REARRANGEMENTS OF ARYLHYDRAZONES OF N-ACYLBENZIMIDAZOLES - SYNTHESIS OF 2-ARYL-1,2,4-TRIAZOLO[4,3-a]QUINOXALINIUM SALTS*

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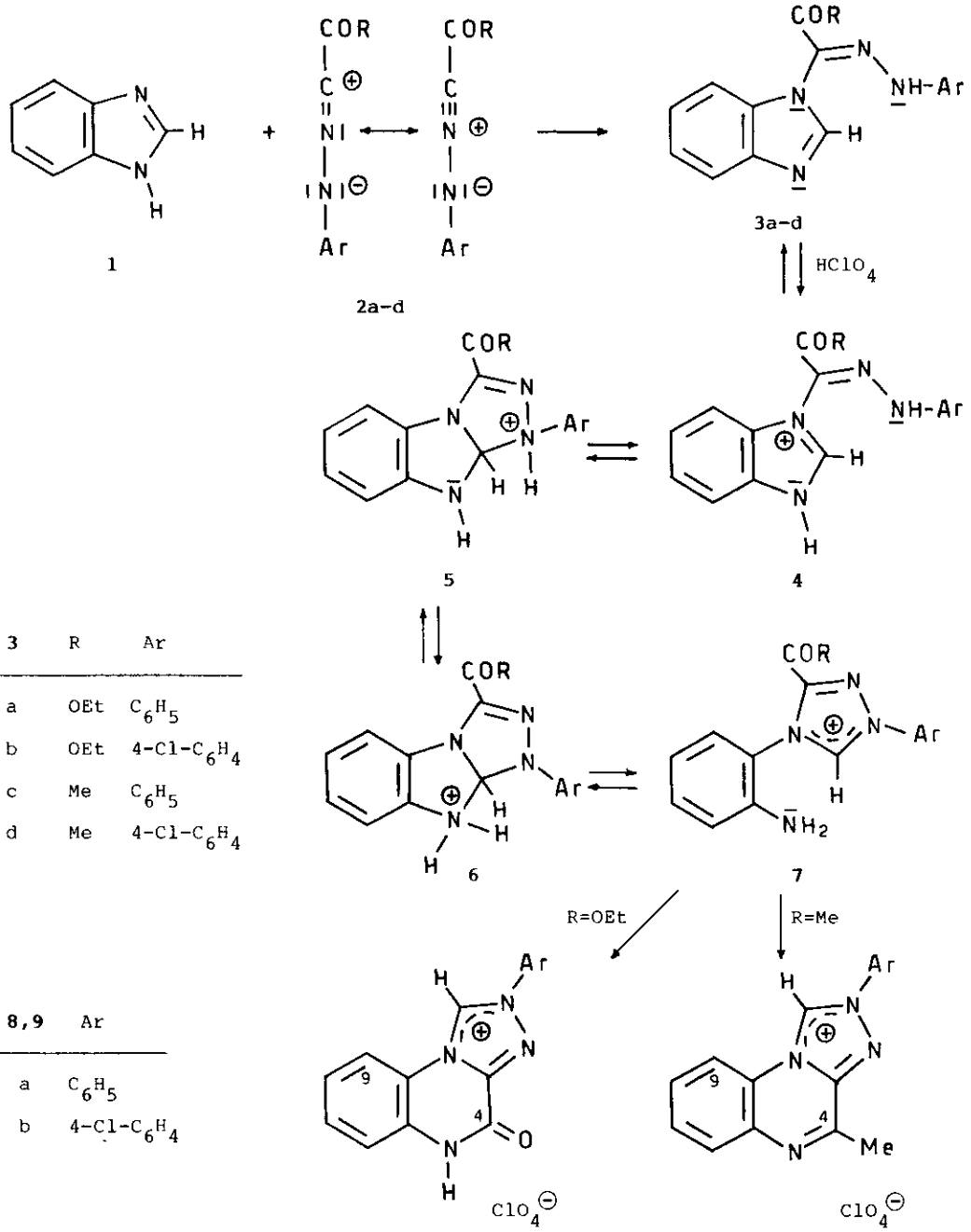
Abstract ——— The acid induced rearrangement of arylhydrazones of N-acylbenzimidazoles has been investigated. An initial 6π heteroelectrocyclic reaction involving the hydrazone side chain and the imidazole moiety, followed by a ring opening gave 4-(2-aminophenyl)-1,2,4-triazolium perchlorate **7** as intermediates. The latter species, depending on the substituent present in the triazole moiety, gave the 2-aryl-1,2,4-triazolo[4,3-a]quinoxalinium perchlorates **8** or **9** as the final rearranged products. Alkaline cleavage of the triazolo[4,3-a]quinoxalinium perchlorates **8** and **9** to 3-(arylformylhydrazino)quinoxaline derivatives **11** and **13** has been pointed out.

Our previous researches[1,2] have shown that rearrangement reactions of heterocyclic compounds, suitably substituted by a hydrazone moiety in the side chain, resulted in an efficient method for the synthesis of nitrogen containing polycondensed heterocyclic systems. The acid induced rearrangement of phenylhydrazones of 3-acylindoles gave directly 2H-pyrazolo[3,4-c]quinoline derivatives in good yield,[1] while the same reaction on phenylhydrazones of 2-acylindazoles gave 5-(2-aminophenyl)-1,2,4-triazoles which were useful intermediates for the synthesis of triazolo[1,5-f]phenanthridines.[2]

The acid catalyzed rearrangement has been interpreted as a result of an initial 6π heteroelectrocyclic reaction involving the hydrazone side chain and the five membered heterocycle, followed by ring opening and final ring closure processes.[1] These results prompted us to extend our studies to the acid induced rearrangements of arylhydrazones of N-acylbenzimidazoles **3**.

It is well known that 1,3-addition reaction of nitrilimines to heterocyclic compounds is a valuable synthetic route to hydrazone derivatives.[2-5] In our case, arylhydrazones **3a-d** were prepared by the reaction of benzimidazole **1** with



1 + 2a-d → 3a-d ⇄ 4 ⇄ 5 ⇄ 6 ⇄ 7

3	R	Ar
a	OEt	C_6H_5
b	OEt	4-Cl-C_6H_4
c	Me	C_6H_5
d	Me	4-Cl-C_6H_4

8,9	Ar
a	C_6H_5
b	4-Cl-C_6H_4

8a,b **9a,b**

the nitrilimines **2a-d** according to a procedure previously reported for **3a**,[5] and the structures were confirmed by spectral (ir, ^{1}H nmr) and analytical data.

The rearrangement reactions were carried out by addition of perchloric acid to a boiling butanol solution of the arylhydrazones **3**. Upon this treatment, compounds **3a-d** gave 2-aryl-1,2,4-triazolo[4,3-a]quinoxalinium perchlorates **8a,b** and **9a,b**, respectively, in high yields depending on the kind of the substituent R. The same rearrangement has been also achieved by refluxing compounds **3a-d** in ethanol containing concentrated hydrochloric acid, affording the corresponding triazolo[4,3-a]quinoxalinium chlorides **8** and **9**, but in lower yields.

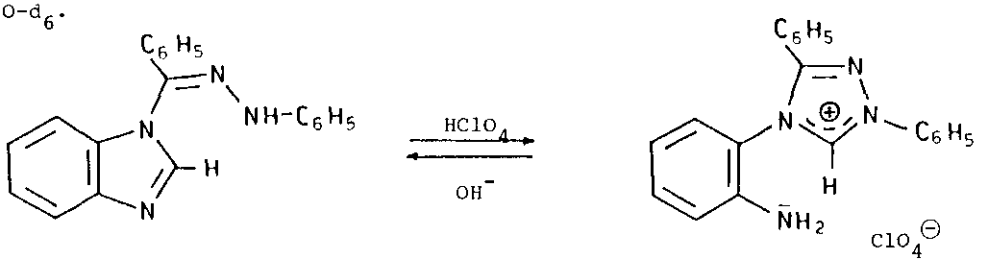
The structures of the 2-aryl-1,2,4-triazolo[4,3-a]quinoxalinium perchlorates **8** and **9** are supported by analytical and spectral data. The ^{1}H nmr spectra of **8** and **9** showed the C_1-H proton signal at δ 12.05-12.40. Compounds **9a,b** exhibited the methyl proton signal at δ 2.97 and 2.94, downfield with respect to the corresponding value of the acetyl protons (δ 2.60 and 2.56) of the starting arylhydrazones because of the ring current effect of the triazoloquinoxalinium ring. The ir spectra of compounds **9** did not show NH or C=O absorptions, while those of compounds **8** exhibited a strong band at 1700 cm^{-1} and weak broad bands at 3250-3100 cm^{-1} assignable to the C=O and NH groups, respectively. Moreover, both series of compounds showed the characteristic ir band due to ClO_4 group near 1100 cm^{-1}.

The obtained results can be explained by a rearrangement proceeding through an initial 6π heteroelectrocyclic ring closure[6] of the protonated form **4**, followed by prototropic equilibrium and ring opening of the intermediates **6** to 1,2,4-triazolium salts **7**. These intermediates **7**, in turn, undergo spontaneous ring closure to **8** or **9** by a condensation reaction between the amino group and the ester or acetyl substituent at C-3 of the triazole ring.

In order to obtain further evidence for this mechanism, we recorded ^{1}H nmr spectra of compounds **3a-d** in DMSO-d_6 containing few drops of TFA. At room temperature the nmr spectra only showed signals due to the protonated form **4** (e.g., singlet at δ 9.72-9.88 for C_2-H proton).[7] However, on heating the sample tube, signals due to the rearranged compounds **8** or **9** appeared (e.g., singlet at δ 12.05-12.40 for C_1-H proton), while signals due to the unrearranged compounds were decreasing in intensity.

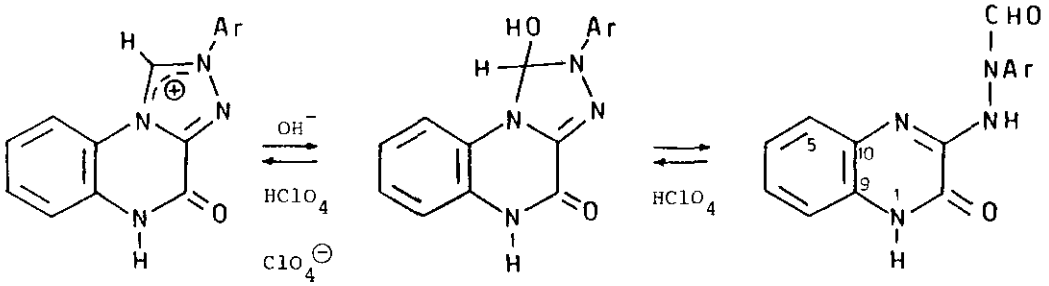
The involvement of an intermediary **7** in the overall rearrangement of **3** into **8** or **9** has been confirmed by the fact that the triazolium perchlorates **7e** was

isolated from the hydrazone **3e** having no carbonyl group. Moreover, in this case the rearrangement reaction was shown to be a reversible process, since the perchlorate **7e**, upon treatment with aqueous sodium carbonate, gave the phenylhydrazone **3e**. The structure of the 4-(2-aminophenyl)-1,3-diphenyl-1,2,4-triazolium perchlorate **7e** was supported by the appearance of the C_5-H proton signal at δ 11.28 and the NH_2 proton signal at δ 4.80 in the nmr spectrum in DMSO-d_6.

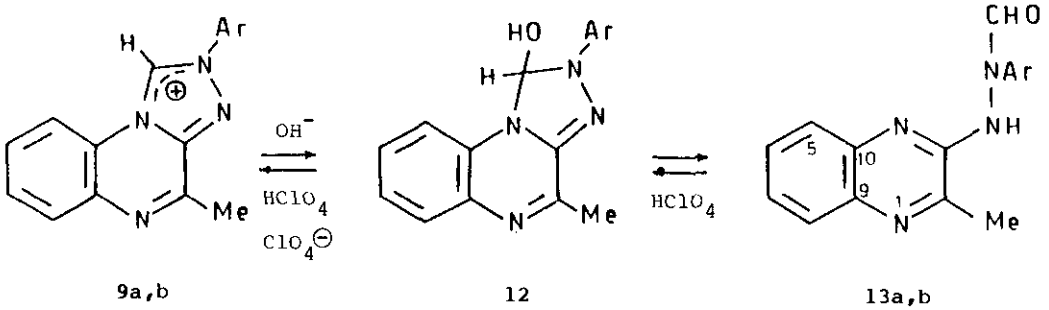


3e **7e**

Treatment of 1,2,4-triazolo[4,3-a]quinoxalinium perchlorates **8a,b** and **9a,b** with a base afforded the arylformylhydrazino derivatives **11a,b** and **13a,b**, respectively, as a result of the ring opening of the 1,2,4-triazole moiety, as well as the ring cleavage of 1,2,4-triazolo[4,3-a]pyridinium, 1,2,4-triazolo[4,3-a]quinolinium, 1,2,4-triazolo[3,4-a]isoquinolinium, and 1,2,4-triazolo[4,3-f]phenanthridinium salts.[8] The reaction is a reversible

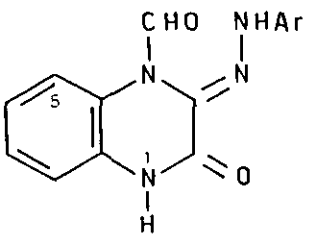


8a,b **10** **11a,b**



9a,b **12** **13a,b**

process. In fact, the obtained formylhydrazino derivatives, upon treatment with aqueous perchloric acid, could be converted into the original triazolo [4,3-a]quinoxalinium salts **8** and **9** quantitatively, presumable via the pseudo bases **10** and **12** as intermediates.



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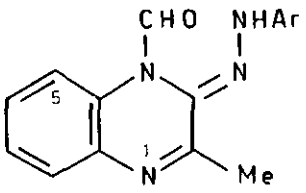

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The ir spectra of both series of the formylhydrazino derivatives **11** and **13** exhibited the NH and CHO bands at 3320-3285 cm^{-1} and at 1680-1660 cm^{-1}, respectively. The ^{1}H nmr spectra of compounds **11** and **13** in DMSO-d_6 showed two sets of signals due to N-H and C-H protons of the formylhydrazino group, suggesting a slow exchange process between two forms, due to the hindered rotation about the N-CHO bond.[9] Isomeric hydrazone structures **14** and **15**, arising from a different triazoline ring opening, were excluded on the basis of the aromatic proton pattern in the ^{1}H nmr spectra. In fact, compounds **11** and **13** showed the aromatic proton signals as one-grouped multiplets at δ 6.9-7.9, whereas structures of type **14** or **15** would exhibit the C_5-H signal downfield from the other aromatic protons, due to anisotropic effect of the adjacent -CHO group.[10] Also ^{13}C nmr data are in agreement with the assigned structures. In the ^{13}C nmr spectra of **11a,b** and **13a,b** two different signals (one for each conformer) can be detected for CHO, C-3, C-5, C-9, C-10, methyl, and N-aryl carbon atoms of the two conformers and their chemical shift difference is a further evidence for the restricted rotation of the N-CHO bond.[10,11] A comparison of the spectra of **11** and **13** indicates that, in the deshielded aromatic carbons region (110-123 ppm), besides the signals for ortho-N-aryl carbons (119,91-122,91 ppm) is only present the signal for C-8 (ortho-amino carbon atom)[10,12] of **11a** and **11b** at 115,44 and 115,50 ppm, respectively. This observation would be considered the most diagnostic in supporting the assigned stuctures **11,13** and excluding both isomeric and tautomeric structures.[13]

EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus; ir spectra (nujol mull) were recorded on a Perkin-Elmer infrared spectrophotometer (model 297); uv spectra (ethanol) were determined with a Varian Superscan 3 spectrophotometer; ^{1}H nmr spectra were recorded on a Varian EM 360 spectrometer; ^{13}C nmr spectra were recorded on a Varian Gemini 200 spectrometer. Chemical shifts are reported as δ values (ppm) relative to TMS as internal standard.

General Method for the Preparation of the Arylhydrazones **3a-e.**

Compounds **3** were prepared by the procedure previously described for **3a.**[5]

To a solution of benzimidazole **1** (25 mmol) and hydrazidoyl chloride[2-5] (25 mmol) in anhydrous THF (100 ml) was added a threefold excess of triethylamine. After standing at room temperature for three days, the resulting triethylamine hydrochloride was filtered off and the filtrate was evaporated under reduced pressure. The solid residue was recrystallized from ethanol to give arylhydrazones **3a-e.**

Compound **3a** (R = OEt, Ar = C_6H_5) (yield 71%), mp 208°C (lit.[5] mp 205°C); ir: 3170 cm^{-1} (NH), 1720 cm^{-1} (CO); ^{1}H nmr (DMSO-d_6) δ: 1.26 (t,J=7 Hz,3H,$OCH_2\underline{CH_3}$), 4.22 (q,J=7 Hz,2H,OCH_2CH_3), 6.7-7.9 (m,9H,Ar<u>H</u>), 8.35 (s,1H,<u>H</u>-2), 10.69 (s,1H,N<u>H</u>).

Compound **3b** (R = OEt, Ar = 4-Cl-C_6H_4) yellow needles (yield 76%), mp 208°C; ir: 3140 cm^{-1} (NH), 1720 cm^{-1} (CO); ^{1}H nmr (DMSO-d_6) δ: 1.23 (t,J=7 Hz,3H,$OCH_2\underline{CH_3}$), 4.23 (q,J=7 Hz,2H,OCH_2CH_3), 7.1-7.9 (m,8H,Ar<u>H</u>), 8.33 (s,1H,<u>H</u>-2), 10.68 (s,1H,N<u>H</u>). Anal. Calcd for $C_{17}H_{15}ClN_4O_2$: C, 59.57; H, 4.41; N, 16.34. Found: C, 59.72; H, 4.38; N, 16.45.

Compound **3c** (R = Me, Ar = C_6H_5) yellow needles (yield 85%), mp 244°C; ir: 3160 cm^{-1} (NH), 1670 cm^{-1} (CO); ^{1}H nmr (DMSO-d_6) δ: 2.60 (s,3H,$C\underline{H_3}$), 6.8-8.0 (m,9H,Ar<u>H</u>), 8.33 (s,1H,<u>H</u>-2), 10.98 (s,1H,N<u>H</u>). Anal. Calcd for $C_{16}H_{14}N_4O$: C, 69.05; H, 5.07; N, 20.13. Found: C, 68.90; H, 4.98; N, 20.45.

Compound **3d** (R = Me, Ar = 4-Cl-C_6H_4) yellow needles (yield 82%), mp 240°C; ir: 3135 cm^{-1} (NH), 1670 cm^{-1} (CO); ^{1}H nmr (DMSO-d_6) δ: 2.56 (s,3H,$C\underline{H_3}$), 6.9-7.9 (m,8H,Ar<u>H</u>), 8.20 (s,1H,<u>H</u>-2), 10.82 (s,1H,N<u>H</u>). Anal. Calcd for $C_{16}H_{13}ClN_4O$: C, 61.45; H, 4.19; N, 17.91. Found: C, 61.58; H, 4.22; N, 17.85.

Compound **3e** (yield 65%), mp 235°C (lit.[14] mp 235°C); ir: 3205 cm^{-1} (NH); ^1H nmr (DMSO-d_6) δ : 6.7-7.9 (m,14H,ArH), 8.42 (s,1H,H-2), 9.95 (s,1H,NH).

Rearrangement Reactions of the Arylhydrazones **3a-d** - Synthesis of 2-Aryl-4,5-dihydro-4-oxo-1,2,4-triazolo[4,3-a]quinoxalinium Perchlorates **8a,b** and 2-Aryl-4-methyl-1,2,4-triazolo[4,3-a]quinoxalinium Perchlorates **9a,b**

To a solution of **3a-d** (5 mmol) in boiling n-butanol (60 ml) was added perchloric acid (60%, 0.6 ml). Cooling down to room temperature precipitated crystals, which were collected and recrystallized from ethanol.

Compound **8a** (Ar = C_6H_5) colourless powder (yield 72%), mp>330°C; ir: 3250, 3180 cm^{-1} (NH), 1700 cm^{-1} (CO), 1140-1070 cm^{-1} (ClO_4); ^1H nmr (DMSO-d_6) δ : 7.2-7.9 (m,6H,ArH), 7.9-8.4 (m,3H,ortho-H of 2-phenyl + H-9), 12.05 (s,1H,H-1), 13.0 (broad s, 1H,NH). Anal. Calcd for $C_{15}H_{11}ClN_4O_5$: C, 49.67; H, 3.06; N, 15.45. Found: C, 49.34; H, 3.07; N, 15.31.

Compound **8b** (Ar = 4-Cl-C_6H_4) colourless powder (yield 70%), mp>330°C; ir: 3200-3110 cm^{-1} (NH), 1700 cm^{-1} (CO), 1100 cm^{-1} (ClO_4); ^1H nmr (DMSO-d_6) δ : 7.4-8.0 (m,5H,ArH), 8.0-8.3 (m,3H,ortho-H of 2-p-Cl-phenyl + H-9), 12.10 (s,1H,H-1), 12.9 (broad s, 1H,NH). Anal. Calcd for $C_{15}H_{10}Cl_2N_4O_5$: C, 45.36; H, 2.54; N, 14.11. Found: C, 45.12; H, 2.67; N, 13.92.

Compound **9a** (Ar = C_6H_5) colourless powder (yield 90%), mp>330°C; ir: 1100 cm^{-1} (ClO_4); ^1H nmr (DMSO-d_6) δ : 2.97 (s,3H,CH_3), 6.9-8.3 (m,8H,ArH), 8.47 (m,1H,H-9), 12.40 (s,1H,H-1). Anal. Calcd for $C_{16}H_{13}ClN_4O_4$: C, 53.27; H, 3.63; N, 15.53. Found: C, 53.43; H, 3.84; N, 15.70.

Compound **9b** (Ar = 4-Cl-C_6H_4) colourless powder (yield 84%), mp>330°C; ir: 1100 cm^{-1} (ClO_4); ^1H nmr (DMSO-d_6) δ : 2.94 (s,3H,CH_3), 7.7-8.3 (m,7H,ArH), 8.45 (m,1H,H-9), 12.30 (s,1H,H-1). Anal. Calcd for $C_{16}H_{12}Cl_2N_4O_4$: C, 48.63; H, 3.06; N, 14.18. Found: C, 48.41; H, 3.04; N, 14.18.

Alkaline Cleavage of Triazolo[4,3-a]quinoxalinium Perchlorates **8a,b** and **9a,b** to 1,2-Dihydro-3-(β-aryl-β-formylhydrazino)quinoxalin-2-one **11a,b** and 2-Methyl-3-(β-aryl-β-formylhydrazino)quinoxaline **13a,b.**

The perchlorates **8a,b** or **9a,b** (2 mmol) were dissolved in hot aqueous ethanol (66%, 100 ml). The solution was made alkaline with aqueous sodium carbonate (2M,

1.4 ml) and cooled down to room temperature. The resulting precipitates were collected by filtration to give **11a,b** or **13a,b**.

Compound **11a** (Ar = C_6H_5) colourless needles from benzene:cyclohexane (1:1) (yield 77%), mp 283°C; ir: 3285, 3180 cm^{-1} (broad) (NH), 1690 and 1665 cm^{-1} (CO); uv λ_{max} nm (log ε) : 235s(4.27), 316(4.05), 328(4.12), 342(3.93); ^1H nmr (DMSO-d_6) δ : two conformers, 6.9-7.9 (m,9H,ArH), 8.43 and 8.95 (2s, [0.45+0.55]H,CHO), 10.20 and 10.90 (broad signals,1H,NH), 12.50 (broad s, 1H,NH); ^{13}C nmr (DMSO-d_6) δ : two conformers, 115.44 (C-8), 120.09 and 121.37 (C-ortho of N-phenyl), 123.84 (C-6), 125.50 and 125,81 (C-5), 125.74 (C-7 or C-para of N-phenyl), 125.93 (C-para of N-phenyl or C-7), 129.00 and 129.60 (C-meta of N-phenyl), 129.42 and 129.52 (C-9 or C-10), 132.24 and 132.33 (C-10 or C-9), 140.44 and 141.60 (C-ipso of N-phenyl), 148.91 and 150.02 (C-3), 150.92 (C-2), 160.19 and 165.36 (CHO). Anal. Calcd for $C_{15}H_{12}N_4O_2$: C, 64.28; H, 4.32; N, 19.99. Found: C, 64,05; H, 4.28; N, 20.13.

Compound **11b** (Ar = 4-Cl-C_6H_4) colourless needles from ethanol (yield 77%), mp 310°C; ir: 3320, 3180 cm^{-1} (broad) (NH), 1690 and 1660 cm^{-1} (CO); uv λ_{max} nm (log ε) : 239s(4.24), 315(4.10), 327(4.18), 343(4.00); ^1H nmr (DMSO-d_6) δ : two conformers, 6.9-7.8 (m,8H,ArH), 8.30 and 8.85 (2s,[0.6+0.4]H,CHO), 10.10 and 10.70 (broad signals, 1H,NH), 12.50 (broad s, 1H,NH); ^{13}C nmr (DMSO-d_6) δ : two conformers, 115.50 (C-8) , 121.71 and 122.91 (C-ortho of N-p-Cl-phenyl), 123.82 (C-6), 125.66 and 126,01 (C-5), 125.86 (C-7), 129.00 and 129.53 (C-meta of N-p-Cl-phenyl), 129.17 and 129.35 (C-9 or C-10), 132.18 and 132.25 (C-10 or C-9), 139.33 and 140.61 (C-ipso of N-p-Cl-phenyl), 148.83 and 149.91 (C-3), 150.91 (C-2), 160.15 and 165.50 (CHO), C-Cl non detected owing to overlap. Anal. Calcd for $C_{15}H_{11}ClN_4O_2$: C, 57.24; H, 3.52; N, 17.80. Found: C, 57.45; H, 3.80; N, 17.87.

Compound **13a** (Ar = C_6H_5) colourless needles from benzene:cyclohexane (1:1) (yield 76%), mp 136°C; ir: 3320 cm^{-1} (NH), 1675 cm^{-1} (CO); uv λ_{max} nm (log ε) : 243s(4.47), 339(3.87); ^1H nmr (DMSO-d_6) δ : two conformers, 2.70 (s,3H,CH_3), 7.0-7.9 (m,9H,ArH), 8.47 and 9.02 (2s,[0.4+0.6]H,CHO), 9.85 and 10.26 (2s,[0.6+0.4]H,NH); ^{13}C nmr (DMSO-d_6) δ : two conformers, 21.11 and 21.17 (CH_3), 119.91 and 121.13 (C-ortho of N-phenyl), 125.57 and 125,65 (C-5), 125.81 (C-para of N-phenyl), 126.53 (C-8 or C-6), 128.02 (C-6 or C-8), 129.24 and 129,34 (C-7), 129.00 and 129.62 (C-meta of N-phenyl), 137.91 and 137.97 (C-10 or C-9), 140.09

and 140.24 (C-9 or C-10), 140.63 and 141.82 (C-ipso of N-phenyl), 145.08 (C-2), 149.63 and 150.54 (C-3), 160.50 and 165.73 (CHO). Anal. Calcd for $C_{16}H_{14}N_4O$: C, 69.05; H, 5.07; N, 20.13. Found: C, 69.17; H, 5.03; N, 20.28.

Compound **13b** (Ar = 4-Cl-C_6H_4) colourless needles from ethanol (yield 80%), mp 145°C; ir: 3310 cm^{-1} (NH), 1680 cm^{-1} (CO); uv λ_{max} nm (log ε) : 243s(4.41), 345(3.81); ^1H nmr (DMSO-d_6) δ : two conformers, 2.70 (s,3H,CH_3), 7.0-7.9 (m, 8H,ArH), 8.45 and 8.72 (2s,[0.4+0.6]H,CHO), 9.50 and 10.45 (2s,[0.4+0.6]H,NH); ^{13}C nmr (DMSO-d_6) δ : two conformers, 21.10 and 21.17 (CH_3), 121.41 and 122.61 (C-ortho of N-p-Cl-phenyl), 125.77 and 125,92 (C-5), 126.55 (C-8 or C-6), 128.00 (C-6 or C-8), 129.31 and 129,38 (C-7), 128.93 and 129.49 (C-meta of N-p-Cl-phenyl), 137.90 and 137.96 (C-10 or C-9), 139.51 and 140.80 (C-ipso of N-p-Cl-phenyl), 139.96 and 140.10 (C-9 or C-10), 145.11 (C-2), 149.42 and 150.30 (C-3), 160.41 and 165.83 (CHO), C-Cl non detected owing to overlap. Anal. Calcd for $C_{16}H_{13}ClN_4O$: C, 61.45; H, 4.19; N, 17.91. Found: C, 61.53; H, 4.20; N, 17.95.

The 3-(arylformylhydrazino)quinoxaline derivatives **11a,b** and **13a,b** were dissolved in ethanol and then treated with equimolar amount of perchloric acid gave to the triazolo[4,3-a]quinoxalinium perchlorates **8a,b** and **9a,b**, respectively, in quantitative yields.

Rearrangement Reaction of the Phenylhydrazone **3e** to 4-(2-Aminophenyl)-1,3-diphenyl-1,2,4-triazolium Perchlorate **7e**.

Perchloric acid (60%, 0.4 ml) was added to a solution of **3e** (1 g) in boiling butanol (30 ml). The reaction mixture was cooled to room temperature, and then the perchlorate **7e** was collected and recrystallized from ethanol (colourless needles, yield 80%), mp 217°C; ir: 3450, 3370 cm^{-1} (NH_2), 1640, 1605 cm^{-1} (C=N), 1115-1070 cm^{-1} (ClO_4); ^1H nmr (DMSO-d_6) δ : 4.80 (broad,2H,NH_2), 6.4-7.9 (m,12H,ArH), 8.05 (m,2H,ortho-H of 1-phenyl), 11.28 (s,1H,H-5). Anal. Calcd for $C_{20}H_{17}ClN_4O_4$: C, 58.19; H, 4.15; N, 13.57. Found: C, 58.34; H, 4.18; N, 13.51.

The perchlorate **7e** (0.6 g) was dissolved in hot aqueous ethanol (50%, 50 ml) and the solution was made alkaline with aqueous sodium carbonate (2M, 1 ml). The phenylhydrazone **3e** was obtained in quantitative yield.

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