

## Free Radicals: XXVII.\* Synthesis of 2,6-Diphenyl-4-[*p*-(2,6-diphenyl-4-pyridyl)phenyl]pyranyl

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**Abstract**—Starting with 2,6-diphenyl-4-(*p*-tolyl)pyridine a synthesis of 2,6-diphenyl-4-[*p*-(2,6-diphenyl-4-pyridyl)phenyl]pyrylium perchlorate was performed. By reduction of the latter the corresponding radical was obtained. The radical was shown to be unstable with respect to oxygen.

2,4,6-Triphenylpyranyl was shown formerly to belong to the “electron-excessive” radicals [2] that should be stabilized by electron-withdrawing substituents.

Therefore we attempted to synthesize 2,6-diphenyl-4-[*p*-(2,6-diphenyl-4-pyridyl)phenyl]pyranyl (**I**). We expected that introduction of the pyridine moiety would stabilize the radical both due to its electron-withdrawing property and because of increased delocalization of the unpaired electron.

The synthesis of the radical was carried out along the scheme.

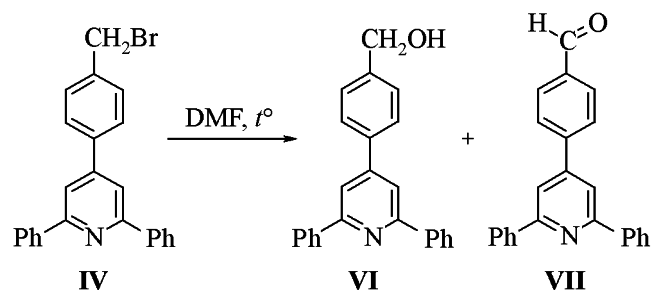
2,4-Diphenyl-4-(*p*-tolyl)pyrylium perchlorate (**II**) was prepared by boiling *p*-methylbenzaldehyde with acetophenone in the presence of perchloric acid. Perchlorate **II** is a yellow crystalline substance, it is well soluble in acetic acid, acetone, dioxane, limitedly soluble in alcohol, and insoluble in water and ether.

Perchlorate **II** was converted into 2,6-diphenyl-4-(*p*-tolyl)pyridine (**III**) by boiling with concentrated ammonia solution. Reaction product **III** is a white crystalline substance well soluble in acetone, chloroform, dioxane, alcohol, ether.

The bromination of 2,6-diphenyl-4-(*p*-tolyl)pyridine (**III**) with *N*-bromosuccinimide in dry carbon tetrachloride with benzoyl peroxide as initiator furnished 2,6-diphenyl-4-(*p*-bromomethylphenyl)pyridine (**IV**) in virtually qualitative yield.

The hydrolysis of compound **IV** in dimethylformamide failed to substitute directly a hydroxy group for the halogen in the methyl group of compound **IV**. We obtained instead a mixture of compounds **IV**, **VI**,

**VII** difficult to separate and having according to TLC on Silufol plates  $R_f$  0.82, 0.30, 0.70 respectively (eluent chloroform).



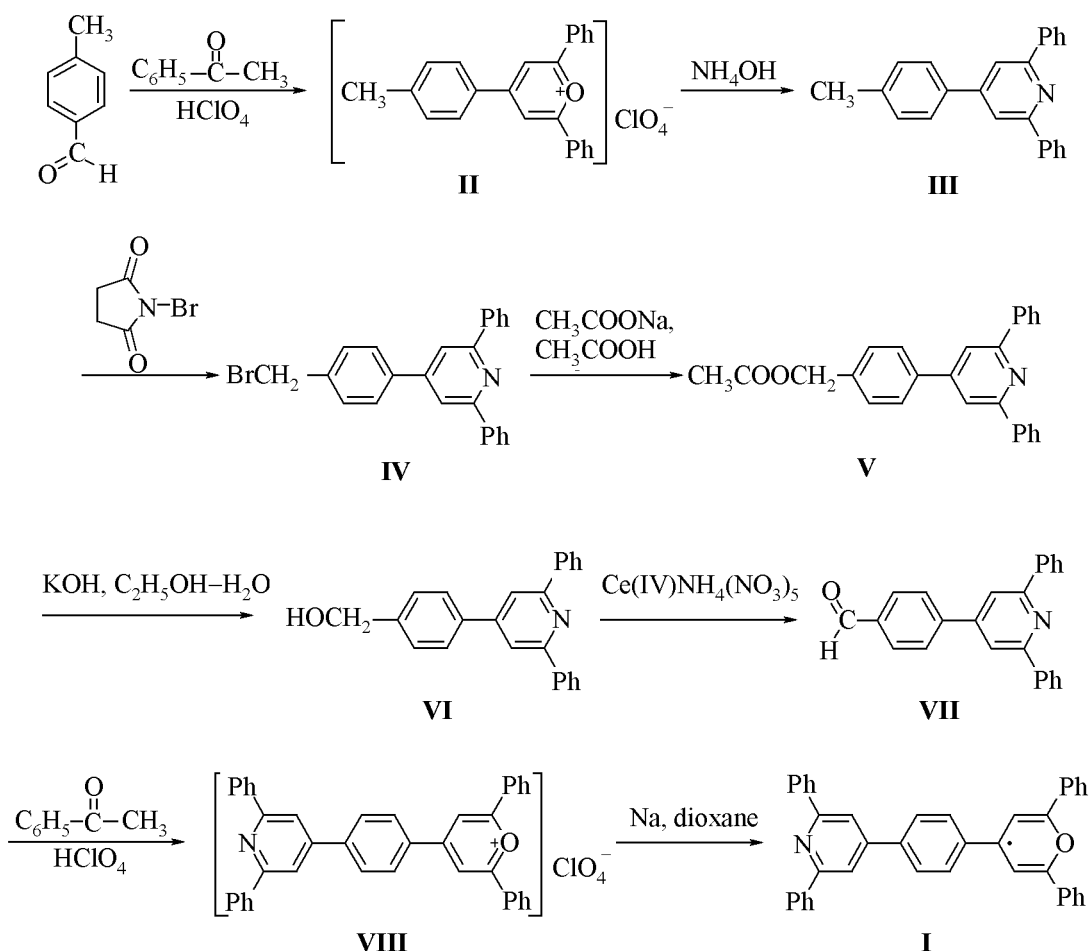
Thus in the reaction mixture alongside the initial bromomethyl derivative **IV** were present products of hydrolysis **VI** and of oxidation **VII**.

Therefore the replacement of halogen in compound **IV** by hydroxy group was carried out via an intermediate stage involving formation of 2,6-diphenyl-4-(*p*-acetoxyethylphenyl)pyridine (**V**) by boiling compound **IV** in glacial acetic acid with anhydrous sodium acetate with subsequent alkaline hydrolysis of compound **V** in alcohol-water mixture (1:1). Reaction products **V** and **VI** were isolated in crystalline state. In the IR spectrum of compound **V** is present an absorption band at  $1730\text{ cm}^{-1}$  characteristic of carbonyl group, and in the IR spectrum of compound **IV** is observed a broad absorption band of hydroxy group in the  $3250\text{--}3400\text{ cm}^{-1}$  region.

Oxidation of 2,6-diphenyl-4-(*p*-hydroxymethylphenyl)pyridine (**VI**) with cerium(IV) ammonium nitrate at boiling in the glacial acetic acid afforded 2,5-diphenyl-4-(*p*-formylphenyl)pyridine (**VII**) as evidenced

\* For communication XXVI, see [1].

## Scheme.



by the presence in the IR spectrum of a carbonyl group band in the  $1720\text{ cm}^{-1}$  region.

2,6-Diphenyl-4-*p*-(2,6-diphenyl-4-pyridyl)phenylpyrylium perchlorate (**VIII**) was prepared by condensation with acetophenone in the same way as compound **II**.

Although the reducing system Zn/benzene-acetic acid-water (1 : 1 : 1) is usually applied to the synthesis of pyrylium radicals [3], salt **VIII** does not practically be reduced with this agent.

The best method of radical **I** preparation is reduction of perchlorate **VIII** with metallic sodium in dry dioxane under inert atmosphere in a Schlenk flask.

Perchlorate **VIII** was also sufficiently readily reduced by 1% sodium amalgam in dioxane under inert atmosphere.

The use of benzene as solvent decelerated the reduction of the salt into the radical. It may be due to

relatively low reaction temperature that cannot be sufficiently increased with benzene as solvent.

The solution of radical **I** in dioxane is crimson, and the color rapidly disappears on contact with air. Thus contrary to expectations radical **I** is instable against oxygen. This fact hampered isolation of the radical in crystalline form. ESR spectrum of the radical is a singlet, and we failed to observe hyperfine structure.

## EXPERIMENTAL

IR spectra were recorded on spectrophotometer UR-20 from solutions in  $\text{CCl}_4$ . ESR spectrum was registered on EPA 2m instrument. The *p*-methylbenzaldehyde was prepared by procedure [4].

**2,4-Diphenyl-4-(*p*-tolyl)pyrylium perchlorate (II).** A mixture of 8 g (8.16 ml, 68 mmol) of *p*-methylbenzaldehyde, 11.3 g (11.5 ml, 94 mmol) of acetophenone, 5 ml of 72% perchloric acid, and

10 ml of toluene was boiled for 1 h. Then the reaction mixture was cooled to room temperature, and 100 ml of ether was added. The separated precipitate was filtered off, washed with ether on filter, and recrystallized from acetic acid. Yield 4.576 g (16%). mp 273–274°C (publ. 275°C [5]). Found, %: C 68.24; H 4.47. C<sub>24</sub>H<sub>19</sub>ClO<sub>4</sub>. Calculated, %: C 68.13; H 4.53.

**2,6-Diphenyl-4-(*p*-tolyl)pyridine (III).** A mixture of 4.58 g (11 mmol) of 2,4-diphenyl-4-(*p*-tolyl)pyrylium perchlorate (II) and 180 ml of 25% aqueous ammonia was boiled for 1.5 h. Then the reaction mixture was cooled to room temperature, the separated precipitate was filtered off, washed on filter with water, and recrystallized from 2-propanol. Yield 2.784 g (78%). mp 120–121°C. Found, %: C 89.64; H 5.94. C<sub>24</sub>H<sub>19</sub>N. Calculated, %: C 89.68; H 5.96.

**2,6-Diphenyl-4-(*p*-bromomethylphenyl)pyridine (IV).** A mixture of 3.21 g (10 mmol) of 2,6-diphenyl-4-(*p*-tolyl)pyridine (III), 1.78 g (10 mmol) of *N*-bromosuccinimide, 27 ml of dry carbon tetrachloride, and 0.005 g of benzoyl peroxide was boiled for 1 h. Then the reaction mixture was cooled, the separated precipitate was filtered off. The mother liquor was evaporated in a vacuum. The crystals obtained were subjected to column chromatography on SiO<sub>2</sub> (eluent carbon tetrachloride). Yield 3.8 g (95%). mp 123–124°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1450, 1585, 1635, 3050 (aromatic ring); 700 (C–Br); 3480 (N–H). Found, %: C 72.35; H 4.55. C<sub>24</sub>H<sub>18</sub>BrN. Calculated, %: C 72.01; H 4.53.

**2,6-Diphenyl-4-(*p*-acetoxymethylphenyl)pyridine (V).** A mixture of 0.84 g (2.1 mmol) of 2,6-diphenyl-4-(*p*-bromomethylphenyl)pyridine (IV), 1 g (12 mmol) of anhydrous sodium acetate, and 12.6 ml (12.6 g, 210 mmol) of glacial acetic acid was boiled for 3 h. Then the reaction mixture was cooled, poured into 35 ml of water, and neutralized by 10% solution of sodium carbonate. The separated precipitate was filtered off and purified by column chromatography on silica gel (eluent ethyl acetate). Yield 0.653 g (82%). mp 74–75°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1450, 1585, 1635, 3050 (aromatic ring); 1730 (C=O); 1260 (C–O–C); 3460 (N–H). Found, %: C 82.70; H 5.75. C<sub>26</sub>H<sub>21</sub>NO<sub>2</sub>. Calculated, %: C 82.32; H 5.54.

**2,6-Diphenyl-4-(*p*-hydroxymethylphenyl)pyridine (VI).** A mixture of 0.653 g (1.7 mmol) of 2,6-diphenyl-4-(*p*-acetoxymethylphenyl)pyridine (V), 0.653 g (5.18 mmol) of potassium hydroxide, 25 ml of ethanol, and 25 ml of water was boiled for 2 h. On cooling the separated precipitate was filtered off and purified by column chromatography on silica gel

(eluent benzene). Yield 0.503 g (88%). mp 121–122°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 700, 1480, 1585, 1635 (aromatic ring); 3250–3400 (OH). Found, %: C 85.51; H 5.12. C<sub>24</sub>H<sub>19</sub>NO. Calculated, %: C 85.43; H 5.38.

**2,5-Diphenyl-4-(*p*-formylphenyl)pyridine (VII).** A mixture of 0.373 g (1.12 mmol) of 2,6-diphenyl-4-(*p*-hydroxymethylphenyl)pyridine (VI), 1.03 g (2.2 mmol) of cerium(IV) ammonium nitrate, 22 ml of acetic acid, and 3 ml of water were boiled for 1 h (till the solution lost its orange color). Then the reaction mixture was cooled and poured into 30 ml of water. The separated precipitate was filtered off and purified by column chromatography on silica gel (eluent chloroform). Yield 0.288 g (78%). mp 99–100°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1700, 1450, 1500, 1600, 3070, 3090 (aromatic ring); 1720 (C=O). Found, %: C 85.75; H 5.25. C<sub>24</sub>H<sub>17</sub>NO. Calculated, %: C 85.95; H 5.11.

**2,6-Diphenyl-4-[*p*-(2,6-diphenyl-4-pyridyl)phenyl]pyrylium perchlorate (VIII).** A mixture of 0.335 g (1 mmol) of 2,5-diphenyl-4-(*p*-formylphenyl)pyridine (VII), 0.73 g (0.75 ml, 6 mmol) of acetophenone, 0.5 ml of 72% of perchloric acid, and 1.5 ml of toluene was boiled for 1 h. Then the reaction mixture was cooled to room temperature, and 20 ml of ether was added. The separated yellow precipitate was filtered off, washed with ether on filter, and recrystallized from acetic acid. Yield 0.51 g (80%), mp 130°C.

**Preparation of solution of 2,6-diphenyl-4-[*p*-(2,6-diphenyl-4-pyridyl)phenyl]pyrylium perchlorate (VIII) in dioxane.** Compound I was prepared in a Schlenk flask in a flow of carbon dioxide. First was charged 50 ml of dry dioxane and 0.01 g of sodium metal, and the system was flushed with carbon dioxide. Then in a flow of carbon dioxide was added 0.13 g of 2,6-diphenyl-4-[*p*-(2,6-diphenyl-4-pyridyl)phenyl]pyrylium perchlorate (VIII). The reaction was boiled for 2 h to formation of a crimson solution.

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