STEREOCHEMISTRY OF THE KOCHI REACTION

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(Received in USA 27 January 1971; received in UK for publication 15 February 1971)

Formation of alkyl halides from carboxylic acids by decarboxylation with lead tetraacetate and halide salt has been described by Kochi.^{2,3} The method of Kochi,^{2,3} particularly useful for chlorodecarboxylation, has been reported to be highly successful in the synthesis of primary,^{2,3} secondary,²⁻⁷ and tertiary^{6,8,9} alkyl chlorides.¹⁰ A free radical chain mechanism was proposed for the reaction.^{2,3} We wish to report on the stereochemistry of the

$$R-COOH + Pb^{IV}(OAc)_4 + LiC1 \xrightarrow{80^\circ, \emptyset H} R-C1 + CO_2 + Pb^{II}(OAc)_2 + HOAc + LiOAc$$

products of the reaction.

Upon chlorodecarboxylation at 80° by the method of Kochi,^{2,3} <u>cis</u>- and <u>trans</u>-4-<u>t</u>-butylcyclohexanecarboxylic acid (1 and 2) each give the same product composition: 67% <u>cis</u>- and 33% <u>trans</u>-4-<u>t</u>-butylcyclohexyl chloride (3 and 4, respectively). The results are like those reported for the reaction of 4-<u>t</u>-butylcyclohexyl radical with chlorine donors.^{14,15} For example dimethyl(<u>cis</u>- or <u>trans</u>-4-<u>t</u>-butylcyclohexyl)carbinyl hypochlorite (5 or 6) at 80° in carbon tetrachloride decomposes to give the same product composition: 67% of 3 and 33% of 4.¹⁴



Similarly, either <u>cis</u>- or <u>trans</u>-4-<u>t</u>-butylcyclohexylmercuric chloride ($\frac{7}{2}$ or $\frac{8}{2}$) gives with sulfuryl chloride at 46° a 70:30 <u>cis</u>:<u>trans</u> distribution.¹⁵ Therefore the stereochemical outcome



of the Kochi reaction of 1 and 2 and is consistent with a mechanism involving a 4- \underline{t} -butylcyclohexyl free radical intermediate, as proposed.^{2,3,16}

Note added: We thank Prof. F. D. Greene for mentioning the article of P. D. Bartlett, <u>et al.</u>, <u>Accounts Chem. Res.</u>, 3, 177 (1970), which reports stereoselectivity of norbornyl and apobornyl radicals with various chlorine donors, and includes product ratios for two Kochi reactions. <u>Acknowledgement</u>: We wish to thank the National Science Foundation, the Research Corporation, and an anonymous donor for support of this work.

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- 16. As stated by Kochi, "t-Butylacetic acid yields neopentyl chloride, and cyclobutanecarboxylic acid affords cyclobutyl chloride in high yields. Products of rearrangement characteristic of carbonium ions are not evident."³ The reaction "is strongly inhibited by oxygen."² Steric effects upon halogen transfer to a cyclohexyl free radical have been discussed in detail.¹⁵