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TRANSFORMATION OF AN EPOXIDE INTO A 1,2-DIBROMOALKANE BY A DIOXODIBROMOMOLYBDENUM(VI) COMPLEX

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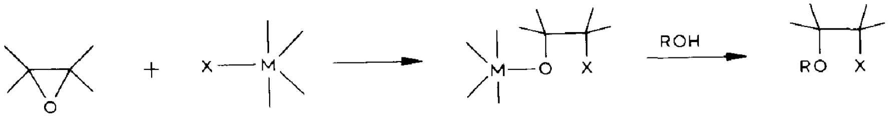
Summary

Dioxodibromomolybdenum(VI) when complexed with acetonitrile reacts with cyclohexane oxide in a 2/1 ratio to give 1,2-dibromocyclohexane. This novel bromination reaction probably proceeds by an initial oxirane ring opening to give the β-bromoalkoxide, which then reacts with a second molecule of molybdenumdibromide to give the 1,2-dibromoalkane.

Epoxides are known to react with various transition metal halides to give β-haloalkoxides, which upon hydrolysis or alcoholysis yield the corresponding halohydrins or β-haloethers [1–3] (eq. 1).

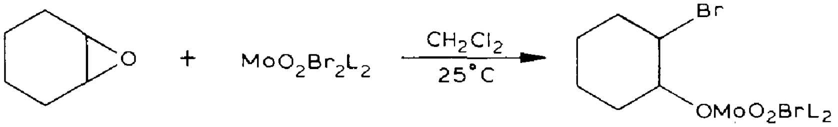


(1)

(R = alkyl, H)

We now report the reaction of a dibromomolybdenum compound under mild conditions which introduces two bromine atoms into the epoxide, to give a 1,2-dibromoalkane.

When various dibromodioxomolybdenum complexes, $MoO_2Br_2L_2$ are treated with cyclohexene oxide in CH_2Cl_2 immediate reaction occurs, as evidenced by the complete disappearance of the epoxide to give the expected β-bromoalkoxide (eq. 2).



(2)

(L = DMSO, DMF, $OPPh_3$, bipyridine, CH_3CN)

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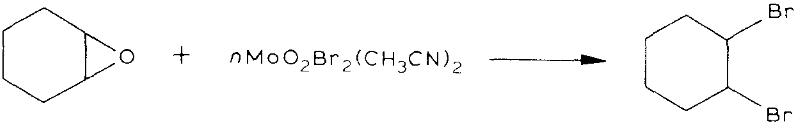
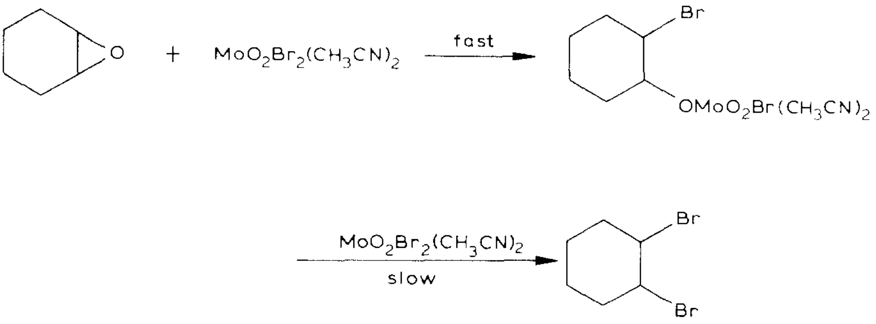
The use of excess $MoO_2Br_2L_2$ had no effect on the reaction except when the ligand was acetonitrile; in that case the reaction proceeded differently to give 1,2-dibromocyclohexane and an unidentified, probably polymeric, molybdenum oxide [4], as in eq. 3.



(3)

When acetonitrile was replaced by benzonitrile analogous results were obtained. This special behaviour shown by nitrile compounds can be attributed to the fact that these ligands are sufficiently labile while keeping their ligating ability [8]. The non-occurrence of reaction 3 with the other ligands used was due probably to their strong ligating character, which makes their displacement difficult. Support for this was provided by the observation that use of a suspension of MoO_2Br_2 in CH_2Cl_2 leads to ready formation of 1,2-dibromocyclohexane.

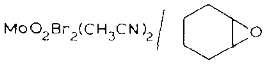
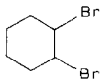
The absence of 1,2-dibromoalkane when a 1/1 ratio of epoxide to $MoO_2Br_2(CH_3CN)_2$ was used indicates that the formation of alkoxide is fast compared to its transformation to 1,2-dibromoalkane. This second step apparently requires the presence of at least one additional mol of molybdenum dibromide, as shown by the results given in Table 1.



(4)

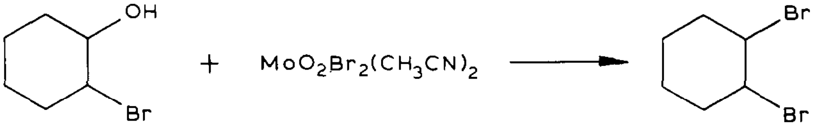
TABLE 1

REACTION OF CYCLOHEXENE OXIDE WITH $MoO_2Br_2(CH_3CN)_2$ [a]

 Mol ratio	 Yield (%) [b]
1	0
2	35
3	60
4	70

[a] Solvent: CH_3CN or CH_2Cl_2, Temp. 25°C, 6 h. [b] Yields by gas chromatography with an internal standard.

Support for this proposal was provided by the observation that 2-bromocyclohexanol reacted under identical reaction conditions with various amounts of $MoO_2Br_2(CH_3CN)_2$ to give 1,2-dibromocyclohexane [9].



(5)

1	1	40 %
1	2	75 %
1	3	90 %

Most reported deoxygenation reactions of epoxides [10–12] were brought about by low valent transition metal species, and can be accounted for in terms of a redox process in which the metal is oxidized. Our results suggest that the driving force for the reaction is not a formal oxidation of the metal but the formation of a new molybdenum–oxygen bond.

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