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SYNTHESIS OF 1H-3-PYRAZOLINES

K. Burger*, H. Schickaneder and F. Hein
Institut für Organische Chemie, Technische Universität München, Lichtenbergstrasse 4, D-8046 Garching bei München, Germany

and

J. Elguero
Laboratoire de Chimie Moléculaire, Université d'Aix-Marseille III, Rue Henri Poincaré, 13397 Marseille Cédex 4, France

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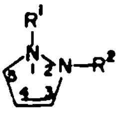
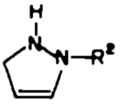
Abstract—Two syntheses of the 1H-3-pyrazoline system **17** are described. The syntheses make use of the ability of the azine system to act as 1,3-dipolar species in [3 + 2] cycloaddition reactions. The spectra data of the new compounds are discussed (IR, ^{1}H NMR and ^{19}F NMR).

Zusammenfassung—Zwei Synthesen für 1H-3-Pyrazoline werden beschrieben. Die Synthesen basieren auf der Fähigkeit des Azinsystems in [3 + 2]-Cycloadditionsreaktionen als 1,3-dipolare Spezies zu fungieren. Die spektralen Daten der neuen Verbindungen werden diskutiert (IR, ^{1}H NMR und ^{19}F NMR).

The majority of the papers on 3-pyrazolines deal with the 1,2-disubstituted system **1a**.[1] Examples of 1-unsubstituted-**1b**, 2-unsubstituted-**1c**, and 1,2-unsubstituted-3-pyrazolines (**1d**) are very rare



1a



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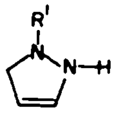

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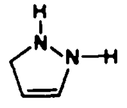
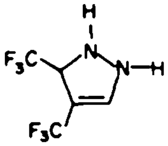


1d

The only 3-pyrazoline known, unsubstituted on both the N atoms (**1d**) was obtained from the reaction of diazomethane with 1,1,1,4,4,4-hexafluoro-2-butene;[2] but when the same olefin was reacted with trifluoro-diazoethane a compound was isolated, which was assigned a 2-pyrazoline structure **3**.[3] Magidson[4] describes a product having structure **4**, but without structural proofs.



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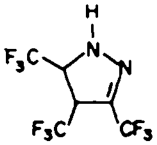

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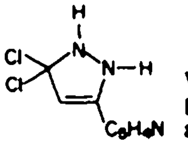

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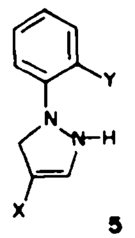
Examples for 2H-3-pyrazolines also are uncommon;[a] in fact only Takamizawa and Hayashi[8,9] have synthesized compounds of type **5**, where X = CN or CO_2Et and Y = NO_2 or SO_2Me. If Y = H, the product exists in the 2-pyrazoline form **6**.

1H-3-Pyrazolines **1b** have been proposed as reactive, not isolated, intermediates.[10–13] Two 1H-3-pyrazolines of type **7**[14a] and **8**[15] have been described, but in both cases it has been shown that the compounds are in fact 2-pyrazolines **9**[12,14b] and **10**.[16]



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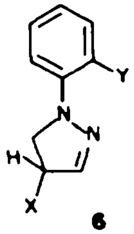

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During the course of this study[17–20] Armstrong and Tipping reported[21] a simple access to the 1H-3-pyrazoline system **1b** starting from hexafluoroacetone azine without giving experimental and spectral data.

RESULTS AND DISCUSSION

The mechanism of the "criss-cross" cycloaddition[22–24] was uncertain until recently.[25] Different mechanistic possibilities like a trimolecular one-step process as well as a bimolecular two-step process, involving the formation and further reaction of a diradical species have been discussed by Forshaw and Tipping.[26] The same authors previously proposed a Diels Alder adduct being the 1:1 intermediate of the "criss-cross" cycloaddition.[21]

We have shown unequivocally by chemical reactions [17–20, 27–31] and X-ray structure analysis[32] that the intermediate of the "criss-cross" cycloaddition reaction is a 1,3-dipolar species, namely an azomethine imine.[33] The reaction therefore being a sequence of two [3 + 2] cycloaddition steps (**11** → **12** → **13**).[17–19,b]

These results for the first time open the way to the mixed "criss-cross" cycloaddition[18,19,35–37] and to a simple general synthetic route to 1H-3-pyrazolines[17–21,34].

Treating hexafluoroacetone azine (**11**)[38,39] with olefins of type R^1 CH=CHR^2 **14** the 2-[3,3-bis(trifluoromethyl) - 1 - pyrazolin - 1 - ylio] - 1,1,1,3,3,3 - hexafluoro - 2 - propanides (**15**) initially formed[17–20,32] can be precursors of 1,5-diazabicyclo[3.3.0] octanes (**16**) and/or 1H-3-pyrazol-

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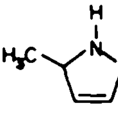
[a] Except of course, when in position 5 there is a CO group: NH-tautomer of pyrazolones.[5] Twice in Chemical Abstracts 2-pyrazolines were classified as 3-pyrazolines **1c**: 1-(phenylsulfonyl)-3-pyrazoline[6] and (1-(2',4'-dinitrophenyl)-3-aryl-4-methyl-3-pyrazoline.[7]

[b] A. E. Tipping *et al.* declined their mechanistical interpretations[21,26] of the "criss-cross" cycloaddition and now fully agree with our interpretation of this cycloaddition process, see[34] lit. 6.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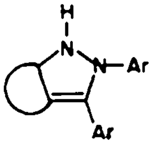
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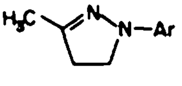
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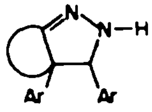
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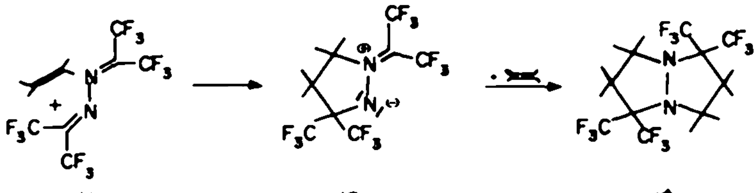

11 12 13

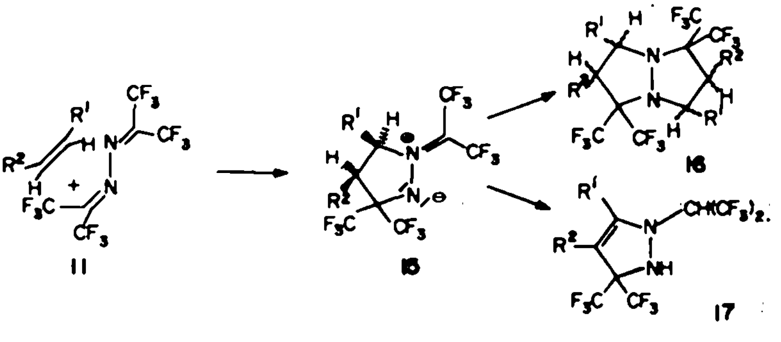
ines (17) depending on the substitution pattern (R[1],R[2]) chosen for the olefins 14 used.[17–20, 34]

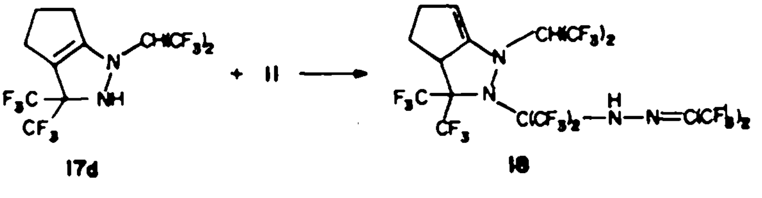
Especially in the case of terminal olefins with bulky groups present [$R^1 = Me_3C$-, Me_2CH-, Me_2CHCH_2-; $R^2 = H$] the yields of 1H-3-pyrazolines (17) are good because of the competing [3+2] cycloaddition process (15→16) is slowed down considerably by steric hindrance.[18,20,21,34] While 17a was found to be the exclusive product under the reaction conditions used, 17b was accompanied by 5–20% of the "criss-cross" cycloadduct 16b, particularly when higher reaction temperatures were used. With decreasing size of the substituent R^1 the reaction rate of the concerted process (15→16) increased.[40] In the case of ethylene, propene and 1-butene no 1H-3-pyrazoline was detected.[20,34] The low yields of 17c could be caused by side reactions, probably of radical nature.[41] In the cycloalkene series (cyclopentene, cyclohexene, cycloheptene) provided the lowest yields for cyclohexene. The crude material 17d was contaminated by a second product, which proved to be a 2:1 adduct of hexafluoroacetone azine and cyclopentene, obtainable in good yields directly from 17d and 11 in a sealed tube reaction. The spectroscopic data are consistent with structure 18.

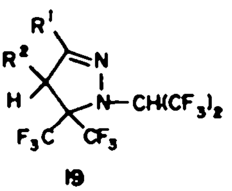
Using indene and acenaphthylene as olefinic compounds the 1H-3-pyrazolines (17g and 17h) could be isolated in high yields. Some electron rich olefins (enol ethers and enamines) also formed 1H-3-pyrazolines (17) on reaction with 11, although sometimes in very low yields.[42]

The structural assignment was based on the spectroscopic data. The spectra indicated the presence of a NH function (3360–3340 cm^{-1}) and of a carbon double bond (1705–1640 cm^{-1}). ^{19}F NMR spectra show two pairs of magnetically equivalent trifluoromethyl groups. The trifluoromethyl groups fixed to C-5 of the pyrazoline ring resonate at −2.0 to −4.7 ppm splitted by a long range coupling $^7J_{FF} = 1.3$–1.85 Hz. The 1,1,1,3,3,3-hexafluoroisopropyl group gives rise to a doublet with fine structure at −11.1 to −11.6 ppm ($^3J_{HF} = 6.9$–7.8 Hz). In the ^1H NMR spectra a broad signal for a NH proton ($\delta = 4.78$–6.07 ppm, exchangable with D_2O/CF_3CO_2H), a septet for the proton of a $(CF_3)_2CH$-group ($\delta = 4.0$–4.7 ppm, $^3J_{HF} = 6.9$–7.8 Hz) as well as the substituents R^1 and R^2, placed at a double bond, are observed (Table 1). Mass spectrometry shows the presence of a hexafluoroisopropyl group by intense peaks at $[M-(CF_3)_2CH]^+$ and $m/e = 151$ $[(CF_3)_2CH]^+$ in the degradation pattern of compounds 17.[43] Other likely candidates as 19 therefore can be ruled out.

An azomethine imine (20) with H atoms present both at C-4 and C-5 of the heterocyclic system could be isolated as the stable product of the reaction of 11 with norbornene,[20] likewise 11 and cyclopentadiene yielded


11 15 16 17


17d 18



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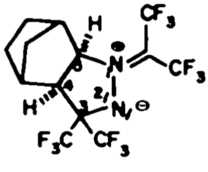

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an azomethine imine at low temperatures.[44] In other cases the intermediacy of 15 was proved by NMR spectroscopy.

The first step of the reaction 11 + 14 → 15 therefore is clearly established. For the second part of the reaction—the rearrangement 15 → 17—two alternative routes must be taken into consideration. We could not decide up to now, whether the rearrangement involves the step of an azomethine ylide or an azomethine imine represented by formula 21 and 22, respectively.[17,18]

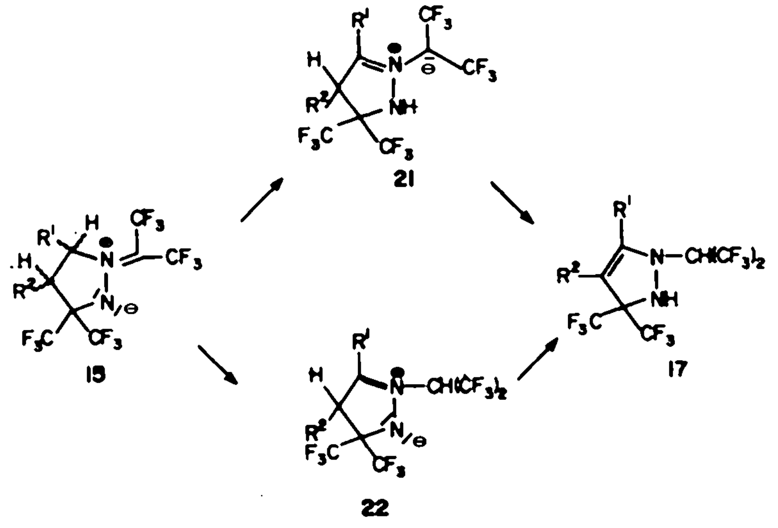
The synthesis of 1,5-diazabicyclo[3.3.0]octa-2,6-dienes from azines and acetylenes[45–50] also passes through an azomethine imine intermediate.[31,50] The 1,3-dipoles 23 having a double bond in the heterocyclic ring system turned out to be considerably more reactive than their saturated analogues and therefore readily undergo rearrangements, but at −20 to +20° they are stable enough to be trapped by dipolarophiles and nucleophiles.[31, 37, 50] The knowledge of the susceptibility of the azomethine imine skeleton to hydrogenation[51–54] consequently offers a further access to the 1H-3-pyrazoline system 17. The new synthetic route is an additional convincing proof for the structural assignment of 17.

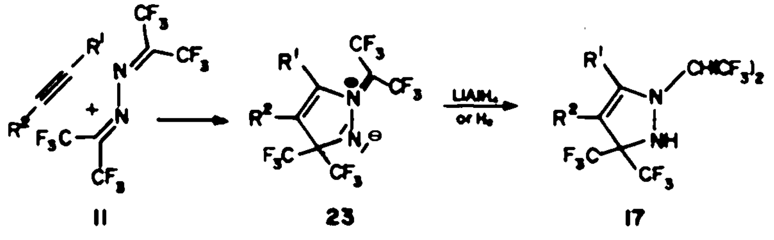
5,5-Bis(trifluoromethyl)-1H-3-pyrazolines 17 were transformed into pyrazoles 24 on flow pyrolysis at 450°.[21,34] We found that this elimination process already occurs below 200°.[c] The temperature required for this aromatization process strongly depends on the nature of the substituents R^1 and R^2. These findings parallel earlier results, namely the pyrazole formation from 3-hydroxypyrazolines by loss of water and methane.[12]

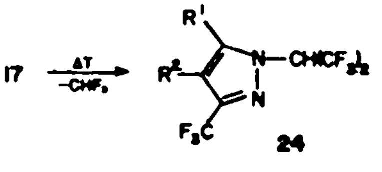
Further work on the reaction behaviour of 17 is under present investigation.

CONCLUSION

We have demonstrated that the reaction of hexafluoroacetone azine with olefins of type R^{1}CH=CHR^2 is a general route to 1H-3-pyrazolines. 2-[3,3-Bis(trifluoromethyl) - 1 - pyrazolin - 1 - ylio] - 1,1,1,3,3,3 - hexafluoro - 2 - propanides are the intermediates of this reaction. Furthermore we have developed a second simple synthetic route to the 1H-3-pyrazoline system by LAH-reduction or hydrogenation of azomethine imines obtained from the reaction of hexafluoroacetone azine (11) with alkoxy acetylenes and ynamines, respectively.







EXPERIMENTAL

IR spectra were measured on a Perkin-Elmer 237 apparatus. ^{1}H NMR spectra were taken with a Varian A 60, ^{19}F NMR

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[c] ^{19}F NMR spectra of the crude compounds 17b–f and h show that small amounts (3–5%) of the corresponding pyrazoles 24 are present when prepared at 80°.

Table 1. ^{1}H NMR and ^{19}F NMR data of 5,5-Bis (trifluoromethyl)-2-[2,2,2-trifluoro - 1 - trifluoromethyl-ethyl]-1H-3-pyrazolines **17a–j**

17	R^1, R^2	$(CF_3)_2C\text{-}\underline{H}$	$N\text{-}\underline{H}$ a)	$C(C\underline{F}_3)_2$ b)	$-CH(C\underline{F}_3)_2$ b)
a	$(CH_3)_3C$, H [34] 1.27 (s) 9H 4.72 (s) 1H	4.63 (h, J = 6.9)	5.15 (broad)	-2.0 6F	-11.5 (d, J = 6.9) 6F
b	$(CH_3)_2CHCH_2$, H 0.99 (d, J = 6.0) 6H 1.50 - 2.25 (m) 3H 4.72 (s) 1H	4.20 (h, J = 7.0)	5.12 (broad)	-2.0 6F	-11.1 (d, J = 7.0) 6F
c	CH_3, CH_3 1.80 (s, broad) 6H	4.17 (h, J = 7.0)	4.96 (broad)	-4.7 6F	-11.5 (d, J = 7.0) 6F
d	$-(CH_2)_3-$ 2.15 - 2.65 (m) 6H	4.02 (h, J = 7.0)	5.60 (broad)	-4.2 6F	-11.5 (d, J = 7.0) 6F
e	$-(CH_2)_4-$ 1.50 - 2.40 (m) 8H	4.12 (h, J = 7.0)	5.02 (broad)	-4.5 6F	-11.3 (d, J = 7.0) 6F
f	$-(CH_2)_6-$ 1.28 - 1.92 (m) 8H 2.05 - 2.55 (m) 4H	4.22 (h, J = 7.1)	4.99 (broad)	-4.7 6F	-11.5 (d, J = 7.1) 6F
g	$-C_7H_6-$ 3.48 (broad) 2H 7.13 - 7.72 (m) 4H	4.67 (h, J = 6.9)	5.86 (broad)	-4.3 6F	-11.2 (d, J = 6.9) 6F
h	$-C_{12}H_6-$ 7.36 - 8.08 (m) 6H	4.71 (h, J = 6.9)	6.07 (broad)	-4.7 6F	-11.6 (d, J = 6.9) 6F
i	OC_2H_5, CH_3 1.34 (t, J = 7.1) 3H 4.11 (q, J = 7.1) 2H 1.78 (broad) 3H	4.36 (h, J = 7.5)	4.86 (broad)	-4.0 6F	-11.2 (d, J = 7.5) 6F
j	$N(C_2H_5)_2$, CH_3 1.07 (t, J = 7.0) 6H 3.04 (q, J = 7.0) 4H 1.78 (broad) 3H	4.65 (h, J = 7.8)	4.78 (broad)	-4.2 6F	-11.3 (d, J = 7.8) 6F

^{1}H NMR spectra recorded in $CDCl_3$ with TMS as internal standard;

^{19}F NMR spectra recorded in $CHCl_3$ with CF_3CO_2H as external standard;

chemical shifts in δ-values, coupling constants in Hz;

a) exchangeable with D_2O/CF_3CO_2H;

b) signals show additional long-range coupling $^7J_{FF}$ = 1.30 - 1.85 Hz.

spectra with a Jeol C 60 HL instrument. TMS was used as internal, trifluoro-acetic acid as external standard, respectively. Mass spectra were obtained on a AEI MS 9 spectrometer at 70 eV. M.ps were determined in a Büchi capillary m.p. apparatus and are uncorrected.

5,5-Bis(trifluoromethyl)-2-[2,2,2 - trifluoro - 1 - trifluoromethyl-ethyl] - 1H - 3 - pyrazolines **17a–h** *from hexafluoroacetone azine* **11** *and olefins* **14**

General procedure. Equimolar amounts of **11** and of the corresponding olefin **14** were heated with or without a solvent (Table 2) in a sealed glass tube or stirred at room temp. in a glass vessel. After removal of the solvent, resulting liquids were purified by distillation, solids by recrystallization from n-hexane. In some cases (indicated in Table 3) an additional column chromatography was necessary to get analytically pure samples.

2,6-Diisobutyl-4,4,8,8-tetrakis(trifluoromethyl) - 1,5 - diazabicyclo[3.3.0]octane (**16b**)

4-Methyl-1-pentene (1.68 g; 20 mmol) and **11** (9.84 g; 30 mmol) were heated to 80-90° in a sealed glass tube for 3 days. The excess of **11** and compound **17b** formed during the reaction were distilled off in vacuum. The remaining solid consisted of a 90:10 mixture of two compounds. Column chromatography (silica gel, n-hexane) and recrystallization from n-hexane yielded 0.75 g (15%) **16b** (with the two i-Bu groups most probably *trans* in respect to the bicyclic ring system[43,55,56]); m.p. 98°. ^{1}H NMR ($CDCl_3$): δ = 0.75–1.10 m (12H), 1.10–1.87 m (6H), 2.10–3.08 m (4H), 3.32–4.00 m (2H). ^{19}F NMR ($CHCl_3$): δ = −5.5 q, J = 10 Hz (6F), − 11.6 q, J = 10 Hz (6F). (Found: C, 43.60; H, 4.89; N, 5.79. $C_{18}H_{24}F_{12}N_2$ requires: C, 43.55; H, 4.87; N, 5.64%). Mass spectrum: M^+ = 496.

2-[2,2,2-*Trifluoro*-1-*trifluoromethyl - ethyl*] - 3 - [5,5,5-*trifluoro* - 1,1,4 - *tris*(*trifluoromethyl*) - 2,3 - *diaza - pent* - 3 - *enyl*] - 4,4 - *bis*(*trifluoromethyl*) - 2,3 - *diazabicyclo*[3.3.0]*oct* - 8 - *ene* (**18**)

Compound **17d** (3.96 g; 10 mmol) and **11** (3.28 g; 10 mmol) were heated to 120° in a sealed tube for 12 hr, yield 1.75 g (24%); m.p.

Table 2. 5,5-Bis(trifluoromethyl)-2-[2,2,2-trifluoro-1-trifluoromethyl - ethyl] - 1H - 3 - pyrazolines **17a-h**

17	R^1, R^2	reaction temperature	reaction time	solvent	yield	b.p./torr m.p.	IR (cm^{-1})
a	$(CH_3)_3C$, H [34]	80 °C	9 d	hexane	79	53 °C	3345, 1640 [a]
b	$(CH_3)_2CHCH_2$, H	80 - 90 °C	3 d	**11**	57	20 °C/0.01	3342, 1655 [b]
c	CH_3, CH_3	80 - 90 °C	21 d	hexane	20	52 °C/12	3348, 1690 [b]
d	$-(CH_2)_3-$	30 °C	14 d	hexane	51	73 °C/12 35-36 °C	3355, 1705 [b]
e	$-(CH_2)_4-$	80 °C	5 d	hexane	32	45 °C/0.2	3350, 1695 [b]
f	$-(CH_2)_6-$	80 - 90 °C	10 d	hexane	65	41 °C/0.01 35 °C	3350, 1675 [b]
g	$-C_7H_6-$ *	80 °C	4 d	hexane	93.5	75 °C	3350, 1645 [a]
h	$-C_{12}H_6-$ **	80 °C	10 d	benzene	80	121 °C	3355, 1605, 1565 [a]

Recorded in KBr [a], as film [b];

* from indene, ** from acenaphthylene.

Table 3. Analytical data of compounds **17a-j**

comp.	formula	Mwt		C	H	N
17a	$C_{12}H_{12}F_{12}N_2$ [34]	412.2	Found:	34.84	3.01	7.26
			required:	34.96	2.93	6.80
17b	$C_{12}H_{12}F_{12}N_2$	412.2	Found:	34.98	2.95	6.86
			required:	34.96	2.93	6.80
17c	$C_{10}H_8F_{12}N_2$	384.2	Found:	31.18	2.19	6.90*
			required:	31.26	2.10	7.29
17d	$C_{11}H_8F_{12}N_2$	396.2	Found:	33.24	2.05	7.33
			required:	33.35	2.05	7.07
17e	$C_{12}H_{10}F_{12}N_2$	410.2	Found:	35.25	2.65	6.87*
			required:	35.14	2.46	6.83
17f	$C_{14}H_{14}F_{12}N_2$	438.3	Found:	38.61	3.45	6.40
			required:	38.37	3.22	6.39
17g	$C_{15}H_8F_{12}N_2$	444.2	Found:	40.72	1.91	6.11*
			required:	40.56	1.82	6.31
17h	$C_{18}H_8F_{12}N_2$	480.3	Found:	45.43	1.73	5.80*
			required:	45.02	1.68	5.83
17i †						
17j	$C_{13}H_{15}F_{12}N_3$	441.3	Found:	35.25	3.46	9.44
			required:	35.39	3.43	9.52

* Column chromatography on silica gel / chloroform - carbon tetrachloride (1:1) was necessary to get analytically pure samples.

† Experiments to purify **17i** by distillation failed. Column chromatography caused decomposition; **17i** therefore was characterized analytically after transformation into **24b**.

94° (from n-hexane). IR (KBr): 3350 (νNH), 1700 (νC=C), 1630 cm^{-1} (νC=N). ^{1}H NMR (D$_6$-acetone): δ = 2.30–3.10 m (4H), 3.83–4.40 broad (1H), 4.70 h, J = 6.9 Hz (1H), 6.97 s (1H), 9.05 broad (1H). ^{19}F NMR (D$_6$-acetone): δ = −4.3 m (3F), −7.3 m (3F), −8.2 q, J = 8.5 Hz (3F), −10.8 m (6F), −12.7 m (3F), −13.5 q, J = 8.5 Hz (3F). (Found: C, 27.74; H, 1.47; N, 7.95. $C_{17}H_8F_{24}N_2$ requires: C, 28.19; H, 1.11; N, 7.73%). Mass spectrum: M$^+$ = 724.

Reaction of 11 *with norbornene.* A mixture of 11 (6.56 g; 20 mmol) and norbornene (1.88 g; 20 mmol) was kept in 50 ml n-hexane at room temp. for 2 days, yield 7.1 g (85%); m.p. 67° (from n-hexane). IR (KBr): 1530 cm^{-1} $(-\overset{\ominus}{\underline{N}}-\overset{\oplus}{N}=C\langle)$. ^{1}H NMR (CDCl$_3$): δ = 0.88–1.98 m (6H), 2.40–2.98 m (3H), 5.07 d, J = 6.5 Hz (1H). ^{19}F NMR (CHCl$_3$): δ = −4.1 q, J = 11.2 Hz (3F), −11.65 q, J = 11.2 Hz (3F), −12.5 q, J = 7.1 Hz (3F), −25.2 q, broad (3F). (Found: C, 37.39; H, 2.84; N, 6.36. $C_{13}H_{10}F_{12}N_2$ requires: C, 36.98; H, 2.39; N, 6.63%). Mass spectrum: M$^+$ = 422.

3-Diethylamino-4-methyl-5,5 - bis(trifluoromethyl) - 2 - [2,2,2 - trifluoro-1-trifluoromethyl - ethyl] - 1H - 3 - pyrazoline (17j)

To a stirred soln of 11 (3.28 g; 10 mmol) in 10 ml abs. hexane at −30° a soln of 1-diethylamino-propyne (1.11 g; 10 mmol), in 10 ml hexane was added dropwise under N$_2$. After 2 hr at −30°, LAH (0.4 g; 10.5 mmol), in 10 ml ether was added. The mixture was allowed to warm up slowly to 0°(2–3 hr). On hydrolytic work-up the 1H-3-pyrazoline 17j was isolated from a mixture of products as a crystalline solid, yield: 0.64 g (14.5%); m.p. 60.5–61° (hexane). IR (KBr): 3350 (νNH), 1675 cm^{-1} (νC=C). ^{1}H NMR and ^{19}F NMR: Table 1; analytical data: Table 3. Mass spectrum: M$^+$ = 441.

Thermolysis of 17h. Compound 17h (2.4 g; 5 mmol) was heated to 190–195°, the course of the reaction was followed by ^{19}F NMR spectroscopy. The crystalline material obtained was purified by column chromatography (silica gel/CCl$_4$), yield: 1.2 g (58.5%) 24a; m.p. 111° (hexane/chloroform). IR (KBr): 1554 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 5.80 h, J = 7 Hz (1H), 7.40–8.15 m (6H). ^{19}F NMR (CDCl$_3$): δ = −10.5 d, J = 7 Hz (6F), −16.3 s (3F). (Found: C, 49.65; H, 1.73; N, 6.71. $C_{17}H_7F_9N_2$ requires: C, 49.77; H, 1.72; N, 6.83%). Mass spectrum: M$^+$ = 410.

5-Ethoxy-4-methyl-3-trifluoromethyl - 1 - [2,2,2 - trifluoro - 1 - trifluoromethyl - ethyl] - pyrazol (24b)

To a stirred soln of 11 (6.56 g; 20 mmol) in 20 ml abs. hexane at −10° a soln of 1-ethoxy-propyne (3.36; 40 mmol) in 10 ml hexane, was added dropwise under N$_2$. The mixture was kept 3 days at 0–5° and 2 days at room temp. before being treated with 0.5 g (13 mmol) LAH, in 10 ml ether, for 4 hr at 0°. On hydrolytic work-up the crude 17l was obtained (NMR data: Table 1).

For pyrazol formation 17l was heated to 150–160° for 18 hr. 24b was purified by column chromatography (silica gel/carbon tetrachloride—under water free conditions) and distillation i. vac, yield: 1.75 g (26%); b.p. 67°/12 torr., IR (film): 1605 cm^{-1}., ^{1}H NMR (CDCl$_3$): δ = 1.43t, J = 7.2 Hz (3H), 2.14 (broad) (3H), 4.33 q, J = 7.2 Hz (2H), 5.36 h, J = 6.8 Hz (1H). ^{19}F NMR (CDCl$_3$): δ = −9.65 d, J = 6.8 Hz (6F), −14.9 s (3F). (Found: C, 35.03; H, 2.51; N, 8.04. $C_{10}H_9F_9N_2O$ requires: C, 34.90; H, 2.64; N, 8.14%). Mass spectrum: M$^+$ = 344.

Thermolysis of 17j. Compound 17j (0.88 g; 2 mmol) was heated to 150° for 5 hr. The resulting liquid was purified by column chromatography and subsequent distillation, yield: 0.74 g (100%) 24c; b.p. 102°/17 torr. IR (film): 1585 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 1.05 t, J = 7.2 Hz (6H), 2.17 (broad) (3H), 3.10 q, J = 7.2 Hz (4H), 5.87 h, J = 6.75 Hz(1H). ^{19}F NMR (CDCl$_3$): δ = −10.0 d, J = 6.75 Hz (6F), −15.3 s (3F). (Found: C, 38.95; H, 3.91; N, 11.18. $C_{12}H_{14}F_9N_3$ requires: C, 38.82; H, 3.80; N, 11.32%). Mass spectrum: M$^+$ = 371.

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[a] The minor compound gives rise to signals at −6.0 q, J = 9 Hz (6F) and −11.1 q, J = 9 Hz (6F) in the ^{19}F NMR spectrum and probably is the "criss-cross" cycloadduct with both the isobutyl groups placed *cis* in respect to the bicyclic ring system

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