

CONVERSION OF 4,5,6-TRIARYL-2-PYRANAMINES AND 4,6-DIARYL-5-BENZOYL-2-PYRAN-AMINES INTO PYRONES, PYRIDONES AND PYRIDINES

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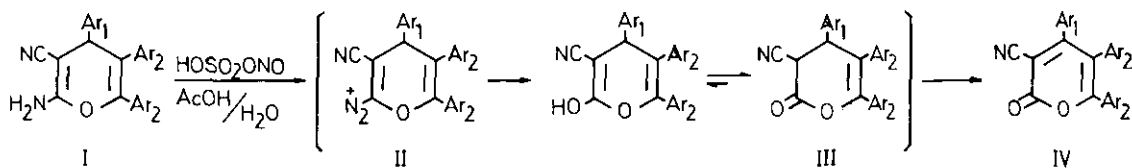
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Abstract - Treatment of 4,5,6-triaryl-2-pyranamines **I** with nitrosylsulfuric acid brings about their conversion into triarylpyrones **IV**. Their 5-benzoyl analogues **V** afford the corresponding 2-pyrones (**VI**), together with pyridones **VII**, resulting from ring opening of **V**. On the other hand, **I** undergoes a ring transformation into aminopyridines **X** by reaction with ammonium acetate.

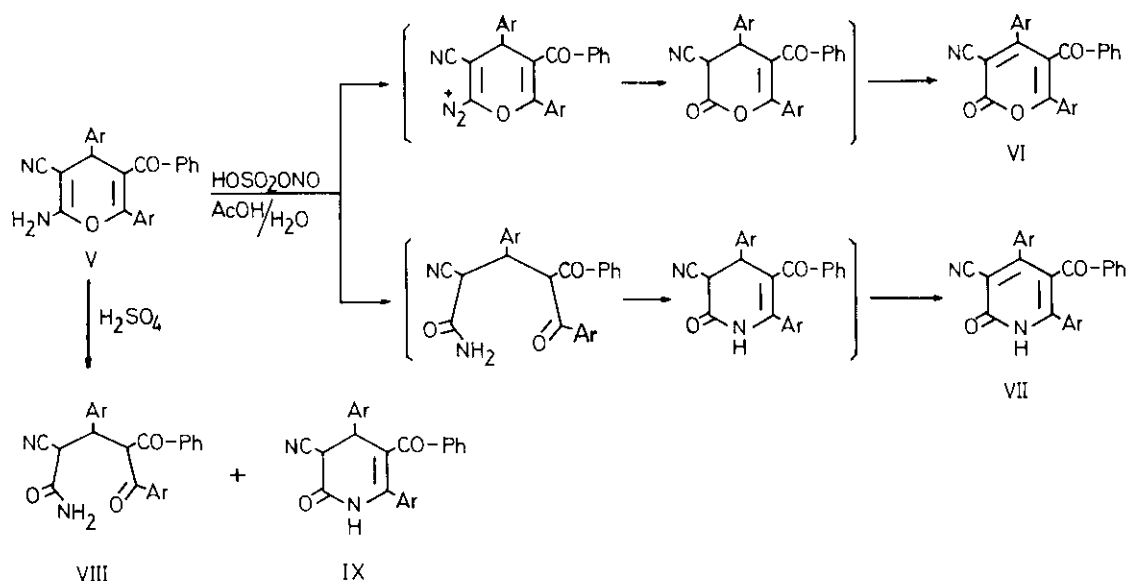
In a previous paper¹, we have described the ring transformation of some 5-cyano and 5-ethoxycarbonyl substituted 2-pyranamines into pyridine derivatives upon treatment with nitrosylsulfuric acid, as a contribution to the rather scarce work on the chemical reactivity of 4H-pyrans²⁻¹² and, in particular, their ring transformations into other heterocycles¹³.

We now report on the ring transformation of the recently prepared¹⁴⁻¹⁵ 2-amino-4,5,6-triaryl-3-cyano-4H-pyran (**I**) and 2-amino-4,6-diaryl-5-benzoyl-3-cyano-4H-pyran (**V**). In contrast with the previously reported results¹, treatment of 4,5,6-triaryl-2-aminopyrans **I** with nitrosylsulfuric acid in acetic acid gave no pyridines but instead α -pyrones with the same substitution pattern as the starting compound (Scheme 1). The reaction involves diazotization of the amino group of **I**, followed by a keto-enolic tautomerism and spontaneous aromatization of the dihydro derivatives **III** by the oxidizing reaction medium (Scheme 1). The IR spectra of these compounds shows, in addition to the cyano stretching band ($\sim 2200\text{ cm}^{-1}$) a strong band at $1720\text{--}1740\text{ cm}^{-1}$ due to the carbonyl group of the α -pyrones¹⁶.



Scheme 1

On the other hand, treatment of the 5-benzoyl compounds V with nitrosylsulfuric acid resulted in the formation of two compounds. The first compound was the corresponding 2-pyrone (VI) formed by a similar diazotization of the amino group. Competing with this reaction, however, a ring opening reaction occurred, leading to a nitrogen heterocycle. Attack by water to the protonated pyran ring gives an open chain intermediate which undergoes recyclization and dehydrogenation to yield aromatic pyridones VII (Scheme 2). In accord with this, acid treatment of V in the absence of an oxidizing agent did not afford any aromatic compound, and a mixture of the open chain compound VIII and its cyclization compound, 3,4-dihydropyridone IX was obtained (Scheme 2). The chromatography of this mixture caused a partial cyclization of VIII to IX, and TLC showed a smaller proportion of VIII after chromatography.



Scheme 2

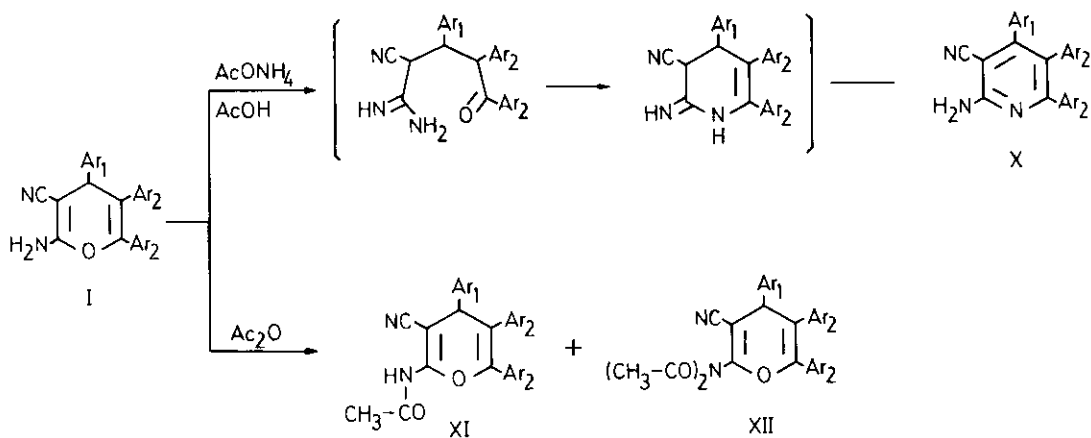
Compounds VII show, in addition to the cyano stretching band at $2200\text{--}2220\text{ cm}^{-1}$, a characteristic broad band at $2800\text{--}3200\text{ cm}^{-1}$ and a strong carbonyl band at about 1650 cm^{-1} . The NH proton signal appearing in the aromatic region could be identified by addition of TFA.

The difference between the behaviour of I and V is probably due to the electron attracting property of the benzoyl group in V. This facilitates the nucleophilic attack by water and the ring opening leading to the nitrogen ring of pyridones VII; This is not the case for I, where the pyrone resulting from diazotization is the only reaction product.

Ammonia can also act as a nucleophile and bring about a ring transformation of aminopyrans.

Treatment of I with ammonium acetate in acetic acid resulted in the formation of pyridines X by cyclization of the intermediate open chain amidine and aromatization (Scheme 3). Attempts to apply

this reaction to the 5-benzoyl-2-aminopyrans V failed.



Finally, taking into account the presence of an amino group and a nitrile one in our aminopyrans, we attempted the preparation of pyranopyrimidines by treatment with sodium ethoxide of the N-acetyl derivatives of I. Acetylation of I gave in fact N-acetylaminopyran XI, together with the diacetyl derivative XII, but no reaction took place upon treatment of XI with sodium ethoxide.

EXPERIMENTAL

Melting points were determined in a Büchi apparatus in capillary tubes and are uncorrected. The IR spectra were performed on a Perkin-Elmer 599 and PYE Unicam SP 1100 spectrophotometers in potassium bromide pellets. The $^1\text{H-NMR}$ spectra were determined on a Varian T-60A at 60 MHz; Chemical shifts are quoted in δ values, using TMS as internal standard. A Varian MAT 711 was used for the recording of mass spectra. Microanalyses were performed by Centro Nacional de Química Orgánica de Madrid. The reactions and purity of compounds were monitored by TLC, performed on silica gel plates (Merck).

I¹⁴ and V¹⁵ were prepared by the methods reported in the literature.

4,5,6-Triaryl-3-cyano-2-pyrones (IV). General Procedure - To a suspension of the appropriate 2-amino-4,5,6-triaryl-3-cyano-4H-pyran (I) in AcOH (2 mmol) at 0°C, a solution of nitrosylsulfuric acid (prepared from 2.2 mmol of NaNO_2 , 23 ml of H_2SO_4 and 7 ml of water) was added. The resulting suspension was stirred at 0°C for 6-7 h. The solution was then poured into ice water to separate a solid. After keeping the mixture in a refrigerator overnight, the precipitate was filtered, washed with water until neutral pH of the liquors, and recrystallized from an appropriate solvent.

3-Cyano-4,5,6-triphenyl-2-pyrone (IVa) - Following the general procedure, this compound was obtained in 81% yield. mp 221-222 °C (EtOH). IR (KBr): ν_{\max} 2230, 1725, 1600, 1570, 1500, 1480, 1440, 1370, 1330, 1250, 1155, 1060, 1040, 1020, 850 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ (ppm) 7.0-7.3 (m, 15H, arom).

Anal. Calcd for $\text{C}_{24}\text{H}_{15}\text{NO}_2$: C, 82.52; H, 4.29; N, 4.01. Found: C, 82.18; H, 4.63; N, 4.12

3-Cyano-5,6-diphenyl-4-(p-tolyl)-2-pyrone (IVb) - This compound was obtained in 76% yield. mp 200-201 °C (EtOH). IR (KBr): ν_{\max} 2195, 1735, 1605, 1565, 1505, 1485, 1445, 1375, 1340, 1245, 1185, 1165, 1065, 1025, 965, 860 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ (ppm) 2.22 (s, 3H, CH_3), 6.9-7.3 (m, 14H, arom) Mass spectrum: m/z (relative intensity) 363(M^+ , 37), 362(5), 335(10), 286(16), 230(4), 202(8), 200(6), 199(4), 106(8), 105(100), 77(33), 51(4), 32(7). Anal. Calcd. for $\text{C}_{25}\text{H}_{17}\text{NO}_2$: C, 82.64; H, 4.68; N, 3.85. Found: C, 82.95; H, 4.98; N, 4.08.

3-Cyano-4-(p-methoxyphenyl)-5,6-diphenyl-2-pyrone (IVc) - This compound was obtained in 73% yield. mp 212-213 °C (EtOH). IR (KBr): ν_{\max} 2225, 1740, 1600, 1520, 1480, 1445, 1370, 1305, 1260, 1180, 1165, 1120, 1030, 960, 840, 790, 710 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ (ppm) 3.66 (s, 3H, CH_3O), 6.6-7.3 (m, 14H, arom.). Anal. Calcd. for $\text{C}_{25}\text{H}_{17}\text{NO}_3$: C, 79.15; H, 4.48; N, 3.69. Found: C, 78.69; H, 4.53; N, 4.04.

4,6-Diaryl-5-benzoyl-3-cyano-2-pyrones (VI) and 4,6-Diaryl-5-benzoyl-3-cyano-2-pyridones (VII).

General Procedure - The corresponding V (2 mmol) was suspended in AcOH at 0 °C and a solution of nitrosylsulfuric acid (previously prepared from 2.2 mmol of NaNO_2 , 23 ml of H_2SO_4 and 7 ml of water) was added. The resulting suspension was stirred at 0 °C for about 7 h. and then poured into ice water. After keeping the mixture cold overnight, the precipitate was filtered off and washed with plenty of water until neutral pH of the liquors. TLC of the resulting solid showed two compounds, which were separated by means of flash column chromatography using the appropriate eluent in each case. Pyrones VI were isolated from the first fraction, whereas pyridones VII were obtained from the last fraction. Both compounds were isolated in good purity, but further purified by recrystallization from an appropriate solvent.

5-Benzoyl-3-cyano-4,6-diphenyl-2-pyrone (VIa) and 5-Benzoyl-3-cyano-4,6-diphenyl-2-pyridone (VIIa)

Following the general procedure, the isolated mixture was chromatographed on silica gel using hexane: AcOEt (7:3) as the eluent. The first fraction was evaporated to dryness and recrystallized from EtOH to give VIa in 34% yield. mp 216-218 °C. IR (KBr): ν_{\max} 2190, 1735, 1660, 1610, 1595, 1580, 1520, 1490, 1440, 1360, 1340, 1260, 1220, 1200, 1140, 1080, 1050, 1025, 1000, 940, 850 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ (ppm) 6.9-7.7 (m, 15H, arom.). Mass spectrum: m/z (relative intensity) 377(M^+ , 51), 376(16), 349(7), 348(9), 300(7), 285(5), 284(26), 272(6), 204(5), 202(21), 201(9), 200(16), 199(12), 198(7), 106(9), 105(100), 101(4), 100(4), 78(4), 77(60), 51(9). Anal. Calcd. for $\text{C}_{25}\text{H}_{15}\text{NO}_3$: C, 79.57; H, 3.98; N, 3.71. Found: C, 79.45; H, 4.33; N, 3.47.

Evaporation of the second fraction and recrystallization gave VIIa in 17% yield. mp 316-318 °C (EtOH). IR (KBr): ν_{\max} 3200-2800, 2220, 1650, 1620, 1570, 1565, 1530, 1485, 1440, 1385, 1310, 1280, 1225, 1160, 1120, 1000, 940, 845, 770 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ (ppm) 6.8-7.6 (m, 15H, arom., NH). Mass spectrum: m/z (relative intensity) 376(M^+ , 24), 375(71), 374(27), 347(7), 346(20), 300(25), 299(100), 281(10), 204(7), 202(32), 201(14), 200(25), 199(18), 198(11), 149(14), 105(86), 104(9), 77(54). Anal. Calcd. for $\text{C}_{25}\text{H}_{16}\text{N}_2\text{O}_2$: C, 79.79; H, 4.26; N, 7.45. Found: C, 79.33; H, 4.28; N, 7.43.

5-Benzoyl-3-cyano-6-phenyl-4-(p-tolyl)-2-pyrone (VIb) and 5-Benzoyl-3-cyano-6-phenyl-4-(p-tolyl)-2-pyridone (VIIf) - The first fraction of chromatography gave VIb in 48% yield. mp 134-136 °C (EtOH). IR (KBr): ν_{\max} 2240, 1740, 1675, 1610, 1530, 1500, 1450, 1340, 1265, 1140, 940, 820 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ (ppm) 2.15 (s, 3H, CH_3), 6.8-7.7 (m, 14H, arom.). Anal. Calcd. for $\text{C}_{26}\text{H}_{17}\text{NO}_3$: C, 79.79; H, 4.35; N, 3.58. Found: C, 79.78; H, 4.30; N, 4.19.

Compound VIIf was obtained from the second fraction and recrystallized from EtOH in 12% yield. mp 303-305 °C. IR (KBr): ν_{\max} 3100-2800, 2220, 1640, 1465, 1445, 1310, 1280, 1230, 1130, 1000, 935 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ (ppm) 2.15 (s, 3H, CH_3), 6.7-7.5 (m, 14H, arom., NH). Anal. Calcd. for $\text{C}_{26}\text{H}_{18}\text{N}_2\text{O}_2$: C, 80.00; H, 4.62; N, 7.18. Found: C, 79.41; H, 4.81; N, 6.79.

5-Benzoyl-3-cyano-4-(p-methoxyphenyl)-6-phenyl-2-pyrone (VIc) and 5-Benzoyl-3-cyano-4-(p-methoxyphenyl)-6-phenyl-2-pyridone (VIIfc) - Compound VIc was isolated from the first fraction of the chromatography in 25% yield. mp 206-207 °C (EtOH). IR (KBr): ν_{\max} 2220, 1735, 1660, 1600, 1520, 1490, 1440, 1360, 1330, 1290, 1250, 1170, 1130, 1020, 920, 840, 820 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ (ppm) 3.6 (s, 3H, CH_3O), 6.6-7.7 (m, 14H, arom.). Anal. Calcd. for $\text{C}_{26}\text{H}_{17}\text{NO}_4$: C, 76.66; H, 4.18; N, 3.44. Found: C, 76.24; H, 4.32; N, 3.61.

The second fraction of the eluate afforded VIIfc in 25% yield. mp 270-273 °C (EtOH). IR (KBr): ν_{\max} 3200-2800, 2230, 1645, 1610, 1565, 1520, 1500, 1450, 1300, 1260, 1240, 1180, 1140, 1035, 930, 840, 830, 780 cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ (ppm) 3.6 (s, 3H, CH_3O), 6.6-7.5 (m, 14H, arom., NH). Anal. Calcd. for $\text{C}_{26}\text{H}_{18}\text{N}_2\text{O}_3$: C, 76.85; H, 4.43; N, 6.90. Found: C, 76.40; H, 4.74; N, 6.86.

Reaction of 2-Amino-5-benzoyl-3-cyano-4,6-diphenyl-4H-pyran (Va) with Sulfuric Acid / Acetic Acid - Pyran Va (8 mmol) was suspended in ca. 20 ml of AcOH and a solution of 94 ml of H_2SO_4 in 28 ml of water was added. The reaction mixture was stirred at 0 °C for 6.5 h. The solution was poured into water and kept in a refrigerator overnight. The deposited solid was filtered and washed with water until neutral pH of the washing liquors. TLC showed that the solid contains two compounds, and they were separated by means of flash column chromatography on silica gel with AcOEt-hexane (6:4). Two compounds thus isolated were enough pure. The first one was 5-benzoyl-3-cyano-4,6-diphenyl-3,4-dihydro-2-pyridone (IXa) (31% yield). mp 240-242 °C (EtOH). IR (KBr): ν_{\max} 3500-2800, 1700,

1600, 1470, 1450, 1380, 1315, 1280, 1250, 1200, 1180, 1150, 1070, 1050, 1020, 1000, 950 cm^{-1} .

$^1\text{H-NMR}$ (DMSO-d_6 + TFA): δ (ppm) 4.3 (d, 1H), 5.1 (d, 1H), 4.6 (bs, 1H, NH), 6.7-7.3 (m, 15H, arom).

Mass spectrum: m/z (relative intensity) 378(M^+ , 47), 377(24), 352(36), 351(72), 350(12), 338(8), 310(8), 301(6), 274(39), 273(43), 206(17), 105(100), 104(22), 77(76). Anal. Calcd. for $\text{C}_{25}\text{H}_{18}\text{N}_2\text{O}_2$: C, 79.36; H, 4.76; N, 7.40. Found: C, 79.15; H, 5.10; N, 7.40.

Evaporation of the last fraction of the eluate gave oxoamide VIIIa in 18% yield. mp 138-140 $^\circ\text{C}$ (EtOH). IR (KBr): ν_{max} 3400-2900, 1680, 1600, 1460, 1350, 1280, 1200, 1140, 1070, 1040, 1000, 900, 780 cm^{-1} . $^1\text{H-NMR}$ (DMSO-d_6): δ (ppm) 3.5 (d, 1H), 4.3 (d, 1H), 6.6-7.4 (m, 15H, arom.), 7.5 (bs, 2H, NH_2), 9.85 (s, 1H, OH). Mass spectrum: m/z (relative intensity) 396(M^+ , 2), 395(5), 353(4), 352(29), 351(100), 274(6), 248(5), 176(3), 115(3), 106(2), 105(33), 77(24). Anal. Calcd. for $\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_3$: C, 75.76; H, 5.05; N, 7.07. Found: C, 74.91; H, 5.13; N, 6.83.

Reaction of 2-Amino-5-benzoyl-3-cyano-4-(p-methoxyphenyl)-6-phenyl-4H-pyran (Vc) with Sulfuric Acid / Acetic Acid - Following the same procedure as described for Va, Vc was treated with H_2SO_4 in AcOH. The resulting solid was a mixture of two compounds (TLC), but only the corresponding 3,4-dihydro-2-pyridone IXc could be isolated by column chromatography in 34% yield. mp 259-261 $^\circ\text{C}$ (EtOH). IR (KBr): ν_{max} 3200-2800, 1700, 1600, 1480, 1450, 1390, 1310, 1250, 1180, 1030, 950, 810 cm^{-1} . $^1\text{H-NMR}$ (DMSO-d_6 + TFA): δ (ppm) 3.7 (s, 3H, CH_3O), 6.5-7.5 (m, 15H, arom.), 5.2 (d, 1H), 4.5 (bs, 1H, NH), 4.3 (d, 1H). Anal. Calcd. for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_3$: C, 76.47; H, 4.90; N, 6.86. Found: C, 76.61; H, 4.84; N, 6.73.

2-Amino-3-cyano-4,5,6-triarylpyridines (X). General Procedure - An appropriate pyran I (3 mmol) was dissolved in ca. 11 ml of glacial acetic acid and 12 mmol of ammonium acetate added. The solution was refluxed for 1-3 h. and then kept at room temperature overnight. The reaction mixture was then poured into water. The deposited solid was filtered, washed with water until neutral pH of the washing liquors, and purified by recrystallization.

2-Amino-3-cyano-4,5,6-triphenylpyridine (Xa) - According to the general procedure, the reaction mixture was refluxed until no starting material was left (TLC). Compound Xa was obtained in 67% yield. mp 238-239 $^\circ\text{C}$ (EtOH)¹⁷. IR (KBr): ν_{max} 3400, 3200, 3050, 2150, 1600, 1500, 1460, 1420, 1400, 1340, 1220, 1000, 980, 900 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 5.35 (bs, 2H, NH_2), 6.6-7.2 (m, 15H, arom). Mass spectrum: m/z (relative intensity) 347(M^+ , 12), 202(18), 201(8), 200(14), 199(11), 198(6), 180(6), 165(4), 106(8), 105(10), 101(4), 77(23).

2-Amino-3-cyano-5,6-diphenyl-4-(p-tolyl)pyridine (Xb) - This compound was obtained in 91% yield. mp 232-233 $^\circ\text{C}$ (EtOH)¹⁷. IR (KBr): ν_{max} 3370, 3200, 3050, 2130, 1580, 1500, 1470, 1400, 1330, 1200, 980, 760 cm^{-1} . $^1\text{H-NMR}$ (DMSO-d_6): δ (ppm) 2.2 (s, 3H, CH_3), 5.4 (bs, 2H, NH_2), 6.6-7.2 (m, 14H, arom).

Reaction of 2-Amino-5-benzoyl-3-cyano-4,6-diphenyl-4H-pyran (Va) with Ammonium Acetate / Acetic acid - Pyran Va (0.3 mmol) and ammonium acetate (1 mmol) were suspended in 6 ml of AcOH. The solution was refluxed until starting material was exhausted (TLC, six hours). The reaction mixture was a very complex mixture of decomposition products, from which no pure compound could be isolated.

Reaction of 2-Amino-3-cyano-4,5,6-triphenyl-4H-pyran (Ia) with Acetic Anhydride - A solution of 8 mmol of Ia in 11 ml of Ac_2O was refluxed for 5 h. After a few hours' standing at room temperature, a precipitate separated. It was filtered and washed with a small amount of diethyl ether. Separation of the two compounds present in the precipitate was carried out by flash column chromatography on silica gel with CH_2Cl_2 -AcOEt (7:3). N,N-Diacetylaminopyran XIIa was eluted first and isolated, upon evaporation of the solvent in 18% yield. mp 164-166 °C (EtOH). IR (KBr): ν_{max} 3050, 3020, 2210, 1725, 1675, 1640, 1600, 1490, 1440, 1365, 1330, 1225, 1150, 1100, 1070, 1025, 1000, 980, 950 cm^{-1} . $^1\text{H-NMR}$ (DMSO-d_6): δ (ppm) 2.35 (s, 6H, CH_3), 4.8 (s, 1H), 6.6-7.3 (m, 15H, arom.). Mass spectrum: m/z (relative intensity) 438(M^+ , 8), 433(26), 392(13), 391(44), 351(13), 350(49), 349(17), 333(22), 315(17), 274(21), 273(100), 202(17), 200(13), 178(23), 165(5), 152(5), 105(72), 77(26). Anal. Calcd. for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_3$: C, 77.42; H, 5.07; N, 6.45. Found: C, 77.64; H, 5.36; N, 6.63. The second fraction of the eluate gave N-acetylaminopyran XIa in 5% yield. mp 285-287 °C (EtOH). IR (KBr): ν_{max} 3000-2600, 1650, 1600, 1490, 1390, 1320, 1250, 1220, 1150, 1120, 1070, 1020, 960, 910, 830 cm^{-1} . $^1\text{H-NMR}$ (DMSO-d_6): δ (ppm) 2.2 (s, 3H, CH_3), 4.6 (s, 1H), 6.6-7.2 (m, 15H, arom., NH). Mass spectrum: m/z (relative intensity) 396(M^+ , 42), 317(3), 316(25), 315(100), 308(4), 307(3), 202(3), 196(5), 178(3), 157(4), 140(3), 105(10), 77(9). Anal. Calcd. for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_2$: C, 79.60, H, 5.10; N, 7.14. Found: C, 79.35; H, 5.31; N, 7.22.

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