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Heterocyclizations of 2-aryl-3-arylamino-4,4,4-trifluoro-2-butenenitrile hydrates to 3-aryl-2-trifluoromethyl-4-quinolones and to 4-*N*-methylamino-3*H*-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-3*H*-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 ($\lambda_{max.}$ 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 **2a–f** do not exist in the azomethine form since the benzylic proton α to CN is absent in their ^{1}H NMR spectra. Signals for sp^3 carbon atoms other than the ring substituent were invisible in the

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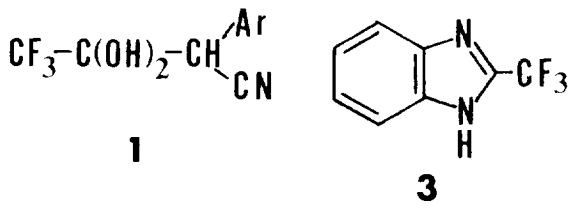
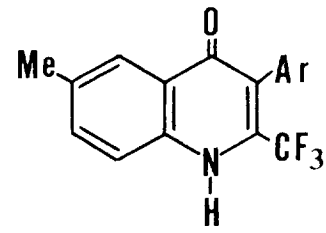


1

a; Ar=Ph

b; Ar=C_6H_4Cl-*p*

c; Ar=C_6H_4OMe-*p*

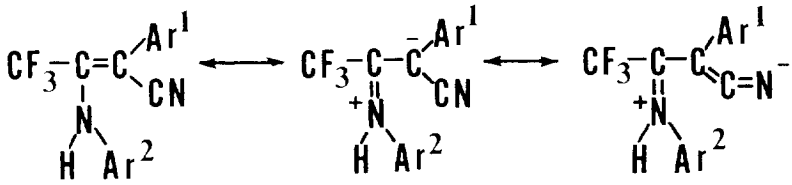


3

4

a; Ar=Ph

b; Ar=C_6H_4OMe-*p*



2A **2B** **2C**

a; Ar^1=Ph, Ar^2=C_6H_4Me-*p*

b; Ar^1=C_6H_4OMe-*p*, Ar^2=C_6H_4Me-*p*

c; Ar^1=C_6H_4Cl-*p*, Ar^2=C_6H_4Me-*p*

d; Ar^1=Ph, Ar^2=C_6H_4Cl-*p*

e; Ar^1=C_6H_4OMe-*p*, Ar^2=C_6H_4Cl-*p*

f; Ar^1=Ph, Ar^2=C_6H_4OMe-*p*

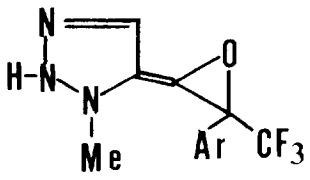
^{13}C NMR spectra [1] of **2a**, **2c** and **2e**, and the IR spectra of **2a–f** suggested that the CN moiety is attached to the vinylic carbon. Furthermore, unlike 3-anilino-2-phenyl- [9] (3320–3260 cm^{-1}) and 2-phenyl-3-(*p*-toluidino)-2-butenenitriles (3320 cm^{-1}), the NH stretch absorption 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 CF_3 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.

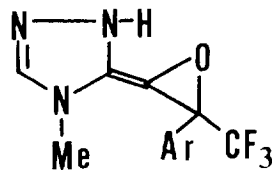
Since neither OH nor C=O stretch frequencies were observed in the IR spectrum of this major product, it is inferred that the oxygen atom is incorporated in an ether linkage with the strong absorption at 3334 cm^{-1} indicating the presence of a secondary amine. The

[1] Owing to the overlap of signals associated with olefinic, aromatic and CF_3, the δ 110–150 ppm region of the ^{13}C 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.



5



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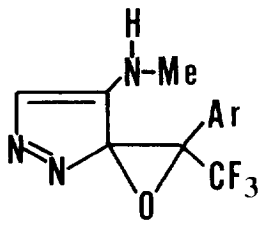

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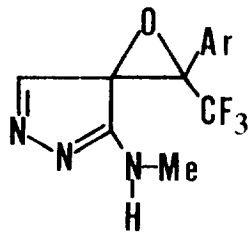


8

a; Ar=Ph

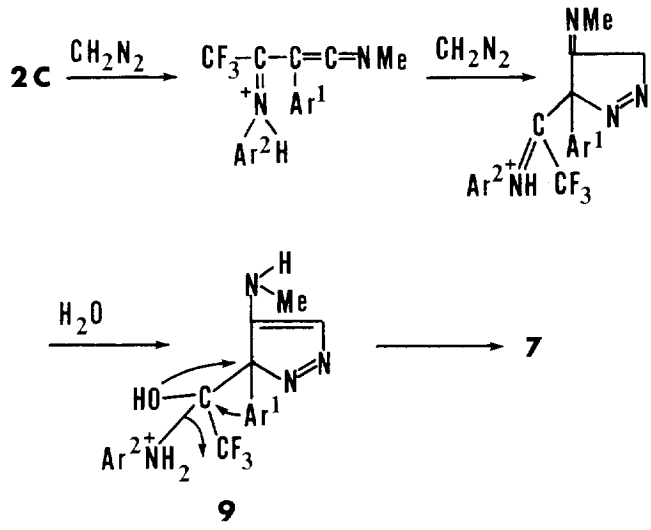
b; Ar=C_6H_4OMe-*p*

c; Ar=C_6H_4Cl-*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 3*H*-pyrazole-3-spiro-2′-oxirane structure **7a** is preferred to **8a** on the basis of ^{13}C NMR spectral data. Two deshielded sp^3 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, $^2J_{C-F}$=30 Hz) to the one attached to the CF_3 group. In addition to benzene ring carbons, the spectrum has two sp^2 carbons at δ 117.8 ppm and δ 136.1 ppm, attributable to those of the olefinic bond of a 3*H*-pyrazole ring. It is known that the sp^2 carbons of 3*H*-pyrazoles appear at δ 125–150 ppm (C-4) and δ 130–170 ppm (C-5), and those of 4*H*-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 3*H*-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

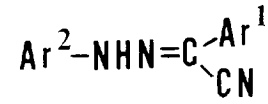
[2] 2-Phenyl-3-(*p*-toluidino)-2-butenenitrile was unreactive to diazomethane under comparable conditions.



Scheme 1.

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)-



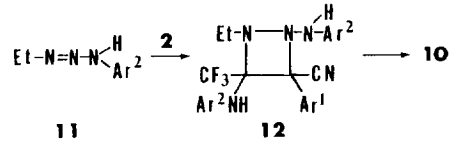
10

a; Ar^1=Ph, Ar^2=C_6H_4Me-*p*

b; Ar^1=Ph, Ar^2=C_6H_4Cl-*p*

phenylacetonitriles **10a** and **10b** (both identical with an authentic specimen), the aniline and **1a** [3]. Fluorine-containing 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**.



11 **12**

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 ^{13}C 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≡N) cm^{-1}.

3.1. 4,4,4-Trifluoro-2-phenyl-3-(p-toluidino)-2-butenenitrile (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%. $C_{17}H_{13}F_3N_2 \cdot H_2O$ 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 [$(CD_3)_2SO$] 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. ^{13}C NMR [$(CD_3)_2SO$] 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%. $C_{18}H_{15}F_3N_2O \cdot H_2O$ 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 [$(CD_3)_2SO$] δ: 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%. $C_{17}H_{12}ClF_3N_2 \cdot H_2O$ 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 [$(CD_3)_2SO$] 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. ^{13}C NMR [$(CD_3)_2SO$] 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 [$(CD_3)_2SO$] 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%. $C_{17}H_{12}ClF_3N_2O \cdot H_2O$ 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 [$(CD_3)_2SO$] 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. ^{13}C NMR [$(CD_3)_2SO$] 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%. $C_{17}H_{13}F_3N_2O \cdot H_2O$ 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 [$(CD_3)_2SO$] 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%. $C_{17}H_{12}F_3NO$ 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). ^{1}H NMR [$(CD_3)_2SO$] 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-4-quinolone (**4b**) was prepared similarly, yield, 5%; m.p. 252–254 °C (chloroform/hexane). (Analysis: Found: C, 65.11; H, 4.15; N, 4.08%. $C_{18}H_{14}F_3NO_2$ 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). ^{1}H NMR [$(CD_3)_2SO$] 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 yellow 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 *p*-toluidine (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%. $C_{12}H_{10}F_3N_3O$ 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). ^{1}H NMR ($CDCl_3$) 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. ^{13}C NMR ($CDCl_3$) δ: 55.5 (Me); 70.3 (3-C); 92.5 (q, $^2J_{C-F}$=30 Hz, 3'-C); 117.8 (4-C); 123.2 (q, $^1J_{C-F}$=286 Hz, CF_3); 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'-p-methoxyphenyl-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%. $C_{13}H_{12}F_3N_3O_2$ 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). ^{1}H NMR ($CDCl_3$) 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. ^{13}C NMR ($CDCl_3$) δ: 54.4 (NMe); 54.8 (OMe); 69.1 (3-C); 90.9 (q, $^2J_{C-F}$=29 Hz, 3'-C); 117.0 (4-C); 122.2 ($^1J_{C-F}$=286 Hz, CF_3); 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'-p-chlorophenyl-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%. $C_{12}H_9ClF_3N_3O$ requires: C, 47.46; H, 2.99; F, 18.77; N, 13.84%.) UV λ_{max} (nm): 224 (ϵ 16 900); 250 (sh) (4200). IR ν_{max} (cm^{-1}): 3344 (NH). ^{1}H NMR ($CDCl_3$) 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. ^{13}C NMR ($CDCl_3$) δ: 55.5 (NMe); 70.0 (3-C); 92.1 ($^2J_{C-F}$=31 Hz, 3'-C); 117.5 (4-C); 123.1 ($^1J_{C-F}$=286 Hz, 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%. $C_{15}H_{13}N_3$ 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). ^{1}H NMR ($CDCl_3$) 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-2-phenyl-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%. $C_{14}H_{10}ClN_3$ 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 ($CDCl_3$) 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*-dimethyl-*p*-phenylenediamine [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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