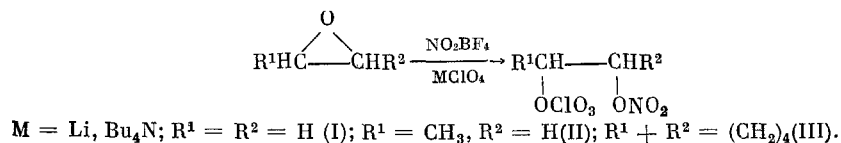


A NEW REACTION OF α -EPOXIDES: RING OPENING
WITH THE FORMATION OF NITRATOPERCHLORATES

N. S. Zefirov, A. S. Koz'min,
N. M. Yur'eva, V. V. Zhdankin,
and V. N. Kirin

UDC 542.97:547.422

The direction of the ring opening of α -epoxides catalyzed by protic acids is affected by the addition of perchlorate salts [1-3]. In a study of tricyclodecane α -epoxides, we found that lithium perchlorate may act as a reagent leading to the formation of covalent perchlorates [4]. In the present communication, we report a new reaction involving the ring opening of epoxides by nitronium tetrafluoroboride in the presence of perchlorate salts. The study was carried out on the α -epoxides of ethylene, propylene, and cyclohexene which were treated with a twofold excess of NO_2BF_4 and LiClO_4 or Bu_4NClO_4 in either ethyl acetate or methylene chloride at 0-25°C. In all cases, chromatography of the reaction mixture gave the corresponding nitratoperchlorates (I)-(III) in 60-90% yield. These products are stable at 25°C but decompose explosively upon heating above 100°C.



The structures of (I)-(III) were shown by PMR and IR spectroscopy as well as by chemical transformations. In the case of propylene oxide, isomeric 1-perchloryloxy-2-propyl nitrate is formed in 30% yield as indicated by PMR spectroscopy in addition to (II) (obtained in 60% yield). The ring opening of cyclohexene oxide proceeds with steric specificity to yield the product with trans configuration.

This is a new reaction of α -epoxides and serves as a convenient, efficient, and safe method for the preparation of a new class of compounds, namely, vicinal nitratoperchlorates.

LITERATURE CITED

1. Y. Pocker and B. P. Ronald, J. Am. Chem. Soc., 102, 5311 (1980).
2. C. Battistini, P. Crotti, M. Ferretti, and F. Macchia, J. Org. Chem., 42, 4067 (1977).
3. P. Costantino, P. Crotti, M. Ferretti, and F. Macchia, J. Org. Chem., 47, 2917 (1982).
4. N. S. Zefirov, A. S. Koz'min, N. M. Yur'eva, V. V. Zhdankin, and V. N. Kirin, Zh. Org. Khim., 18, 2211 (1982).