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Pyridazinium Ylides II. New Carbanion Disubstituted Ylides.

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Abstract: The first report of reaction between diazinium ylides and diazonoium salts to give C-disubstituted ylides is proposed. A mechanism is postulated for the reaction, which proceeds via nucleophilic attack rather than by 3+2 cycloaddition, to give C-disubstituted ylides. The intense colour of the products is attributed to an intramolecular charge transfer transition, for which a mechanism is proposed. © 1997 Elsevier Science Ltd.

Introduction.

We have previously reported[1, 2] the reaction between arylpyridazinium ylides and isocyanate that leads to stable disubstituted ylides. In order to obtain new stable C-disubstituted ylides in the pyridazine series and to establish structure stability reactivity correlations, we have investigated the reaction between 3-(4-halogenophenyl) pyridazinium ylides and diazoaromatic compounds. The reaction pathway of nitrogen ylides with diazoaromatic compounds depends on the structure of the ylide heterocycle and diazoaromatic compound.[3, 4, 5] The 3+2 dipolar cycloaddition with diazoaromatic compounds gives azabicycles whereas nucleophilic attack of the ylide carbanion on the diazoaromatic compound gives C-disubstituted ylides.

Results and discussion.

Previously we have devised a method for the preparation of monosubstituted 3-(4-halogenophenyl) pyridazinium ylides **5** - **8**,[6, 7] based on an adaptation of the Kröhnke salt reaction.[8] Monosubstituted pyridazinium ylides can be represented by a zwitterionic structure (**a**) or by a 1,3- dipolar structure (**b**), Fig.1. Theoretically, the reaction between ylides **5** - **8** and diazoaromatic compounds **9** and **10** could give carbanion disubstituted ylides or azabicyclic compounds. Experimentally it was found that the product formed between 3-(4-halogenophenyl) pyridazinium ylides **5** - **8** (generated in situ from the corresponding cycloimmonium salts **1** - **4**) with dioazoaromatic compounds gave the stable C-disubstituted ylides **12** - **19** (Fig. 1).

As the reaction mechanism we suggest, in the first step, nucleophilic attack of the ylide carbanion at the positive diazo group with formation of a cycloimmonium salts **11** (nonisolated); in the second step, salt **11** undergoes dehydrohalogenation in the basic reaction medium to give the carbanion disubstituted ylides **12-19.**

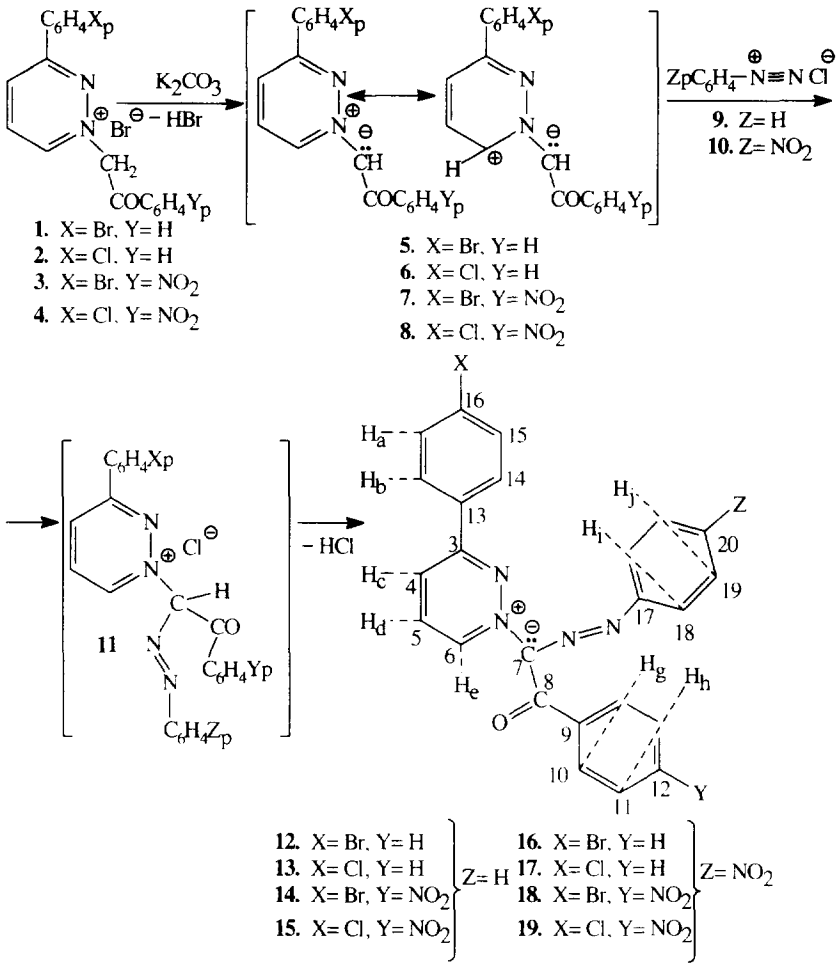

Figure 1. Reaction between pyridazinium ylides and diazoaromatic compounds.

The structure of the ylides **12** - **19** was proved through elemental and spectral (IR, UV- VIS, ^{1}H NMR, ^{13}C NMR) analysis. Thus, if we consider compound **14** as a representative of the series, the spectral analysis yields the following data:

It is known[9, 10] that in IR spectra it is difficult to attribute the band for the diazo group. Making use of the literature data[9, 10] and the intensity (low) and the position of the band from 1450 cm^{-1}, we consider that this band could be attributed to the valence vibration of diazo group. An other important band appear at 1485 cm^{-1}, with a very strong intensity, and it was attributed to a ketone group. The displacement of the ketone band to such low wave numbers (there is precedence for this in related cases[11]) might be explained by conjugation of the ketone group with the ylide carbanion and diazo group, as we suggest in Fig. 2. Moreover we consider that this extended conjugation phenomenon it is responsible for the great stability of this ylide.

^{1}H NMR spectra confirm the proposed structure. The most significant signal is that of the H_e proton

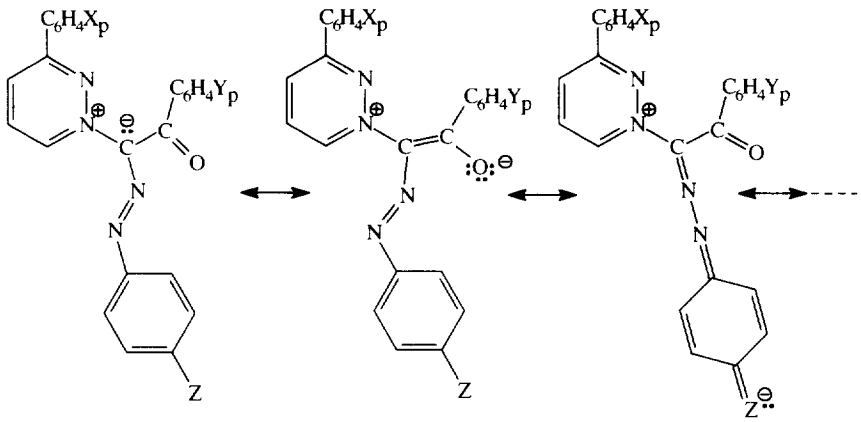

Figure 2. Possible canonical forms of ylides **12- 19**.

which appears at 8. 563- 8. 541 ppm, as a doublet (J_{cd} = 3. 40 ppm). The fact that this proton appears at such low chemical shifts as compared with the corresponding monosubstituted ylide[6, 7] (2. 50 ppm less), could be explained through the neighbourhood effect induced by the diazo group.

In the ^{13}C NMR spectra the carbon from the ketone group (C_8) appears at 155. 428 ppm with a low intensity. We should remark that this ketone carbon appears at very low chemical shifts compared with the monosubstituted ylide[12] (20 ppm less) and the related alkyl- aryl ketones (70 ppm less). We explain this through the extended conjugation phenomena of the negative charge from the ylide carbanion on the ketone and diazo groups as we already suggest in Fig. 2. We should also remark and the fact that the ylide carbon (C_7) appears at very high chemical shifts (112. 228 ppm) as compared with a saturated carbon. This could also be explained through the extended conjugation phenomena, Fig. 2.

All the remaining signals from IR, ^1H NMR and ^{13}C NMR are in accordance with the proposed structure.

The ylides **12- 19** are very intensely coloured compounds, which prompted us to make a study of the electronic absorption spectra. The literature data[13] for the corresponding monosubstituted ylides **5- 8** show that, in the electronic absorption spectra these ylides present a band with a reduced intensity around 500 nm. This band disappears in the protonation process with H_2SO_4 which means that this band might be attributed to an intramolecular charge transfer transition. Similar results have been obtained for other similar nitrogen ylides.[14, 15] The electronic absorption spectra of ylides **12- 19** were taken in acetone and the results are listed in Table 1.

Table 1. Results of the UV- VIS spectra for ylides **12- 19**.

Ylides/	λ_{ICT} (nm)							
solvent	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
Acetone	476. 00	474. 60	470. 20	466. 64	474. 40	472. 80	463. 40	459. 20
Acetone +H_2SO_4	←----------		disappears in the protonation process					----------→

As Table 1 show the ylides **12- 19** present an absorption band around 470 nm, which disappears in the protonation process. This band could be attributed to an intramolecular charge transfer transition (ICT) from the ylide carbanion to heterocycle and it is responsible for the appearance of colour (Fig. 3). As shown in Table 1, the wave number of the intramolecular charge transfer band depends essentially on the ylide carbanion substituents. To explain the value of the wave number [λ_{ICT} (nm)] in the intramolecular charge transfer spectra, we use the following equation[16]: $hc/\lambda_{ICT} = I - A - W$ (**1**)

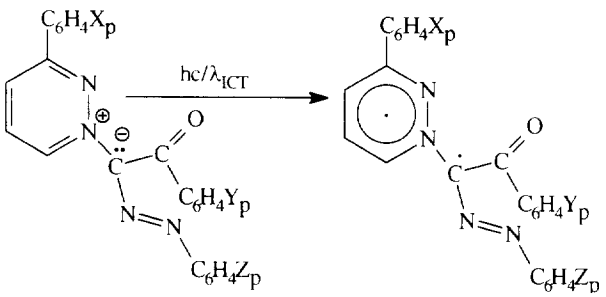

Figure 3. ICT in the ylides **12- 19**.

where : I is the ionisation potential of heterocycle; A is the electron affinity of carbanion and W the electrostatic interaction between the anionic and cationic charge.

The fact that the intramolecular charge transfer band is shifted to blue in the carbanion disubstituted ylides **12- 19** (with approximately 30 nm) as compared with the corresponding carbanion monosubstituted ylides **5- 8** could be explained through the introduction of the diazo group. The diazo group increases the electron-withdrawing effect in the molecule and this decreases the electrostatic interaction from equation 1. Consequently the intramolecular charge transfer band appears at inferior wave numbers. This shift to blue it is also consistent evidence for the extended conjugation phenomena in the carbanion disubstituted ylides **12- 19**. We also observed that, when the substituents Y and Z are electron-withdrawing groups (as NO_2) the shift to blue is greater. The same explanation furnished before (extended conjugation phenomena) remains valid.

Conclusions.

1. For the first time in the diazinium ylides series we have accomplished the reaction with diazoaromatic compounds. The reaction between 3-(4-halogenophenyl) pyridazinium ylides and diazoaromatic compounds yield carbanion disubstituted ylides. No cycloaddition reaction was observed. This means that 3-(4-halogenophenyl) pyridazinium ylides have a strong nucleophilic character with regard to the ylide carbanion.

2. The ylides are stable compounds. Their stability could be explained through the extended conjugation phenomena between the ketone group, the ylide carbanion and diazo group.

3. The reaction mechanism involves, in the first step, the nucleophilic attack of the ylide carbanion to the positive nitrogen of diazo group with formation of unisolated cycloimmonium salts; in the second step, the salt (in the basic reaction medium) by dehydrohalogenation leads to the carbanion disubstituted ylides **12- 19**.

4. The intense colour of the ylides **12 - 19** is considered to be due an intramolecular charge transfer transition

(the colour is lost on protonation).

5. Eight new stable carbanion disubstituted ylides have been obtained.

Experimental.

The ^{1}H NMR and ^{13}C NMR spectra were obtained on a Gemini 200 MHz spectrometer and were recorded in ppm downfield from an internal standard, TMS in $CDCl_3$. The coupling constants are given in Hertz. The IR spectra were recorded with a SPECORD-71 spectrometer in KBr. The UV- VIS spectra were recorded with a Shimandzu UV- 260 spectrometer in acetone.

General procedure. 0. 002 Mol aromatic amine and 0. 006 mol mineral acid (0. 006 mol HCl 1:1 in the case of aniline and 0.006 mol concentrated H_2SO_4 in the case of 4- nitroaniline) was placed in a beaker. The mixture was cooled to -5 ^{0}C and then 0. 40 g $NaNO_2$ (dissolved in 6 ml water) was added (stirring, maintaining the temperature between -5 and 5 ^{0}C). To the obtained diazonium salt, 0. 001 mol pyridazinium salt was added followed by the dropwise addition of an aqueous solution of K_2CO_3 40% to pH 8- 8. 50. The mixture was stirred for 3 hours more (2 hours between -5 and 5 ^{0}C and 1 hour at room temperature). The crude product was filtered, dried, and then washed with chloroform. The chloroformed extract was evaporated to give the product.

3-(4-Bromophenyl) Pyridazinium-1-benzoyl-1-azophenyl Methylide. 12. Brown product, mp. 147- 149°C. Yield 76%. Anal. $C_{24}H_{17}BrN_4O$: N%- calcd.- 12. 25, found- 11. 65, 11. 80. **IR** (KBr, cm^{-1}): 1455 $\nu_{N=N}$; 1490 $\nu_{C=O}$; 1610, 1435 $\nu_{C=C, C=N\ arom}$; 3100-3000 $\nu_{C\text{-}Harom}$. **^{1}H NMR** ($CDCl_3$, TMS, δ, ppm): 8. 556- 8. 534, d, $1H_e$ (J_{ed}= 3. 36 Hz); 8. 018- 7. 866, m, 6H: $1H_c$, $1H_d$, $2H_b$, $2H_g$, 7. 635- 7. 412, m, 8H: $2H_h$, $2H_a$, $2H_i$, $2H_j$; 7. 141- 7. 097, d, $2H_a$ (J= 8. 71 Hz). **^{13}C NMR** ($CDCl_3$, TMS, δ, ppm): 155. 418 C_8 (ketone carbon), 152. 435 C_6 (*alpha* pyridazine ylid nitrogen), 150. 096 C_3 (*alpha* carbon endocycle pyridazine), 146. 153 C_{17} (*para* hydrogen atom, *ipso* azo group), 136. 618 C_{12} (*para* ketone group, *ipso* hydrogen atom), 132. 172 C_{13} (*para* bromine atom, *ipso* carbon C_3 pyridazine), 131. 610 C_{15} (*orto* bromine atom, *meta* carbon C_3 pyridazine), 130. 664 C_9 (*para* hydrogen atom, *ipso* ketone group), 129. 390 C_{14} (*orto* C_3 pyridazine ring, *meta* bromine atom), 129. 100 C_{19} (*orto* hydrogen atom, *meta* azo group), 129. 029 C_{10} (*meta* hydrogen atom, *orto* ketone group), 128. 775 C_{11} (*orto* hydrogen atom, *meta* ketone group), 128. 534 C_{20} (*ipso* hydrogen atom, *para* azo group), 126. 929 C_{16} (*ipso* bromine atom, *para* carbon C_3 pyridazine), 122. 641 C_4 (carbon *beta* pyridazine, *beta* *4*-bromophenyl ring), 122. 347 C_5 (carbon γ- pyridazine, γ- *4*-bromophenyl ring), 118. 801 C_{18} (*meta* hydrogen atom, *orto* azo group), 116. 033 ppm C_7 (ylid carbon).

3-(4-Chlorophenyl) Pyridazinium-1-benzoyl-1-azophenyl Methylide. 13. Brown product, mp. 145- 147°C.

Yield 76%. Anal. $C_{24}H_{17}ClN_4O$: N%- calcd.- 13. 57, found- 12. 90, 13. 10. **IR** (KBr, cm^{-1}): 1450 $\nu_{N=N}$; 1480 $\nu_{C=O}$; 1585, 1435 $\nu_{C=C, C=N\ arom}$; 3100-3000 $\nu_{C\text{-}Harom}$. **^{1}H NMR** ($CDCl_3$, TMS, δ, ppm): 9. 156- 9. 130, d, $1H_e$ (J_{ed}= 3. 40 Hz); 8. 022- 7. 772, m, 6H: $1H_c$, $1H_d$, $2H_b$, $2H_g$, 7. 657- 7. 268, m, 8H: $2H_h$, $2H_a$, $2H_i$, $2H_j$; 7. 100- 6. 980. d. $2H_a$ (J= 8. 76 Hz). **^{13}C NMR** ($CDCl_3$, TMS, δ, ppm): 155. 820 C_8, 152. 212 C_6, 150. 112 C_3, 146. 225 C_{17}, 136. 812 C_{12}, 133. 214 C_{13}, 132. 524 C_{16}, 130. 285 C_9, 130. 004 C_{15}, 129. 198 C_{19}, 128. 876 C_{10}, 128. 745 C_{11}, 128. 575 C_{20}, 128. 272 C_{14}, 126. 988 C_4, 124. 675 C_5, 122. 321 C_{18}, 115. 926 ppm C_7.

3-(4-Bromophenyl) Pyridazinium-1-(4- nitrobenzoyl)-1-azophenyl Methylide. 14. Dark brown product, mp. 154- 156°C. Yield 71%. Anal. $C_{24}H_{16}BrN_5O_3$: N%- calcd.- 13. 94, found- 13. 12, 13. 42. **IR** (KBr, cm^{-1}): 1450 $\nu_{N=N}$; 1485 $\nu_{C=O}$; 1510, 1335 ν_{NO2}; 1590, 1435 $\nu_{C=C, C=N\ arom}$; 3100-3000 $\nu_{C\text{-}Harom}$. **^{1}H NMR** ($CDCl_3$, TMS, δ, ppm): 8. 563- 8. 541, d, $1H_e$ (J_{ed}= 3. 40 Hz); 8. 026- 8. 013, m, 6H: $1H_c$, $1H_d$, $2H_b$, $2H_g$, 7. 559- 7. 445, m, 7H: $1H_f$, $2H_b$, $2H_h$, $2H_i$; 7. 148- 7. 103, d, $2H_a$ (J= 8. 87 Hz). **^{13}C NMR** ($CDCl_3$, TMS, δ, ppm): 155. 418 C_8, 152. 460 C_{12}, 150. 114 C_6, 146. 172 C_3, 136. 636 C_9, 132. 194 C_{17}, 131. 596 C_{13}, 130. 653 C_{15}, 129. 388 C_{10}, 129. 026 C_{14}, 128. 818 C_{19}, 128. 528 C_{20}, 126. 935 C_4, 123. 643 C_{16}, 122. 659 C_{11}, 122. 355 C_5, 118. 805 C_{18}, 112. 00 C_7.

3-(4-Chlorophenyl) Pyridazinium-1-(4-nitrobenzoyl)-1-azophenyl Methylide. 15. Brown product, mp. 151- 152°C. Yield 70%. Anal. $C_{24}H_{16}ClN_5O_3$: N%- calcd.- 15. 30, found- 14. 57, 14. 90. **IR** (KBr, cm^{-1}): 1445 $\nu_{N=N}$; 1485 $\nu_{C=O}$; 1510, 1335 ν_{NO2}; 1590, 1430 $\nu_{C=C, C=N\ arom}$; 3100-3000 $\nu_{C\text{-}Harom}$. **^{1}H NMR** ($CDCl_3$, TMS, δ, ppm): 8. 573- 8. 550, d, $1H_e$ (J_{ed}= 3. 44 Hz); 8. 033- 7. 881, m, 6H: $1H_c$, $1H_d$, $2H_b$, $2H_g$, 7. 562- 7. 444, m, 7H: $1H_f$, $2H_b$, $2H_h$, $2H_i$; 7. 155- 7. 110, d, $2H_a$ (J= 8. 92 Hz). **^{13}C NMR** ($CDCl_3$, TMS, δ, ppm): 155. 979 C_8, 153. 023 C_{12}, 150. 688 C_6, 146. 743 C_3, 137. 205 C_9, 132. 159 C_{17}, 131. 215 C_{13}, 129. 955 C_{16}, 129. 793 C_{10}, 129. 589 C_{15}, 129. 383 C_{19}, 129. 050 C_{20}, 128. 805 C_{14}, 127. 500 C_4, 123. 406 C_{11}, 122. 923 C_5, 119. 376 C_{18}, 112. 801 C_7.

3-(4-Bromophenyl) Pyridazinium-1-benzoyl-1-azo-(4-nitrophenyl) Methylide. 16. Brown product, mp. 152- 154°C. Yield 68%. Anal. $C_{24}H_{16}BrN_5O_3$: N%- calcd.- 13. 94, found- 13. 30, 13. 40. **IR** (KBr, cm^{-1}): 1450 $\nu_{N=N}$; 1485 $\nu_{C=O}$; 1510, 1335 ν_{NO2}; 1590, 1410 $\nu_{C=C, C=N\ arom}$; 3100-3000 $\nu_{C\text{-}Harom}$. **^{1}H NMR** ($CDCl_3$, TMS, δ, ppm): 9. 113- 9. 086, dd, $1H_e$ (J_{ed}= 4. 62 Hz, J_{ec}= 1. 42 Hz); 8. 193- 8. 151, d, $2H_j$ (J= 8. 43 Hz), 7. 907- 7. 865, d, $2H_i$ (J= 8. 43 Hz), 7. 800- 7. 759, m, 2H: $1H_c$, $1H_d$, 7. 571- 7. 330, m, 9H: $2H_b$, $2H_g$, $1H_y$, $2H_h$, $2H_a$. **^{13}C NMR** ($CDCl_3$, TMS, δ, ppm): 149. 303 C_8, 148. 636 C_6, 147. 934 C_{17}, 147. 483 C_3, 140. 410 C_{12}, 139. 232 C_{20}, 132. 847 C_{13}, 132. 416 C_9, 131. 642 C_{15}, 128. 690 C_{14}, 128. 156 C_{10}, 127. 968 C_{11}, 126. 451 C_4, 124. 812 C_{19}, 124. 363 C_{16}, 123. 228 C_5, 117. 850 C_{18}, 110. 557 C_7.

3-(4-Chlorophenyl) Pyridazinium-1-benzoyl-1-azo-(4-nitrophenyl) Methylide. 17. Brown product, mp.

150- 152°C. Yield 65%. Anal. $C_{24}H_{16}ClN_5O_3$: N%- calcd.- 15. 30, found- 14. 80, 14. 90. **IR** (KBr, cm^{-1}): 1445 $\nu_{N=N}$; 1480 $\nu_{C=O}$; 1510, 1335 ν_{NO2}; 1585, 1410 $\nu_{C=C,\ C=N\ arom}$; 3100-3000 $\nu_{C\text{-}Harom}$. **^{1}H NMR** ($CDCl_3$, TMS, δ, ppm): 9. 154- 9. 122, dd, $1H_e$ (J_{ed}= 4. 84 Hz, J_{ec}= 1. 50 Hz); 8. 292- 8. 250, d, $2H_j$ (J= 8. 67 Hz), 8. 014- 7. 971, d, $2H_i$ (J= 8. 71 Hz), 7. 885- 7. 792, m, 2H: $1H_c$, $1H_d$, 7. 596- 7. 391, m, 9H: $2H_b$, $2H_g$, $1H_y$, $2H_h$, $2H_a$. **^{13}C NMR** ($CDCl_3$, TMS, δ, ppm): 149. 924 C_8, 148. 882 C_6, 147. 980 C_{17}, 147. 628 C_3, 140. 050 C_{12}, 138. 880 C_{20}, 133. 120 C_{13}, 132. 010 C_{16}, 130. 912 C_9, 129. 905 C_{15}, 129. 186 C_{10}, 128. 917 C_{11}, 128. 247 C_{14}, 126. 905 C_4, 125. 241 C_{19}, 123. 694 C_5, 118. 211 C_{18}, 112. 212 C_7.

3-(4-Bromophenyl) Pyridazinium-1-(4-nitrobenzoyl)-1-azo-(4-nitrophenyl) Methylide. 18. Dark brown product, mp. 158- 160°C. Yield 60%. Anal. $C_{24}H_{15}BrN_6O_5$: N%- calcd.- 15. 35, found- 14. 40, 14. 60. **IR** (KBr, cm^{-1}): 1450 $\nu_{N=N}$; 1485 $\nu_{C=O}$; 1510, 1335 ν_{NO2}; 1585, 1430 $\nu_{C=C,\ C=N\ arom}$; 3100-3000 $\nu_{C\text{-}Harom}$. **^{1}H NMR** ($CDCl_3$, TMS, δ, ppm): 9. 186- 9. 156, dd, $1H_e$ (J_{ed}= 4. 97 Hz, J_{ec}= 1. 30 Hz); 8. 495- 8. 224, m, $2H_h$, $2H_j$, 8. 055- 8. 010, d, $2H_g$ (J_{gh}= 8. 91 Hz) 7. 960- 7. 872 m, 4H: $1H_c$, $1H_d$, $2H_i$, 7. 683- 7. 531, m, 4H: $2H_b$, $2H_a$. **^{13}C NMR** ($CDCl_3$, TMS, δ, ppm): 162. 474 C_8, 157. 632 C_{12}, 152. 609 C_6, 149. 174 C_3, 143. 262 C_{17}, 139. 414 C_9, 134. 336 C_{20}, 131. 962 C_{13}, 131. 646 C_{15}, 130. 445 C_{10}, 128. 023 C_{14}, 126. 553 C_4, 124. 885 C_{11}, 124. 418 C_{19}, 123. 317 C_{16}, 123. 114 C_5, 117. 837 C_{18}, 111. 888 C_7.

3-(4-Chlorophenyl) Pyridazinium-1-(4-nitrobenzoyl)-1-azo-(4-nitrophenyl) Methylide. 19. Brown product, mp. 151- 153°C. Yield 60%. Anal. $C_{24}H_{15}ClN_6O_5$: N%- calcd.- 16. 71, found- 16. 00, 16. 20. **IR** (KBr, cm^{-1}): 1445 $\nu_{N=N}$; 1480 $\nu_{C=O}$; 1510, 1330 ν_{NO2}; 1580, 1430 $\nu_{C=C,\ C=N\ arom}$; 3100-3000 $\nu_{C\text{-}Harom}$. **^{1}H NMR** ($CDCl_3$, TMS, δ, ppm): 9. 180- 9. 150, dd, $1H_e$ (J_{ed}= 4. 68 Hz, J_{ec}= 1. 30 Hz); 8. 429- 8. 224, m, $2H_h$, $2H_j$, 8. 034- 7. 989, d, $2H_g$ (J_{gh}= 8. 84 Hz), 7. 857- 7. 740 m, 4H: $1H_c$, $1H_d$, $2H_i$, 7. 587- 7. 464, m, 4H: $2H_b$, $2H_a$. **^{13}C NMR** ($CDCl_3$, TMS, δ, ppm): 159. 339 C_8, 157. 885 C_{12}, 155. 024 C_6, 153. 339 C_3, 144. 008 C_{17}, 136. 820 C_9, 133. 226 C_{20}, 133. 000 C_{13}, 130. 939 C_{16}, 130. 420 C_{10}, 128. 700 C_{15}, 127. 764 C_{14}, 126. 407 C_4, 124. 891 C_{11}, 124. 311 C_{19}, 122. 845 C_5, 117. 839 C_{18}, 115. 620 C_7.

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