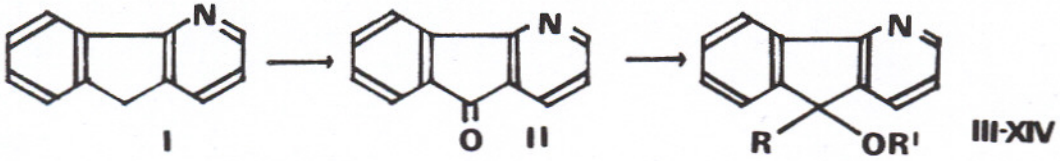
SYNTHESIS OF 9-ARYL(ARALKYL)-4-AZAFLUORENOLS-9 AND DERIVATIVES

G. Alvarado U., G. Quiroz G., R. García M.

Facultad de Ciencias Químicas e Industriales, División de Estudios Superiores, Universidad Autónoma del Estado de Morelos, Cuernavaca, Morelos, México.

Azafluorenes still remain a little studied group of compounds and information in the literature is limited. They are of definite interest, for among them have been found quite effective physiologically active substances with sedative, neuroleptic and adrenolitic activity. (Neth. Patent 6.500.312,(1966)).

Recently we described a convenient synthesis for 4-azafluorene (I) by dehydrocyclisation of 3-methyl-4-phenylpyridine in the vapour phase. (Khim. Geterotsikl. Soed. 124 (1977)). This finding suggested to us to continue our studies in this series. Oxidation of I afforded 4-azafluorenone (II). Reaction of II with phenyllithium, o-tolyllithium and benzylmagnesium bromide gave: 9-phenyl (III); 9-o-tolyl (IV) and 9-benzyl (V)--4-azafluorenol-9 respectively.



I III-XIV

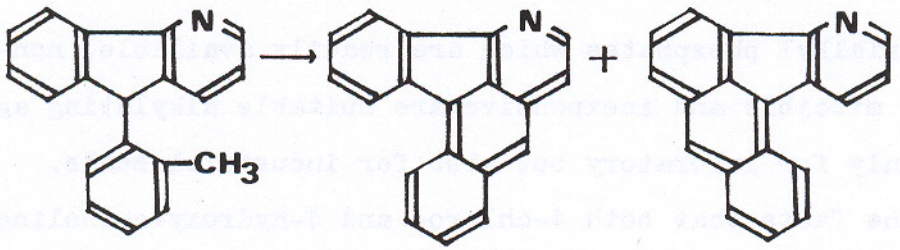
III,VI,IX ; $R=C_6H_5$
IV,VII,X ; $R=o\text{-}CH_3C_6H_4$
V ,VIII,XI; $R=CH_2C_6H_5$

III–V ; $R'=H$
VI–VIII; $R'=COCH_3$
IX–XI ; $R'=COC_2H_5$
XII–XIV; $R'=COC_7H_{15}$

In this series of azafluorenols (III-V) we did not detect the anomaly in the melting point that was observed in the 2-azafluorenols series. (Khim. Geterotsikl. Soed., 1087 (1971)).

The esters of acetic (VI-VIII), propionic (IX-XI) and heptanoic (XII-XIV) acids have been prepared in quantitative yields using 4-dimethyl--aminopyridine (DMAP) as catalyst. The reaction goes to completion in 10 minutes using 0.1 equivalent of DMAP vs. 6-12 hours and 40-50% yield in the case of the corresponding anhydride in pyridine. Factors affecting reactivity will be presented.

Reduction of IV with Sn/ HCl gave the corresponding 9-o-tolyl-4-aza--fluorene (XV) which was used for the synthesis of a new heterocyclic syst em: benzo(f)azafluoranthenes (XVI and XVII). Dehydrocyclisation of XV at 520-530°C in the vapour phase gave a mixture of three compounds; elucidation of their structures was accomplished by UV, IR, NMR and elemental analysis.



XV XVI XVII

Supported by Secretaría de Educación Pública de México (SEP), grant 78/ 64.