

THE OXIDATION OF ACENAPHTHYLENE WITH LEAD TETRAACETATE IN VARIOUS SOLVENTS

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In a preceding paper⁽¹⁾ we described the reaction of anthracene with lead tetraacetate in various solvents. Here we report the oxidation of acenaphthylene with the same reagent. The results are shown in the table. The unknown compounds (III-VI) were prepared from the corresponding diols (VII) and (VIII)⁽²⁾ by complete methylation or by monomethylation and acetylation.

The data shown in the table indicate that the presence of methanol in the solvent mixture favours the formation of mono- and dimethoxylated species where the trans isomer is the most abundant, in accord with the results of anthracene. In this case it can be thought that the electrophilic attack of a Pb^{IV} methoxylated species (i.e. Pb(OAc)₂(OMe)₂) occurs preferentially with a concerted mechanism leading to the intermediate (XI) having a cis stereochemistry. The nucleophilic S_N2 attack at the carbon bearing the lead atom gives then (II) and (IV).

In contrast with anthracene, acenaphthylene gives preference to the trans isomer even in the formation of the diacetoxo derivatives. This can be explained by postulating the production of (XII) and (XIII) through a positive charge intermediate as the first reaction step. The S_N2 attack of an acetate ion to the carbon bearing the lead atom in (XII) leads to the trans diacetoxo compound (II). An S_N1 mechanism in the splitting of this bond in the case of (XIII) gives a cyclic acetoxonium ion (XIV) which affords (II) by a trans opening reaction.

REFERENCES

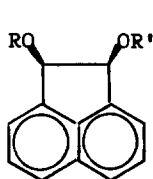
- 1) B. Rindone and C. Scolastico, J. Chem. Soc. (C), 3983, (1971).
- 2) L. D. Hayward and I. G. Csizmadia, Tetrahedron, 19, 2111, (1963).

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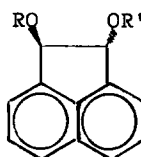
Compound	I	II	III	IV	V	VI	Reac. time	Reac. temp.
ϕ H	18*	82			**		48 h	reflux
MeOH		10	13	56		21	2 h	"
ϕ H-MeOH 1:1	5	19	7	54		15	2 h 30'	"
ϕ H-MeOH 15:2	6	34	16	24		23	6 h 30'	"
CHCl_3	31	69					50 h	"

* Values calculated by quantitative GLC and NMR measurements. Accuracy: $\pm 3\%$

** Values below the accuracy of the determination method.



I R = Ac R' = Ac
 III R = Me R' = Me
 V R = Me R' = Ac
 VII R = H R' = H
 IX R = H R' = Me



II R = Ac R' = Ac
 IV R = Me R' = Me
 VI R = Me R' = Ac
 VIII R = H R' = H
 X R = H R' = Me

