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Heterocyclizations of 2-aryl-3-arylamino-4,4,4-trifluoro-2butenenitrile hydrates to 3-aryl-2-trifluoromethyl-4-quinolones and to 4-N-methylamino-3H-pyrazole-3-spiro-2'-(3'-aryl-3'trifluoromethyl)oxiranes

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Abstract

2-Aryl-3-arylamino-4,4,4-trifluoro-2-butenenitriles were obtained as hydrates from 3-oxo-2-aryl-4,4,4-trifluorobutyronitriles and anilines and their structure and heterocyclizations studied. Cyclization with polyphosphoric acid gave poor yields of 3-aryl-2-trifluoromethyl-4-quinolones, but they underwent an interesting cyclization with diazomethane to give a 25%-40% yield of 4-N-methylamino-3H-pyrazole-3-spiro-2'-(3'-aryl-3'-trifluoromethyl)oxiranes. However, the related reaction with diazoethane yielded only aryl(arylhydrazono)acetonitriles and other fragmentation products.

Keywords: Heterocyclizations; Fluorinated oxiranes; NMR spectroscopy; IR spectroscopy; UV spectrophotometry

1. Introduction

3-Oxo-2-aryl-4,4,4-trifluorobutyronitriles 1a-c have been found to be building blocks for 3-aryl-4-trifluoromethylbenzo[b]pyran-2-ones [1]. Of these, 1c was an oily mixture of the hydrate and ketonic forms [2] and a means of characterization as a crystalline derivative was required. With this objective in mind, the reactions of 1a-c with anilines or o-phenylenediamine in the presence of acid have been studied. In the light of their unique structure, it was also of interest to study the heterocyclizations of the Schiff bases thus obtained.

2. Results and discussion

The 2-aryl-3-arylamino-4,4,4-trifluoro-2-butenenitriles **2a-f** obtained are crystalline materials which were purified by recrystallization from a non-hydroxylic solvent, but they invariably crystallized with a molecule of water as shown by elemental analyses. However, the reaction of either **1a** or **1b** with *o*-phenylenediamine gave the known 2-trifluoromethylbenzimidazole (3) [3] by cyclization of an intermediate Schiff base with the loss of arylacetonitrile; the reaction resembles that of 1,1,1-trifluoro-2,4-pentanedione with o-phenylenediamine to produce 3 [4].

Consistent with the behaviour of Schiff bases [5], compounds 2a and 2b were cyclized with polyphosphoric acid (PPA) to the 3-aryl-2-trifluoromethyl-4-quinolones 4a,b whose IR spectrum exhibited a peak around or below 1600 cm⁻¹ corresponding to ν (C=O) which is lower than that of the 3-unsubstituted 2-trifluoromethyl-4-quinolones [6] and closer to that of 4-quinolone itself [7]. The UV spectrum of 4 resembled that of 6-methyl-2-trifluoromethyl-4-quinolone [6], but each absorption maximum of the former showed a red shift of 3-10 nm compared to those of the latter (λ_{max} 231, 293, 327 and 341 nm). However, the yields of 4a and 4b did not exceed 10%, despite conducting experiments under various conditions.

The products $2\mathbf{a}-\mathbf{f}$ do not exist in the azomethine form since the benzylic proton α to CN is absent in their ¹H NMR spectra. Signals for sp³ carbon atoms other than the ring substituent were invisible in the

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¹³C NMR spectra ¹ of 2a, 2c and 2e, and the IR spectra of 2a-f suggested that the CN moiety is attached to the vinylic carbon. Furthermore, unlike 3-anilino-2phenyl- [9] (3320-3260 cm⁻¹) and 2-phenyl-3-(p-toluidino)-2-butenenitriles (3320 cm^{-1}), the NH stretch absorption was invisible above 3000 cm^{-1} , but rather an absorption associated with a $C=N^+H-$ group was clearly seen at ca. 2600 cm^{-1} . We thus inferred that the Schiff bases of 1 may be better formulated as the iminium form 2B rather than the enaminonitrile 2A reported for the Schiff bases of β -ketonitriles [9,10] and there may be a contribution of the keteneimine form 2C. The strongly electron-withdrawing CF₃ group must obviously favour the iminium form. If this is true, nucleophilic character may be imparted to the nitrile nitrogen and the Schiff base 2, when treated with a diazoalkane, would be expected to undergo alkylation and, if the reaction proceeds further, 1,3-dipolar cycloaddition on the keteneimine moiety.

The reaction of 2a with diazomethane afforded many products as shown by TLC. The major one (25% yield) was a crystalline material that was not a nitrile. The empirical formula $C_{12}H_{10}F_3N_3O$ indicated that 2 equiv. of diazomethane had been consumed and *p*-toluidine had been lost. One equivalent of diazomethane was presumably used to produce an *N*-methylketeneimine, as reported for sulfonylacetonitriles [11,12], because an *N*-Me singlet was seen at δ 3.10 ppm. The other equivalent is presumed to have reacted to form a cycloadduct either on the C=N or C=C bond of the keteneimine [13,14]. The product formed by addition to the C=N bond must contain a 1,2,3- or 1,2,4-triazoline ring, and the one obtained by addition to the C=C bond must possess either a 3*H*- or 4*H*-pyrazole ring.

Since neither OH nor C=O stretch frequencies were observed in the IR spectrum of this major product, it is inferred that the oxygen atom is incorporated in an ether linkage with the strong absorption at 3334 cm⁻¹ indicating the presence of a secondary amine. The

¹ Owing to the overlap of signals associated with olefinic, aromatic and CF₃, the δ 110–150 ppm region of the ¹³C NMR spectra of 2a, 2c and 2e were too complex to be analyzed. The only signal which could be definitely assigned was the CN carbon at δ 121–123 ppm, which was found to be deshielded by ca. 2 ppm as compared to that of 3-amino-3-arylpropenenitriles as reported by Chiacchio et al. [8].

structures bearing an oxirane ring, i.e. 5, 6, 7 and 8, satisfy these spectral observations.



- b; $Ar = C_6 H_4 OMe p$
- c: $Ar = C_6 H_4 C_1 p$

Although diazomethane has been reported to add to a keteneimine C=N bond to form a 1,2,3-triazole derivative [15], the triazoline structures 5 and 6 are unlikely because the ¹H NMR spectrum of our product includes a singlet at δ 6.96 ppm that is very shielded for a triazoline CH=N proton which usually resonates at ca. δ 8 ppm [16,17]. Among the remaining two possibilities, the 3H-pyrazole-3-spiro-2'-oxirane structure 7a is preferred to 8a on the basis of ¹³C NMR spectral data. Two deshielded sp³ carbons at δ 70.3 and δ 92.5 ppm are observed, the former being assigned to the one bearing two heteroatoms and the latter (q, ${}^{2}J_{C-F} = 30$ Hz) to the one attached to the CF₃ group. In addition to benzene ring carbons, the spectrum has two sp² carbons at δ 117.8 ppm and δ 136.1 ppm, attributable to those of the olefinic bond of a 3Hpyrazole ring. It is known that the sp^2 carbons of 3Hpyrazoles appear at δ 125–150 ppm (C-4) and δ 130–170 ppm (C-5), and those of 4H-pyrazoles are more deshielded, resonating at δ 178–182 ppm (C-3 and C-5) [18]. The reactions of 2b and 2c with diazomethane proceeded similarly, furnishing the 3H-pyrazole derivatives 7b (30%) and 7c (40%), respectively 2 .

Methylation of the keteneimine anion 2C, followed by the 1,3-dipolar cycloaddition of diazomethane across the C=C bond, and addition of the water involved in



2, would give a protonated hemiaminal 9. Removal of p-toluidine from 9 and concomitant migration of a phenyl group and epoxidation would produce the 3*H*-pyrazole-3-spiro-2'-oxirane ring 7 (Scheme 1).

The reactions of 2a and 2d, respectively, with ethereal diazoethane were dramatically different from those with diazomethane. A yellow solution gradually became more intense within a few hours and work-up gave a number of products as shown by TLC, but there was no ¹H NMR spectral indication that *N*-ethylation had occurred. The materials characterized were (arylhydrazono)-

$$Ar^{2}-NHN=C Ar^{1}$$

$$CN$$

$$IO$$
a; Ar^{1}=Ph, Ar^{2}=C_{6}H_{4}Me-p
b; Ar^{1}=Ph, Ar^{2}=C_{6}H_{4}Cl-p

phenylacetonitriles 10a and 10b (both identical with an authentic specimen), the aniline and 1a³. Fluorinecontaining products other than 1a could not be characterized. Such fragmentation of 2 by diazoethane did not occur with diazomethane, as shown by the absence of the characteristic UV absorptions of 10 for all materials eluted by chromatography.

³ Although we were unable to identify minor fragmentation products and to ascertain the mode of aniline formation, we do not discount the possibility that 1-ethyl-3-aryltriazine (11) may be transiently generated from diazoethane and aniline and react with 2 to form a 1,2-diazetidine 12 which, by cycloreversion, may lead to 10.



² 2-Phenyl-3-(*p*-toluidino)-2-butenenitrile was unreactive to diazomethane under comparable conditions.

3. Experimental details

Melting points were determined in capillary tubes and are uncorrected. All solutions were dried over sodium sulfate. The ¹H NMR spectra were obtained on a Hitachi R-250 spectrometer at 250 MHz with tetramethylsilane as internal standard and the assignments were confirmed by deuterium exchange where necessary. The proton-decoupled ¹³C NMR spectra were taken on the same instrument with tetramethylsilane as internal standard. The J values refer to H-H couplings unless otherwise indicated. IR spectra were determined as Nujol mulls and UV spectra were run in ethanol. Kieselgel 60 was used for column chromatography. Molar concentrations of 3-oxo-4,4,4-trifluoro-2-(p-methoxyphenyl)butyronitrile (1c), which is a mixture of the keto and hydrate forms [2], and yields of products derived therefrom are based on the hydrate form. 2-Phenyl-3-(p-toluidino)-2-butenenitrile, prepared as reported [9], had IR frequencies at 3320 (NH) and 2182 $(C \equiv N) \text{ cm}^{-1}.$

3.1. 4,4,4-Trifluoro-2-phenyl-3-(p-toluidino)-2butenenitrile (2a)

A mixture of 1a (2.31 g, 10 mmol), *p*-toluidine (1.07 g, 10 mmol), benzene (5 ml) and acetic acid (0.5 ml) was heated under reflux for 3 h and evaporated to dryness. The nitrile (1.98 g, 62%) was recrystallized from chloroform/hexane as needles, m.p. 142–143 °C. (Analysis: Found: C, 63.57; H, 4.54; F, 17.80; N, 8.71%. C₁₇H₁₃F₃N₂·H₂O requires: C, 63.74; H, 4.72; F, 17.80; N, 8.75%.) IR ν_{max} (cm⁻¹): 2616 (C=N⁺H–); 2208 (CN). ¹H NMR [(CD₃)₂SO] δ : 2.31 (3H, s, Me); 6.92 (1H, t, *J*=7.3 Hz, Ar); 7.16 (2H, d, *J*=7.3 Hz, Ar); 7.21 (2H, s, Ar); 7.29 (2H, d, *J*=7.3 Hz, Ar); 7.89 (2H, d, *J*=7.3 Hz, Ar); 9.60 (1H, br s, NH) ppm. ¹³C NMR [(CD₃)₂SO] δ : 20.4 (Me); 122.7 (C≡N) ppm.

The following 4,4,4-trifluoro-2-butenenitriles were prepared similarly.

2-(*p*-Methoxyphenyl)-3-(*p*-toluidino)- (2b): yield, 57%; m.p. 139–141 °C (chloroform/hexane). (Analysis: Found: C, 61.67; H, 4.89; F, 16.32; N, 8.02%. C₁₈H₁₅F₃N₂O·H₂O requires: C, 61.71; H, 4.89; F, 16.27; N, 8.00%.) IR ν_{max} (cm⁻¹): 2632 (C=N⁺H-); 2206 (C=N). ¹H NMR [(CD₃)₂SO] &: 2.30 (3H, s, Me); 3.70 (3H, s, MeO); 6.80 (2H, d, J=8.6 Hz, Ar); 7.18 (2H, d, J=8.6 Hz, Ar); 7.27 (2H, d, J=8.6 Hz, Ar); 7.81 (2H, d, J=8.6 Hz); 9.60 (1H, br s, NH) ppm.

2-(*p*-Chlorophenyl)-3-(*p*-toluidino)- (2c): yield, 33%; m.p. 141–143 °C (methylene chloride/hexane). (Analysis: Found: C, 57.49; H, 3.88; F, 16.08; N, 7.90%. C₁₇H₁₂ClF₃N₂·H₂O requires: C, 57.55; H, 3.98; F, 16.07; N, 7.90%.) IR ν_{max} (cm⁻¹): 2600 (C=N⁺H-); 2204 (C=N). ¹H NMR [(CD₃)₂SO] δ : 2.32 (3H, s, Me); 7.25 (6H, m, Ar); 7.94 (2H, d, J=9.2 Hz, Ar); 9.80 (1H, br s, NH) ppm. ¹³C NMR [(CD₃)₂SO] δ : 20.4 (Me); 122.7 (C=N) ppm.

3-(*p*-Chloroanilino)-2-phenyl- (**2d**): yield, 61%; m.p. 124–125 °C (Chloroform/hexane). (Analysis: Found: C, 56.29; H, 3.63; F, 16.73; N, 8.27%. $C_{16}H_{10}ClF_3N_2 \cdot H_2O$ requires: C, 56.40; H, 3.55; F, 16.73; N, 8.22%.) IR ν_{max} (cm⁻¹): 2610 (C=N⁺H⁻); 2200 (C=N). ¹H NMR [(CD₃)₂SO] δ : 6.96 (m, 1H, Ar); 7.20 (m, 4H, Ar); 7.47 (d, 2H, J=9.2 Hz, Ar); 7.87 (d, 2H, J=9.2 Hz, Ar); 8.40 (br s, NH) ppm.

3-(*p*-Chloroanilino)-2-(*p*-methoxyphenyl)- (2e): yield, 50%; m.p. 117 °C (chloroform/hexane). (Analysis: Found: C, 54.79; H, 3.78; F, 15.46; N, 7.57%. C₁₇H₁₂ClF₃N₂O·H₂O requires: C, 55.07; H, 3.81; F, 15.37; N, 7.56%.) IR ν_{max} (cm⁻¹): 2600 (C=N⁺H-); 2206 (C=N). ¹H NMR [(CD₃)₂SO] δ : 3.72 (3H, s, MeO); 6.85 (2H, d, J=8.5 Hz, Ar); 7.12 (2H, d, J=8.5 Hz, Ar); 7.41 (2H, d, J=8.5 Hz, Ar); 7.78 (2H, d, J=8.5 Hz, Ar); 9.60 (1H, br s, NH) ppm. ¹³C NMR [(CD₃)₂SO] δ : 55.0 (MeO); 120.9 (C=N) ppm.

3-(*p*-Methoxyanilino)-2-phenyl- (**2f**): yield, 69%; m.p. 147–148 °C (chloroform/hexane). (Analysis: Found: C, 60.73; H, 4.39; F, 16.94; N, 8.27%. $C_{17}H_{13}F_{3}N_{2}O \cdot H_{2}O$ requires: C, 60.71; H, 4.50; F, 16.95; N, 8.33%.) IR ν_{max} (cm⁻¹): 2632 (C=N⁺H-); 2216 (C=N). ¹H NMR [(CD₃)₂SO] δ : 3.77 (s, 3H, MeO); 6.91 (m, 1H, Ar); 7.05 (dd, 2H, J=8.5, 1.8 Hz, Ar); 7.18 (m, 2H, Ar); 7.28 (dd, 2H, J=8.5, 1.8 Hz, Ar); 7.89 (d, 2H, J=8.5 Hz, Ar); 9.73 (br s, 1H, NH) ppm.

3.2. 2-Trifluoromethylbenzimidazole (3)

A mixture of **1a** (1.15 g, 5 mmol), *o*-phenylenediamine (0.54 g, 5 mmol), benzene (15 ml) and acetic acid (2 ml) was heated for 3 h and worked-up. Chromatography with benzene gave **3** (0.46 g, 50%), m.p. 204–205 °C after recrystallization from cyclohexane, as identified by IR spectroscopy [19]. (Analysis: Found: C, 51.92; H, 2.70; N, 14.99%. Calc. for $C_8H_5F_3N_2$: C, 51.62; H, 2.71; N, 15.05%.) A 47% yield of **3** was obtained from **1b**.

3.3. 3-Aryl-6-methyl-2-trifluoromethyl-4-quinolone (4)

A mixture of 2a (2.30 g, 7.6 mmol) and PPA (20 g) was heated at 130–140 °C for 1 h and the reaction mixture then poured into crushed ice and extracted with ether. Evaporation of the dried extracts and chromatography of the residue with chloroform gave 6-methyl-3-phenyl-2-trifluoromethyl-4(1*H*)-quinolone (4a) (0.21 g, 9%), recrystallized from benzene/hexane as pale yellow microneedles, m.p. 243–244 °C. (Analysis: Found: C, 67.39; H, 3.95; N, 4.43%. C₁₇H₁₂F₃NO requires: C, 67.32; H, 3.99; N, 4.62%.) IR ν_{max} (cm⁻¹): 1608 (C=O). UV λ_{max} (nm): 216 (ϵ 33 200); 240 (19 200); 248 (sh) (17 200); 286 (sh) (3400); 296 (4600); 332

(8300); 346 (9100). ¹H NMR [(CD₃)₂SO] δ : 2.47 (3H, s, Me); 7.24 (2H, d, J=8.0 Hz, 3-Ph); 7.42 (3H, m, 3-Ph); 7.65 (1H, d, J=8.5 Hz, 7-H); 7.87 (1H, d, J=8.5 Hz, 8-H); 7.98 (1H, s, 5-H) ppm (the NH proton was not visible).

3-(*p*-Methoxyphenyl)-6-methyl-2-trifluoromethyl-4quinolone (**4b**) was prepared similarly, yield, 5%; m.p. 252–254 °C (chloroform/hexane). (Analysis: Found: C, 65.11; H, 4.15; N, 4.08%. C₁₈H₁₄F₃NO₂ requires: C, 64.86; H, 4.23; N, 4.20%.) IR ν_{max} (cm⁻¹): 1552 (CO). UV λ_{max} (nm): 216 (ϵ 36 100); 236 (23 100); 246 (sh) (19 800); 280 (sh) (5900); 294 (5200); 334 (sh) (8500); 346 (9400). ¹H NMR [(CD₃)₂SO] δ : 2.43 (3H, s, Me); 3.81 (3H, s, MeO); 6.99 (2H, d, J=7.9 Hz, 3-Ar); 7.13 (2H, s, 3-Ar); 7.63 (1H, d, J=7.9 Hz, 7-H); 7.88 (2H, m, 5- and 8-H); 12.2 (1H, s, NH)] ppm.

3.4. 4-N-Methylamino-3H-pyrazole-3-spiro-2'-(3'-phenyl-3'-trifluoromethyl)oxirane (7a)

Ethereal diazomethane was added to a solution of 2a (0.302 g, 1.0 mmol) in ether (35 ml) and the solution set aside at room temperature for 2 h. Excess of diazomethane was decomposed with acetic acid and the brown oil remaining after evaporation of the solvent was chromatographed. Elution with benzene gave a vellow oil and elution with chloroform gave a brown oil (0.15 g). Further chromatography of the latter oil with chloroform eluted a brown oil (0.14 g) and ptoluidine (0.04 g, 37%), successively. The oil solidified to give 7a (0.068 g, 25%) which was recrystallized from hexane as hexagonal plates, m.p. 86-88 °C. (Analysis: Found: C, 53.69; H, 3.69; F, 21.21; N, 15.84%. C₁₂H₁₀F₃N₃O requires: C, 53.53; H, 3.74; F, 21.17; N, 15.61%.) UV λ_{max} (nm): 211 (ϵ 9200); 245 (4300). IR ν_{max} (cm⁻¹): 3334 (NH). ¹H NMR (CDCl₃) δ : 3.10 (s, 3H, Me); 6.81 (s, 1H, NH); 6.96 (s, 1H, 5-H); 7.41 (m, 3H, 3'-Ar); 7.57 (m, 2H, 3'-Ar) ppm. ¹³C NMR (CDCl₂) δ: 55.5 (Me); 70.3 (3-C); 92.5 (q, ${}^{2}J_{C-F}$ =30 Hz, 3'-C); 117.8 (4-C); 123.2 (q, ${}^{1}J_{C-F} = 286$ Hz, CF₃); 136.1 (5-C); 128.2, 129.1, 130.5, 130.7 (3'-Ar) ppm.

3.5. 4-N-Methylamino-3H-pyrazole-3-spiro-2'-(3'-pmethoxyphenyl-3'-trifluoromethyl)oxirane (7b)

Ethereal diazomethane was added to a solution of 2e (0.353 g, 1.0 mmol) in ether (10 ml). Chromatography with chloroform gave a yellow oil (0.16 g), which was further chromatographed with chloroform to give *p*-chloroaniline (0.02 g, 16%) and then **7b** (0.09 g, 30%) which recrystallized from hexane as needles (0.026 g), m.p. 88–89 °C. (Analysis: Found: C, 52.26; H, 4.07; F, 18.89; N, 14.20%. C₁₃H₁₂F₃N₃O₂ requires: C, 52.17; H, 4.04; F, 19.05; N, 14.04%.) UV λ_{max} (nm) 231 (ϵ 12 300); 280 (sh) (1100). IR ν_{max} (cm⁻¹): 3344 (NH). ¹H NMR (CDCl₃) δ : 3.17 (s, 3H, NMe); 3.84 (s, 3H, OMe); 6.79

(s, 1H, NH); 6.95 (d, 2H, J=9.2 Hz, 3'-Ar); 7.02 (s, 1H, 5-H); 7.54 (d, 2H, J=9.2 Hz, 3'-Ar) ppm. ¹³C NMR (CDCl₃) δ : 54.4 (NMe); 54.8 (OMe); 69.1 (3-C); 90.9 (q, ² $J_{C-F}=29$ Hz, 3'-C); 117.0 (4-C); 122.2 (¹ $J_{C-F}=286$ Hz, CF₃); 135.2 (5-C); 113.5, 121.1, 128.6, 160.3 (3'-Ar) ppm.

3.6. 4-N-Methylamino-3H-pyrazole-3-spiro-2'-(3'-pchlorophenyl-3'-trifluoromethyl)oxirane (7c)

Ethereal diazomethane was added to a solution of 2c (0.55 g, 1.6 mmol) in ether (20 ml). Chromatography with benzene gave a yellowish semi-oily solid (0.41 g)and chloroform eluted p-toluidine (0.10 g, 58%). Further chromatography of the above oily solid with benzene/ hexane (1:1) removed a yellow oil and elution with benzene furnished 7c (0.20 g, 41%) which recrystallized from hexane as rods, m.p. 107-109 °C. (Analysis: Found: C, 47.67; H, 2.81; F, 18.74; N, 14.07%. C₁₂H₉ClF₃N₃O requires: C, 47.46; H, 2.99; F, 18.77; N, 13.84%.) UV $\lambda_{\rm max}$ (nm): 224 (ϵ 16 900); 250 (sh) (4200). IR $\nu_{\rm max}$ (cm⁻¹): 3344 (NH). ¹H NMR (CDCl₃) δ: 3.18 (s, 3H, NMe); 6.91 (s, 1H, NH); 7.02 (s, 1H, 5-H); 7.41 (2H, dd, J=9.2, 2.4 Hz, 3'-Ar); 7.56 (dd, 2H, J=9.2, 2.4 Hz, 3'-Ar) ppm. ¹³C NMR (CDCl₃) δ : 55.5 (NMe); 70.0 (3-C); 92.1 (${}^{2}J_{C-F}$ = 31 Hz, 3'-C); 117.5 (4-C); 123.1 $({}^{1}J_{C-F} = 286 \text{ Hz}, \text{ CF}_{3}); 136.8 (5-C); 129.2, 129.3, 129.8,$ 136.3 (3'-Ar) ppm.

3.7. Reaction of 4,4,4-trifluoro2-phenyl-3-(p-toluidino)-2-butenenitrile (2a) with diazoethane

Ethereal diazoethane was added to a solution of 2a (1.21 g, 4 mmol) in ether (150 ml), the mixture set aside at room temperature for 3.5 h and then decomposed with acetic acid. The solvent was evaporated and the residue chromatographed. Elution with benzene gave a yellow solid (0.47 g) and elution with chloroform afforded p-toluidine (0.14 g, 33%). Further elution with chloroform and ether, successively, gave 1a (0.33 g, 36%), while elution with ethyl acetate gave an oil (0.20) g). The yellow solid was further chromatographed with benzene/hexane (1:3), benzene/hexane (1:1) and benzene. The first solvent gave (p-tolylhydrazono)phenylacetonitrile (10a) (0.20 g, 21%) which recrystallized from cyclohexane as yellow needles, m.p. 120 °C. (Analysis: Found: C, 76.69; H, 5.43; N, 18.06%. C₁₅H₁₃N₃ requires: C, 76.57; H, 5.57; N, 17.86%.) UV λ_{max} (nm): 244 (ϵ 20 700); 294 (4100); 302 (sh) (3400); 378 (25 000). IR ν_{max} (cm⁻¹): 3256 (NH); 2212 (CN). ¹H NMR (CDCl₃) δ : 2.33 (3H, s, Me); 7.16 (4H, s, Ar); 7.40 (3H, m, Ar); 7.79 (2H, m, Ar); 8.75 (1H, s, NH) ppm, identical (mixed m.p. and IR) with an authentic specimen. The yellow materials from the second and third solvents were combined (0.27 g) and separated into several materials by means of preparative TLC with hexane/ethyl acetate (3:1), but each was found to contain *p*-toluidine and several other substances.

3.8. Reaction of 3-(p-chloroanilino)-4,4,4-trifluoro-2phenyl-2-butenenitrile (2d) with diazoethane

Ethereal diazoethane was added into a solution of 2d (1.61 g, 5 mmol) in ether (100 ml). Elution with hexane/benzene (5:1) gave (p-chlorophenylhydrazono)phenylacetonitrile (10b) (0.05 g, 4%) which recrystallized from hexane as yellow needles, m.p. 164-165 °C. (Analysis: Found: C, 65.65; H, 3.85; N, 16.31%. C₁₄H₁₀ClN₃ requires: C, 65.75; H, 3.94; N, 16.44%.) UV λ_{max} (nm): 244 (ϵ 15 500); 296 (3300); 306 (sh) (3200); 374 (19 700). IR ν_{max} (cm⁻¹): 3264 (NH); 2212 (CN). ¹H NMR (CDCl₃) δ : 7.19 (2H, dd, J=8.5, 1.8 Hz, Ar); 7.33 (2H, m, Ar); 7.43 (3H, m, Ar); 7.80 (2H, dd, J=8.5, 1.8 Hz, Ar); 8.75 (1H, s, NH) ppm, identical (mixed m.p. and IR) with an authentic specimen. Elution was continued with hexane/benzene (1:1), benzene, chloroform, ether and ethyl acetate. The first and second solvents gave p-chloroaniline (0.58 g, 91%), the third and fourth 1a (0.79 g, 68%) and the fifth an oil (0.19 g).

3.9. Preparation of authentic (arylhydrazono)phenylacetonitrile (10)

A solution of (α -cyanobenzylidene)-N,N-dimethylphenylenediamine [20] (1.00 g, 4 mmol) in ethanol (45 ml) was mixed with a solution of *p*-tolylhydrazine hydrochloride (1.90 g, 12 mmol) in water (20 ml) and heated under reflux for 2 h [21]. The yellow hydrazone **10a** (0.44 g, 46%) had m.p. 119–120 °C after recrystallization.

The hydrazone 10b (72%), when similarly prepared, had m.p. 165 °C.

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