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THALLIUM NITRATE AS A REAGENT FOR THE CONVERSION OF EPOXIDES INTO α-HYDROXY-NITRATE ESTERS AND FOR THE CLEAVAGE OF ALIPHATIC ETHERS*

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SUMMARY - Simple as well as steroidal oxiranes are converted into the corresponding α-hydroxy nitrate esters by treatment with $Tl(NO_3)_3$ in hexane solution. Moreover aliphatic ethers react with $Tl(NO_3)_3$ in acetic anhydride via cleavage of the ethereal bond and formation of the corresponding acetoxy derivatives.

The efficient and versatile reactivity of thallium(III) nitrate with ketones and alkenes is well known (1). We reported that this salt is also able to react with weakly nucleophilic functional groups such as epoxides and aliphatic ethers. In fact, simple as well steroidal oxiranes are converted at room temperature, in acetic acid or hexane solution, on treatment with a molar equivalent of $Tl(NO_3)_3$, into the corresponding α-hydroxy nitrate esters (Table 1). In a similar way, aliphatic ethers, in acetic anhydride solution, undergoe cleavage of the ethereal bond with the formation of the corresponding acetoxy derivatives.

TABLE 1. Reaction of epoxides and aliphatic ethers with $Tl(NO_3)_3$

Starting materials	solvent	Products, yield %	
cyclohexene oxide I	acetic acid	cyclohexanediol mononitrate ester II (62)	cyclohexanediol monoacetate III (30)
	hexane	II (76)	
styrene oxide IV	acetic acid	1-phenyl-2-hydroxy-1-ethyl nitrate V (40)	1-phenyl-2-hydroxy-1-ethyl acetate VI (44)
	hexane	V (65)	
2α,3α-cholestane oxide VII	acetic acid	3α-hydroxy-5α-cholestan-2β-yl nitrate VIII (57)	3α-hydroxy-5α-cholestan-2β-yl acetate IX (21)
	methanol	3α-hydroxy-5α-cholestan-2β-yl methyl ether X (76)	
	hexane	VIII (80)	
3β-acetoxy-5α,6α-cholestane oxide XI	acetic acid	3β-acetoxy-5α-hydroxy-cholestan-6β-yl nitrate XII (75)	5α-hydroxy-3β,6β-diacetoxy cholestane XIII (21)
	hexane	XII (81)	
3β-acetoxy-5β,6β-cholestane oxide XIV	acetic acid	3β-acetoxy-6β-hydroxy-cholestan-5α-yl nitrate XV (25)	6β-hydroxy-3β,5α-diacetoxy cholestane XVI (57)
	hexane	XV (68)	

3β-methoxy-cholestane	acetic anhydride	3ξ-acetoxy-cholestane (91)
2-methoxy-trans-decalin	"	2-acetoxy-trans-decalin (68)
dibutyl ether	"	butyl acetate (57)
tetrahydrofuran	"	4-acetoxybutan-1-ol (62)

As regards the stereochemical course of the oxirane ring opening in the steroidal compounds (VII) (XI) (XIV), the formation of the trans diol mononitrate, as expected, is observed.

The nitrate esters are partly transesterified in the reaction medium to the corresponding acetoxy derivatives, with retention of configuration. This acetolysis is complete if the reaction temperature is raised to 80-100°C. Moreover, by examination of solvent effects on the reaction course we conclude that in hexane solution the reaction proceeds to give the best yields of nitrate esters (Table 1), although with a slower conversion rate, while in methanol solution the formation of monomethoxy diols such as (X) is observed. As regards the influence of the salt anion on the effectiveness of the reaction, by utilising a thallium salt with a less electronegative anion, such as the thallium (III) acetate, the opening reaction proceeds very slowly and in low yield (20%). Hydroxy nitrate esters appear to be very unstable and reactive compounds; in order to isolate them, by the initially reported method (2), very mild and convenient conditions are necessary.

As to the effectiveness on the ethereal linkage, while no reaction is observed by thallium nitrate in acetic acid, also after prolonged warming of the ethereal solution at 50-80°C, a effective breaking of the aliphatic ethereal bond takes place even at room temperature in acetic anhydride solution by a molar excess of $Tl(NO_3)_3$, with subsequent formation of the corresponding acetoxy derivatives (Table 1.) This is a useful and promising result if we consider the severe conditions required for the cleavage of the ethereal linkage.

NOTES AND BIBLIOGRAPHY

1. A. McKillop and E.C. Taylor, Endeavour, 88-93 (1976).
2. Formation of α-nitratoketones from the reaction of enolisables ketones with $Tl(NO_3)_3$ (3) and formation of nitrate esters from reaction of alkenes with $Tl(NO_3)_3$ (4) has been reported recently.
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