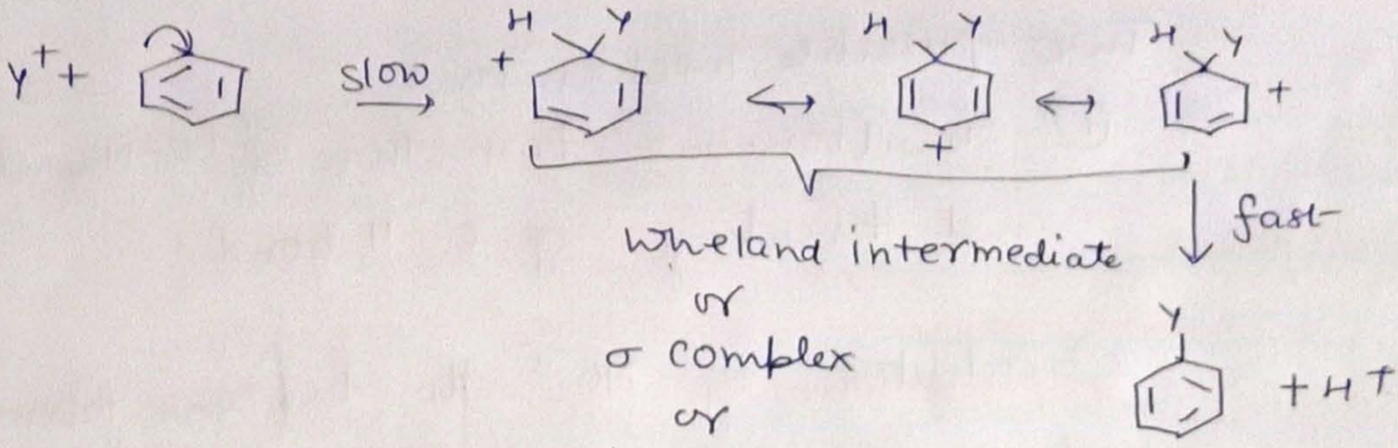
AROMATIC ELECTROPHILIC SUBSTITUTION

(Part-I)

Aromatic electrophilic substitution



Wheland intermediate
or
σ complex
or
benzenonium cation

→ Resonance hybrid of the intermediate

Nitration

$$HO-NO_2 + H_2SO_4 \overset{fast}{\rightleftharpoons} HSO_4^- + H_2\overset{+}{O}-NO_2$$

$$\upharpoonleft\!\downharpoonright \text{slow}$$

$$H_3O^+ + HSO_4^- \overset{H_2SO_4}{\rightleftharpoons} NO_2^+ + H_2O$$

The overall equation

$$HNO_3 + 2\,H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

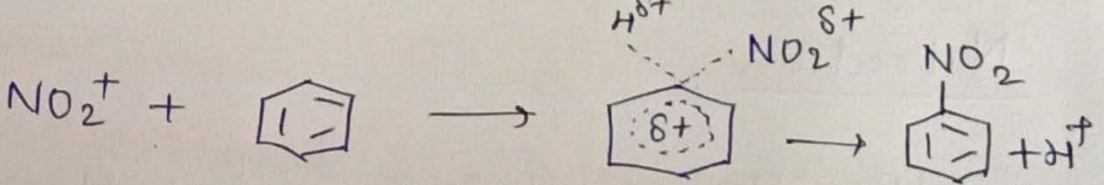
Rate = K [substrate] $[NO_2^+]$

Two possible mechanisms:

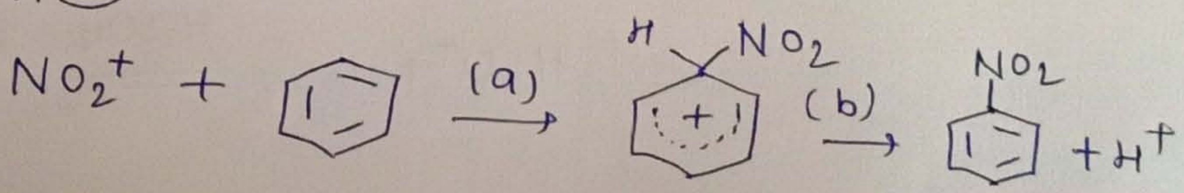
① Simultaneous formation of C–N bond and breaking of C–H bond

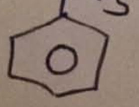
② addition of NO_2^+ to benzene followed by expulsion of a H^+. In this either ~~may be~~ addition of NO_2^+ or expulsion of H^+ may be r.d.s.

mechanism ①



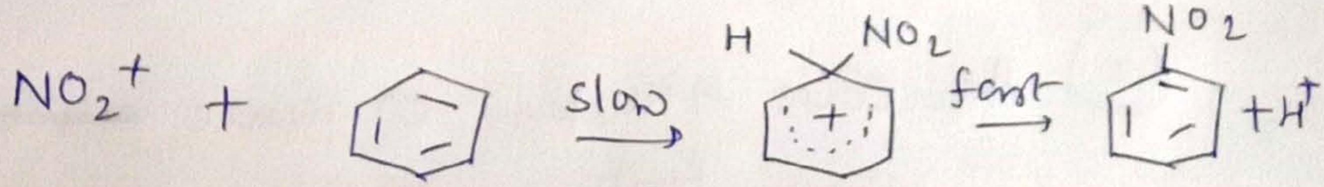
mechanism ②

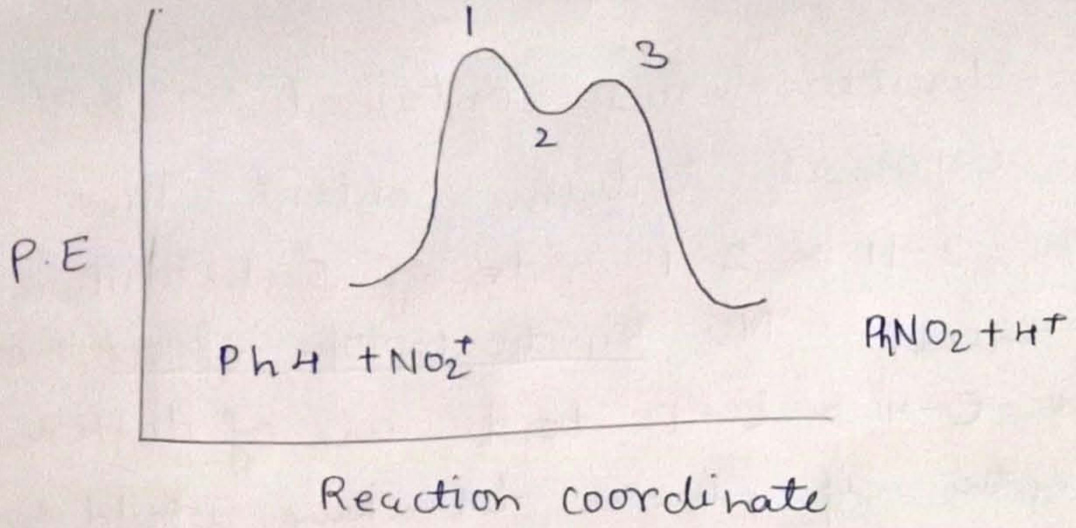


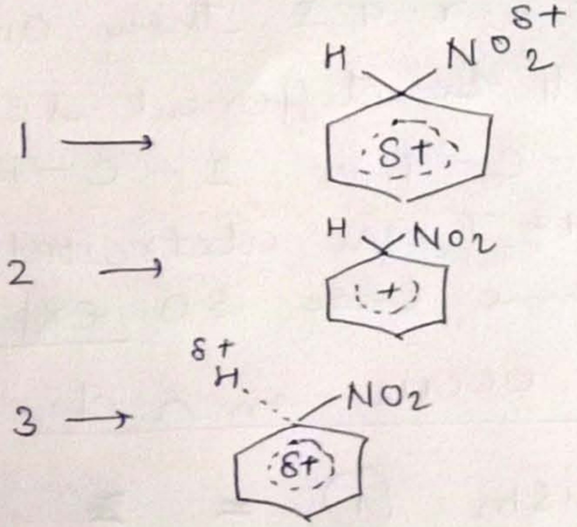
To establish the actual mechanism  containing a tritium instead of H in 2-position showed that the product

2,4 - dinitrotoluenes contained 50% of the original tritium content. Thus both 2-H & 2-T rate of substitution is equal. No Kinetic isotope effect means (since C-H & C-T bonds are of different strength if there breaking would be involved in the r.d.s then amount of products will be different ie those containing 2-C-T or 2-C-H.) Since both H & T are abstracted by same amount & same ease so expulsion of H^+ does not occur in r.d.s as a result mechanism ① & 3 is ruled out. & for mechanism 2 step a is r.d.s.

So the final mechanism is







Nitration can be done with

① mixed acids conc. HNO_3 + conc. H_2SO_4

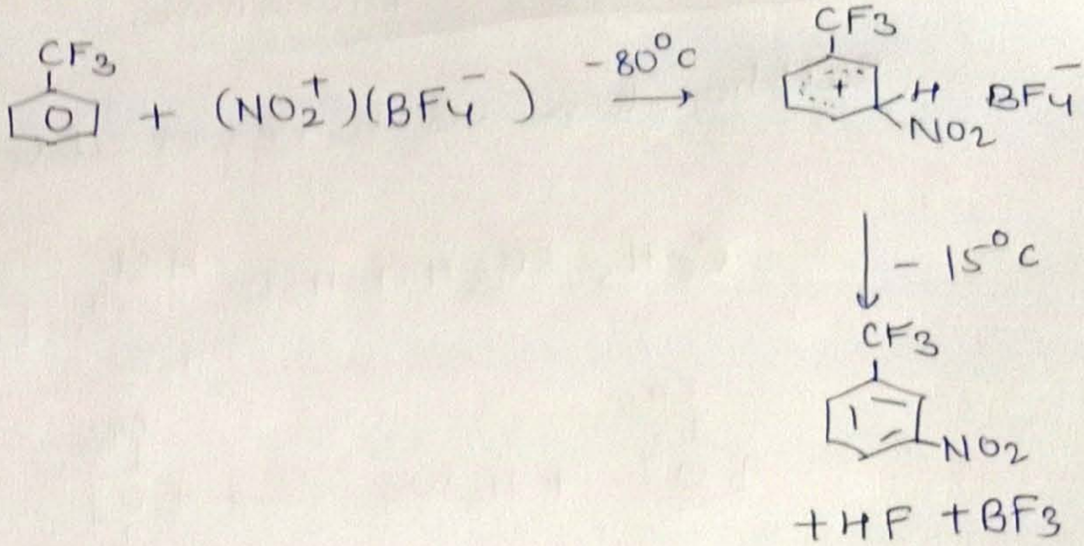
② Aqueous HNO_3 in organic ~~acid~~ solvents

$$2HNO_3 \xrightleftharpoons{fast} H_2O^+-NO_2 + NO_3^- \xrightleftharpoons{slow} NO_2^+ + H_2O$$

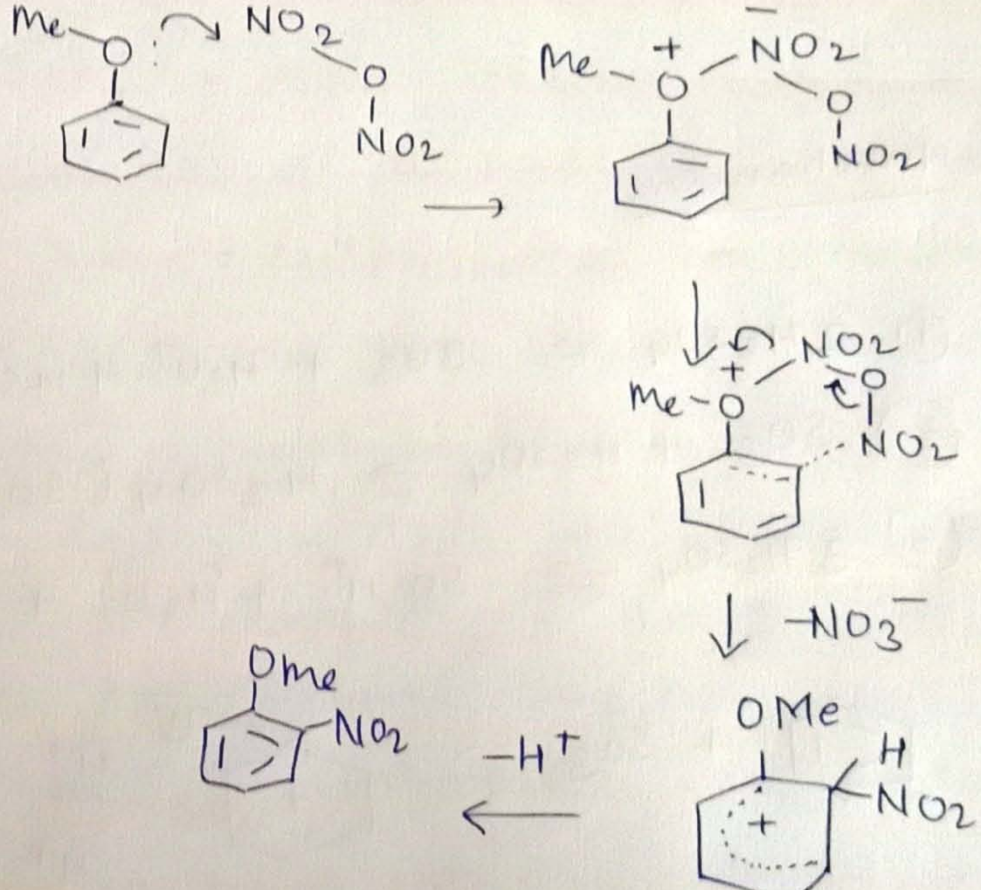
③ In dilute HNO_3

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^-$$

④

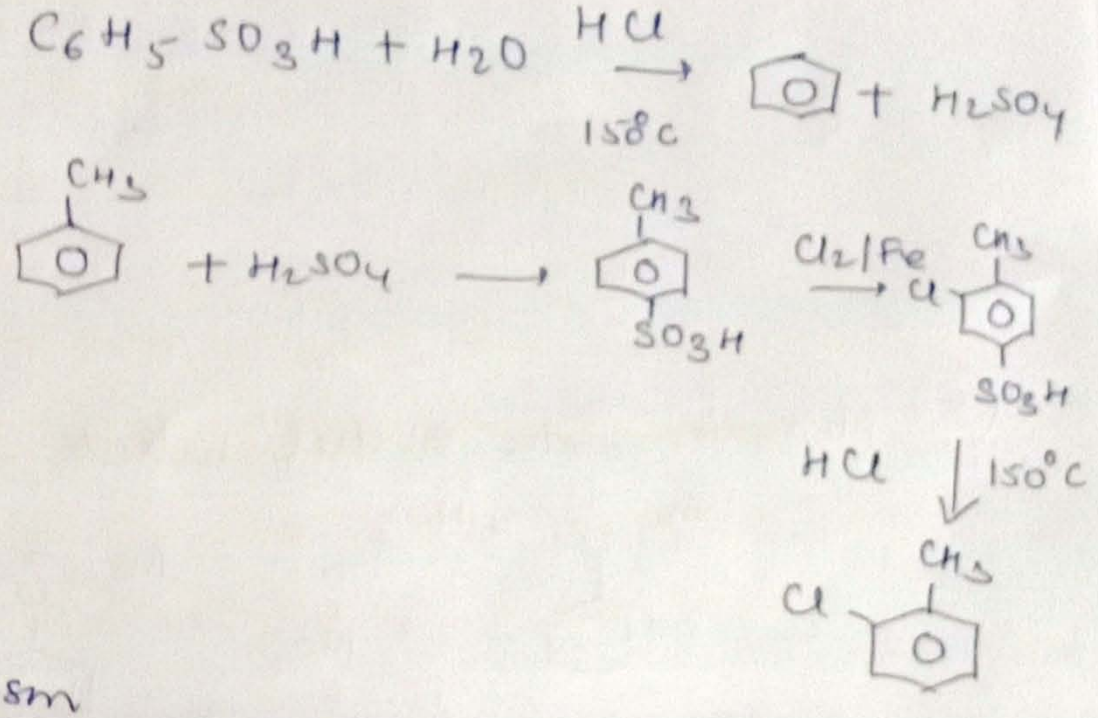


⑤ Nitration with acetyl nitrate



mechanism of sulphonation

Sulphonation is a reversible reaction.

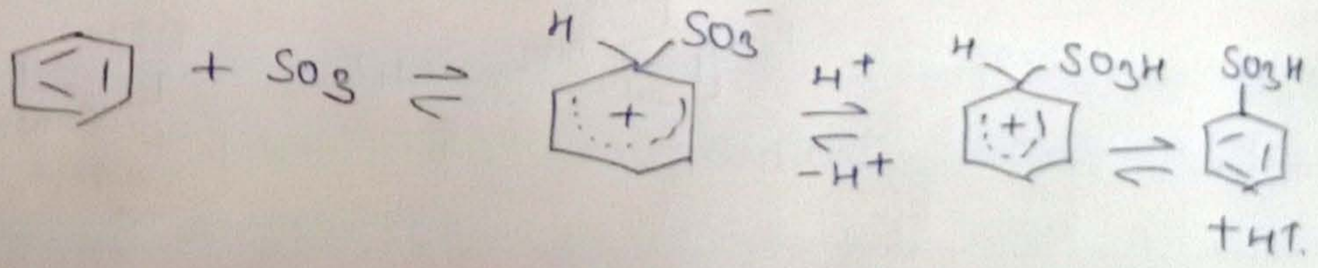


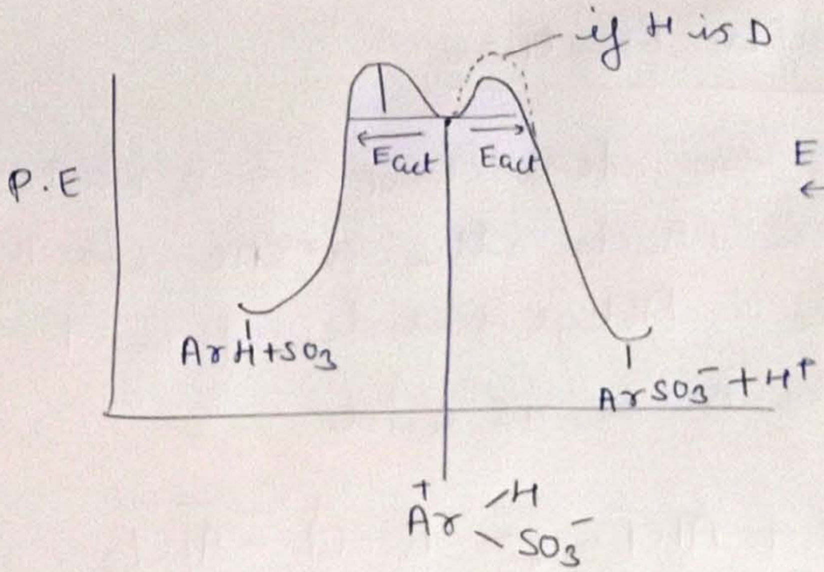
mechanism

① $2H_2SO_4 \rightleftharpoons SO_3 + H_3O^+ + HSO_4^-$

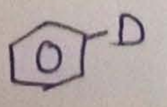
② $SO_3 + H_2SO_4 \rightleftharpoons H_2SO_4(SO_3)$ or $H_2S_2O_7$

③ $3H_2SO_4 \rightleftharpoons SO_3H^+ + H_3O^+ + 2HSO_4^-$

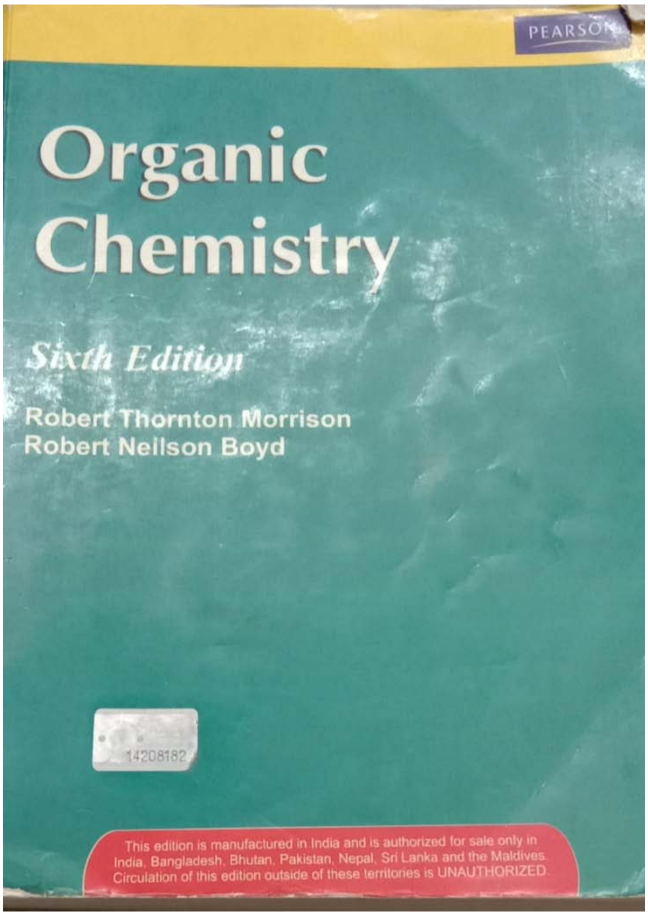




$\overleftarrow{E_{act}} \sim \overrightarrow{E_{act}}$

If H & D both are there
Products some $\overset{+}{Ar}{<}^{H}_{SO_3^-}$ or
$\overset{+}{Ar}{<}^{D}_{SO_3^-}$ & some original compound.
Sulphonation shows a moderate isotope effect. Since sulphonation is a reversible reaction Eact on both sides of the carbo-cation $\overset{+}{Ar}{<}^{H}_{SO_3^-}$ must be roughly the same so both $ArSO_3^-$ & ArH are formed. But when H is replaced by D reaction Eact to go to the forward direction is higher ~~than~~ for $\overset{+}{Ar}{<}^{D}_{SO_3^-}$ carbocation as compared to $\overset{+}{Ar}{<}^{H}_{SO_3^-}$. So more starting deuterated benzene & ∴ overall sulfonation is slower for .

References and suggested further reading



PEARSON

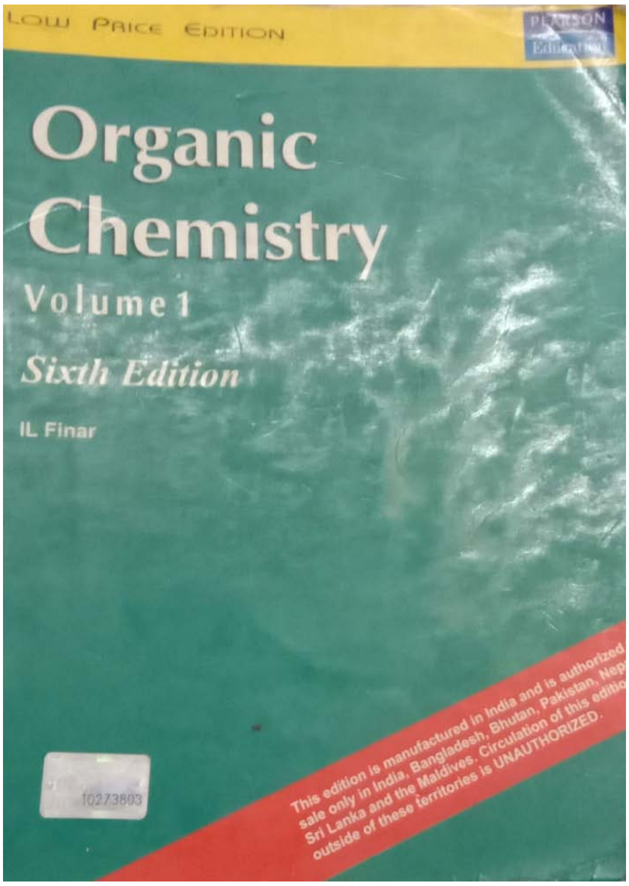
Organic Chemistry

Sixth Edition

Robert Thornton Morrison
Robert Neilson Boyd

14208182

This edition is manufactured in India and is authorized for sale only in India, Bangladesh, Bhutan, Pakistan, Nepal, Sri Lanka and the Maldives. Circulation of this edition outside of these territories is UNAUTHORIZED.



LOW PRICE EDITION

PEARSON Education

Organic Chemistry

Volume 1

Sixth Edition

IL Finar

10273803

This edition is manufactured in India and is authorized for sale only in India, Bangladesh, Bhutan, Pakistan, Nep Sri Lanka and the Maldives. Circulation of this editio outside of these territories is UNAUTHORIZED.