Synthesis, ^{1}H, ^{13}C and ^{15}N NMR Study of Azo Coupling Products from Enaminones[‡]

Petr Šimůnek,*[a] Antonín Lyčka,[b] and Vladimír Macháček[a]

Dedicated to Professor Vojeslav Štěrba on the occasion of his 80th birthday

Keywords: Diazo compounds / NMR spectroscopy / Enaminones / Azo coupling

Compounds **2** were prepared by the reaction of 3-amino-5,5-dimethylcyclohex-2-en-1-one and its *N*-phenyl derivative with substituted benzenediazonium tetrafluoroborates, and their ^{1}H, ^{13}C and ^{15}N NMR spectra were measured and analysed. The active components react with enaminones in molar ratios of 2:1. Only in the case of 4-methoxybenzenediazonium tetrafluoroborate and 3-amino-5,5-dimethylcyclohex-2-en-1-one were traces of the product of the 1:1 reaction observed. The attack by the diazonium component occurs at carbon atoms C-2 and C-4, and the hydrazo form is always formed at the 2-position. ^{15}N NMR spectroscopy was adopted to study the position of the tautomeric equilibrium (arylazo – arylhydrazono) at the 4-position: this equilibrium depends predominantly on the substituents of the amino group and, to a lesser extent, on the substituents of the diazonium component.

Introduction

There is not much information in the literature about reactions of β-enaminones with arenediazonium salts. Elnagdi et al.[2] reported the reaction of 1-diethylamino-5-arylpenta-1,4-diene-3-one with diazonium ions in aqueous ethanol: they isolated the corresponding 5-aryl-2-arylhydrazono-3-oxopent-4-enals presumably formed by hydrolysis of the enamine primary products. Macháček et al.[3] prepared the respective azo coupling products by the reaction of 4-amino- or 4-arylaminopent-3-en-2-ones with diazonium salts in aqueous acetone acetate buffers. They discovered that the pure azo coupling products are formed from enaminones only in the first phase of reaction, and that as the reaction progresses the product becomes more and more contaminated by the hydrolysis product − the corresponding pentane-2,3,4-trione 3-phenylhydrazone. In two cases these authors studied the structure of the products by means of ^{1}H NMR spectroscopy (at 100 MHz), dealt with the reaction kinetics, and suggested a mechanism for the azo coupling reaction.

In order to prevent the hydrolysis of both the starting enaminones and the products of their azo coupling reaction, the azo coupling reactions of enaminones are usually performed in diisopropyl ether using the respective dry diazonium tetrafluoroborates.[1] In this way a series of 4-arylaminopentan-2,3-dione 3-phenylhydrazones, 4-methylamino-3-arylazopent-3-en-2-ones and 4-amino-3-arylazopent-3-en-2-ones have been prepared. (The names have been derived from the prevalent tautomeric forms of the respective compounds in $CDCl_3$.) The tautomeric structure of these substances was determined by means of ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy. In the case of the 4-amino and 4-methylamino derivatives, the dynamics of intramolecular exchange of the acidic protons was also studied by means of TPPI-NOESY.[1] Information about the tautomerism of the above-discussed azo coupling products in $CDCl_3$ obtained by means of multinuclear NMR was confirmed in the case of 4-(4-methoxyphenylamino)-3-phenylazopent-3-en-2-one by a crystallographic study,[4] too.

All the azo coupling products studied so far have been derived from acyclic β-enaminones obtained from pentane-2,4-dione. We report here on the behaviour of alicyclic enaminones (3-amino-5,5-dimethylcyclohex-2-en-1-one or 5,5-dimethyl-3-phenylaminocyclohex-2-en-1-one) in their reactions with diazonium ions.

Results and Discussion

Products of the Azo Coupling Reaction with 5,5-Dimethyl-3-phenylaminocyclohex-2-en-1-one

The main product of the reaction of 3-phenylamino-5,5-dimethylcyclohex-2-en-1-one (**1a**) with 4-methylbenzenedia-

[‡] Enaminones Derived from Dimedone, 2. Part 1: Ref.[1]

[a] Department of Organic Chemistry, University of Pardubice
Nám. Čs. Legií 565, Pardubice, 53210, Czech Republic
Fax: (internat.) +42-040/603-7068
E-mail: p.simunek@email.cz
vladimir.machacek@upce.cz
[b] Research Institute for Organic Syntheses
Pardubice-Rybitví, 53218, Czech Republic
Fax: (internat.) +42-040/682-2971
E-mail: antonin.lycka@vuosas.cz

zonium tetrafluoroborate is compound **2a**, which is isolated in a yield of 50%. On the basis of the ^{1}H NMR spectrum it can be stated that:

i) the enaminone molecule is attacked at the C-2 carbon atom (the signal of the olefinic proton at δ = 5.55 ppm disappeared), and ii) the molecule of product **2a** contains two *p*-disubstituted benzene nuclei (Figure 1), which indicates a double azo coupling reaction even in cases where the mol ratio of reacting components is 1:1.

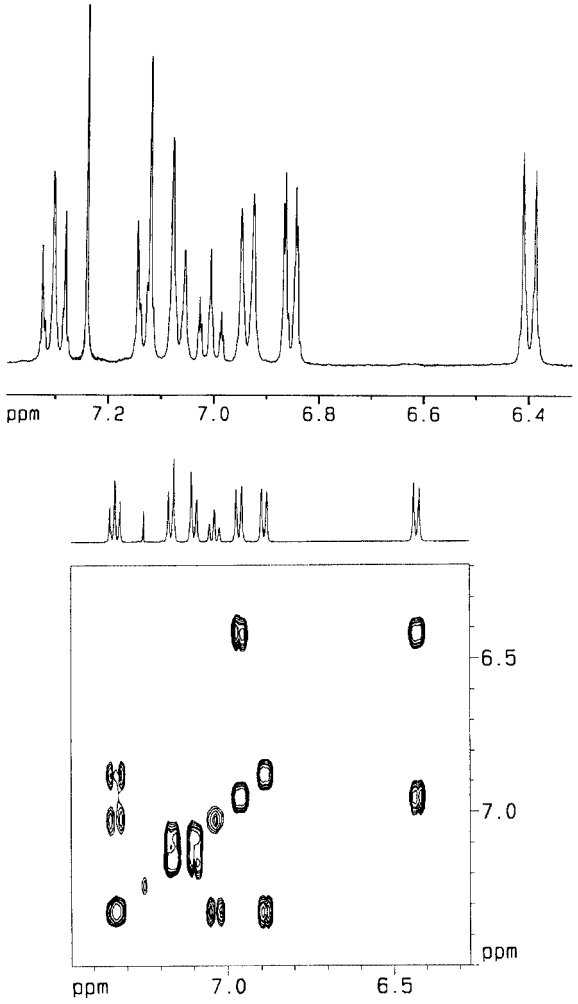
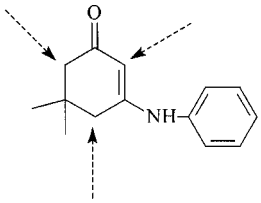


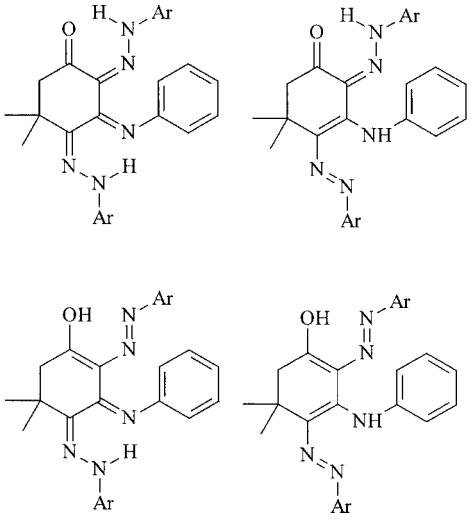
Figure 1. (top) 360 MHz ^{1}H NMR spectrum of the compound **2a** in $CDCl_3$, detail of the aromatic region; (bottom) 500 MHz H,H-COSY spectrum of the compound **2a** in $CDCl_3$, detail of the aromatic region

The enaminone **1a** contains three carbon atoms that can be attacked by a diazonium ion (Scheme 1). The first molecule of diazonium ion attacks carbon C-2. From the gradient selected (gs) ^{1}H-^{13}C HMBC spectrum of compound **2a** it is obvious [from the occurrence of the corresponding cross-peak *via* $^2J(^{13}C,^1H)$] that there is a methylene group in the neighbourhood of the carbonyl group and, hence, the attack of the second diazonium ion must have taken place at the C-4 carbon atom.



Scheme 1

The azo coupling reaction products from arenediazonium salts and enaminones can exist in several different forms due to very rapid azo-hydrazone and ketimine-enamine tautomerism a keto-enol tautomerism can also be considered. Compound **2a** can therefore exist in a number of tautomeric forms out of which the four that are more probable are given in Scheme 2. The possibility of keto-enol tautomerism can be excluded in the case of compound **2a** on the basis of the fact that the azo coupling product exhibits the δ(^{13}C=O) chemical shift almost identical to that of the starting enaminone **1a** (δ = 196.27 and 197.62 ppm, respectively). The position of the azo-hydrazone equilibrium can most reliably be determined by means of ^{15}N NMR spectroscopy[5,6] from the values of the δ(^{15}N) chemical shifts and/or the ^1J (^{15}N, ^{1}H) coupling constants.



Scheme 2

From the ^{15}N chemical shifts found for compound **2a** (δ = −200.40, −6.74 and −218.40, −41.0 ppm) it follows that the two substituents introduced into the molecule by means of the diazonium salt are present in product **2a** in the hydrazono form. The difference in chemical shifts between nitrogen atoms of the same type is probably caused by the different environments of the two groups (in one case, the hydrogen of NH group is bound by an intramolecular hydrogen bond to the carbonyl oxygen atom, while in the other case it is bound to the nitrogen atom of the phenylimino group). The presence of two hydrazone groups was confirmed by means of the *gs* ^{1}H-^{15}N HMBC spectrum (Figure 2). The structure of compound **2a** is shown in Scheme 3 and its NMR parameters are presented in Table 1−3.

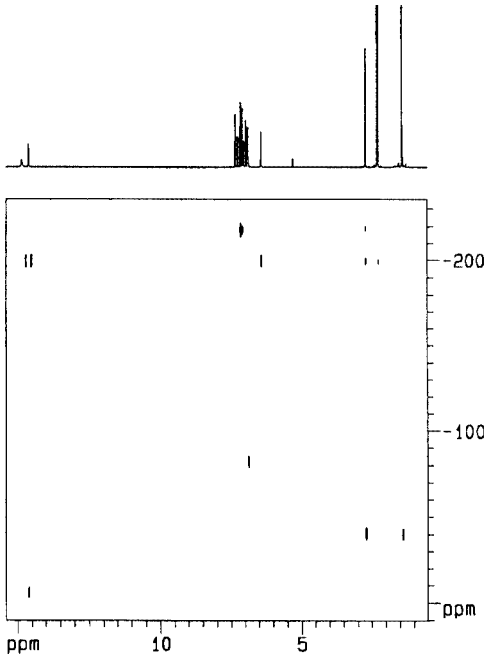
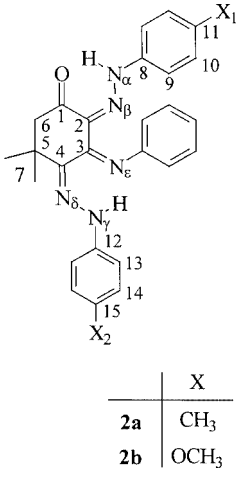


Figure 2. 500 MHz gs ^{1}H-^{15}N HMBC spectrum of the compound **2a** in $CDCl_3$, d6 ($1/^{n}J$) = 70 ms



	X
2a	CH_3
2b	OCH_3

Scheme 3

In order to find out the effect of the substituents of the diazonium component on the position of the tautomeric equilibrium, we carried out the azo coupling reaction of enaminone **1a** with 4-methoxybenzenediazonium tetrafluoroborate. This reaction gave product **2b**, and its NMR parameters (Table 1−3) indicate practically the same structure as that of compound **2a**. Therefore, the substituents of the diazonium components have no significant effect on the tautomerism of the reaction products obtained from enaminone **1a** in this case. The structure of compound **2b** is also shown in Scheme 3.

Table 2. ^{13}C NMR chemical shifts of the compounds **2a**−**e** in $CDCl_3$

Y	**2a** Ph	**2b** Ph	**2c** H	**2d** H	**2e** H
C-1	196.27	196.16	195.78	196.11	195.85
C-2	125.41	125.14	126.25	126.98	125.66
C-3	153.94	153.51	149.13	151.14	142.40
C-4	135.18	135.94	133.35	134.65	132.04
C-5	37.50	37.51	37.90	37.35	36.92
C-6	52.38	52.43	53.22	53.08	53.45
C-7	28.15	28.29	29.15	28.99	29.56
C-8	138.83	134.84	139.43	140.69	135.49
C-9	115.79	117.30	115.55	117.07	116.69
C-10	129.41	114.24	130.07	132.57	114.22[a]
C-11	135.24	157.61	135.09	118.02	157.22
C-12	142.09	138.67	147.15	147.54	145.87
C-13	113.84	115.17	117.11	118.21	119.97
C-14	129.45	114.50	129.54	131.94	114.81[a]
C-15	130.73	154.85	133.85	116.51	157.91
X_1	20.63	55.31	20.87	–	55.46[b]
X_2	20.49	55.44	20.87	–	55.41[b]
Y	[c]	[d]	–	–	–

[a] May be interchanged. [b] May be interchanged. [c] C_{ipso} 151.05, C_{ortho} 119.04, C_{meta} 128.82, C_{para} 122.18. [d] C_{ipso} 151.08, C_{ortho} 119.04, C_{meta} 128.93, C_{para} 122.20.

Products of Azo Coupling Reaction with 3-Amino-5,5-dimethylcyclohex-2-en-1-one

The conclusions that can be made about the structure of compound **2c**, formed by the reaction of 4-methylbenzenediazonium tetrafluoroborate with 3-amino-5,5-dimethylcyclohex-2-en-1-one (**1b**), are similar to those made in the case of compound **2a**:

i) the missing signal of the olefinic proton =C−H (δ = 5.28 ppm) indicates that the attack by the diazonium ion takes place at C-2, ii) the presence of two 1,4-disubstituted benzene nuclei indicates a double azo coupling reaction even when the ratio of reacting components is 1:1, iii) the attack by the second diazonium ion takes place at the C-4

Table 1. ^{1}H NMR chemical shifts of the compounds **2a**−**e** in $CDCl_3$

Compound	Y	H-6	H-7	H-9	H-10	H-13	H-14	$N_\alpha H$	$N_\gamma H$	X_1	X_2	Y
2a	Ph	2.69	1.37	6.40	6.94	7.13	7.07	14.62	14.75	2.25	2.28	[a]
2b	Ph	2.67	1.36	6.66	6.44	7.19	6.85	14.71	14.87	3.72	3.75	[b]
2c	H	2.66	1.37	7.29	7.19	7.37	7.15	14.55	12.98	2.32	2.33	8.38
2d	H	2.68	1.36	7.25	7.49	7.42	7.28	14.50	13.25	–	–	11.27
2e	H	2.66	1.38	7.29	6.90	7.51	6.90	14.50	–	3.80[c]	3.81[c]	11.75

[a] H_{ortho} 6.85, H_{meta} 7.30, H_{para} 7.01. [b] H_{ortho} 6.86, H_{meta} 7.30, H_{para} 7.00. [c] May be interchanged.

carbon atom in the vicinity of amino group, and iv) the product contains a carbonyl group (δ = 195.78 ppm).

The following facts can be stated on the basis of the ^{15}N NMR spectra (Figure 3): i) molecule **2c** involves a pure hydrazone group [δ(^{15}N) = −206.40 and −31.30 ppm], and ii) the second substituent introduced by the diazonium ion is present in the form of an equilibrium mixture of azo and hydrazone tautomers [δ(^{15}N) = −88.0 and 30.70]. 2-Hydroxy-5-*tert*-butylazobenzene, which is considered to be the standard example of a pure azo compound, has δ(^{15}N) = 69.4 and 126.9 ppm (ref.[7]).

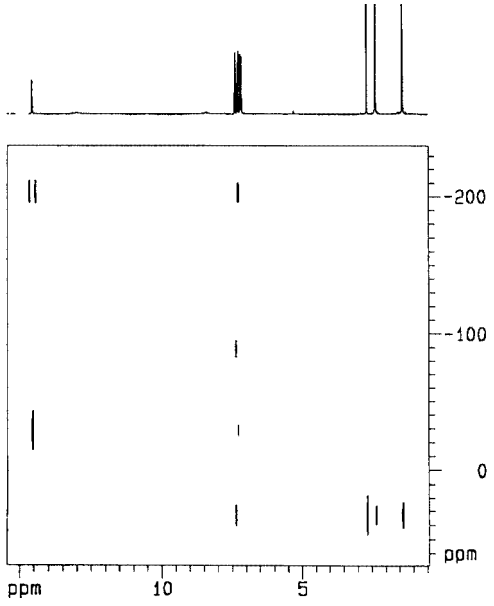
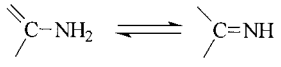


Figure 3. 500 MHz gs ^{1}H-^{15}N HMBC spectrum of the compound **2c** in $CDCl_3$, d6 ($1/^{n}J$) = 70 ms

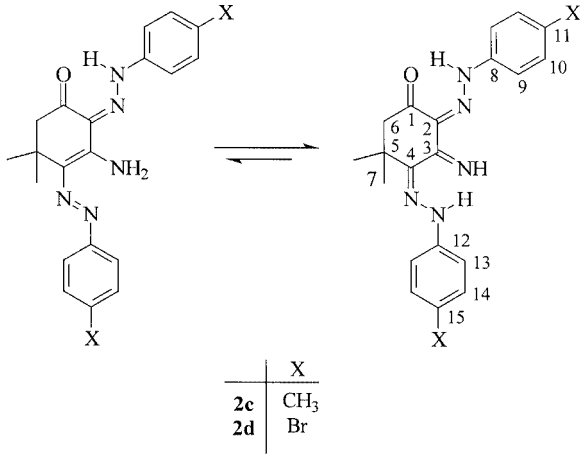
The conclusion (ii) about the tautomeric forms of the second substituent is supported by the presence of a broad signal with δ = −213.80 ppm in the ^{15}N spectrum, which corresponds to a nitrogen atom involved in an enamino-imino tautomeric equilibrium as shown in Scheme 4 [in enaminone **1b** δ($^{15}NH_2$) = −264.70 ppm; δ($H^{15}N$=) ≈ −80 ppm[8]]. Hence the structure of product **2c** can be described by the equilibrium presented in Scheme 5. The NMR parameters of compound **2c** are given in Table 1−3.

Table 3. ^{15}N NMR chemical shifts of the compounds **2a**−**e** in $CDCl_3$

Compound	N_α	N_β	N_γ	N_δ	N_ε
2a	−200.40	−6.74	−218.40	−41.00	−82.50
2b	−199.60	−7.10	−212.60	−37.40	−93.30
2c	−206.40	−31.30	−88.00	30.70	−213.80
2d	−209.20	−31.80	−110.00	18.00	−197.30
2e	−207.70	−34.60	not found	60.70	−259.80



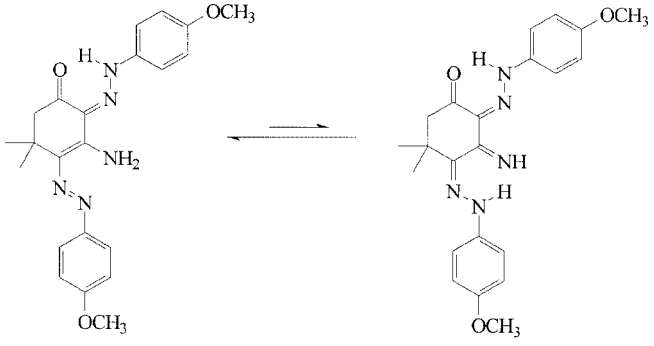
Scheme 4



Scheme 5

Practically the same conclusions as those made in the case of compound **2c** can also be made in the case of the product **2d** formed by the reaction of 4-bromobenzenediazonium tetrafluoroborate with enaminone **1b**. From the values of the ^{15}N chemical shifts (Table 3) it is obvious that there is only a small shift of the 4-substituent towards the hydrazone form. The structure of **2d** is shown in Scheme 5.

A more distinct shift towards the azo form can be seen in the case of compound **2e** formed by the azo coupling reaction from 4-methoxybenzenediazonium tetrafluoroborate and enaminone **1b**. This can be seen particularly clearly from the presence of a broadened signal with a chemical shift of δ(^{15}N) = −259.80 ppm, which is a value quite close to that found for the starting enaminone (δ = −281.87 ppm). It is well-known[11] that β-enaminones are present almost exclusively in their keto-enamino forms, hence the proposed structure of compound **2e** shown Scheme 6.



2e

Scheme 6

Conclusion

A comparison of the structures of products obtained from azo coupling reactions of benzenediazonium ions with enaminones derived from pentane-2,4-dione and 5,5-dimethylcyclohexane-1,3-dione shows some identical and some different features. An identical feature is the fact that

the replacement of an amino group by a phenylamino group causes a distinct shift in the tautomeric equilibrium towards the hydrazone form of the neighbouring group introduced by azo coupling.

The main difference lies in the fact that while 4-aminopent-3-ene-2-one only reacts with one equivalent of diazonium salt at the 3-position,[1] 3-amino-5,5-dimethylcyclohex-2-ene-1-one derivatives undergo two azo coupling reactions (at the 2- and 4-positions) even if the molar ratio of starting components is only 1:1. The formation of only traces of the 1:1 product (from one molecule of benzenediazonium ion and one molecule of enaminone) was observed in the preparation of compound **2e**. The reason for the different behaviour of the two types of enaminones during azo coupling reactions is not known at present. The azo coupling reactions of 3-amino-5,5-dimethylcyclohex-2-ene-1-one gave the respective 5,5-dimethylcyclohexane-1,2,3-trione 2-(subst. phenyl) hydrazones as minor side products.

Experimental Section

General Remarks: The NMR spectra were measured with Bruker AMX 360 or Avance 500 spectrometers in $CDCl_3$ at 25 °C. Measuring frequencies were 360.14 MHz and 500.13 MHz for ^1H, 90.57 MHz and 125.77 MHz for ^{13}C, 36.50 MHz and 50.69 MHz for ^{15}N. The proton chemical shifts are referenced to hexamethyldisiloxane (δ = 0.05 ppm); the carbon chemical shifts are referenced to the middle signal of the solvent triplet (δ = 76.9 ppm). The ^{15}N NMR spectra were standardised by referencing to external neat nitromethane placed in a coaxial capillary (δ = 0.00 ppm). The individual signals were assigned on the basis of H,H-COSY, HETCOR, gradient-selected (gs) HSQC, HMQC and HMBC techniques. The ^{13}C NMR spectra were measured in the standard way and by pulse sequence APT.

The melting points were determined on a Kofler hot stage microscope and were not corrected. The elemental analyses were carried out on an automatic analyser FISONS EA 1108.

Dichloromethane was pre-dried by standing over calcium chloride overnight. It was then filtered into a distilling flask and distilled from over phosphorus pentoxide; the fraction boiling at 39−40 °C was collected.

A commercial sample of anhydrous sodium acetate was remelted on a porcelain dish and left to cool in a desiccator.

Tetrafluoroborates of Benzenediazonium Salts: The respective aromatic amine (0.05 mol) was dissolved in 22 mL of hot HCl (1:1). The solution was then cooled with stirring to 5 °C, and an aqueous solution of sodium nitrite (3.62 g, 0.053 mol) was added drop by drop with cooling. The temperature of the reaction mixture was kept below 10 °C. The excess of HNO_2 was monitored by drop tests on KI-starch paper. The final excess nitrous acid was removed by addition of amidosulfonic acid. The resulting solution of diazonium chloride was treated with a saturated aqueous solution of $NaBF_4$ (10 g, 0.09 mol) added with stirring. The precipitated diazonium tetrafluoroborate was collected by suction, washed with cold methanol and (several times) with ether and dried in a desiccator.

5,5-Dimethyl-3-(phenylamino)cyclohex-2-en-1-one (1a): A flask equipped with an adapter for the azeotropic removal of water was charged with dimedone (3.5 g, 25 mmol), toluene (50 mL), aniline (2.33 g, 25 mmol), and glacial acetic acid (0.5 mL). The mixture was heated in an oil bath until the distillate consisted of pure toluene only (ca. 7 h). The product precipitated by cooling was collected by suction and dried in air. A second portion was obtained by concentrating the mother liquor. The enaminone obtained was recrystallized from toluene. Yield 3.54 g (65%); m.p. 182−183 °C (ref.[9] m.p. 184−185 °C).

3-Amino-5,5-dimethylcyclohex-2-en-1-one (1b): This compound was prepared as above. Gaseous ammonia was introduced into the apparatus, and the water formed in the reaction was again removed by azeotropic distillation. The product was recrystallized from acetone; yield 56%, m.p. 160−162 °C (ref.[10] m.p. 164−165 °C).

Preparation of Azo Coupling Products: A flask was charged with the respective enaminone (1.08 g, 5 mmol) dissolved in 30 mL of dichloromethane. This solution was treated with sodium acetate (1.23 g, 15 mmol) and 10 mmol of the respective benzenediazonium tetrafluoroborate. The mixture was stirred at room temperature 24 h. The solid portion was collected by suction on a sintered glass filter and washed with dichloromethane. The dichloromethane extracts obtained were distilled until dry, and the evaporation residue was submitted to column chromatography on silica gel with CH_2Cl_2 as eluent. The product obtained was recrystallized from the solvent mixtures specified below.

The following compounds were prepared in the above-described way:

5,5-Dimethyl-3-(phenylimino)cyclohexane-1,2,4-trione 2,4-Bis(4-methylphenylhydrazone) (2a): After the above-mentioned chromatography, recrystallization from a chloroform/ethanol mixture gave red-brown needles. Yield 50%. M.p. 222−225 °C. $C_{28}H_{29}N_5O$ (451.57): calcd. C 74.48, H 6.47, N 15.51; found C 74.22, H 6.49, N 15.50.

5,5-Dimethyl-3-(phenylimino)cyclohexane-1,2,4-trione 2,4-Bis(4-methoxyphenylhydrazone) (2b): Recrystallization from a chloroform/ethanol mixture. Black-brown needles. Yield 34%. M.p. 197−202 °C. $C_{28}H_{29}N_5O_3$ (483.56): calcd. C 69.55, H 6.04, N 14.48; found C 69.80, H 6.16, N 14.50.

3-Imino-5,5-dimethylcyclohexane-1,2,4-trione 2,4-Bis(4-methylphenylhydrazone) (2c): Recrystallization from ethanol. Black needles. Yield 60%. M.p. 185−186 °C. $C_{22}H_{25}N_5O$ (375.47): calcd. C 70.38, H 6.71, N 18.65; found C 70.29, H 6.89, N 18.95.

5,5-Dimethyl-3-(phenylimino)cyclohexane-1,2,4-trione 2,4-Bis(4-bromophenylhydrazone) (2d): After the above-mentioned chromatography, recrystallization from ethanol gave black-green needles with a metallic lustre. Yield 19%. M.p. 168−170 °C. $C_{20}H_{19}Br_2N_5O$ (505.21): calcd. C 47.55, H 3.79, N 13.86; found C 47.30, H 3.70, N 13.91.

3-Amino-4-(4-methoxyphenylazo)-5,5-dimethylcyclohex-3-ene-1,2-dione 2-(4-Methoxyphenylhydrazone) (2e): Recrystallization from ethanol gave black-violet needles. Yield 51%. M.p. 137−140 °C. $C_{22}H_{25}N_5O_3$ (407.47): calcd. C 64.85, H 6.18, N 17.19; found C 64.74, H 6.19, N 17.15.

Preparation of Selectively ^{15}N-Labelled Azo Coupling Products: The respective aniline (2.8 mmol) was dissolved in 3 mL (≈30%) of HBF_4. The solution obtained was treated with sodium nitrite (210 mg, 3.04 mmol) (15% ^{15}N) dissolved in a minimum amount of

water and added with stirring and cooling. The temperature was kept below 10 °C. After adding the whole amount of nitrite, the mixture was stirred for another 5 min. The precipitated diazonium tetrafluoroborate was filtered off, washed with cold methanol and several times with ether and then dried in a desiccator.

A flask was charged with 0.5 mmol of the respective enaminone dissolved in 6 mL of dichloromethane. With stirring, this solution was treated with sodium acetate (250 mg, 3 mmol) and 1 mmol of the selectively labelled diazonium tetrafluoroborate (15% $^{15}N_{\beta}$). The mixture was stirred at room temperature for 24 h, whereupon it was filtered by suction on a sintered glass filter, and the filter cake was washed with dichloromethane. The filtrates were combined and distilled under reduced pressure at room temperature until dry, and the evaporation residue was submitted to column chromatography and/or recrystallization.

The following compounds were prepared in this way:

5,5-Dimethyl-3-(phenylimino)cyclohexane-1,2,4-trione 2,4-Bis[$^{15}N_{\beta}$]-(4-methylphenylhydrazone) (3a): Chromatography over silica gel with dichloromethane as eluent. Yield 45%. M.p. 219−222 °C.

5,5-Dimethyl-3-(phenylimino)cyclohexane-1,2,4-trione 2,4-Bis[$^{15}N_{\beta}$]-(4-methoxyphenylhydrazone) (3b): Recrystallization from a chloroform/ethanol mixture. Yield 40%. M.p. 198−199 °C

3-Imino-5,5-dimethylcyclohexane-1,2,4-trione 2,4-Bis[$^{15}N_{\beta}$] (4-methylphenylhydrazone) (3c): Recrystallization from ethanol. Yield 50%. M.p. 185−187 °C.

3-Amino-4-[$^{15}N_{\beta}$](4-methoxyphenylazo)-5,5-dimethylcyclohex-3-en-1,2-dione 2-[$^{15}N_{\beta}$](4-Methoxyphenylhydrazone) (3e): Recrystallization from ethanol. Yield 45%. M.p. 138−140 °C

Acknowledgments

The authors are indebted to the Ministry of Education, Youth and Sports of the Czech Republic for financial support (Research Project CI/MSM 253 100001).

[1] V. Macháček, A. Lyčka, P. Šimůnek, T. Weidlich, *Magn. Reson. Chem.* **2000**, *38*, 293−300.
[2] S. Al-Mousawi, M. M. Abdel Khalik, S. El-Sherbiny, E. John, M. H. Elnagdi, *J. Heterocycl. Chem.* **2001**, *38*, 949−953.
[3] V. Macháček, A. Čegan, A. Halama, O. Rožňavská, V. Štěrba, *Collect. Czech. Chem. Commun.* **1995**, *60*, 1367−1379.
[4] V. Kettmann, J. Lokaj, P. Šimůnek, V. Macháček, *Acta Crystallogr., Sect. C* **2001**, *57*, 737−739.
[5] A. Lyčka, *Annu. Rep. NMR Spectrosc.* **1993**, *26*, 247−281.
[6] A. Lyčka, *Annu. Rep. NMR Spectrosc.* **2000**, *42*, 1−57.
[7] A. Lyčka, D. Šnobl, V. Macháček, M. Večeřa, *Org. Magn. Reson.* **1981**, *16*, 17−19.
[8] M. Witanowski, L. Stefaniak, G. A. Webb, *Annu. Rep. NMR*, Vol. 25 (Ed.: G. A. Webb), p. 336, Academic Press, London, 1993.
[9] K. Yamada, T. Konkahara, H. Iida, *Bull. Soc. Chem. Jpn.* **1973**, *46*, 2504−2511.
[10] J. V. Greenhill, *J. Chem. Soc. C* **1971**, 2699−2703.
[11] J. V. Greenhill, *J. Chem. Soc. B* **1969**, 299−300.

Received January 23, 2002
[O02030]