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A NOVEL TYPE OF INTRAMOLECULAR DIELS-ALDER REACTION IN THE FURAN SERIES [x)]

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RECENTLY [1] an interesting example of intramolecular Diels-Alder reaction in the furan series, observed in experiments with 5,5'-ethylene-1,2-di-(2-furyl)-ethane [2], a (furano) heterocyclophane, has been reported.

In our work on tertiary furfurylamines [xx)] it was found that some allyl-aryl-(2-furfuryl)-amines, on standing at room temperature, spontaneously isomerized to hitherto undescribed

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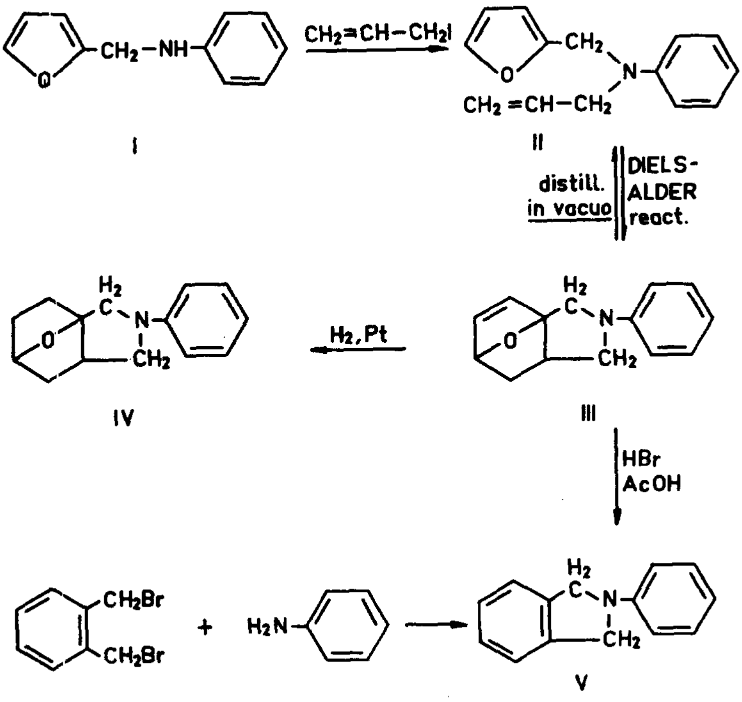
[x)] Studies in the Furan Series.VI. Part V, Ž.Stojanac and V.Hahn, Croat.Chem.Acta, 34, 237 (1962).

[xx)] Described in detail in the Doctor's Thesis of D.Bilović, University of Zagreb, 1963.

N-aryl-4H-5,7a-epoxyisoindolines, evidently formed by intramolecular Diels-Alder reaction.

When (2-furfuryl)-aniline (I) [3], b.p. 150-153°/14 mm, was allowed to react with allyl iodide and the resulting crystalline hydriodide of II, m.p. 88-89° (Anal. Found: C 49.47 ; H 4.83. Calc'd for $C_{14}H_{15}NO.HI$: C 49.28 ; H 4.73.) treated with sodium hydroxide, oily allyl-(2-furfuryl)-aniline (II),

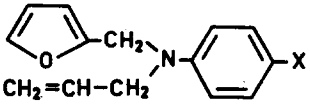


b.p. 165-168°/13 mm, n_D^{20} 1.5757, (Picrate, m.p. 109-110°), was obtained in a 51 % yield. On standing, the oily amine (II) soon began to crystallize and within a few days it transformed completely to a solid mass, melting at 114-119°. After recrystallization from ethanol pure N-phenyl-4H-5,7a-epoxyisoindoline (III), m.p. 120-121° (Anal. Found: C 78.60 ; H 6.91 ; N 6.65. Calc'd for $C_{14}H_{15}NO$: C 78.84 ; H 7.09 ; N 6.57.) could be obtained. The picrate of III melted at 145°(decomp.).

The isomerization of II to III proved to be reversible. When III was subjected to distillation in vacuo, oily II was obtained again, its IR spectrum being identical with the spectrum of the product (II) first obtained and different from the spectrum of III ; it showed in every respect the same properties as described before.

The structure of III could be established unequivocally by the following facts: a) Catalytic hydrogenation of III over Pt led to uptake of one mole of hydrogen and the formation of N-phenyl-5,7a-epoxyperhydroisoindole (IV), m.p. 84-85° (Anal. Found: C 78.15 ; H 7.82 ; N 6.64. Calc'd for $C_{14}H_{17}NO$: C 78.10 ; H 7.96 ; N 6.51.).- b) By heating the mixture of III with a solution of hydrobromic acid in glacial acetic acid at 60° for 2 hours, N-phenylisoindoline (V) could be obtained in a good yield. After several recrystallizations it melted at 171-172° and proved to be identical with an authentical sample, prepared from α,α'-dibromo-o-xylene and aniline [4] (m.p.172-173°). The IR spectra of both samples were superimposable and the mixed melting point showed no depression.

N-allyl-N-(2-furfuryl)-p-toluidine (VI), b.p. 178-181°/13 mm, and N-allyl-N-(2-furfuryl)-p-anisidine (VII), b.p. 192-194°/13 mm, oily bases prepared in an analogous way



VI: X = CH_3; VII: X = OCH_3

as II, showed the same behaviour and the same reactions as described for II. However, the time needed for solidification of VI was sensibly longer than in the case of II and VII.

Further studies in the reported field are in course.

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