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COMPARATIVE ALKYL TRIFLATE SYNTHESIS WITH MONO- AND DIBROMO-ALKANES

S. A. Shackelford*

European Office of Aerospace Research and Development, Box 14, FPO New York, NY 09510 (U.S.A.)

R. D. Chapman, J. L. Andreshak, S. P. Herrlinger

Air Force Rocket Propulsion Laboratory, Edwards AFB, CA (U.S.A.)

R. A. Hildreth and J. C. Smith

Frank J. Seiler Research Laboratory, USAF Academy, CO (U.S.A.)

When reacted with the silver triflate reagent, lower α , ω -dibromoalkanes in the 1, 2-dibromoethane homologous series display a unique reaction stability and product selectivity over their higher homologues and corresponding primary monobromoalkanes. Often monobromoalkanes and α , ω -dibromoalkanes greater than 1,4-dibromobutane undergo alkylation in benzene solvent and polymerize in CCl_4 ; but the lower 1,2- through 1,4-dibromoalkanes produce desired monobromotriflate and ditriflate products. These same lower α , ω -dibromoalkanes also resist product

$$Br-(CH_2)_n-Br + xAgOTf \longrightarrow TfO-(CH_2)_n-Br + TfO-(CH_2)_n-OTf + xAgBr \downarrow$$

rearrangement to 2°-triflate products while the higher homologues and 1°-monobromoalkanes do not. The 1,2- through 1,4-dibromoalkanes potentially offer a selective synthesis route to key difunctional derivatives through sequential metathesis. The unique stability and selectivity of the lower homologues are best explained by bromonium ion anchimeric assistance in the first metathesis step followed by a rare example of cyclic triflate group anchimeric stabilization. This subject reaction offers distinct synthetic advantages but is very susceptible to several reaction parameters. These parameters and the potential synthetic advantages of this reaction system will be discussed.

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