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Mendeleev Commun., 2009, **19**, 276–278

Mendeleev Communications

Ionic-liquids-assisted reaction of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes with β-nitrostyrenes

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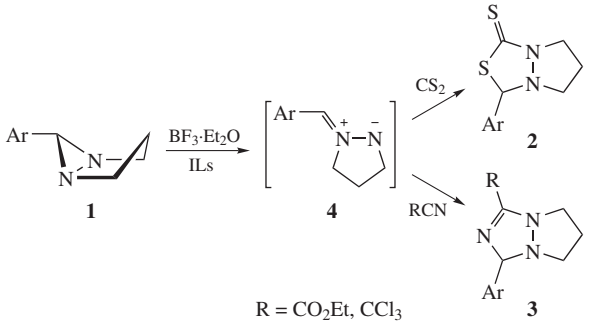
DOI: 10.1016/j.mencom.2009.09.016

5,6-Diaryl-2,3-dihydro-1*H*-pyrazolo[1,2-*a*]pyrazolium tetrafluoroborates (hexafluorophosphate) were unexpectedly synthesized along with expected 1,3-diaryl-2-nitrotetrahydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazoles, under the action of 1-nitro-2-(3-nitrophenyl)-ethylene on 6-aryl-1,5-diazabicyclo[3.1.0]hexanes in ionic liquids with the $Et_2O{\cdot}BF_3$ catalyst, whereas the same reaction with unsubstituted β-nitrostyrene produced only 1,3-diaryl-2-nitrotetrahydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazole derivatives.

Recently,[1–3] we have found that reactions of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **1** with carbon disulfide and activated nitriles in the ionic liquids (ILs) [bmim][BF_4] and [bmim][PF_6] with the $Et_2O{\cdot}BF_3$ catalyst resulted in bicyclic 3-(aryl)dihydro-5*H*-pyrazolo[1,2-*c*][1,3,4]thiadiazole-1-thiones **2** and 1-aryl-6,7-dihydro-1*H*,5*H*-pyrazolo[1,2-*a*][1,2,4]triazoles **3**, respectively. The first stage of these reactions is the formation of azomethine imine **4**, which is generated by the interaction of initial bicyclic diaziridine **1** with $Et_2O{\cdot}BF_3$ followed by addition of corresponding dipolarophiles (Scheme 1). The formation of compounds **2** and **3** does not occur in common organic solvents.

This research was undertaken to continue examining the reactions of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **1a–d** with dipolarophiles in ionic liquids. β-Nitrostyrenes **5a**,**b** were used as dipolarophiles and [bmim][BF_4] and [bmim][PF_6], as ionic liquids. By analogy with papers,[1–3] $Et_2O{\cdot}BF_3$ in a catalytic amount was added to the reaction mixture to break the diaziridine ring in initial compounds **1a–d** to reactive azomethine iminic intermediates **4a–d**. It could be expected that the addition of β-nitrostyrenes **5a**,**b** to dipolar intermediates **4a–d** should run *via* the Michael addition pathway through intermediates **6** generating 1,3-diaryl-2-nitrotetrahydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazoles **7a–d**, which are potential inhibitors of neuronal NO synthase.[4] The reaction was carried out at room temperature or with moderate heating. Compounds **7** were obtained in all the cases; however, apart from them, tetrafluoroborates of 5,6-diaryl-2,3-dihydro-1*H*-pyrazolo[1,2-*a*]pyrazolium **8b–d** and hexafluorophosphate of 5,6-diaryl-2,3-dihydro-1*H*-pyrazolo[1,2-*a*]-pyrazolium **8c′** were unexpectedly isolated, the anions of ionic liquids (BF_4 and PF_6) serving as counterions for pyrazolium cations. Assumingly, compounds **8** were formed as a result of the interaction of β-nitrostyrene **5a** with dipolar intermediates **4b–d**, contrary to the Michael addition mechanism, generating second intermediates **6′**, which were then cyclized to bicycles **9**. The latter underwent aromatization with the detachment of HNO_2 and the hydride ion. The oxidizers were likely to be either atmospheric oxygen or N_2O_3 (HNO_2 decomposition product) (Scheme 2).



Scheme 1

The structures of compounds **7** and **8** were established by aggregating elemental analysis data and spectral characteristics (mass spectra, IR, ^1H, ^{13}C and ^{15}N NMR spectra with the use of COSY, NOESY, ^1H–^{13}C HMBC, ^1H–^{13}C HSQC and ^1H–^{15}N HMBC methods).† It was found that compounds **7** were formed in the stereospecific manner: the aromatic fragments were *cis*-positioned toward each other and *trans*-positioned toward the NO_2 group.

The confirmation of the structure of salt **8c** was supplemented by X-ray data‡ (Figure 1). According to the analysis of the cation geometry, the 2,3-dihydro-1*H*-pyrazolo[1,2-*a*]pyrazolium fragment is practically planar. Although the pyrazolidine ring conformation is an envelope with the C(2) atom deviating from the mean plane of the others by 0.48 Å, the angle between the planes of two fused heterocycles is only 1.2°. The sums of the CCN and CNN angles for N(1) and N(2) atoms are 359.3 and 359.1°, respectively and the electron density is partly delo-

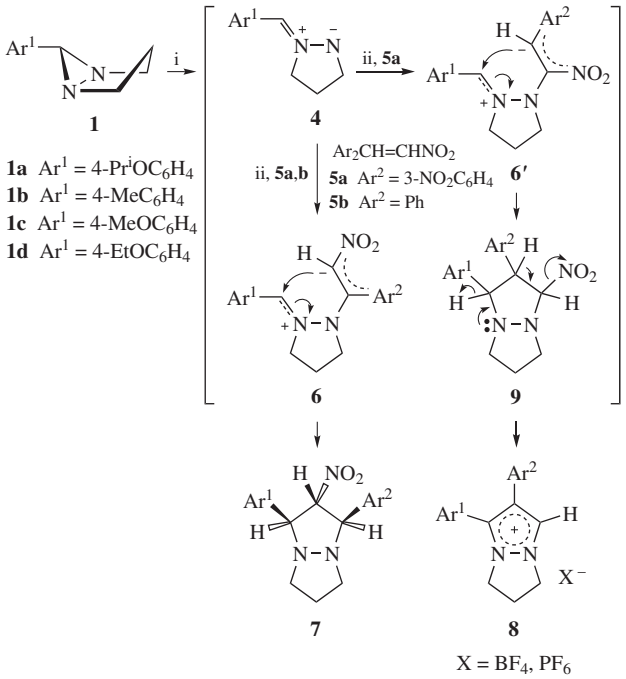
† All new compounds exhibited satisfactory elemental analyses. IR spectra were measured on a UR-20 spectrometer. ^1H and ^{13}C NMR spectra for **7e–g** were recorded on Bruker AC200-31 (200 MHz for ^1H and 50.3 MHz for ^{13}C) and Bruker AM300 (300 MHz for ^1H and 75.5 MHz for ^{13}C) spectrometers ($CDCl_3$ was used as the internal standard). ^{13}C NMR spectra were recorded under proton decoupling conditions. NMR spectra for **7a–d** and **8b–d** were measured on a Bruker AV-600 instrument (600.13, 150.90 and 60.81 MHz for ^1H, ^{13}C and ^{15}N, respectively). The chemical shifts of the signals of DMSO and $CDCl_3$ residual protons (2.50 and 7.27 ppm) and their carbons (39.5 and 77.0 ppm) were used as the internal standard. The ^{15}N spectra were measured with $MeNO_2$ (δ_N 0.0 ppm) as the external standard. All 2D-spectra were recorded using standard Bruker methods with Z-gradient. The mixing time in NOESY spectra was 0.7 s. The spectra were measured at 30 °C. Mass spectra were measured on a Finnigan MAT INCOS-50 instrument. TLC was carried out on Silufol UV-254 plates. R_f [*n*-hexane–ethyl acetate, 2:1 (v/v)]. Melting points were measured on a Gallenkamp instrument (Sanyo). 6-Aryl-1,5-diazabicyclo-[3.1.0]hexanes **1a–d** were synthesized by the published method.[14]

calized over the pirazolium fragment. No conjugation with aryl substituents (dihedral angles with the heterocycle are 133.1° for the methoxyphenyl group and 39.6° for the nitrophenyl group) is observed due to steric reasons.

Ions in the crystal of **8c** form close ion pairs *via* bifurcated B–F(4)···N contact [F···N 2.804(2) and 2.956(2) Å] that can be attributed to the F···π type of interactions.[5] Moreover, one can conclude that this ion pair is additionally stabilized by the C–H···F bonds[6] involving the $C(3)H_2$ group [C···F 3.108(2) Å].

To examine this interaction with the tetrafluoroborate moiety in more detail, we performed the topological analysis of the theoretical (B3LYP/6-311G**) electron density $\rho(r)$ for the close ion pair.§

The optimization of the ion pair geometry resulted in the reorientation of the tetrafluoroborate anion in respect to its partner. Now two B–F bonds are directed toward the nitrogen atoms of pyrazolo[1,2-*a*]pyrazolium fragment; the corresponding F(4)···N(2) and F(1)···N(1) distances are slightly bigger (2.919 and 2.925 Å, respectively). Although both the nitrogen atoms are of the same sign of charge [N(1) by –0.76 e and N(2) by –0.75 e] as the fluorine atoms of anion, search for the bond critical points (3, –1) or BCP revealed the attractive character of these bonds. Their energy calculated *via* the Espinosa's correlation scheme[7] was found to be 2.44 and 2.52 kcal mol^{-1}, respectively. Despite the observed variation of the cation-to-anion bonding type, these values could be a good approximation to the above B–F(4)···N bond strength. Thus, the bifurcated B–F(4)···N interaction in the crystal of **6c** can contribute 5 kcal mol^{-1} in total. The BCPs were also found for the C–H···F contacts linking these two nitrogen atoms with the nearest CH_2 groups [F(1)···C(1) 3.121 Å, F(4)···C(3) 3.246 Å]. The latter are somewhat weaker (1.66 and 2.39 kcal mol^{-1}), that is, apparently, the case of the C(3)–H···F(4) bond in crystal. Moreover, their CPs (3, –1) are very close to the CPs (3, +1), and the corresponding molecular graph is unstable; *i.e.*, minor variations of geometrical parameters will cause these interactions to disappear. As a result, the interac-



Scheme 2 *Reagents and conditions*: i, 0.5 mmol of **1**, 0.4–0.6 g [bmim][BF_4] or [bmim][PF_6] and 2 drops of $Et_2O{\cdot}BF_3$; ii, 0.5 mmol of β-nitrostyrene **5**.

*1-(4-Isopropoxyphenyl)-2-nitro-3-(3-nitrophenyl)tetrahydro-1*H,5H-*pyrazolo[1,2-*a*]pyrazole* **7a**: R_f 0.60, mp 90 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ: 1.30 (d, 6H, Me_2CHO), 2.15, 2.40 (2m, 2H, $CH_2CH_2CH_2$), 3.08, 3.28 (td, m, 2H, PriOArCNCH_2, ^2J 9.8 Hz, ^3J 5.6 Hz), 3.28, 3.39 (m, td, 2H, NO_2ArCNCH_2, ^2J 9.8 Hz, ^3J 4.8 Hz), 4.51 (sp, 1H, Me_2CHO, ^3J 6.1 Hz), 4.66 (d, 1H, PriOArC*H*, ^3J 6.8 Hz), 4.90 (d, 1H, NO_2ArC*H*, ^3J 5.2 Hz), 4.98 (t, 1H, NO_2CH, ^3J 5.0 Hz), 6.84, 7.28 (2d, 4H in PriO*Ar*, ^3J 8.5 Hz), 7.55 [t, 1H, C(5)H in NO_2Ar, ^3J 8.0 Hz], 7.84 [d, 1H, C(4)H in NO_2Ar, ^3J 8.0 Hz], 8.15, [d, 1H, C(6)H in NO_2Ar, ^3J 8.0 Hz], 8.44 [s, 1H, C(2)H in NO_2Ar]. ^{13}C NMR ($CDCl_3$) δ: 21.90 (Me_2CHOAr), 23.89 (NCH_2CH_2), 50.23 (PriOArCNCH_2), 51.23 (NO_2ArCNCH_2), 69.86 (Me_2CHOAr), 70.44 (NO_2ArC_{ring}), 71.53 (PriOArC_{ring}), 102.79 (NO_2C_{ring}), 116.14, 128.56, 129.40, 158.16 (PriO*Ar*), 122.20, 122.92, 129.82, 133.11, 142.76, 148.63 (NO_2*Ar*). ^{15}N NMR ($CDCl_3$) δ: +6.8 (NO_2C_{ring}H), –9.7 (NO_2Ar), –247.1 (MeOArCN), –249.6 (NO_2ArC*N*).

*1-(4-Methoxyphenyl)-2-nitro-3-phenyltetrahydro-1*H,5H-*pyrazolo[1,2-*a*]pyrazole* **7f**: nondistilled oil, R_f 0.56. ^{1}H NMR ($CDCl_3$) δ: 2.14, 2.40 (2m, 2H, $CH_2CH_2CH_2$, ^3J 5.87 Hz, Δν 77.03 Hz), 3.25 (m, 4H, NCH_2, ^3J 5.87 Hz), 3.81 (s, 3H, ArO*Me*), 4.68 (d, 1H, MeOArC*H*, ^3J 5.87 Hz), 4.77 (d, 1H, ArC*H*, ^3J 5.87 Hz), 5.06 (t, 1H, NO_2CH, ^3J 5.87 Hz), 6.90, 7.38 (2d, 4H, H in MeO*Ar*, ^3J 8.80 Hz), 7.35, 7.50 (2m, 5H, H_{Ph}, ^3J 7.34 Hz). ^{13}C NMR ($CDCl_3$) δ: 23.99 (NCH_2CH_2), 50.74 (MeArCNCH_2), 51.13 (ArCNCH_2), 55.32 (*Me*OAr), 71.76 (MeArC_{ring}), 71.87 (ArC_{ring}), 103.51 (NO_2C_{ring}), 114.36, 127.20, 131.15, 159.63 (MeO*Ar*), 128.20, 128.55, 128.96, 139.82 (Ph).

*5-(4-Methoxyphenyl)-6-(3-nitrophenyl)-2,3-dihydro-1*H-*pyrazolo[1,2-*a*]pyrazol-4-ium tetrafluoroborate* **8c**: mp 195.5–196.0 °C. ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.90 (m, 2H, $CH_2CH_2CH_2$), 3.84 (s, 3H, ArO*Me*), 4.54 (t, 2H, MeArCNCH_2, ^3J 6.9 Hz), 4.68 (t, 2H, NO_2ArCNCH_2, ^3J 7.1 Hz), 7.15, 7.48 (2d, 4H, H in MeO*Ar*, ^3J 7.9 Hz), 7.70 [m, 2H, C(5)H, C(6)H in NO_2Ar, ^3J 8.0 Hz], 8.14 [s, 1H, C(2)H in NO_2Ar], 8.23 [d, 1H, C(4)H in NO_2Ar, ^3J 8.0 Hz], 8.99 (s, 1H, NO_2ArC*H*). ^{13}C NMR ([$^2H_6$]DMSO) δ: 26.21 (NCH_2CH_2), 48.19 (MeOArCNCH_2), 49.22 (CHNCH_2), 55.46 (*Me*OAr), 122.39 (NO_2ArC_{ring}), 130.04 (NC_{ring}), 139.58 (MeOArC_{ring}), 115.09, 116.64, 130.80, 161.25 (MeO*Ar*), 122.48, 123.04, 130.68, 130.96, 134.31, 148.09 (NO_2Ar). ^{15}N NMR ([$^2H_6$]DMSO) δ: –10.3 (NO_2Ar), –167.7 (MeArCN), –168.6 (CHN). IR (ν/cm^{-1}): 688, 736, 1084, 1188, 1252, 1307, 1344, 1448, 1520, 1612, 2856, 2952, 3074, 3152. MS, *m*/*z* (%): 377 (M – NO_2, 10), 324 (M – BF_4 – Me, 12), 308 (M – BF_4 – MeO, 23), 295 (M – BF_4 – NO_2, 7), 278 (M – BF_4 – NO_2 – Me, 8), 190 [$MeOC_6H_4$-$CHN_2(CH_2)_3$, 17], 121 ($C_6H_4NO_2$, 7), 76 (C_6H_4, 35), 41 [$(CH_2)_3$ – H, 100].

*5-(4-Methoxyphenyl)-6-(3-nitrophenyl)-2,3-dihydro-1*H-*pyrazolo[1,2-*a*]pyrazol-4-ium hexafluorophosphate* **8c′**: mp 216.0–216.5 °C. IR (ν/cm^{-1}): 688, 736, 820, 1188, 1256, 1300, 1344, 1448, 1520, 1612, 2888, 2952, 3088, 3136.

For characteristics of compounds **7b**–**e**,**g** and **8b**,**d**, see Online Supplementary Materials.

‡ *Crystallographic data*. Crystals of **8c** ($C_{19}H_{18}N_3O_3BF_4$, M = 423.17) are monoclinic, space group $P2_1/c$, at 100 K: a = 7.9345(5), b = 10.6218(6) and c = 22.2185(13) Å, β = 98.585(5)°, V = 1851.56(19) Å^3, Z = 4 (Z' = 1), d_{calc} = 1.518 g cm^{-3}, μ(MoKα) = 1.29 cm^{-1}, F(000) = 872. Intensities of 17949 reflections were measured with a Bruker SMART APEX2 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans, 2θ < 58°] and 4917 independent reflections (R_{int} = 0.0360) were used in the further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The H(C) atom positions were calculated. The hydrogen atoms were refined in the isotropic approximation in riding model. For **6c** the refinement converged to wR_2 = 0.1098 and GOF = 1.000 for all independent reflections [R_1 = 0.0413 was calculated against F for 3947 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.[15]

CCDC 745852 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2009.

§ The DFT calculations of the isolated cation of **6c** and the ion pair were performed with the Gaussian98 program package[16] using B3LYP functional. Full optimization of their geometry was carried out with the 6-311G(d,p) basis set starting from the X-ray structural data. The extremely tight threshold limits of 2×10^{-6} and 6×10^{-6} a.u. were applied for the maximum force and displacement, respectively. The topological analysis of the computed electron densities was performed using AIMall program package.[17]

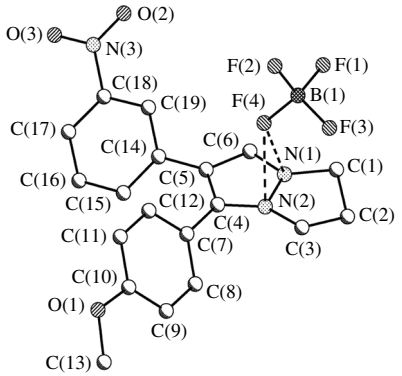


Figure 1 General view of compound **8c** showing the formation of B–F···N contacts. Selected bond lengths (Å): N(1)–N(2) 1.3536(15), N(1)–C(1) 1.4710(16), N(1)–C(6) 1.3287(18), N(2)–C(3) 1.4736(17), N(2)–C(4) 1.3415(17), C(4)–C(5) 1.4116(18), C(5)–C(6) 1.3994(17); selected bond angles (°): N(1)–N(2)–C(4) 109.47(11), N(2)–N(1)–C(6) 109.54(11), C(4)–C(5)–C(6) 106.03(12).

tions of this type cannot be the driving force of the B–F···N binding.

Additional stabilization of the model ion pair is also achieved by interionic interactions of F(2) fluorine atom with C(1)H_2 and C(3)H_2 groups of pyrazolium cycle – F(2)···C(1) (2.966 Å, 3.18 kcal mol^{-1}) and F(2)···C(3) (3.009 Å, 2.86 kcal mol^{-1}) ones. However, the mutual disposition of ions in crystalline **6c** prevents the formation of such contacts; the smallest F(n) [n = 1–3] to C(m) [m = 1, 3] distance is 3.497(2) Å between F(3) and C(3) atoms. The interaction of tetrafluoroborate anion with the methoxyphenyl moiety of cation [F(4)···C(3) 3.109 Å, 2.17 kcal mol^{-1}] *in vacuo* does not persist in crystal [F(2)···C(3) 3.313 Å]. Although in model ion pair the contribution from C–H···F (12.3 kcal mol^{-1}) binding overcomes that for the B–F···N (4.96 kcal mol^{-1}), in crystal of **8c** it decreases down to ~2.5 kcal mol^{-1} with B–F···N interaction energy being presumably the same. This means that they are equally responsible for the formation of close ion pair of **8c**.

Salts similar to compounds **8** have been described in the literature.[8,9] They are of interest as highly conductive organic plastic crystals[8] patented as active herbicides, fungicides and antibacterial agents.[10,11] Bromides of pyrazolo[1,2-*a*]pyrazolium derivatives are obtained by alkylation of corresponding pyrazole sodium salts with 1,3-dihalogenides and trifluoromethane sulfoimide is formed by a bromide ion substitution in the interaction with trifluoromethane sulfoimide sodium salt.[8] Also there are a few examples of preparing compounds similar to salts **8** through aromatization of pyrazolinium analogues under the action of atmospheric oxygen.[9] Compounds similar to products **7** are also known.[9,12] They display activity as tyrosine kinase inhibitors and can be effective for immunity disturbance.[13]

Regioselectivity of the reaction between compounds **1** and β-nitrostyrene **5a** depends on the nature of substituents in the aromatic fragment of initial bicyclic diaziridines **1** and evidently relates to steric hindrances. The predominant products for reaction of compounds **1a**,**b**,**d** proved to be predicted structures **7a**,**b**,**d**. Note that the reaction of compound **1a** (the Pr^{i}O substituent) gave exclusively compound **7a**. The predominant formation of the pyrazolium cation (compound **8c** or **8c′**) was observed only in the reaction of compound **1c** (the MeO substituent in the aromatic ring). The interaction of β-nitrostyrene **5b** without substituents in the aromatic ring with diaziridines **1b–d** merely resulted in Michael reaction products **7e–g** (Table 1).

Table 1 Reaction of β-nitrostyrene **5a**,**b** with 6-aryl-1,5-diazabicyclo[3.1.0]-hexanes **1a–d** in [bmim][BF_4] with $Et_2O{\cdot}BF_3$ catalyst.

Substituent Ar^1 in initial **1a–d**	β-Nitrostyrene **5a** (Ar^2 = 3-$NO_2C_6H_4$)				β-Nitrostyrene **5b** (Ar^2 = Ph)			
	Yield (%)		*t*/h	*T*/°C	Yield (%)		*t*/h	*T*/°C
	7	**8**			**7**	**8**		
a 4-Pr^{i}OC_6H_4	**a** 76	**a** 0	3	20				
b 4-MeC_6H_4	**b** 55	**b** 35	4[a]	20	**e** 72	**e** 0	2	60
c 4-MeOC_6H_4	**c** 20	**c** 65	3 (7[b])	20	**f** 75	**f** 0	7	20
d 4-EtOC_6H_4	**d** 52	**d** 20	5	20	**g** 78	**g** 0	9	20

[a]Reaction occurs equally both in the presence and in the absence of catalyst $Et_2O{\cdot}BF_3$. [b]Reaction was carried out in [bmim][PF_6] with formation of compounds **7c** and hexafluorophosphate derivative **8c′** in the same yields.

This work was partially supported by the programme of the Presidium of the Russian Academy of Sciences 'Development of Methods for Synthesizing Chemical Compounds and Creating New Materials' and the Russian Foundation for Basic Research (grant no. 09-03-01091-a).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2009.09.016.

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Received: 16th February 2009; Com. 09/3284