Tetrahedron Letters No.47, pp. 5921-5923, 1966. Pergamon Press Ltd.
Printed in Great Britain.

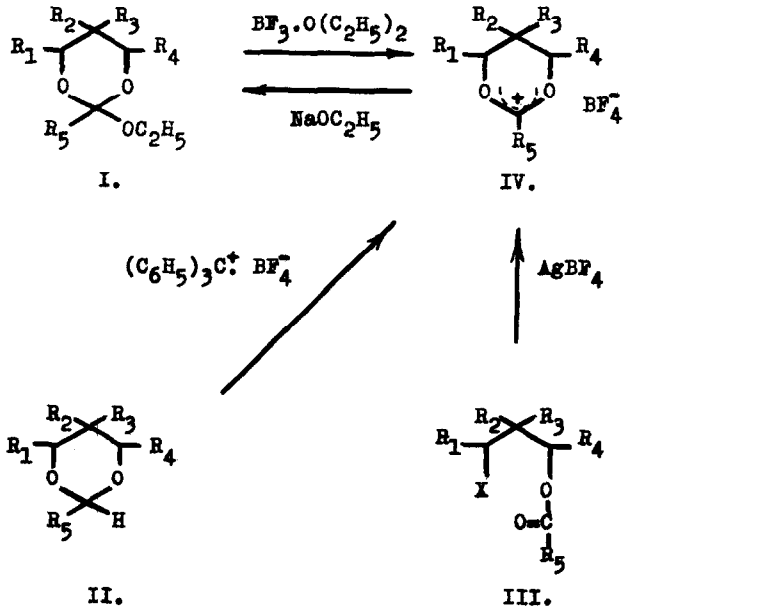
SYNTHESIS OF SUBSTITUTED 1,3-DIOXENIUM SALTS.

Gy.Schneider
Institute of Organic Chemistry
József Attila University
Szeged, Hungary

(Received 16 September 1966)

Previously we had proved both in a preparative way and kinetically (1) that the solvolysis of cis-2-toluene-p-sulphonyloxymethylcyclohexyl acetate and of trans-2-acetoxymethylcyclohexyl p-tosylate yielded cis-2-methyl-1,3-dioxadecalene-1-ium cation as the intermediary product. Recently, on basis of the results published on the preparation and investigation of the corresponding 1,3-dioxolenium salt (2), we succeeded in isolating the tetrafluoroborate salt of cis-2-methyl-1,3-dioxadecalene-1-ium cation in three ways (3).

Considering the difference in reactivity between cis- and trans-1,3-dioxolane and 1,3- dioxane systems anellated to the cyclohexane skeleton, we extended our investigations, in a way analogous to researches made with aliphatic 1,2-diols (4), to various substituted propan-1,3-diol derivatives.



I. IV. II. III.

X = Cl, Br, $H_3C.C_6H_4.SO_2O$, $Br.C_6H_4.SO_2O$,

R_1, R_2, R_3, R_4 = H, CH_3, C_2H_5, C_3H_7, C_4H_9,

R_5 = CH_3, C_6H_5

It was found that the variously substituted cyclic 2-methyl-2-ethoxy- and 2-phenyl-2-ethoxy-1,3-dioxanes (I.) yielded dioxenium salts (IV.) with boron trifluoride etherate in a reversible way, whilst the 2-methyl and 2-phenyldioxanes (II.) gave the corresponding salts with triphenylmethyl fluoroborate in yields

depending on the substituent. The open-chain 1,3-propanediol halogeneacetates and halogenebenzoates, as well as their tosylates and brosylates (III.) also afforded the corresponding dioxenium fluoroborates (IV.) with silver fluoroborate.

Concerning the tendency for dioxenium salt formation, we found that in case of pre-formed cyclic compounds (I. and II.) the dioxenium salt (IV.) was obtained in highes yield with $R_1=R_4=$ H and $R_2=R_3$. In case of open-chain derivatives(III.) the corresponding cyclic dioxenium salt (III.)was yielded in the best yield when $R_2=R_3=$ H.

REFERENCES

1. Ö.K.J.Kovács, Gy.Schneider, L.K.Láng, Proc.Chem.Soc., 1963, 374.
2. C.A.Anderson, E.C.Friedrich, S.Winstein, Tetrahedron Letters, 29,2037,(1963).
3. Gy.Schneider, Ö.K.J.Kovács, Chem.Comm. 10,202,(1965).
4. H.Meerwein, K.Bodenbrenner, P.Borner, K.Kunert, K.Wunderlich, Ann. 632,38,(1960).