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SYNTHESIS OF COMPOUNDS OF INTEREST IN PROTON TRANSFER SPECTROSCOPY

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Abstract: A new series of compounds has been prepared for use in proton transfer spectroscopy. The complexes **6a**-**6d** have been converted into the fully characterised perchlorates **7a**-**7d** and the corresponding anhydro bases **8a**-**8d**.

Proton transfer spectroscopy is a subject of current importance and of great potential interest.[1] 3-Hydroxyflavone and its congeners have been extensively studied.[1] It seemed to us that an extended molecule of the same general family might show even more interesting behavior. Thus, a series of compounds of general formula **1a** would afford by proton transfer zwitterionic tautomer **1b**. "X" would be typically oxygen, sulfur, selenium, tellurium and nitrogen.

We set as our first synthetic target the compounds **2a** and **2b**. The presence of the two methyl groups in the pyrone derived ring makes the syntheses easier. These structures are the anhydrobases of the corresponding pyrylium salts **3a** and **3b**.

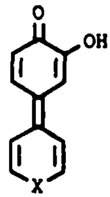
There is already considerable literature on the synthesis and reactivity of pyrylium salts.[2] Pyrylium salts of type **3** have been conveniently synthesized[2a,b] from the addition of Grignard or organo-lithium reagents to 4-(H)-pyranones. However, in some cases, electrophilically activated 4(H)-pyranones have been substituted into electron-rich aromatics, for example, using phosphorus oxychloride[3] or phosgene.[4]

We first examined the condensation of 2,6-dimethyl-4(H)-pyranone with catechol under the conditions[3] used with success for resorcinol. Catechol is less nucleophilic than resorcinol and we were unable to obtain any of the desired pyrylium salt.

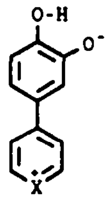
We then turned to the traditional Grignard reagents. We prepared two different protected derivatives of 4-bromocatechol. The hitherto unknown catechol derivative **4a** was obtained from catechol in two steps. The reaction of catechol with cyclohexanone in boiling toluene catalyzed by p-toluene-sulfonic acid[5] followed by bromination with N-bromosuccinimide[6] gave crystalline **4a** in good (67%) overall yield. The reverse sequence of bromination of catechol followed by ketalization was found to be less effective.

The catechol derivative **4b** was prepared in the following way. Treatment of guaiacol with bromine according to a slightly modified literature procedure[7] gave 4-bromoguaiacol. Without purification this was reacted in dimethylformamide with sodium hydride and chloromethyl methyl ether. This afforded the desired derivative **4b** in satisfactory yield (63%) after distillation.

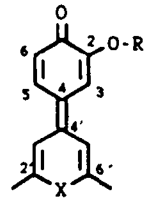
The bromo-derivatives **4a** and **4b** in tetrahydrofuran were converted into Grignard reagents in the normal way. The solutions thus prepared were added to 2,6-dimethyl-4(H)-pyranone in the same solvent.[8] This type



1a

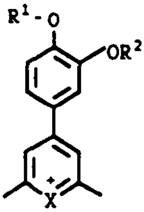


1b



2a R=H, X=O

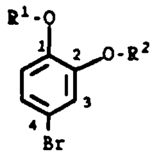
2b R=Me, X=O



3a R^1 = R^2 = H

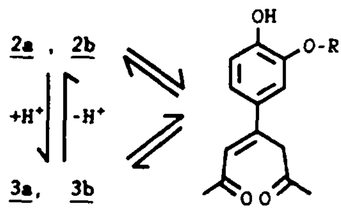
3b R^1 = H, R^2 = Me

3c R^1, R^2 = C_6H_{10}



4a R^1, R^2 = C_6H_{10}

4b R^1 = CH_2OCH_3, R^2 = Me



5a R = H

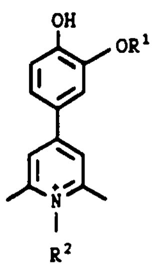
5b R = Me

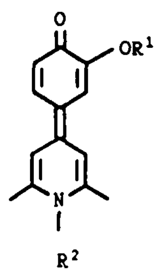
6a = 7a : 8a 1:1

6b = 7b : 8b 1:1

6c = 7c : 8c 1:1

6d = 7d : 8d 1:1





7a R^1 = H, R^2 = *n*-Bu

7b R^1 = H, R^2 = Ph

7c R^1 = Me, R^2 = Ph

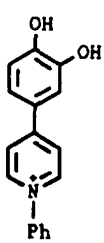
7d R^1 = H, R^2 = *p*-$NMe_2C_6H_4$

8a R^1 = H, R^2 = *n*-Bu

8b R^1 = H, R^2 = Ph

8c R^1 = Me, R^2 = Ph

8d R^1 = H, R^2 = *p*-$NMe_2C_6H_4$



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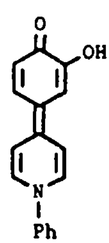

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of reaction is usually carried out [2a-b,8] and quenched at O°. We modified the procedure with improved yields by allowing the reaction solutions to warm to room temperature before quenching with perchloric acid. The pyrylium salt **3c** was obtained in crystalline form (56%) from **4a**. Further hydrolysis with ethanol-perchloric acid gave the perchlorate **3a** (47% overall).

A perchlorate mixture was obtained from **4b** with some loss of the methoxymethyl group. Further hydrolysis with ethanolic aqueous perchloric acid gave the pyrylium salt **3b** in satisfactory overall yield (36%).

We also tried to synthesize a compound like **3a** but without the two methyl groups. Thus the Grignard from **4a** was reacted as above with 4(H)-pyranone. Unlike other reports in the literature we were unable under a variety of conditions to obtain the di-demethyl derivative of **3a**. The anhydro-bases **2a** and **2b** have not been described in the literature before, but similar more substituted compounds have been prepared.[4,9] We found that the perchlorate **3a**, on treatment with tributylamine in dry methylene dichloride, gave a good yield of the crystalline anhydrobase **2a**. We did not succeed in transforming **3b** into pure **2b** under a variety of conditions. However, the N.M.R. spectrum of the crude **2b** showed that it was present.

During the transformation of the pyrylium salts **3a,b** into their anhydrobases, our observations suggested that compounds **2a,b** might exist in the presence of water. To prove this we examined the u.v. spectra of **3a**, **3b** and **2a** at pH=7 in water. All three compounds gave very similar spectra with the strongest absorption at 478 nm, but the intensity of this band diminished and a new band at 331 nm grew until an equilibrium state was reached after about 2h. In contrast the pyrylium salts were deprotonated instantaneously with base forming the anhydrobases which slowly hydrated to the diketone **5a** (λ max=331nm). When the sample was acidified with hydrochloric acid to pH=1 the pyrylium salts with maximum absorption at 402 nm was present. Compound **3a** was also tested at pH=6. The U.V. spectrum showed that the conversion of this into **2a** was not complete and at an equilibrium state all three species **2a**, **3a**, **5a** were observed.

This type of observation is very well known for pyrylium salts unable to form stable anhydro-bases.[2b,10] Normally aqueous media are used without any precautions for the conversion of pyrylium salts into their anhydro-bases.[1b,4,9]

From the point of view of proton transfer spectroscopy, compound **2b** was to provide negative evidence of the need for the proton transfer. Since pyrylium salts, as well as anhydro-bases [2b,10-15], react rapidly with primary amines to give the corresponding aza-analogues, the same sort of information about proton transfer can be obtained if X in formulae of type **2** and **3** is nitrogen. Pyrylium salt **3a** reacted readily with *n*-butylamine in presence of tributylamine to give in good yield (over 80%) a 1:1 crystalline complex **6a** of the pyridinium perchlorate **7a** and its anhydrobase **8a**. The structure of this complex was established by N.M.R. and U.V. spectroscopy. The exchange rate at the -OH protons between **7a** and **8a** was very fast on the N.M.R. time scale. Therefore, only an averaged spectrum was seen. For the complex **6a** the chemical shifts values were, within error limits the arithmetic mean of the chemical shifts of the corresponding protons of **7a** and **8a**. We assume that **6a** is a charge transfer complex of **7a** as an acceptor and **8a** as a donor. The U.V. spectrum of **6a** was the sum of the spectra of **7a** and **8a** in 1:1 molar proportions.

Complex **6a** was easily converted into the pyrylium perchlorate **7a** by an excess of perchloric acid in ethanol. To transform the complex **6a** into the anhydro-base **8a** needed an excess of diazabicycloundecane (D.B.U).

The reaction of **3a** with aniline and tributylamine afforded a 1:1 complex **6b** of **7b** and **8b**. Treatment with the excess perchloric acid gave the crystalline perchlorate **7b**. The same reaction carried out with **3b** gave 1:1 complex **6c** of **7c** and **8c**. The perchlorate **7c** and the anhydrobase **8c** were prepared from complex **6c** as before. Thus in **8c** we had a suitable compound lacking a mobile proton for proton transfer spectroscopy.

We also prepared the complex **6d** of the *p*-dimethylaminophenyl derivatives **7d** and **8d** using the techniques already described. The anhydro-base **8d** contains the longest chromophore of all the compounds described here.

Finally, in order to complete the series, we prepared the desmethyl compounds **9** and **10**. The Grignard reagent from **4a** was added to 4(H)-pyranone. The resulting mixture was treated with aniline and acetic acid. The cyclohexylidene residue was removed with the ethanolic perchloric acid, and eventually, a small yield of pyrylium salt **9** was secured. This was smoothly converted to the desired anhydro-base **10** on treatment with D.B.U.

Experimental

N.M.R. spectra were recorded at 200MHz with a Varian GEMINI 200 spectrometer. Chemical shifts are in ppm with respect to internal TMS. Coupling constants are in Hz. The first order approximation was used for determination of spectral parameters. IR spectra were measured with a Perkin-Elmer 881 spectrometer. U.V. spectra were measured in acetonitrile (J.T. Baker Inc., for spectrophotometry) with a Beckman DU-7 spectometer. For the pyrylium salts **3a** and **3b** and for pyridinium salt **9** a small quantity (3 drops per 50ml of the solvent) of 70% perchloric acid was added. Electron impact (70eV) mass spectra were carried out with a Hewlett-Packard 5995c quadrupole GC-MS instrument. Exact mass measurements were performed with a VG Analytical 705 high resolution double focusing magnetic sector mass spectrometer with an attached VG Analytical 11/250J data system. Melting points were determined on a Kofler hot stage and are uncorrected. All solvents and reagents were purified by standard procedures. Buffer solution pH=7 (potassium phosphate monobasic sodium hydroxide, 0.05 molar) was purchased from Fisher Scientific company and buffer solution pH=6 (acetate buffer, ionic strength 0.2) was prepared according to the literature.[16] Reaction mixtures after work-up were dried over anhydrous sodium sulfate. This was filtered and the solvent was evaporated under reduced pressure on a rotary evaporator.

Cyclohexylidene Derivative of 4-Bromocatechol (4a).

Catechol (22g, 0.2 mol) was converted into its cyclohexylidene derivative according to the literature.[5] The crude product was purified by filtration through silica gel (60g, Aldrich, 130-270 mesh) with hexanes as eluent. The yield was 34.5g (90.7%). The cyclohexylidene derivative (5.7g, 0.03mol) was dissolved in dry methylene chloride (40ml) and cooled to 0°, then NBS (5.35g, 0.0309 mol) was added portionwise during 15 minutes. The mixture was stirred at O° to 10° for 3.5h and kept in a refrigerator (at ca. 10°) overnight. The pale yellow solution was washed with water, sodium hydroxide (10%), water, brine and dried. The product was crystallized twice from methanol giving 5.9g (67% calculated based on catechol) of compound **4a** m.p. 55-57°. Calc'd for: $C_{12}H_{13}BrO_2$ (M^+): 268.0099 and 270.0097; found: 268.0099 and 270.0087 respectively. NMR ($CDCl_3$): δ 6.90-6.86 (m,2H), 6.59 (m,1H), 1.95-1.40 (m,10H). IR(CCl_4): 2934, 1478, 1278, 1229, 1068cm^{-1}.

4-Bromo-2-methoxy-1-methoxymethylenoxybenzene (4b).

4-Bromoguaiacol was synthesized by a modified literature procedure.[7] Thus guaiacol (7.44g, 0.06 mol) in carbon tetrachloride (50ml) was cooled to -25°. At this temperature bromine (3.1ml, 0.06 mol) in CCl_4 (10ml) was added dropwise over a period of about 50 min. The resulting mixture was stirred for 30 min. and was allowed to warm to -15°. Routine work-up afforded a crude product which was used without further purification.

In a round-bottomed flame-dried flask equipped with magnetic bar, dropping funnel and inlet/outlet for argon sodium hydride (2.9g, 0.07 mol) as 60% suspension in mineral oil was placed. The oil was removed by washing with dry hexanes followed by addition of dry DMF (50ml). To this 4-bromoguaiacol (13.18g, 0.065 mol) in dry DMF (20ml) was added dropwise during 30 min. with cooling (cold water). When addition of the phenol was complete, the sodium hydride went into solution. Chloromethyl methyl ether (5.5ml, 0.072 mol) was added dropwise within 30 min and the mixture was stirred for an additional 2h at room temperature. The reaction mixture was diluted with water. The organic layer was separated and the water layer was extracted three times with hexanes. The organic layers were combined and washed subsequently with water, sodium hydroxide (5%), water, brine and dried. The crude product was purified by distillation *in vacuo*. The product was collected from 125° to 130° at 2.5 mm Hg. The yield was 10.87g (63% calculated based on guaiacol). Calc'd for : $C_9H_{11}BrO_3$(M^+): 245.9892 and 247.9871, found: 245.9895 and 247.9874 respectively; IR(neat): 2953, 2827, 1589, 1495, 1400, 1246, 1078, 991, 853cm^{-1}; NMR ($CDCl_3$): δ 7.01 (S,3H), 5.19 (S,2H), 3.86 (S,3H), 3.49 (S,3H).

2,6-Dimethyl-4-(2",2"-pentamethylenebenzodioxole-5'-yl)pyrlium Perchlorate (3c).

A flame-dried, round-bottomed flask equipped with a magnetic stirring bar, reflux condenser with protection against moisture and an argon inlet was flushed with argon and charged with magnesium (1.23g, 0.0506 mol) and dry THF (50ml). To this mixture 2 drops of 1,2-dibromoethane were added and the resulting mixture was refluxed for a few minutes and then cooled to ambient temperature followed by addition of compound **4a** (13.49g, 0.05mol). The resulting mixture was gently refluxed for about 1.5h. During this time most of the magnesium went into solution. The solution of the Grignard reagent was tranfered by a canula to an ice cold suspension of 2,6-dimethyl-4H-pyranone (6.3g, 0.0507 mol) in dry THF (40ml) within 10 min. The resulting dark red solution was stirred for 5 min. at 0° and 30 min. at ca 20°. This was then added to an ice cold solution of perchloric acid (40 ml of 70% $HClO_4$ in 250 ml of water). Dark yellow crystals were precipitated. This was diluted with water (500ml) and left in the refrigerator for 3h. The crystals were filtered off, washed with water and hexanes-ethyl acetate mixture (3:2, v/v). After drying in vacuum over phosphorus pentaoxide the yield was 11.25g (56.2%). This was pure enough (by NMR) to be used in the next step. An analytical sample was recrystallized from ethanol. It had m.p. 180-193° decomp.; calc'd for: $C_{19}H_{21}ClO_7$ (M^+-$HClO_4$): 296.1412; found: 296.1417; IR($CHCl_3$): 3011, 2933, 1631, 1091cm^{-1}; NMR ($CDCl_3$): δ 7.94 (s,2H), 7.81 (dd,J=2.0,J=8.4,1H), 7.38 (d,J=2.0,1H), 6.95 (d,J=8.4,1H), 2.85 (s,6H), 2.00-1.48 (m,10H); UV: λ max (lgε): 275.5 (4.06), 295.0 (4.05), 332.5 (3.83), 420.5 (4.38)nm.

4-(3′,4′-Dihydroxyphenyl)-2,6-dimethylpyrylium Perchlorate (3a).

The stirred mixture of compound 3c(5.0g, 0.0126 mol), 95% ethanol (75ml) and 70% perchloric acid (15ml) was slowly brought to the boil. The starting material went into solution. After ca. 40 min. yellow crystals precipitated. After 1.5h the mixture was cooled for a few hours. The crystals were filtered off, washed with ethanol and finally with ethyl acetate. The yield of **3a**, after recrystallization from ethanol, was 3.3g (83%). It had m.p. 285-288° decomp. calc'd for : $C_{13}H_{13}ClO_7$ (m^+-$HClO_4$): 216.0786; found: 216.0786; IR(nujol): 3243, 1641, 1603, 1531, 1336, 1276, 1060 cm^{-1}; NMR(DMSO-d_6): δ 8.23 (s,2H), 7.78 (dd,J=2.4, J=8.5,1H), 7.64 (d,J=2.4,1H), 7.03 (d,J=8.5,1H), 2.77 (s,6H); UV: λ max (lgε): 265.5 (3.85), 295 (4.08), 352 shoulder (3.97), 405 (4.39)nm.

4-(2′,6′-Dimethyl-4′H-pyran-4′-ylidene)-2-hydroxy-2,5-cyclohexadien-1-one (2a).

The finely powdered perchlorate 3a (0.1294, 0.41 mmol) was suspended in dry methylene chloride (20ml). Dry tributylamine (0.11ml, 0.46 mmol) was added to this suspended solution in one portion under stirring. A dark red solution was obtained. The mixture was stirred at room temperature for 15 min, filtered and put into a freezer for a few hours. The dark red, almost black, crystals of **2a** were filtered off, washed with the same solvent and dried *in vacuo*. The yield was 0.0664g (75%). It decomposed above 150°C; IR (nujol): 3200, 1661, 1609, 1553, 1518, 1339, 1211, 914 cm^{-1}; NMR($CDCl_3$):δ 7.54 (dd,J=2.7, J=9.4, 1H), 7.03 (d,J=2.7,1H), 6.72 (s,2H), 6.56 (d,J=9.4, 1H), 2.31(s,6H); UV: λ max(lgε): 268.5 (3.94), 347 (3.45), 457 shoulder (4.42), 479.5 (4.60), 510.5 (4.56)nm.

4-(4'-Hydroxy-3'-methoxyphenyl)-2,6-dimethylpyrylium Perchlorate (3b).

From 5.33g (0.0207 mol) of bromo derivative **4b**, 2.9g of crude perchlorate was obtained according to the procedure previously described. The NMR spectrum showed it was the mixture of protected and deprotected (**3b**) derivative. This mixture was added to 30ml of ethanol, 3ml of water and 1 ml of 70% perchloric acid and refluxed with stirring for 1h, cooled and kept in the freezer overnight. The yellow crystals were filtered off, washed with ethanol and ethyl acetate. Crystallization from ethanol gave 2.45g (36%) of compound **3b** with m.p. 210-217° decomp. calc'd for: $C_{14}H_{15}ClO_7$ (M^+-$HClO_4$): 230.0941; found: 230.0943 IR(nujol): 3358, 1641, 1578, 1522, 1338, 1298, 1064cm^{-1}; NMR (DMSO-d6): δ 8.44 (s,2H), 7.93 (dd,J=2.1,J=8.6,1H), 7.78(d,J=2.1,1H), 7.07(d,J=8.6, 1H), 3.94 (s,3H), 2.79 (s,6H), UV λ max (lgε): 269.5 (3.82), 295.5 (4.05), 345 (3.86), 407.5 (4.41)nm.

4-(N-Butyl-1',4'-dihydro-2',6'-dimethylpyridine-4'ylidene)-2-hydroxy-2,5- cyclohexadien-1-one (8a).

To a stirred suspension of **3a** (0.106g, 0.33 mmol) in dry methylene chloride (5ml), dry n-butylamine (0.036ml, 0.36 mmol) and tributylamine (0.079ml, 0.33 mmol) were added in sequence. The color of the mixture turned to dark red and after a few minutes yellow crystals precipitated. The reaction was stirred for four hours. The crystals were filtered, washed with dichloromethane and then with ethyl acetate. The yield of complex **6a** was 0.0913g (86%; pure by NMR and UV) with m.p. 231-235° decomp. Recrystallization from ethanol gave 0.08g (75%) with m.p. 234-240° decomp. NMR (DMSO-d6): δ 7.91 (s,2H), 7.40 (dd,J=2.3, J=8.5,1H), 7.31 (d,J=2.3,1H), 6.63 (d,J=8.5, 1H), 4.24 (m,2H), 2.62 (s,6H), 1.73 (m,2H), 1.44 (sx, J=7.5,2H), 0.96 (t,J=7.5,3H); UV: λ max (lgε): 260 (4.32), 288 (4.16), 349.5 (4.30), 475.5 (4.67)nm.

Complex **6a** (0.123g), ethanol (ca. 7ml) and 70% perchloric acid (0.3ml) were mixed together and brought to boil. The hot solution was filtered. The crystals precipitated on cooling were filtered, washed with cold ethanol and dried. The yield of perchlorate **7a** with m.p. 189-191° was 0.129g. NMR(DMSO-d6): 8.13 (s,2H), 7.43 (m,2H), 6.95 (d,J=8.8,1H), 4.37 (m,2H), 2.85 (s,6H), 1.78 (m,2H), 1.48 (sx,J=7.1,2h), 0.98 (t,J=7.1,3H); IR (nujol): 3373, 1635, 1604, 1566, 1167, 1117, 1029, 722cm^{-1}; UV: λ max (lgε): 255.5 (3.98), 288.5 (400), 347 (4.31)nm.

Complex **6a** (0.0643g, 0.1 mmol) was suspended in 4ml of acetonitrile and DBU (0.031ml, 0.21 mmol) was added at once with stirring. The color of the mixture turned to dark red and the crystal of the complex went into solution. After a few minutes new crystals precipitated. The mixture was stirred for 15 min at room temperature and kept in a freezer for a few hours. The crystals were filtered off and washed with ethyl acetate. The yield of compound **8a** with m.p. 215-218° (decomp) was 0.035g (65%). Calc'd for: $C_{17}H_{21}NO_2$ (m^+): 271.1572; found 271.1572; NMR (DMSO-d6): δ 7.64 (s,2H), 7.40 (dd,J=2.7, J=8.7,1H), 7.15 (d,J=2.7,1H), 6.17 (d,J=8.7,1H), 4.10 (m,2H), 2.62 (s,6H), 1.68 (m,2H), 1.42 (sx,J= 7.1, 2H) 0.96 (t,J=7.1,3H); IR (nujol): 3200, 1636, 1585, 1329, 1227, 1120cm^{-1}; UV: λ max (lgε): 262.5 (4.05), 286.5 (3.70), 300.5 (3.50), 476 (4.70)nm.

4-(1',4'-Dihydro-N-phenyl-2',6'-dimethylpyridine-4'-ylidene)-2-hydroxy-2,5- cyclohexadien-1-one (8b).

According to the procedure described for the synthesis of **8a** (see above) **3a** (0.106g, 0.33 mmol), aniline (0.06ml, 0.67 mmol) and tributylamine in dry dichloromethane (5ml) gave after 24h of stirring 0.108g (95%) of complex **6b** with m.p. 255-265° decomp. It was recrystallized from acetonitrile (89%) NMR(DMSO-d6): δ 8.05 (s,2H), 7.68-7.57 (m,5H), 7.53 (dd,J=2.4,J=8.6,1H), 7.39 (d,J=2.4,1H), 6.63 (d,J=8.6,1H), 2.22 (s,6H); UV: λ max (lgε): 261(4.33), 289(4.14), 354(4.32), 487.5(4.74)nm.

Perchlorate **7b** was obtained according to procedure described for **7a**. It had m.p. 280-284° decomp.;NMR(DMSO-d6): δ 8.31 (s,2H), 7.75-7.70 (m,3H), 7.66-7.61 (m,2H), 7.55-7.51 (m,2H), 6.99 (d,J=8.7,1H), 2.33 (s,6H) IR (nujol): 3369, 1632, 1602, 1326, 1278, 1210, 1101, 702cm^{-1}, UV: λ max (lgε): 258.5(3.97), 290(3.97), 323(4.02), 355(4.32) nm.

Complex **6b** (0.050g,0.073 mmol) in acetonitride (2ml) was converted into **8b** by DBU (0.025ml,0.17 mmol) as was described for **8a**. The yield of **8b** was 0.035g (83.5%). This decomposed slowly above 190° without melting up to 270°. Calc'd for: $C_{19}H_{17}NO$ (M^{+}): 291.1259; found 291.1263; NMR(DMSO-d6): δ 7.76 (s,2H), 7.68-7.63 (m,3H) 7.58-7.50 (m,3H), 7.24 (d,J=2.1,1H) 6.21 (d, J=8.8,1H), 2.10 (s,6H); IR=(nujol): 1642, 1585, 1535, 1330, 1202, 1122, 700cm^{-1}; UV: λ max (lgε): 263 (4.09), 300 (3.56), 3.25 (3.53), 487.5 (4.76) nm.

4-[1'-N-(4"-dimethylaminophenyl)-1,4-dihydro-2,6-dimethylpyridine-4'-ylidene]-2-hydroxy-2',5'-cyclo hexadien-1-one(8d).

N,N-dimethylamino-1,4-phenylenediamine converted **3a** (0.106g, 0.33 mmol) into complex **6d** (0.122g,96%) under conditions described for the reaction with aniline (see above). Complex **6d** was recrystallized from acetonitride (83%). It showed rapid decomposition at 258-265°. NMR (DMSO-d6): δ 8.13(s,2H),7.51(dd,J=2.2,J=8.4,1H) 7.45(d,J=2.2, 1H), 7.34(d,J=9.0,2H) 6.90(d,J=9.0,2H),6.80 (d,J=8.4,1H), 3.02(s,6H), 2.30(s,6H);UVλ max(lgε):264.5(4.79), 318(4.27), 351.5(4.37), 485.5(4.76) nm; UV(CH_3CN+HCl)(lgε): 260(4.02), 290(3.98), 320(4.00),360 (4.35)nm. Complex **6d** (0.0769,0.1mmol) in acetonitrile (4ml) was converted into the anhydro-base **8d** (0.0691g, 93%) by DBU (0.06ml, 0.4 mmol). Anhydro-base **8d** decomposed above 190°and did not melt up to 270°. Calc'd for:$C_{21}H_{22}N_2O_2$(M+): 334.1681; found: 334.1681; NMR (DMSO-d_6):δ 7.73 (s,2H), 7.50 (dd,J=2.6,J=8.8,1H), 7.27(d,J=9.0, 2H),7.22(d,J=2.6,1H), 6.81(d,J=9.0,2H), 6.20(d,J=8.8,1H), 3.00 (s,6H), 2.13 (s,6H);IR(nujol): 1638, 1584, 1506, 1331, 1210, 1112cm^{-1}; UV: λ max (lgε): 264 (4.49), 300.5 (3.75), 313.5 (3.72), 486 (4.80)nm

4-(1',4'-Dihydro-2',6'-dimethyl-1'-N-phenylpyridine-4'-ylidene)-2-methoxy-2,5-cyclohexadien-1-one (8c).

Perchlorate **3b** (0.2g, 0.605 mmol), aniline (0.15ml,1.6 mmol), tributamine (0.15ml,0.62 mmol) and dry methylene chloride (8ml) gave complex **6c** (0.19),89%). This was recrystallized from acetonitrile (80%). It decomposed at 245-250°;NMR(DMSO-d_6): 8.08(s,2H,7.72-7.59 (m,6H), (d,J=2.0,1H), 6.64 (d,J=8.6,1H) 3.83 (s,3H), 2.22 (s,6H); UV λmax (lgε): 255.5(3.9), 289.5 (3.94), 356 (4.36)nm.

Complex **6c** (0.0719,0.1mmol) in acetonitrile (2ml) was converted into **7c** (0.042,69%). It showed rapid decomposition at 215-220°C. Calc'd for $C_{20}H_{19}NO_2$ (M+): 305.1416;found: 305.1459; NMR (DMSO-d_6): δ 7.70-7.40 (m,8H), 7.16 (d,J=2.6,1H) 6.11 (d,9.0,1H, 3.69 (s,3H),2.06 (s,6H); IR(nujol): 1634, 1578, 1538, 1339, 1212, 1029, 709cm^{-1}; UV: λmax (lgε): 264.5 (4.09), 287.5(3.72), 340 (3.40), 498 (4.81)nm.

4-(1',4'-Dihydro-1'-N-phenylpyridine-4'-ylidene)-2-hydroxy-2,5-cyclohexadi en-1-one (10).

A Grignard reagent in THF was prepared from **4a** (2.02g,7.4mmol) as already described (see above). The solution was added to an ice cold solution of 4(H)-pyranone[17](0.708,7.4mmol) in 15ml of dry THF. When addition was complete the resulting mixture was stirred for 30 min. at O°, then aniline (0.25ml) and acetic acid (1ml) were added. The reaction mixture was stirred at room temperature for 23h. A yellow hygroscopic precipitate was filtered off and washed with THF. This was digested by THF (30ml), filtered off and washed with THF yielding a yellow powder (1.16g). This was partially soluble in $CDCl_3$. The NMR showed the presence of the cyclohexylidene derivative of **9**. The mixture (0.49g), 13ml Of 95% ethanol, water (0.5ml) and 70% perchloric acid were refluxed and stirred for 2.5 h. The solvent was distilled off. After several distillations with benzene-ethanol under reduced pressure a semi-crystalline product was formed. Crystallization from isopropanol-ethyl acetate and then from isopropanol gave **9** as yellow crystals (0.081g, 9% from pyranone), m.p. 249-255° decomp.; NMR (DMSO-d_6):δ 9.15 (d,J=6.9,2H), 8.25 (d,J=6.9,2H), 7.90-7.86 (m,2H), 7.76-7.71 (m,3H), 7.63 (dd,J=2.00,J=8.2,1H), 7.00 (d,J=8.2,1H):IR (nujol): 3367, 1635, 1613, 1316, 1259, 1094, 765cm^{-1};UV: λ max (lgε): 265.5(3.99), 324.5(3.87), 377(4.31)nm. Perchlorate **9** (0.036g, 0.05mmol)in acetonitrile (1ml) was converted into anhydro-base **10** by DBU(0.03,0.02mmol). The yield was 0.017g (65%). It decomposed above 190° without melting up to 290°; calc'd for :$C_{17}H_{13}NO_2$ (M+): 263.0946; found:263.0943; NMR (DMSO-d_6) δ 8.29 (d,J=7.5,2H), 7.75-7.52 (m,8H), 7.19 (d,J=2.6,1H), 6.24 (d,J=9.1,1H); IR(nujol): 1640, 1580, 1327, 1211, 1114, 760cm^{-1} ; UV: λ max (lgε): 265 (3.71), 340 (3.24), 513 (4.53)nm.

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