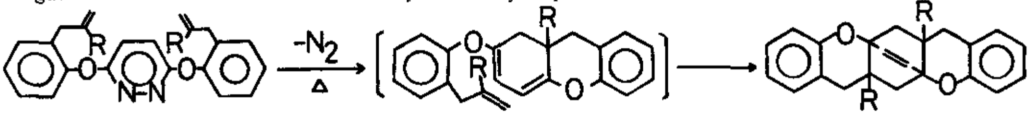
DOUBLE INTRAMOLECULAR CYCLOADDITION OF 3,6-BIS(2-ALLYLPHENOXY)PYRIDAZINES.

Hideo Takeshiba, Takao Kinoto and Teruomi Jojima

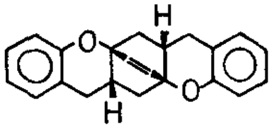
Agricultural Chemicals Research Laboratory, Sankyo Co., Ltd.

During the studies on the synthesis of 2-allylphenoxypyridazines as herbicides, we found that 3,6-bis(2-allylphenoxy)pyridazines (1) gave rise to novel ring-fused heterocycles,5a,12a-etheno-6H,6aH,7H,13H,13aH,14H-[1]benzopyrano[2,3-b]xanthenes (3) on heating. These compounds (3) were formed by the intramolecular cycloaddition of initially formed 2-(2-allylphenoxy)1,9a-dihydroxanthenes (2) which were also formed by the cyclization of the starting material (1), followed by nitrogen gas elimination in the manner as previously reported.[1), 2)]

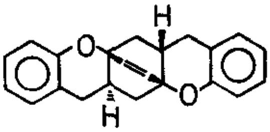


1 2 3a,b (R=H, CH_3)

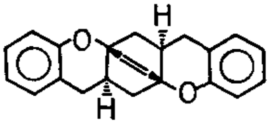
These compounds (3) have four asymmetric carbon atoms. But, considering the cis-orientation of the etheno bridge and the molecular symmetry, possible numbers of diastereoisomers of 3 are only three. The proton configuration of these isomers 3a (R=H) at 6a and 13a positions is β-β (s_1), α-β (q) and α-α (s_2), respectively as shown. Among them, two diastereoisomers; q and s_2, were actually separated by the column chromatography.



s_1 (β-β)



q (α-β)



s_2 (α-α)

1 : 19 : 13

The formation ratio of three diastereoisomers of 3a (R=H) was s_1:q:s_2 = 1:19:13, while the corresponding value for 3b (R=CH_3) was 11:22:1.

The detailed physical data and a plausible mechanism of the formation of these diastereoisomers will be discussed.

Lit. 1) Teruomi Jojima, Hideo Takeshiba and Takao Kinoto, Chem. Pharm. Bull. 20, 2191 (1972).

2) Teruomi Jojima, Hideo Takeshiba and Takao Kinoto, Chem. Pharm. Bull. 24, 1581 (1976).