarized in Table I.

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TABLE I

t-Distributions in the 1-Propyl Products from Reactions of Cyclopropane with Tritiated Sulfuric Acid or with Tritiated Lucas Reagent

Reaction Conditions	<u>t</u> -Distribution, %								
	C-1			C-2			C-3		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
I. 9.2 M H_2SO_4 - <u>t</u> 1- $C_3H_7HSO_4$ not hydrolyzed ^a	36.5	36.8	-	27.8	26.0	-	35.7	37.2	-
II. 9.2 M H_2SO_4 - <u>t</u> 1- $C_3H_7HSO_4$ hydrolyzed ^b	37.6	37.1	-	25.9	24.8	-	36.5	38.1	-
III. 13.8 M H_2SO_4 - <u>t</u> 1- $C_3H_7HSO_4$ not hydrolyzed ^a	37.8	36.2	-	26.0	27.5	-	36.2	36.3	-
IV. 13.8 M H_2SO_4 - <u>t</u> 1- $C_3H_7HSO_4$ hydrolyzed ^{b, c}	41.0	40.0	-	26.0	26.3	-	33.0	33.7	-
V. $ZnCl_2$ in 12 M HCl - <u>t</u>	38.6	37.2	37.7	16.6	19.7	18.8	44.7	43.1	43.5

^aThe reaction mixture was not heated. ^bThe reaction mixture was heated at $50 \pm 2^\circ C$ for 30 hr to hydrolyze any 1-propyl hydrogen sulfate. ^cUnder these conditions, some 2-propanol was also obtained.

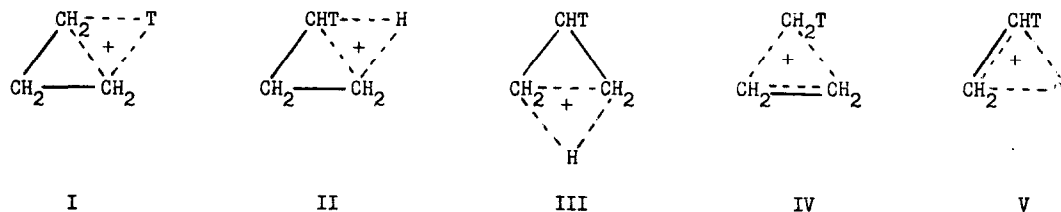
In the studies with tritiated Lucas reagent, purified cyclopropane was bubbled through 40.8 g. (0.3 mole) of $ZnCl_2$ in 25 ml. (0.3 mole) of 12 M HCl -t for 24 hr. at room temperature. The product, found by v.p.c. analysis to be solely 1-chloropropane with no 2-chloropropane, was swept out by the excess cyclopropane and collected in cold traps containing inactive 1-chloropropane as carrier. This removal of the product as it is formed minimized any possible isotopic rearrangements that might result from prolonged contact between the Lucas reagent and 1-chloropropane (5). The 1-chloropropane obtained in these experiments was converted to the Grignard reagent, treated with oxygen to give 1-propanol and then the latter was degraded the usual way (4) to give the t-distribution. The results are also given in Table I.

Under reaction conditions I, II, III or V (Table I), there was no H-T exchange between the 1-propyl product and the tritiated acidic reagent. Under reaction conditions IV, a more complex situation resulted because the 1-propanol originally formed undergoes further reactions

during the subsequent heating of the reaction mixture. After ordinary 1-propanol was heated in 13.8 M H_2SO_4-t at $50 \pm 2^\circ C$ for 30 hr., about 30% recovery of a mixture of 1-propanol and 2-propanol was obtained, and of this mixture, only about one-third was 1-propanol. The recovered 2-propanol showed an extraordinarily high specific activity, obviously derived from exchange with H_2SO_4-t . This finding is in agreement with that of Deno (3b), who found that between 2-propyl hydrogen sulfate and concentrated D_2SO_4 , H-D exchange takes place rapidly at C-1 and C-3 and more slowly at C-2. The 1-propanol recovered from such experiments also showed small amounts of t -activity, but whether this was due to exchange or to slight contaminations by 2-propanol has not been definitely ascertained.

When 1- t -1-propanol ($CH_3CH_2CHO + LiAlH_4-t$) was heated in ordinary 13.8 M H_2SO_4 at $50 \pm 2^\circ C$ for 30 hr. and the resulting 1-propanol and 2-propanol were recovered, the 2-propanol showed a considerable loss of activity, again indicating exchange with the H_2SO_4 . In the recovered 1-propanol, a total of about 5-7% of the isotopic label was rearranged from C-1, and distributed approximately equally at C-2 and C-3. Thus the small differences in overall t -distributions obtained from experiments under reaction conditions IV compared to those from reaction conditions I - III were likely due to changes in the 1-propanol that took place during the subsequent heating of the reaction mixture.

The data in Table I clearly show that in the reactions studied, the 1-propyl products contain isotopic label in all three carbon positions, with the smallest amount of the label located at C-2.* These results could be explained, as originally suggested by Baird and Aboderin (1), in terms of product formation from equilibrating edge-protonated cyclopropanes I, II and III, with the equilibration probably proceeding via methyl-bridged ions IV and V.



* The t -distributions obtained under reaction conditions I - III (Table I), which were free from subsequent changes in the 1-propanol, are somewhat different from the d -distribution reported by Baird and Aboderin (1). This difference, if significant, might be explicable in terms of a difference in H-T and H-D isotope effects, since D or T shifts will give the equivalent of I which only leads to a product labeled at C-3.

The low isotopic concentration at C-2 was observed because formation of the C-2-labeled product from III would require more extensive equilibrations (1, 4). The inequality of t-distribution over the three carbon positions also eliminated symmetrical face-protonated cyclopropane as reaction intermediate. Furthermore, product formation arising solely from equilibrating methyl-bridged ions IV and V without involving edge-protonated species would not be adequate since such a mechanism could not provide for an explanation of the presence of the smallest amount of label at C-2.

References

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