Formation of Pyridazinium Salts by Azo Coupling of *N*-Substituted 3-Amino-1-phenylbut-2-en-1-ones and Diazonium Salts

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Dedicated to Professor Otto Exner on the occasion of his 80th birthday[‡]

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Treatment of 3-(2,4-dimethoxyphenylamino)- and 3-methylamino-1-phenylbut-2-en-1-ones with some benzenediazonium tetrafluoroborates gives, besides the usual azo coupling products [i.e., 3-(substituted imino)-1-phenylbutane-1,2-diones 2-(4-substituted phenylhydrazones) and 2-(4-methoxyphenyldiazenyl)-3-methylamino-1-phenylbut-2-en-1-one, respectively], the previously unreported 1,4,5,6-tetrasubstituted pyridazinium tetrafluoroborates. The pyridazinium salts have been identified by X-ray analysis and by their ^{1}H, ^{13}C, ^{15}N, ^{11}B and ^{19}F NMR spectra. Their formation is most probably the result of nucleophilic attack on the carbonyl carbon by the nitrogen of the hydrazone group and subsequent dehydration.

Introduction

Enaminones are useful intermediates for syntheses of heterocyclic compounds[1,2] and also currently serve as medical drugs.[3–7] A typical feature of β-enaminones is their reactions with electrophilic reagents. In previous papers[8–12] we have dealt with reactions between various types of β-enaminones and benzenediazonium salts from the standpoints of the constitutions of the products and their tautomeric behaviour, both in solution ($CDCl_3$) and in the crystalline state. These compounds exhibit azo-hydrazone and ketimine-enamine tautomerism, both fast on the NMR timescale,[13,14] and a somewhat slower rotation around the polarised and partially double bond $\mathrm{C}_\alpha \overset{\cdots}{-} \mathrm{C}_\beta$ in the $\mathrm{N} \overset{\cdots}{-} \mathrm{C}_\beta \overset{\cdots}{-} \mathrm{C}_\alpha \overset{\cdots}{-} \mathrm{C} \overset{\cdots}{-} \mathrm{O}$ grouping (ref.[9]). The positions of the tautomeric equilibria depend predominantly on the structures of the starting enaminones and, to a lesser extent, on the substitution on the benzenediazonium ions.[15] This paper deals with a study of the reactions of the *N*-substituted 3-amino-1-phenylbut-2-en-1-ones **1** and **2** with benzenediazonium and 4-methoxy- and 4-methylbenzenediazonium cations, which give some products with structures entirely different from those of the azo coupling products described so far.

Results and Discussion

The reaction between 4-methylbenzenediazonium tetrafluoroborate and 3-(2,4-dimethoxyphenylamino)-1-phenylbut-2-en-1-one (**1**) in dichloromethane gives a mixture of two compounds. One of them is the expected azo coupling product **3a**, which according to ^{15}N NMR spectroscopy exists in deuteriochlorofom solution predominantly as the hydrazone [3-(2,4-dimethoxyphenylimino)-1-phenylbutane-1,2-dione) 2-(4-methylphenyl)hydrazone]. The side product is a dark red crystalline substance **4a**, formed in a yield of 17% (Scheme 1).

The elemental analysis of compound **4a** corresponds to a molecular formula of $C_{32}H_{30}BF_4N_5O_2$, which was confirmed by ^{11}B and ^{19}F NMR spectroscopy, the boron[16] and fluorine[17] chemical shifts corresponding to the BF_4^- anion.

The cationic moiety of the molecule was identified by X-ray analysis of the corresponding single crystal. Compound **4a** is 4-(2,4-dimethoxyphenylamino)-1-(4-methylphenyl)-5-(4-methylphenyldiazenyl)-6-phenylpyridazinium tetra-

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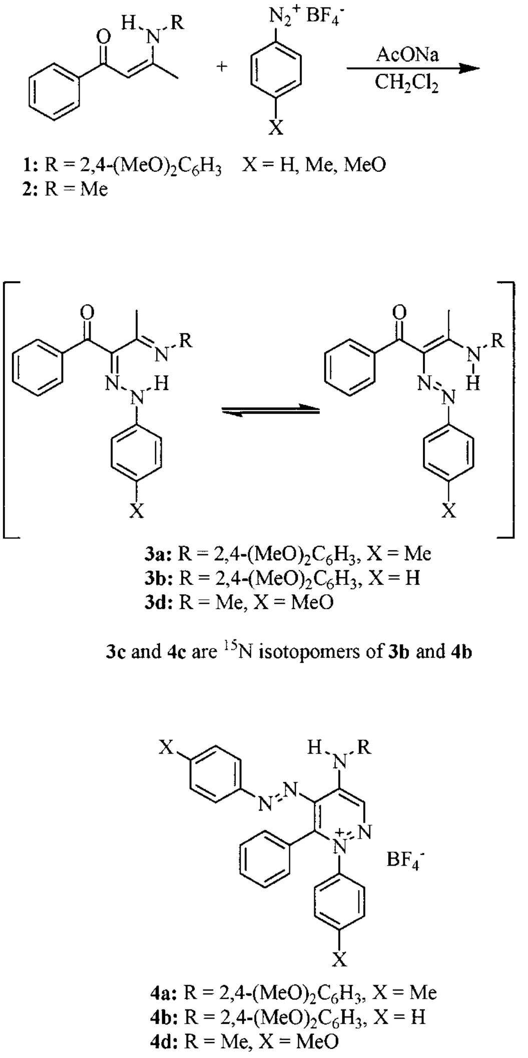
[‡] In recognition of his outstanding contributions to physical organic chemistry



1: R = 2,4-$(MeO)_2C_6H_3$ X = H, Me, MeO
2: R = Me

3a: R = 2,4-$(MeO)_2C_6H_3$, X = Me
3b: R = 2,4-$(MeO)_2C_6H_3$, X = H
3d: R = Me, X = MeO

3c and **4c** are ^{15}N isotopomers of **3b** and **4b**

4a: R = 2,4-$(MeO)_2C_6H_3$, X = Me
4b: R = 2,4-$(MeO)_2C_6H_3$, X = H
4d: R = Me, X = MeO

Scheme 1

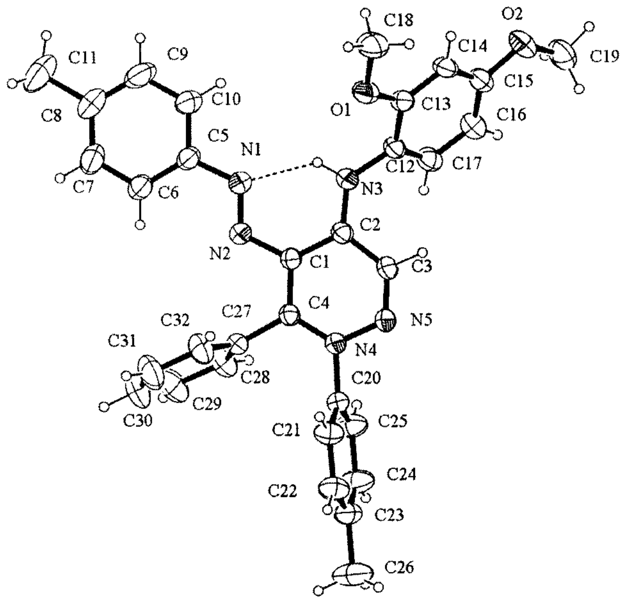


Figure 1. ORTEP plot of compound **4a**

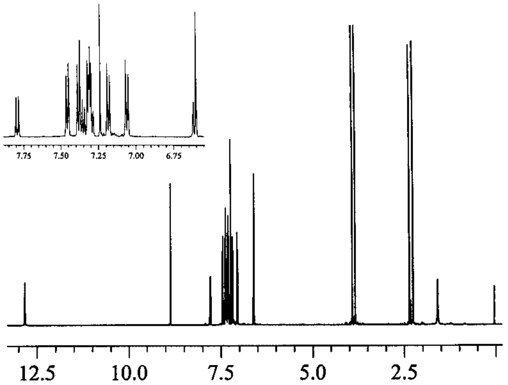


Figure 2. 500 MHz proton NMR spectrum of compound **4a** in $CDCl_3$

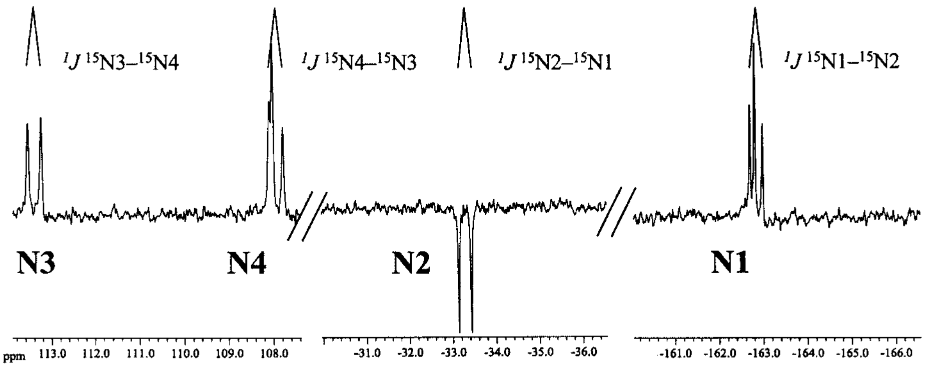
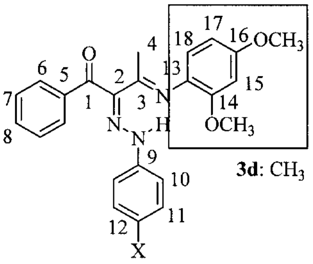


Figure 3. 50.7 MHz $^{15}N\{^1H\}$ NMR spectrum of **4c** in $CDCl_3$

fluoroborate (Scheme 1, Figure 1), and its proton NMR spectrum is shown in Figure 2.

A similar pyridazinium salt (compound **4b**) was also obtained from the reaction between enaminone **1** and benzenediazonium tetrafluoroborate. For unambiguous assignment of individual ^{15}N chemical shifts we prepared the ^{15}N isotopomer **4c** with different degrees of enrichment at the nitrogen atoms of the aniline (95% ^{15}N) and the nitrite (55.5% ^{15}N). The different degrees of ^{15}N enrichment enable unambiguous differentiation between the nitrogen

Table 1. ^{1}H NMR parameters of the azo-coupled enaminones **3** in $CDCl_3$



	3a (X = Me)	**3b** (X = H)	**3d** (X = MeO)
H-4	2.34 s	2.33 s	2.54 s
H-6	7.92−7.94 m	7.95−7.96 m	7.72−7.73 m
H-7	7.42−7.45 m	7.44−7.47 m	7.34−7.37 m
H-8	7.50−7.53 m	7.52−7.55 m	7.40−7.43 m
H-10	7.06−7.10 m	7.17−7.18 m	7.23−7.26 m
H-11	7.06−7.10 m	7.25−7.28 m	6.78−6.81 m
H-12		7.01−7.04 m	
H-15	6.58, d, J = 2.5 Hz	6.59, d, J = 2.4 Hz	
H-17	6.53, dd, J = 2.6, 8.3 Hz	6.53, dd, J = 2.4, 8.5 Hz	
H-18	6.89, d, J = 8.5 Hz	6.89, d, J = 8.5 Hz	
OCH_3 (C-14)	3.88, s	3.89, s	
OCH_3 (C-16)	3.84, s	3.84, s	
Other	2.28, s (CH_3), 15.86, br. s (NH)	15.80, br. s (NH)	3.13, s ($N-CH_3$), 3.75 s (OCH_3), 14.59 br. s (NH)

Table 2. ^{13}C chemical shifts of the azo-coupled enaminones **3** in $CDCl_3$

	3a (X = Me)	**3b** (X = H)	**3d** (X = MeO)
C-1	192.99	192.91	193.77
C-2	133.34	133.99	128.48
C-3	165.00	165.10	162.51
C-4	20.79	20.52	16.07
C-5	139.45	139.16	141.56
C-6	130.44	130.44	130.00
C-7	127.41	127.48	129.93
C-8	131.15	131.32	127.01
C-9	141.75	143.78	145.08
C-10	116.00	115.84	121.06
C-11	129.75	129.18	114.01
C-12	133.68	123.76	158.39
C-13	128.49	128.73	
C-14	152.01	151.94	
C-15	99.29	99.30	
C-16	158.44	158.47	
C-17	103.74	103.75	
C-18	122.27	122.09	
OCH_3 (C-14)	55.50	55.50	
OCH_3 (C-16)	55.58	55.60	
Other	20.45 (CH_3)		30.36 ($N-CH_3$), 55.27 (OCH_3)

shifts, and the $^{1}J(^{15}N,^{15}N)$ coupling constants determine the nitrogen connectivities. The ^{15}N NMR spectrum of compound **4c** measured by direct detection with proton decoupling is presented in Figure 3, and the NMR spectroscopic data of compounds **3a** and **3b** and of **4a** and **4b** are given in Tables 1−6.

The formation of pyridazinium salts from diazonium salts has been described in the literature.[18−22] Among several variants of such reactions, two alternatives can be considered in the case of the formation of compound **4a**, and we have not found any direct analogies for them in the literature:

i) [4+2] cycloaddition between the enol form of compound **3a** and the second diazonium ion and subsequent dehydration (Scheme 2), and

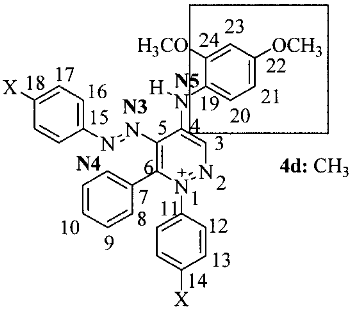
ii) azo coupling of enaminone **1**, step by step, with two diazonium salt molecules to form intermediate **Im**, followed by nucleophilic attack by the hydrazone NH group on the carbonyl of the benzoyl group and splitting off of a water molecule (Scheme 2).

We do not know which of the given reaction pathways is taken in the formation of pyridazinium salt **4a**, because we only know its structure and the structures of the starting

Table 3. ^{15}N NMR parameters of the azo-coupled enaminones **3** in $CDCl_3$

	3a (X = Me)	**3b** (X = H)	**3d** (X = MeO)
N1	−183.6, $^{1}J(^{15}N,^{1}H)$ = 82.0 Hz	−192.3, $^{1}J(^{15}N,^{1}H)$ = 87.9 Hz	−18.4
N2	not detected	−9.4, $^{2}J(^{15}N,^{1}H)$ = 2.6 Hz	82.8
N3	−90.1, $^{1}J(^{15}N,^{1}H)$ = 10.9 Hz	−82.5	−232.2, $^{1}J(^{15}N,^{1}H)$ = 72.3 Hz

Table 4. ^{1}H NMR parameters of the pyridazinium salts **4**



	4a ($CDCl_3$) X = Me	**4b** ($CDCl_3$) X = H	**4d** ([D$_6$]DMSO) X = MeO
H-3	8.86 s	8.91 s	9.40 s
H-8	7.44−7.46 m	7.44−7.50 m	7.41−7.52 m
H-9	7.28−7.32 m	7.28−7.32 m	7.41−7.52 m
H-10	7.34−7.39 m	7.35−7.38 m	7.41−7.52 m
H-12	7.28−7.32 m	7.44−7.50 m	7.41−7.52 m
H-13	7.04−7.05 m	7.29−7.32 m	6.97−7.00 m
H-14		7.44−7.50 m	
H-16	7.34−7.39 m	7.44−7.50 m	7.72−7.76 m
H-17	7.18−7.19 m	7.38−7.40 m	7.11−7.14 m
H-18		7.29−7.32 m	
H-20	7.76, d, J = 8.6 Hz	7.83, d, J = 8.6 Hz	
H-21	6.58, dd, J = 2.5, 8.7 Hz	6.64, dd, J = 2.5, 8.7 Hz	
H-23	6.61, d, J = 2.5 Hz	6.61, d, J = 2.4 Hz	
OCH_3 (22)	3.84, s	3.85, s	
OCH_3 (24)	3.92, s	3.94, s	
other	2.37, s, CH_3 (18) 2.26, s, CH_3 (14) 12.84, s, NH	12.87, s, NH	3.50, d, J = 5.3 Hz, NCH_3 10.94, q, J = 5.5 Hz, NH 3.78, s, OCH_3 (14) 3.88, s, OCH_3 (18)

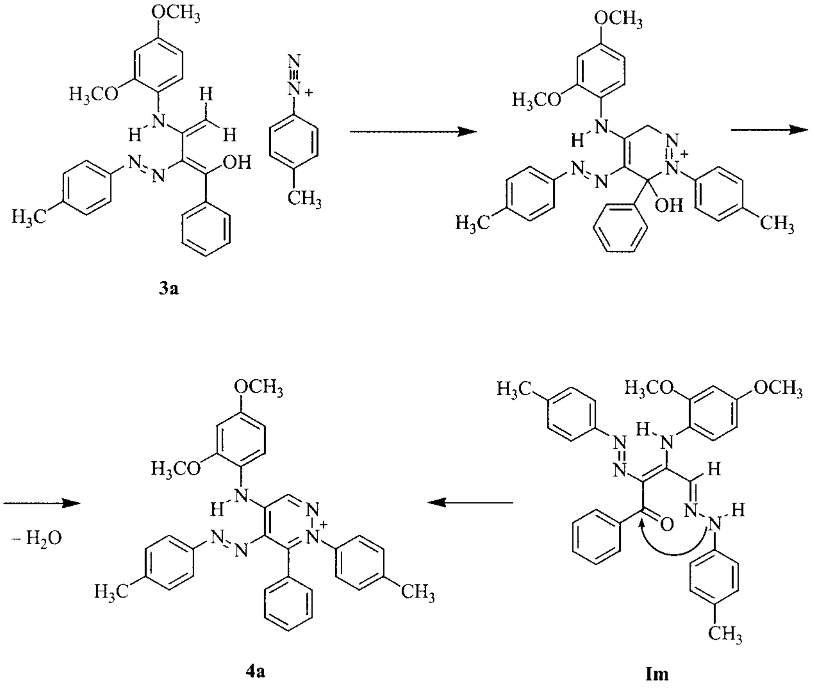
Table 5. ^{13}C chemical shifts of the pyridazinium salts **4**

	4a ($CDCl_3$) X = Me	**4b** ($CDCl_3$) X = H	**4d** ([D$_6$]DMSO) X = MeO
C-3	141.41	141.74	141.24
C-4	128.87	128.92	128.78
C-5	139.20	139.45	140.85
C-6	158.14	158.64	156.47
C-7	128.89	128.79	129.59
C-8	130.77	130.89	130.57
C-9	127.61	127.69	127.67
C-10	126.35	126.73	130.01
C-11	140.41	142.80	135.90
C-12	130.00	129.56	128.16
C-13	129.50	129.01	114.15
C-14	139.71	130.16	159.64
C-15	149.67	151.51	146.20
C-16	123.27	123.30	125.31
C-17	130.06	129.37	114.97
C-18	144.15	132.86	163.45
C-19	115.85	115.91	
C-20	126.39	126.81	
C-21	105.19	105.23	
C-22	161.09	161.29	
C-23	99.49	99.72	
C-24	153.86	153.94	
OCH_3 (22)	55.69	55.73	
OCH_3 (24)	56.00	56.04	
other	21.02 CH_3 (14) 21.57 CH_3 (18)		30.74 N-CH_3 55.61 OCH_3 (14) 55.97 OCH_3 (18)

Table 6. ^{15}N, ^{11}B and ^{19}F NMR parameters of the pyridazinium salts **4**

	4a ($CDCl_3$) X = Me	**4b** ($CDCl_3$) X = H	**4d** ([D_6]DMSO) X = MeO
N-1	−162.5	−162.8 $^1J(^{15}N, ^{15}N)$ = 14.4 Hz[a]	−165.9
N-2	−33.1	−33.3 $^1J(^{15}N, ^{15}N)$ = 14.4 Hz[a]	−33.3
N-3	not detected	113.4 $^1J(^{15}N, ^{15}N)$ = 15.5 Hz[a]	not detected
N-4	106.5	108.0 $^1J(^{15}N, ^{15}N)$ = 15.2 Hz[a]	110.6
N-5	−265.6	−265.0	−274.9
^{11}B	−2.20	−2.19	−1.80
^{19}F	−153.82[b]	−153.74[b]	−148.83[b]
	−153.76[c]	−153.69[c]	−148.78[c]

[a] Obtained by measuring of ^{15}N isotopomer **4c**. [b] Fluorine atom bound to ^{11}B isotope. [c] Fluorine atom bound to ^{10}B isotope.



Scheme 2

compounds. 4-Dimethylamino-5-(phenyldiazenyl)pent-4-ene-2,3-dione 3-phenylhydrazone, which is formed in the reaction between 4-(dimethylamino)pent-3-en-2-one and two molecules of benzenediazonium salt, does not undergo ring closure.[12]

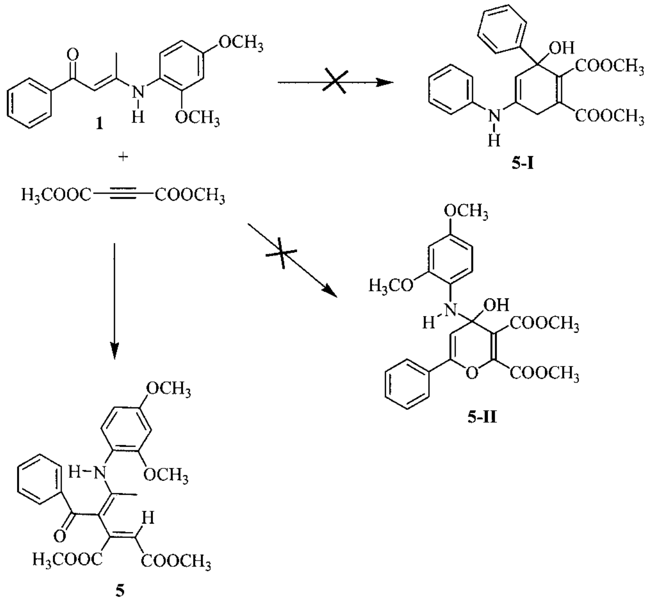
In order to confirm that enaminone **1** can undergo [4+2] cycloaddition, we carried out the reaction in the presence of the very reactive dienophile dimethyl butynedioate in acetonitrile. The cycloaddition could give a derivative of dimethyl phthalate **5-I** or a derivative of 1,4-dihydropyran **5-II** (Scheme 3). However, we found that the [4+2] cycloaddition did not take place: only the addition of enaminone **1** to the triple bond of butynedioate to form compound **5** occurred.

Pyridazinium salts were only formed in cases in which enaminone **1** reacted with benzenediazonium tetrafluoroborate or 4-methylbenzenediazonium tetrafluoroborate. Attempts to obtain similar compounds from reactions with 4-methoxy- or 4-nitrobenzenediazonium tetrafluoroborates failed, only the singly coupled products analogous to **3a** being obtained in these cases.

Products (**3d** and **4d**) analogous to those obtained in the case of the reaction of enaminone **1** were also isolated from azo coupling between 3-methylamino-1-phenylbut-2-en-1-one (**2**) and 4-methoxybenzenediazonium tetrafluoroborate (Scheme 1). Compound **3d** exists in $CDCl_3$ solution predominantly as 2-(4-methoxyphenyldiazenyl)-3-methylamino-1-phenylbut-2-en-1-one. NMR parameters are given in Tables 1−6, and an ORTEP plot of compound **4d** is depicted in Figure 4.

With equimolar ratio of enaminones and the corresponding diazonium salts, only compounds **3** were formed.

When the ratio of enaminones and diazonium salts was 1:2, both compounds **3** and **4** were formed. An increase in this ratio (1:3 and higher), however, did not result in any increase in the pyridazinium content in the reaction prod-



Scheme 3

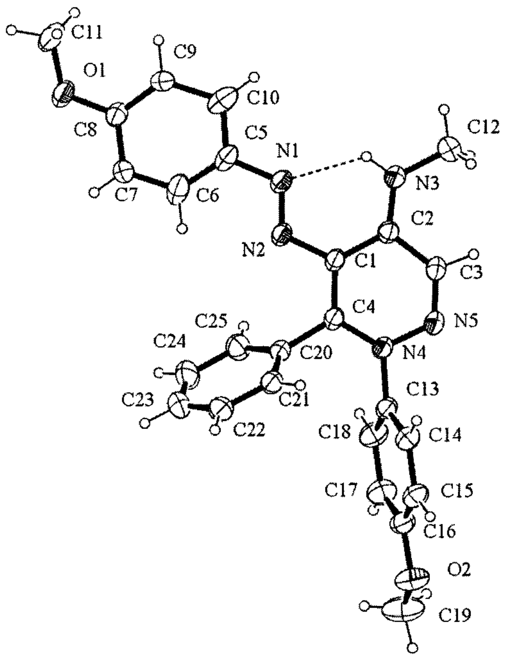


Figure 4. ORTEP plot of compound **4d**

ucts, only increases in the decomposition products being detected.

Only very small amounts of compounds **4** (besides some diazonium salt decomposition products) were detected when the appropriate diazonium salt was added to compound **3** under the same reaction conditions as used in the case of the reaction between compound **1** and the same diazonium salt (see Exp. Sect.).

Experimental Section

General Remarks: The NMR spectra were measured with a Bruker AVANCE 500 spectrometer fitted with a 5-mm broad-band probe with a magnetic field gradient in the direction of the z axis at frequencies of 500.13 MHz (^{1}H), 125.77 MHz (^{13}C), 50.69 MHz (^{15}N) and 470.56 MHz (^{19}F), and with a Bruker AMX 360 spectrometer at a frequency of 115.55 MHz (^{11}B). The ^{1}H NMR spectra were calibrated in CDCl$_3$ on hexamethyldisiloxane (δ = 0.05 ppm) and in [D$_6$]DMSO on the central signal of the solvent multiplet (δ = 2.55 ppm). The ^{13}C NMR spectra were calibrated on the central signal of the solvent multiplet (δ = 39.6 ppm for [D$_6$]DMSO and δ = 76.9 ppm for CDCl$_3$). The ^{15}N NMR spectra were calibrated on external neat ^{15}N nitromethane placed in a coaxial capillary (δ = 0.0 ppm). The ^{11}B NMR spectra were calibrated on external B(OCH$_3$)$_3$ placed in a coaxial capillary (δ = 18.1 ppm). In order to suppress the signals of ^{11}B nuclei from glass, the measurements were carried out in Teflon sample tube liners (Aldrich) inserted into 5 mm tubes in which the bottom part (about 25 mm length) had been cut off. The ^{19}F NMR spectra were calibrated on internal CFCl$_3$ (δ = 0.0 ppm, central signal of multiplet of the standard) and were measured with use of a 5 mm ^{1}H/^{19}F dual probehead with proton noise decoupling. The individual proton signals were assigned by H,H-COSY spectra. The ^{13}C signals were assigned on the basis of APT, ^{1}H−^{13}C HMQC, ^{1}H−^{13}C HSQC and ^{1}H−^{13}C HMBC spectra. The δ(^{15}N) values were measured with the aid of inversion detection techniques (^{1}H−^{15}N HMBC) and, in the case of the ^{15}N-labelled compounds, also by direct detection. The crystal data for compounds **4a** and **4d** were collected at room temperature on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-K_α radiation and corrected for Lorentz polarization effects. The structures were solved by direct methods (SIR99[28]) and refined by full-matrix, least-squares. All non-hydrogen atoms were refined anisotropically and hydrogens included on calculated positions, riding on their carrier atoms, except for the N3−H and C3−H3 hydrogen atoms, which were refined isotropically. All the calculations were performed with SHELXL-97[29] and PARST[30] implemented in the WINGX[31] system of programs. The melting points were determined with a Kofler hot stage microscope and were not corrected. The elemental analyses were carried out with a FISONS EA 1108 automatic analyser. Dichloromethane was predried by standing over anhydrous calcium chloride and subsequent distillation with phosphorus pentoxide. The anhydrous sodium acetate was fused on a porcelain dish and left to cool in a dessiccator. The diazonium tetrafluoroborates used were prepared by procedures described elsewhere.[10]

3-(2,4-Dimethoxyphenylamino)-1-phenylbut-2-en-1-one (1): A 100 ml three-necked flask fitted with a Dean−Stark extension was charged with toluene (30 mL), benzoylacetone (12.15 g, 75 mmol), 2,4-dimethoxyaniline (11.50 g, 75 mmol) and p-methylbenzenesulfonic acid (0.1 g). The mixture was heated at reflux for 3 h, and the toluene distilling off was continuously replaced with fresh toluene. Finally, the solvent was distilled off at reduced pressure. The distillation residue solidified on cooling and gave a dark substance. After recrystallisation from toluene, the yield was 16.74 g (75%) brown green crystals melting at 105−107 °C. C$_{18}$H$_{19}$NO$_3$ (297.35): calcd. C 72.71, H 6.44, N 4.71; found C 72.93, H 6.48 and N 4.86. ^{1}H NMR (360 MHz, CDCl$_3$): δ = 2.00 [s, 3 H, COCH$_3$], 3.76 [s, 3 H, OCH$_3$], 3.79 [s, 3 H, OCH$_3$], 5.84 [s, 1 H, CH=], 6.42 [dd, $^3J_{\mathrm{H,H}}$ = 8.6, $^4J_{\mathrm{H,H}}$ = 2.6 Hz, 1 H], 6.48 [d, $^4J_{\mathrm{H,H}}$ = 2.6 Hz, 1 H], 7.03 [d, $^3J_{\mathrm{H,H}}$ = 8.6 Hz, 1 H], 7.35−7.41 [m, 3 H], 7.89−7.91 [m, 2 H], 12.65 [br. s, 1 H, NH] ppm. ^{13}C NMR (90.56 MHz, CDCl$_3$): δ = 20.03 [CH$_3$], 55.36, 55.61 [2 × OCH$_3$], 93.46, 99.11, 103.75 [3 ×

CH], 120.66 [C$_q$], 126.72, 126.94, 128.04, 130.48 [4 × CH], 140.20, 154.47, 158.91, 163.61 [4 × C$_q$], 188.07 [C=O] ppm.

3-Methylamino-1-phenylbut-2-en-1-one (2): This compound was prepared by the procedure described in ref.[32]

General Procedure Used for Azo Coupling Reactions: The enaminone (2.5 mmol) was dissolved in dichloromethane (20 mL) in a 100 ml Erlenmeyer flask. The reaction mixture was treated with anhydrous sodium acetate (1.23 g, 15 mmol) with stirring, after which the appropriate benzenediazonium tetrafluoroborate (5 mmol) was added. The mixture was stirred at room temperature for 72 h, and the solid was then removed by suction and washed with a little dichloromethane. The combined dichloromethane filtrates were evaporated to dryness. The evaporation residue was dried in vacuo, mixed with ethyl acetate and again filtered under suction. The solution in ethyl acetate was placed on a silica gel column and subjected to chromatography (silica gel/ethyl acetate). The portion insoluble in ethyl acetate was recrystallised from ethanol to give the corresponding pyridazinium salt. In this way the following compounds were prepared.

3-(2,4-Dimethoxyphenylimino)-1-phenylbutane-1,2-dione 2-(4-Methylphenyl)hydrazone (3a): Recrystallisation from cyclohexane. Yield 0.82 g (79%). M.p. 120−122 °C. $C_{25}H_{25}N_3O_3$ (415.49): calcd. C 72.27, H 6.06, N 10.11; found C 72.19, H 6.28, N 10.26.

3-(2,4-Dimethoxyphenylimino)-1-phenylbutane-1,2-dione 2-Phenylhydrazone (3b): Recrystallisation from *n*-hexane. Yield 0.8 g (80%). M.p. 112−115 °C. $C_{24}H_{23}N_3O_3$ (401.46): calcd. C 71.80, H 5.77, N 10.47; found C 71.84, H 5.96, N 10.42.

2-(4-Methoxyphenyldiazenyl)-3-methylamino-1-phenylbut-2-en-1-one (3d): Recrystallisation from cyclohexane. Yield 0.15 g (19%). M.p. 109−110.5 °C. $C_{18}H_{19}N_3O_2$ (309.36): calcd. C 69.88, H 6.19, N 13.58; found C 69.96, H 6.49, N 13.58.

4-(2,4-Dimethoxyphenylamino)-1-(4-methylphenyl)-5-(4-methylphenyldiazenyl)-6-phenylpyridazinium Tetrafluoroborate (4a): Recrystallisation from ethanol. Yield 0.26 g (17%). M.p. 255−265 °C. $C_{32}H_{30}BF_4N_5O_2$ (603.42): calcd. C 63.69, H 5.01, N 11.61; found C 63.71, H 4.91, N 11.53.

4-(2,4-Dimethoxyphenylamino)-1-phenyl-5-phenyldiazenyl-6-phenylpyridazinium Tetrafluoroborate (4b): Recrystallisation from ethanol. Yield 0.25 g (17%). M.p. 260−265 °C. $C_{30}H_{26}BF_4N_5O_2$ (575.37): calcd. C 62.63, H 4.55, N 12.17; found C 62.75, H 4.39, N 12.04.

4-(2,4-Dimethoxyphenylamino)-1-phenyl-5-[$^{15}N_\alpha$,$^{15}N_\beta$]phenyldiazenyl-6-phenylpyridazinium Tetrafluoroborate (4c): The compound was prepared in the same way as the unlabelled isotopomer. Recrystallisation from ethanol. Yield 0.21 g (14%). M.p. 257−267 °C.

1-(4-Methoxyphenyl)-5-(4-methoxyphenyldiazenyl)-4-methylamino-6-phenylpyridazinium Tetrafluoroborate (4d): Recrystallisation from ethanol. Yield 0.28 g (22%). M.p. 211−214 °C. $C_{25}H_{24}BF_4N_5O_2$ (513.29): calcd. C 58.50, H 4.71, N 13.64; found C 58.50, H 4.88, N 13.81.

Methyl 4-Benzoyl-5-(2,4-dimethoxyphenylamino)-3-methoxycarbonylpenta-2,4-dienoate (5): A 100-ml three-necked flask was charged with enaminone **1** (1.49 g, 5 mmol) and dry acetonitrile (30 mL). The reaction was carried out under argon. A solution of dimethyl butynedioate (0.71 g, 5 mmol) in dry acetonitrile (10 mL) was added from a dropping funnel with stirring. The mixture was further stirred at room temperature for 120 h. The solvent was then evaporated in vacuo, and the residue was subjected to column chromatography (silica gel, CH_2Cl_2/EtAc, 5:1) to give an orange oil (1.35 g, 61%), which gradually solidified. After recrystallisation from ethanol, m.p. 137−139 °C. $C_{24}H_{25}NO_7$ (439.46): calcd. C 65.59, H 5.73, N 3.19; found C 65.35, H 5.98, N 3.13. ^{1}H NMR (500.13 MHz, CDCl$_3$): δ = 1.84 [s, 3 H], 3.61 [s, 3 H], 3.70 [s, 3 H], 3.79 [s, 3 H], 3.85 [s, 3 H], 6.46 [dd, $^4J_{H,H}$ = 2.5, $^3J_{H,H}$ = 8.5 Hz, 1 H], 6.51 [d, $^4J_{H,H}$ = 2.5 Hz, 1 H], 6.69 [s, 1 H], 7.09 [d, $^3J_{H,H}$ = 8.5 Hz, 1 H], 7.22−7.29 [m, 3 H], 7.35−7.37 [m, 2 H], 13.51 [s, 1 H] ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 17.75 [CH$_3$], 51.51,

Table 7. Crystal data of compounds **4a** and **4d**

Compound	4a	4d
Empirical formula	$(C_{32}H_{30}N_5O_2)^+\cdot(BF_4)^-$	$(C_{25}H_{24}N_5O_2)^+\cdot(BF_4)^-\cdot1/2(CH_3OH)$
M	603.42	529.33
System	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	10.7035(2)	10.0433(2)
b (Å)	19.9731(4)	10.5873(2)
c (Å)	15.5525(3)	12.5838(2)
α (°)	90	80.512(1)
β (°)	109.728(1)	84.640(1)
γ (°)	90	88.804(1)
U (Å^3)	3129.7(1)	1314.0(1)
Z	4	2
$D_{calcd.}$ (g cm^{-3})	1.281	1.338
T (K)	295	295
μ (cm^{-1})	0.97	1.07
$\theta_{min.}-\theta_{max,}$ (°)	2.5−27.0	2.8−27.0
Unique reflns.	6822	5714
R_{int}	0.030	0.018
Obsd. reflns. [$I > 2\sigma(I)$]	3831	4161
R (obsd. reflns.)	0.0562	0.0572
wR (all reflns.)	0.1721	0.1889
S	1.00	1.04
$\Delta\rho_{max.}$; $\Delta\rho_{min.}$/e·Å^{-3}	0.18;−0.24	0.39;−0.33

52.38, 55.30, 55.58 [4 × OCH_3], 99.19 [CH], 102.11 [C_q], 103.92 [CH], 120.28 [C_q], 127.04, 127.15, 127.28, 128.83, 128.85 [5 × CH], 142.20, 143.93, 154.60, 159.16, 163.92, 165.51, 168.02 [7 × C_q], 191.64 [C=O] ppm.

X-ray Crystallographic Study: The BF_4^- anion in compound **4a** was found to be disordered and the four fluorine atoms were refined with two independent orientations with multiplicities of 0.6 and 0.4, respectively. In compound **4d** the C7(H)C8(H)O1C11(H3) moiety of the 4-methoxyphenyl substituent was found to be disordered, and the atoms were refined with two independent orientations with multiplicities of 0.55 and 0.45, respectively. The BF_4^- anion contains two disordered fluorine atoms, F3 and F4, which were refined with two independent orientations with multiplicities of 0.5. This crystal also includes molecules of methanol disordered around centres of symmetry. The crystal data and refinement parameters are summarized in Table 7, selected interatomic distances and angles are given in Table 8, and hydrogen bond parameters are listed in Table 9. ORTEP[23] views of compounds **4a** and **4d** are shown in Figure 1 and 4, respectively. In both structures the pyridazinium rings are essentially planar, with maximum deviations from the least-squares planes defined by the ring atoms of 0.024(2) and 0.019(2) Å for **4a** and **4d**, respectively. Both rings display extended conjugations, and the C4−N4 [1.342(1) in **4a** and 1.350(2) Å in **4d**] and N4−N5 [1.362(2) in **4a** and 1.357(2) Å in **4d**] bond lengths support pyridazinum structures with positive charge mainly located on nitrogen N4, consistently with other similar structures.[24−27]

Table 8. Selected bond lengths (Å), angles (°) and short contact distances (Å) of compounds **4a** and **4d**

	4a	**4d**
N1−N2	1.262(2)	1.259(2)
N1−C5	1.420(2)	1.420(2)
N2−C1	1.399(2)	1.403(2)
C1−C2	1.417(3)	1.426(2)
N3−C2	1.335(3)	1.315(2)
C1−C4	1.393(3)	1.391(2)
N4−C4	1.342(2)	1.350(2)
N4−N5	1.362(2)	1.357(2)
N5−C3	1.297(3)	1.290(3)
C2−C3	1.416(3)	1.430(3)
N2−N1−C5	114.4(2)	113.6(2)
N1−N2−C1	115.9(2)	115.9(1)
N2−C1−C2	126.8(2)	126.7(1)
N2−C1−C4	114.2(2)	114.5(1)
C2−C1−C4	118.5(2)	118.8(1)
N3−C2−C1	122.1(2)	124.8(2)
C1−C2−C3	115.5(2)	114.8(2)
N3−C2−C3	122.4(2)	120.4(2)
N5−C3−C2	125.5(2)	125.5(2)
N4−C4−C1	119.8(2)	119.9(2)
N5−N4−C4	123.6(2)	123.2(1)
N4−N5−C3	117.0(2)	117.7(2)
C1···F3	2.989(10)	
C2···F3	3.107(10)	
C4···F3	2.988(8)	
N4···F1(x,1/2 − y,z − 1/2)	3.071(8)	
C4···F1(x,1/2 − y,z − 1/2)	3.060(6)	
C2···F1		2.982(2)
C3···F1		2.987(3)

Table 9. Hydrogen bond parameters (Å and degrees) of compound **4a** and **4d**

Compound **4a**				
D−H···A	D−H	H···A	D···A	D−H···A
N3−H···N1	0.85(2)	1.98(2)	2.649(2)	135(2)
Compound **4d**				
D−H···A	D−H	H···A	D···A	D−H···A
N3−H···N1	0.83(2)	2.11(2)	2.701(2)	128(2)
N3−H···F1(−x, −y, 1 − z)	0.83(2)	2.41(3)	3.023(3)	131(2)

Each compound forms a short intramolecular N−H···N hydrogen bond assisted by resonance in which the enaminic N3−H group is linked to the nitrogen N1 of a diazenyl moiety through a π-conjugated heterodienic group HN3−C2=C1−N2=N1.[11] In spite of the very similar π-conjugation, the N1···N3 distances have significant different values of 2.649(2) and 2.701(2) Å in **4a** and **4d**, respectively. The lengthening and weakening of the hydrogen bond in compound **2** can be ascribed to the formation of a second bifurcated N3−H···F1 hydrogen bond between the enaminic group and a fluorine of the BF_4^- anion.[28] Furthermore, the BF_4^- anions in both crystals are implicated in short interactions, with distances less than sums of the van der Waals radii, towards atoms in the pyridazinium rings, as shown in Table 8.

CCDC-229729 and -229730 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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