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AN UNUSUAL REACTION OF 2-(2-PYRIDYLCARBONYL)- AND 2-(2-QUINOLYLCARBONYL)BENZOYL CHLORIDES WITH p-NITROANILINE

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In the reaction of 2-(2-pyridylcarbonyl)benzoyl chloride, which exists in the form of 6,11-dioxo-6,11-dihydrobenzo[b]quinolizinium chloride, with p-nitroaniline, 2-(4-nitrophenylimino)-6,11-dihydro-2H-benzo-[b]quinolizine-6,11-dione is unexpectedly formed. When it reacts with water or methanol there is an opening of the quinolizine ring and aromatization of the quinoid fragment with the formation of 2-[4-(4-nitrophenylamino)-2-pyridylcarbonyl]benzoic acid or its methyl ester. Under the action of antimony pentachloride, 2-(2-quinolylcarbonyl)benzoylchloride—3-(2-quinolyl)-3-chloro-1,3-dihydrobenzo[c]furan-1-one — is converted to 3-(2-quinolyl)-1,3-dihydrobenzo[c]furan-1-on-3-ylium hexachloroantimonate, which undergoes isomerizing recyclization upon heating to 7,12-dioxo-7,12-dihydrobenzo[b,f]quinolizinium hexachloroantimonate. The latter enters into an analogous reaction with p-nitroaniline, thereby forming 5-(4-nitrophenylimino)-7,12-dihydro-5H-dibenzo[b,f]quinolizine-7,12-dione.

We have proposed [1, 2] a convenient method for producing a number of 2-pyridyl- and 2-quinolylcarbonylarenecarboxylic acids. It was shown that in the reaction of 2-(2-pyridylcarbonyl)benzoic acid (I) with thionyl chloride a product of intramolecular acylation of the pyridine nitrogen atom is formed — 6,11-dioxo-6,11-dihydrobenzo[b]quinolizinium chloride (II). It was established [4] that in its reaction with ammonia and a number of primary aliphatic and aromatic amines, the C=O group bonded to the onium nitrogen atom is subjected to nucleophilic attack, and the amines formed immediately cyclize to 2-substituted 3-hydroxy-3-(2-pyridyl)isoindolinones (III), with the exception of cases in which cyclization is prevented by a voluminous substituent at the nitrogen atom (R in compound III).

In the reaction of the chloride II with p-nitroaniline, we isolated a compound that differed from the isoindolinones III and their open isomers in its chemical properties and spectroscopic characteristics. This observation was evidence of a different direction of nucleophilic attack and it became the subject of the present investigation.

In the reaction of the chloride II with p-nitroaniline, carried out at room temperature in a solution of acetonitrile in the presence of an equimolar amount of triethylamine, a red compound is formed, which we identified as 2-(4-nitrophenylimino)-6,11-dihydro-2H-benzo[b]quinolizine-6,11-dione (V). Let us assume that first a product of nucleophilic addition of p-nitroaniline to C_2 of the benzoquinolizinium II is formed — 2-(4-nitrophenylamino)-6,11-dihydro-2H-benzo[b]quinolizine-6,11-dione (IV), which, as is characteristic of 1,4-dihydroderivatives of pyridine, is already oxidized in the reaction medium to compound V. The quinoid structure of V was stabilized by the presence of a long system of conjugation, which is confirmed by the long-wave absorption bands at 335 and 437 nm.

The addition of nucleophilic agents to the α- and γ-carbon atoms of N-substituted pyridines and their benzanalogs is known in the literature [5-9].

The chloride II is a polydentate system, which has at least four electrophilic sites — the carbon atoms in the 2-, 4-, 6-, and 11-positions. p-Nitroaniline attacks only the $C_{(2)}$ position, since no other products were detected.

Compound V is readily hydrolyzed, which leads to opening of the ring, aromatization of the quinoid fragment, and the formation of 2-[4-(4-nitrophenylamino)-2-pyridylcarbonyl]benzoic acid (VIa). Under the action of methanol on compound

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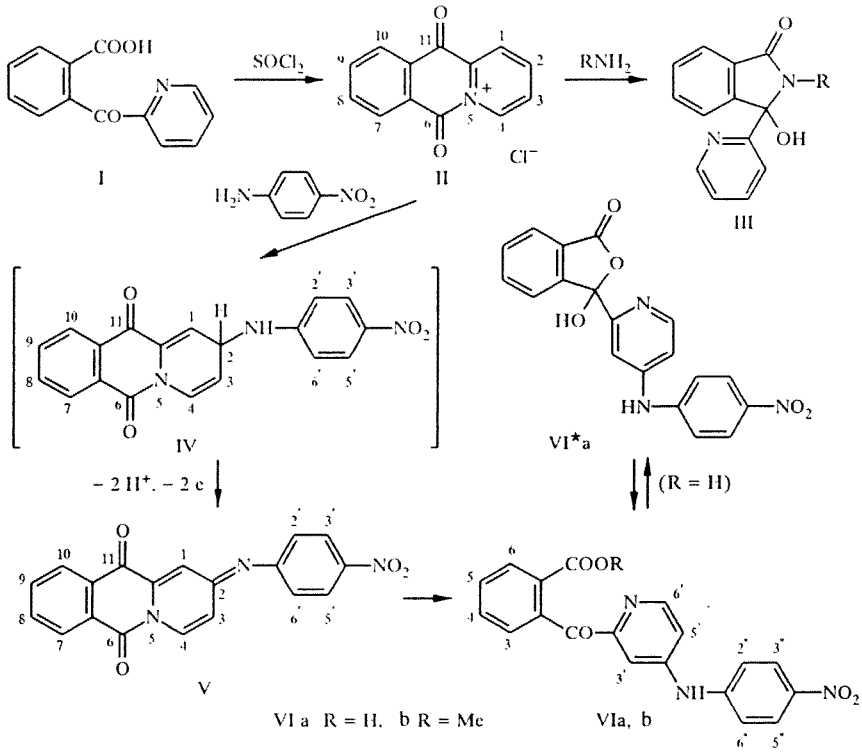


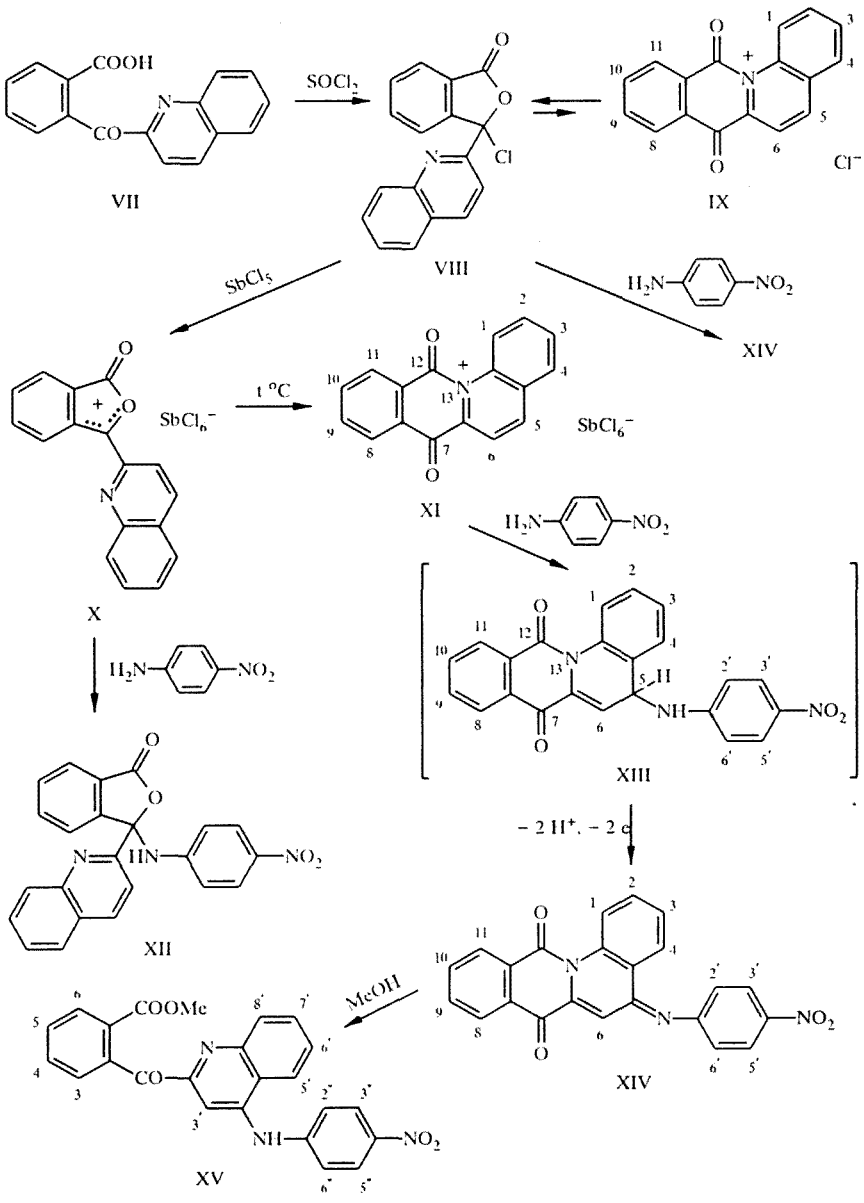
V in the presence of triethylamine, the methyl ester of 2-[4-(4-nitrophenylamino)-2-pyridylcarbonyl]benzoic acid VIb is obtained.

In the IR spectrum of compound V the C=O bands 1708 (ketone) and 1636 cm^{-1} (CON) are observed, which corresponds to the literature data [10]. Evidently on account of the tendency to hydrolysis, a satisfactory PMR spectrum of compound V could not be obtained: A signal appears in the spectrum at 9.87 ppm (N−H), indicating an admixture of the acid VIa. Signals of the protons C_7−H, C_8−H, and C_{10}−H, as well as the AA'XX' system of protons of the p-nitrophenyl ring, can be identified; however, the assignment of the C_1−H, C_3−H, and C_4−H signals is ambiguous.

Bands of the carboxyl C=O at 1680 cm^{-1} and the ketone C=O at 1660 cm^{-1} appear in the IR spectrum of the acid VIa, which confirms an open structure of the acid VIa in the crystalline state (see [11]). However, in the IR spectrum of the acid VIa, taken for a solution in DMSO, in addition to the carboxyl C=O (1705 cm^{-1}) and ketone C=O (1690 cm^{-1}) bands, a C=O band of hydroxylactone is observed at 1764 cm^{-1}, which is evidence of ring-chain tautomeric equilibrium VIa ⇌ VI*a. This equilibrium (for information on the rates of tautomeric conversions of ketocarboxylic acids relative to the NMR time scale, see [12]), as well as the possibility of intra- or intermolecular exchange $-COOH + N \equiv \rightleftharpoons -COO^- + HN^+ \equiv$ in a solution of the acid VIa, complicates the picture of the PMR spectrum: The lines of the protons of the pyridine ring are broadened.

The most convenient derivative of compound V, permitting confirmation of its structure by the PMR method, proved to be the methyl ester VIb, for which the exchange processes that complicate the PMR spectrum of the acid VIa are impossible. The IR spectrum of the ester VIb contains ketone and ester C=O bands (see [11]). In the PMR spectrum, in addition to the signals of the CH_3O, NH (disappears when D_2O is added), C_3−H, C_4−H, C_5−H, and C_6−H protons, as well as the AA'XX' system of the p-nitrophenyl ring, the protons of the pyridine ring clearly appear: $C_{3'}$−H (7.93 ppm, d, ^4J = 2.1 Hz), $C_{5'}$−H (7.11 ppm, d.d, ^3J = 5.6, ^4J = 2.1 Hz), and $C_{6'}$−H (8.40 ppm, d, ^3J = 5.6 Hz). The spin−spin coupling constants correspond to the literature data [10] for 2,4-disubstituted pyridine and indirectly confirm the structure of the precursor V: If the original attack on the chloride II by p-nitroaniline proceeded at C_4, then the 2,6-disubstituted pyridine derivative formed would have a different picture of spin−spin splitting of the pyridine protons.

In contrast to the acid I, 2-(2-quinolylcarbonyl)benzoic acid (VII) reacts with thionyl chloride to form an acid chloride of cyclic structure — 3-(2-quinolyl)-3-chloro-1,3-dihyrobenzo[c]furan-1-one (VIII) [4]. The formation of stable clorolactones is characteristic of 2-acylbenzoyl chlorides in general [11, 13]. It can be assumed that the difference between the cyclic structures of the acid chlorides I and VII is due to the fact that for the latter the formation of an onium chloride is hindered on account of steric hindrances between C=O and C_1−H (see the formula IX). It was shown in [4] that in the reaction of the chlorolactone VIII with ammonia and primary amines, exclusively 3-hydroxy-3-(2-quinolyl)isoindolinones are formed.



In the reaction of the chlorolactone VIII with p-nitroaniline, a red product was also obtained in a small yield; by analogy to compound V, the structure 5-(4-nitrophenylamino)-7,12-dihydro-5H-dibenzo[b,f]quinolizine-7,12-dione (XIV) was assigned to it. Such a compound can be formed from the chlorolactone VIII only if the equilibrium VIII ⇄ IX exists in solution, and the tautomeric form IX reacts with p-nitroaniline. We attempted to find conditions for the conversion VIII → IX. Under the action of antimony pentachloride on the chlorolactone VIII, a colorless crystalline complex — 3-(2-quinolyl)-1,3-dihydrobenzo[c]furan-1-on-3-ylium hexachloroantimonate (X) — is formed with a quantitative yield. The synthesis of complex salts of analogous structure in the reactions of cyclic isomers of salicyl chloride and certain other α- or β-acyloxycarboxylic acid chlorides with antimony pentachloride is known [14, 15]. In the IR spectrum of compound X, the C=O band appears at 1804 cm^{-1}.

Compound X, when heated around 140°C, acquires a yellow color and isomerizes to 7,12-dioxo-7,12-dihydrodibenzo[b,f]-quinolizinium hexachloroantimonate (XI), which is a structural analog of the chloride II. In the IR spectrum of compound XI, C=O bands are observed at 1770 (CON^+) and 1694 cm^{-1} (C=O), which is close to the positions in the spectrum of the chloride II (see [3, 4]). This is the first time that such a thermal isomerizing recyclization (X → XI) has been observed.

In the reaction of the hexachloroantimonate X with p-nitroaniline, 3-(4-nitrophenylamino)-3-(2-quinolyl)-1,3-dihydrobenzo[c]furan-1-one (XII) is formed. The IR spectrum of compound XII is in good agreement with the data for 3-arylamino-3-(2-pyridyl or aryl)-1,3-dihydrobenzo[b]furan-1-ones [16, 17].

In the reaction of the hexachloroantimonate XI with p-nitroaniline, which evidently proceeds similarly to the conversions II → IV → V, at first the nucleophilic addition product XIII formed is subjected to oxidation in the reaction mixture and is converted to 5-(4-nitrophenylimino)-7,12-dihydro-5H-dibenzo[b,f]quinolizine-7,12-dione (XIV). Evidently p-nitroaniline acts as an oxidizing agent for the conversion of XIII → XIV. The necessity of the presence of an oxidizing agent was confirmed by the fact that the addition of nitrobenzene to the reaction mixture (XI + nitroaniline) increased the yield of XIV from 20 to 70%.

Compound XIV is converted in the reaction with methanol in the presence of triethylamine to the methyl ester of 2-[4-(4-nitrophenylamino)-2-quinolylcarbonyl]benzoic acid (XV).

The IR spectrum of compound XIV contains the ketone and lactam C=O bands at 1706 and 1686 cm^{-1}, respectively. A complete assignment of the signals in the PMR spectrum of compound XIV was made by the double resonance method; the C_6-H signal appears in the form of a single singlet at 7.16 ppm ($CDCl_3$). In the PMR spectrum of the ester XV the signals of the C_4-H, C_5-H, $C_{5'}-H$, $C_{6'}-H$, and $C_{7'}-H$ protons appear in the form of a difficult-to-resolve multiplet; the assignment of the signals of the remaining protons is given in the experimental section.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 instrument for suspensions in nujol (region 1900-1500 cm^{-1}, NaCl prism) and hexachlorobutadiene (region 3800-2000 cm^{-1}, LiF prism) (microlayer), and the remaining spectra were also recorded for solutions in dioxane and DMSO. The electronic spectra were taken on a Specord M-40 instrument for solutions in acetonitrile ($c = 5 \cdot 10^{-5}$ M). The PMR spectra were obtained on a Bruker AM-360 spectrometer (^1H 360 MHz) in solutions of DMSO-D_6 and $CDCl_3$; the chemical shifts were measured relative to a TMS internal standard. To monitor the course of the reaction and the purity of the compounds obtained we used a method of thin-layer chromatography on plates with a fixed layer of Silufol UV-254 silica gel; the eluent was acetone–hexane; development with UV light and iodine.

The data of elementary analysis for C, H, N, and Cl correspond to the calculated data.

6,11-Dioxo-6,11-dihydrobenzo[b]quinolizinium chloride (II) was produced according to the procedure of [3].

3-(2-Quinolyl)-3-chloro-1,3-dihydrobenzo[c]furan-1-one (VIII) was produced by the method of [4].

2-(4-Nitrophenylimino)-6,11-dihydro-2H-benzo[b]quinolizine-6,11-dione (V). A 0.55 g (4 mmoles) portion of p-nitroaniline was dissolved in 45 ml of acetonitrile; 0.98 g (4 mmoles) of the chloride II was added to the solution, and a solution of 0.7 ml (5 mmoles) of triethylamine in 5 ml of acetonitrile was added to the suspension obtained with mixing (magnetic stirrer) at 20°C from a dropping funnel. In the course of the reaction all of the chloride passes into solution, and 2-3 min after addition of the entire triethylamine solution, a precipitate begins to separate from the red solution. The reaction mixture was mixed for 2 h, then exposed for 20 h at 20°C. The precipitate was filtered off, washed with acetonitrile, and recrystallized from acetonitrile. Shining red plates of compound V were obtained, yield 0.2 g (29%). Mp 281-282°C, R_f 0.35 (acetone–hexane, 1:1). IR spectrum (microlayer): 1708 (C=O), 1636 (CON), 1596, 1584, 1560, 1508 cm^{-1} (dioxane); 1706 (C=O), 1642 (CON), 1584, 1516 cm^{-1}. UV spectrum (acetonitrile), λ_{max} (lgε): 236 (4.47), 335 (4.21), 437 nm (4.16).

2-[4-(4-Nitrophenylamino)-2-pyridylcarbonyl]benzoic Acid (VIa). Method A. 0.2 g of compound V and 5 ml of hydrolyzing mixture (prepared from 5 ml of acetic acid, 5 ml of water, and 0.5 ml conc. sulfuric acid) were boiled with a reflux condenser for 0.5 h. After the precipitate of the initial compound V dissolved, the color of the solution changed from red to yellow. The hot solution was filtered off; 10 ml of water was added to the cool filtrate, then it was neutralized with a sodium hydroxide solution to pH ~3. The precipitate formed was filtered off, washed with water, and dried. Yield 0.2 g (95%) of light-yellow crystals of the acid VIa. Mp 274-275°C (dec.). IR spectrum (microlayer): 3306 (NH), 3230, 3194, 3148, 3114, 2440 (broad band, OH); 1680 (C=O carboxyl), 1660 (C=O ketone), 1614, 1590, 1542 (NO_2), 1509 cm^{-1}; (DMSO): 1764 (hydroxylactone), 1705 (C=O carboxyl), 1690 (C=O ketone), 1580 (arom), 1534 (NO_2), 1509 cm^{-1}. PMR spectrum (DMSO-D_6): 7.30 (1H, broad signal, $C_{5'}$-H), 7.38 (2H, AA'XX', J_{AX} = 9.1 Hz, $C_{2''}-H$ and $C_{6''}-H$), 7.46 (1 H, d.d, ^3J = 7.5, ^4J = 1.2 Hz, C_3-H), 7.62 (1H, t.d, ^3J = 7.5, ^4J = 1.2 Hz, C_4-H or C_5-H), 7.70 (1H, t.d, ^3J = 7.5, ^4J = 1.2 Hz, C_4-H or C_5-H), 7.79 (1 H, broad signal, $C_{3'}-H$), 7.91 (1H, d.d, ^3J = 7.5, ^4J = 1.2 Hz, C_6-H), 8.24 (2H, AA'XX', J_{AX} = 9.1 Hz, $C_{3''}-H$ and $C_{6''}-H$), 8.31 (1H, d, ^3J = 5.5 Hz, $C_{6'}-H$), 9.87 ppm (1H, s, N–H).

Method B. A mixture of 0.2 g of compound V and 10 ml of a 5% aqueous solution of sodium hydroxide was boiled with a reflux condenser for 1 h. The precipitate of compound V dissolved, and the solution took on an intense red color. It was cooled to 20°C, diluted with water to a volume of 20 ml, and acidified with dilute hydrochloric acid to pH 3-4. After some time, the precipitate that formed was filtered off, washed with water, and dried. Yield 0.18 g (86%) of light-yellow crystals of the acid VIa, identical with a sample obtained according to method A.

Methyl Ester of 2-[4-(4-Nitrophenylamino)-2-pyridylcarbonyl]benzoic Acid (VIb). A mixture of 0.35 g (1 mmole) of compound V and 0.14 ml (1 mmole) triethylamine in 30 ml of methanol was boiled with a reflux condenser for 1.5 h until the initial compound dissolved completely, then the solution was evaporated under vacuum, and the residue was recrystallized from ethanol (cooled at 0°C). The precipitate formed was filtered off, washed with ethanol, and dried. Yellow crystals of the ester VIb were obtained, yield 0.3 g (80%). Mp 279-280°C (dec.). IR spectrum: 3366 (N−H), 1714 (C=O ester), 1668 (C=O ketone), 1578, 1534 (NO_2), 1506 cm^{-1}. UV spectrum (acetonitrile), λ_{max} (lgε): 245 (4.47), 367 nm (4.42). PMR spectrum ($CDCl_3$): 3.63 (3H, s, OCH_3), 6.80 (1H, s, NH, disappears after addition of D_2O), 7.11 (1H, d.d, ^3J = 5.6, ^4J = 2.1 Hz, $C_{5'}$−H), 7.26 (2H, AA'XX', J_{AX} = 8.8 Hz, $C_{2''}$−H and $C_{6''}$−H), 7.52 (1H, d.d, ^3J = 7.6, ^4J = 1.1 Hz, C_3-H), 7.58 (1H, t.d, ^3J = 7.6, ^4J = 1.1 Hz, C_4−H or C_5−H), 7.67 (1H, t.d, ^3J = 7.6, ^4J = 1.1 Hz, C_4−H or C_5−H), 7.93 (1H, d, ^4J = 2.1 Hz, $C_{3'}$−H), 8.02 (1H, d.d, ^3J = 7.6, ^4J = 1.1 Hz, C_6−H), 8.24 (2H, AA'XX', J_{AX} = 8.8 Hz, $C_{3''}$−H and $C_{5''}$−H), 8.40 m.d, (1H, d, ^3J = 5.6 Hz, $C_{6'}$−H).

3-(2-Quinolyl)-1,3-dihydrobenzo[c]furan-1-on-3-ylium Hexachloroantimonate (X). To 2.8 g (10 mmoles) of the acid VII 4 ml of thionyl chloride was cautiously added; a vigorous reaction occurred, and the acid dissolved completely. The mixture was kept at 20°C for 0.5 h, then 5 ml of methylene chloride was added, after which a solution of 3 ml (24 mmoles) antimony pentachloride in 5 ml methylene chloride was slowly added. A yellow precipitate immediately formed and subsequently became colorless. The reaction mixture was kept at 20°C for 10 h, then the precipitate was filtered off, washed with methylene chloride, and dried in a vacuum desiccator over conc. sulfuric acid. Yield 5.9 g (99%) of colorless crystals of the hexachloroantimonate X. The melting point could not be determined, since isomerization of X → XI occurred upon heating (see the following experiment). IR spectrum: 3272, 3244, 3212, 1804 (C=O), 1640, 1598, 1538 cm^{-1}.

7,12-Dioxo-7,12-dihydrobenzo[b,f]quinolizinium Hexachloroantimonate (XI). A 0.6 g (1 mmole) portion of the hexachloroantimonate X was heated at 140°C for 1.5 h. We obtained 0.6 g (100%) of yellow crystals of the hexachloroantimonate XI. Mp 250-251°C (dec.). IR spectrum: 3072, 1770 (CON^+), 1694 (C=O), 1618, 1590, 1570, 1526 cm^{-1}.

3-(4-Nitrophenylamino)-3-(2-quinolyl)-1,3-dihydrobenzo[c]furan-1-one (XII). To a solution of 0.6 g (1 mmole) of the hexachloroantimonate X in 2 ml of acetonitrile we added a solution of 0.14 g (1 mmole) of p-nitroaniline and 0.28 ml (2 mmoles) triethylamine in 3 ml of acetonitrile. The reaction mixture was exposed at 20°C for 72 h. The precipitate formed was filtered off, and colorless crystals of compound XII were obtained. Yield 0.1 g (25%), mp 228-231°C. The filtrate was poured out into 50 ml of water, the precipitate was removed, recrystallized from ethanol with an addition of activated charcoal, and an additional 0.1 g of compound XII was obtained. The total yield is 50%. IR spectrum (microlayer): 3295 (NH), 3071, 2927, 2859, 1770 (C=O), 1604, 1530 (NO_2), 1506 cm^{-1}; (dioxane): 1779 (C=O), 1599, 1530 (NO_2), 1509 cm^{-1}.

5-(4-Nitrophenylimino)-7,12-dihydro-5H-dibenzo[b,f]quinolizine-7,12-dione (XIV). To a suspension of 0.6 g (1 mmole) of the hexachloroantimonate XI in 4 ml of acetonitrile we added 3 drops of nitrobenzene, and a solution of 0.14 g (1 mmole) p-nitroaniline and 0.28 g (2 mmoles) triethylamine in 5 ml of acetonitrile was added with mixing at 20°C. The mixture was exposed for 24 h at 20°C, the precipitate was removed, and 0.28 g (70%) of dark-red crystals or compound XIV, mp 275-280°C, was obtained. After recrystallization from acetonitrile, mp 281-282°C. IR spectrum: 3158, 3102, 3070, 2930, 1706 (C=O), 1686 (CON), 1610, 1594, 1586, 1564 (NO_2), 1502 cm^{-1}. UV spectrum (acetonitrile), λ_{max} (lgε): 284 (4.17), 314 (4.12), 437 nm (3.94). PMR spectrum ($CDCl_3$): 7.05 (2H, AA'XX', J_{AX} = 8.9 Hz, $C_{2'}$−H and $C_{6'}$−H), 7.16 (1H, c, C_6−H), 7.53 (1H, d.d.d, ^3J = 8.8, ^3J = 8.2, ^4J = 1.0 Hz, C_3−H), 7.71 (1H, d.d.d, ^3J = 8.8, ^3J = 8.2, ^4J = 1.3 Hz, C_2−H), 7.86 (1H, t.d, ^3J = 7.6, ^4J = 1.3 Hz, C_9−H), 7.94 (1H, t.d, ^3J = 7.6, ^4J = 1.3 Hz, C_{10}−H), 8.23 (1H, d.d, ^3J = 7.6, ^4J = 1.3 Hz, C_8−H), 8.29 (2H, AA'XX', J_{AX} = 8.9 Hz, $C_{3'}$−H and $C_{5'}$-H), 8.49 (1H, d.d, ^3J = 7.6, ^4J = 1.3 Hz, C_{11}−H), 8.53 (1H, d.d, ^3J = 8.2, ^4J = 1.6 Hz, C_4−H), 8.71 m.d (1H, d.d, ^3J = 8.2, ^4J = 1.0 Hz, C_1−H). A vicinal (^3J) spin coupling between the signals 7.71 and 8.71 (C_2−H and C_1−H), 7.53 and 8.53 (C_3−H and C_4−H), 7.86 and 8.23 (C_9−H and C_8−H), 7.94 and 8.49 (C_{10}−H and C_{11}−H), respectively, was established by a double resonance method.

Methyl Ester of 2-[4-(4-Nitrophenylamino)-2-quinolylcarbonyl]benzoic Acid (XV). A mixture of 0.4 g (1 mmole) of compound XIV and 0.1 ml of triethylamine in 30 ml of methanol was boiled with a reflux condenser for 2 h. After cooling, shining yellow plates or compound XV precipitated. Yield 0.4 g (94%), mp 265-266°C. IR spectrum: 3356 (NH), 1734 (C=O

ester), 1674 (C=O ketone), 1608, 1586, 1564 (NO_2), 1534, 1506 cm^{-1}. UV spectrum (acetonitrile), λ_{max} (lgε): 221 (4.53), 389 nm (4.37). PMR spectrum (DMSO-D_6): 3.37 (3H, c, OCH_3), 7.56 (2H, AA'XX', J_{AX} = 9.2 Hz, $C_{2''}$–H and $C_{6''}$–H), 7.62 (1H, d.d.d, ^3J = 7.5, ^4J = 1.5, ^5J = 0.6 Hz, C_3–H), 7.69-7.82 (5H, m, C_4–H, C_5–H, $C_{5'}$–H, $C_{6'}$–H, $C_{7'}$–H), 7.95 (1H, d.d.d, ^3J = 7.6, ^4J = 1.5, ^5J = 0.5 Hz, C_6–H), 8.04 (1H, c, $C_{3''}$–H), 8.31 (2H, AA'XX', J_{AX} = 9.2 Hz, $C_{3'}$–H and $C_{6''}$–H), 8.38 (1H, d, ^3J = 8.6 Hz, $C_{8'}$–H), 9.87 m.d. (1H, N–H).

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