Aryl trifluoromethyl-1,2,3-triazoles

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Abstract

Diaryl-substituted trifluoromethyl-1,2,3-triazoles have been synthesized from aromatic azides and various substituted 1-aryl-3,3,3-trifluoro-1-propynes. The spectroscopic characteristics of the products and the regioselectivity of the reaction are discussed. An improved method for the synthesis of 1-aryl-3,3,3-trifluoro-1-propynes from 1-aryl-2-chloro-3,3,3-trifluoro-1-propenes is presented.

Introduction

Fluorinated heterocyclic compounds are of potential interest as intermediates for pharmaceuticals and agrochemicals, but the introduction of fluorine-containing groups into heterocyclic rings has been limited [1, 2]. As a part of our work devoted to the synthesis of new compounds possessing biological activity as agrochemicals, we have explored the usefulness of fluorinated intermediates in the construction of heterocyclic structures.

It is well known that acetylenic compounds readily undergo cycloaddition reactions to give several heterocyclic systems [3–5], thus fluorinated alkynes may be used as building blocks in the synthesis of fluorinated heterocycles [6–8]. Previously, we have investigated the reaction of aryl trifluoromethyl alkynes and nitrile oxides [7]; here we describe the synthesis of aryl trifluoromethyl-1,2,3-triazoles starting from various aryl trifluoromethyl alkynes and azides.

Experimental

General techniques

Analytical TLC plates and silica gel (230–400 mesh) were purchased from Merck. Melting points were determined using a Büchi SMP-20 apparatus and are reported uncorrected. GC analyses were carried out on a Carlo Erba HRGC 5300 chromatograph. Microanalyses were obtained using a Hewlett–Packard 185 element analyser. Mass spectra were obtained using a Varian Matt 1125 spectrometer with an electron impact source at 70 eV. IR spectra were obtained using a Perkin–Elmer 1420 spectrophotometer. ^{19}F NMR spectra were obtained using a Bruker AC 200 spectrometer, with $CDCl_3$ as the solvent and $CFCl_3$ as the internal standard.

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Alkenes (**2**) [7], phenylazide [9] and 4-nitro-phenylazide [10] were prepared as described previously.

2,6-Dichloro-phenylazide

2,6-Dichloro-phenylhydrazine hydrochloride (20 g, 0.093 mol) was treated with an aqueous 3% hydrochloric acid solution (105 ml). The solution was cooled to 0 °C, ethyl ether (30 ml) added and a solution of sodium nitrite (7.5 g, 0.108 mol) in 12 ml water added dropwise at such a rate as to keep the temperature below 5 °C. The reaction mixture was stirred at 5 °C for a further 30 min, then the layers were separated and the aqueous phase extracted with ethyl ether (3×50 ml). The organic phase was dried with sodium sulphate and the solvent evaporated. The crude product was purified by chromatography on a short silica gel column using n-hexane as the eluant, yielding 6.5 g (37%) of a solid with m.p. <35 °C; IR (neat): 2110 cm^{-1}.

*1-Aryl-3,3,3-trifluoro-1-propynes (**3a–h**); general procedure*

To a stirred solution of **2a–h** (10 mmol) in DMSO (60 ml) was added finely powdered 85% KOH (12 mmol). The dark mixture was stirred at room temperature overnight, then diluted with water (100 ml) and extracted with ethyl ether. The organic phase was washed with water and dried with sodium sulphate. The solvent was evaporated and the crude product was purified via silica gel chromatography to give **3a–h** (Table 1).

*1,5-Diaryl-4-trifluoromethyl-1,2,3-triazoles (**5**) and regioisomeric 1,4-diaryl-5-trifluoromethyl-1,2,3-triazoles (**6**); general procedure*

Alkyne **3** (5.0 mmol) and azide **4** (5.0 mmol) were dissolved in toluene (5 ml) and heated at 110 °C for 12–30 h. The solvent was evaporated and the crude products separated by silica gel chromatography using the appropriate n-hexane/ethyl acetate mixture as eluant. Analytical data for the compounds obtained are as follows:

5a: m.p., 106–108 °C. ^{19}F NMR: δ −59.57 ppm. IR (Nujol): 1150 cm^{-1}. Mass spectrum *m/z* (%): 323 (M^+, 22); 295 ($M^+ - N_2$, 29); 260 ($M^+ - N_2 - Cl$, 6); 240(17); 218($M^+ - N_2 - C_6H_5$, 3); 191(8); 165(7); 77(100). Analysis, found (calc.): C, 55.94 (55.66); H, 2.71 (2.80); F, 17.18 (17.61); N, 13.00 (12.98)%.

6a: m.p., 79–81 °C. ^{19}F NMR: δ −55.31 ppm. IR (Nujol): 1150 cm^{-1}. Mass spectrum *m/z* (%): 323 (M^+, 5); 295 ($M^+ - N_2$, 100); 260 (15); 240 (98); 226 ($M^+ - N_2 - CF_3$, 23); 190 (31); 165 (28); 123 ($C_7H_4Cl^+$, 15); 77 (38). Analysis, found (calc.): C, 55.68 (55.66); H, 2.70 (2.80); F, 17.44 (17.61); N, 12.69 (12.98)%.

5b: m.p., 102–103 °C. ^{19}F NMR: δ −60.64 ppm. IR (Nujol): 1150 cm^{-1}. Mass spectrum *m/z* (%): 323 (M^+, 11); 295 ($M^+ - N_2$, 15); 260 ($M^+ - N_2 - Cl$, 20); 240 (14); 218 ($M^+ - N_2 - C_6H_5$, 3); 190 (10); 165 (7); 77 (100). Analysis, found (calc.): C, 56.06 (55.66); H, 2.72 (2.80); F, 17.26 (17.61); N, 13.13 (12.98)%.

6b: m.p., 67–68 °C. ^{19}F NMR: δ −57.05 ppm. IR (Nujol): 1140 cm^{-1}. Mass spectrum *m/z* (%): 295 ($M^+ - N_2$, 33); 260 (100); 240 (79); 226 (7); 190 (29); 165 (30); 77 (62). Analysis, found (calc.): C, 55.34 (55.66); H, 2.80 (2.80); F, 17.30 (17.61); N, 12.83 (12.98)%.

5c: m.p., 95–96 °C. ^{19}F NMR: δ −59.59 ppm. IR (Nujol): 1530; 1350; 1150 cm^{-1}. Mass spectrum *m/z* (%): 334 (M^+, 31); 306 ($M^+ - N_2$, 25); 276 ($M^+ - N_2 - NO$, 14); 260 (8); 240 (12); 191 (31); 157 (8); 137 (6); 77 (100). Analysis, found (calc.): C, 54.09 (53.90); H, 2.69 (2.71); F, 17.18 (17.05); N, 16.58 (17.76)%.

6c: m.p., 130–132 °C. ^{19}F NMR: δ −55.35 ppm. IR (Nujol): 1520; 1345; 1150 cm^{-1}. Mass spectrum *m/z* (%): 334 (M^+, 55); 306 ($M^+ - N_2$, 100); 276 (12); 260 (14); 240 (23); 191 (77); 164 (25); 152 (9); 77 (54). Analysis, found (calc.): C, 54.11 (53.90); H, 2.60 (2.71); F, 17.08 (17.05); N, 16.48 (16.76)%.

5d: m.p., 71–72 °C. ^{19}F NMR: δ −59.24 ppm. IR (Nujol): 1150; 1040 cm^{-1}. Mass spectrum *m/z* (%): 319 (M^+, 30); 291 ($M^+ - N_2$, 21); 276 ($M^+ - N_2 - CH_3$, 60); 214 ($M^+ - N_2 - C_6H_5$, 7); 77 (100). Analysis, found (calc.): C, 60.26 (60.19); H, 3.75 (3.79); F, 18.05 (17.85); N, 13.10 (13.16)%.

6d: m.p., 111–112 °C. ^{19}F NMR: δ −54.96 ppm. IR (Nujol): 1140; 1030 cm^{-1}. Mass spectrum *m/z* (%): 319 (M^+, 14); 291 ($M^+ - N_2$, 100); 276 ($N^+ - N_2 - CH_3$, 72); 222 ($M^+ - N_2 - CF_3$, 33); 152 (22); 77 (43). Analysis, found (calc.): C, 59.93 (60.19); H, 3.90 (3.79); F, 18.24 (17.85); N, 13.05 (13.16)%.

5e: ^{19}F NMR: δ −59.25 ppm.

5e ac: m.p., 150–152 °C. ^{19}F NMR: δ −59.61 ppm. IR (Nujol): 3360; 1680; 1130 cm^{-1}. Mass spectrum *m/z* (%): 346 (M^+, 16); 318 ($M^+ - N_2$, 9); 276 (54); 207 (22); 77 (59); 43 (CH_3CO^+, 100). Analysis, found (calc.): C, 58.98 (58.96); H, 3.61 (3.78); F, 16.80 (16.46); N, 16.27 (16.18)%.

6e: ^{19}F NMR: δ −54.94 ppm.

6e ac: m.p., 174–175 °C. ^{19}F NMR: δ −54.36 ppm. IR (Nujol): 3360; 1680; 1130 cm^{-1}. Mass spectrum *m/z* (%): 346 (M^+, 4); 318 ($M^+ - N_2$, 11); 276 (95); 207 (84); 77 (29); 43 (CH_3CO^+, 100). Analysis, found (calc.): C, 57.16 (58.96); H, 3.62 (3.78); F, 16.41 (16.46); N, 16.10 (16.18)%.

5f: m.p., 152–153 °C. ^{19}F NMR: δ −59.71 ppm. IR (Nujol): 1130 cm^{-1}. Mass spectrum *m/z* (%): 391 (M^+, 79); 363 ($M^+ - N_2$, 100); 328 ($M^+ - N_2 - Cl$, 66); 308 (26); 293 (34); 258 (30); 233 (65); 218 ($M^+ - N_2 - C_6H_3Cl_2$, 12); 145 ($C_6H_3Cl_2^+$, 27); 123 (79); 109 (73). Analysis, found (calc.): C, 45.69 (45.89); H, 1.81 (1.80); F, 14.28 (14.52); N, 10.60 (10.70)%.

6f: m.p., 138–140 °C. ^{19}F NMR: δ −57.91 ppm. IR (Nujol): 1135 cm^{-1}. Mass spectrum *m/z* (%): 363 ($M^+ - N_2$, 30); 328 (100); 308 (19); 293 (10); 258 (13); 233 (34); 224 (18); 123 (21); 109 (6). Analysis, found (calc.): C, 46.00 (45.89); H, 1.71 (1.80); F, 14.28 (14.52); N, 10.39 (10.70)%.

5g: m.p., 159–161 °C. ^{19}F NMR: δ −61.60 ppm. IR (Nujol): 1155 cm^{-1}. Mass spectrum *m/z* (%): 391 (M^+, 13); 363 ($M^+ - N_2$, 18); 328 (29); 308 (4); 233 (12); 218 (7); 192 (10); 157 (43); 145 (29); 137 (25); 123 (96);

109 (100). Analysis, found (calc.): C, 45.54 (45.89); H, 1.73 (1.80); F, 14.34 (14.52); N, 10.46 (10.70)%.

6g: m.p., 134–136 °C. ^{19}F NMR: δ −59.87 ppm. IR (Nujol): 1140 cm^{-1}. Mass spectrum *m/z* (%): 363 ($M^+ - N_2$, 5); 328 (40); 308 (8); 233 (19); 224 (12); 157 (15); 145 (17); 137 (11); 123 (100); 109 (47). Analysis, found (calc.): C, 45.90 (45.89); H, 1.65 (1.80); F, 14.17 (14.52); N, 10.58 (10.70)%.

5h: m.p., 125–126 °C. ^{19}F NMR: δ −59.62 ppm. IR (Nujol): 1530; 1365; 1150 cm^{-1}. Mass spectrum *m/z* (%): 402 (M^+, 41); 374 ($M^+ - N_2$, 27); 344 ($M^+ - N_2 - NO$, 39); 339 ($M^+ - N_2 - Cl$, 12); 328 ($M^+ - N_2 - NO_2$, 12); 293 (41); 258 (42); 224 (41); 157 (100); 145 (41); 137 (77); 109 (45). Analysis, found (calc.): C, 44.96 (44.69); H, 1.75 (1.75); F, 13.48 (14.14); N, 13.73 (13.90)%.

6h: m.p., 144–145 °C. ^{19}F NMR: δ −57.84 ppm. IR (Nujol): 1530; 1360; 1140 cm^{-1}. Mass spectrum *m/z* (%): 374 ($M^+ - N_2$, 65); 339 (100); 328 (56); 293 (41); 281 (65); 258 (47); 224 (50); 157 (35); 145 (24); 137 (29); 109 (26). Analysis, found (calc.): C, 44.46 (44.69); H, 1.67 (1.75); F, 13.82 (14.14); N, 13.70 (13.90)%.

5i: m.p., 115–117 °C. ^{19}F NMR: δ −59.71 ppm. IR (Nujol): 1150; 1040 cm^{-1}. Mass spectrum *m/z* (%): 387 (M^+, 46); 359 ($M^+ - N_2$, 29); 344 ($M^+ - N_2 - CH_3$, 100); 214 ($M^+ - N_2 - C_6H_3Cl_2$, 14); 145 ($C_6H_3Cl_2^+$, 34); 109 (18). Analysis, found (calc.): C, 49.90 (49.51); H, 2.47 (2.60); F, 15.19 (14.68); N, 10.71 (10.82)%.

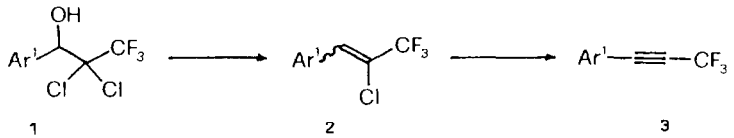
6i: m.p., 150–152 °C. ^{19}F NMR: δ −57.91 ppm. IR (Nujol): 1135; 1040 cm^{-1}. Mass spectrum *m/z* (%): 359 ($M^+ - N_2$, 4); 325 ($M^+ - Cl - F$, 100); 310 (33). Analysis, found (calc.): C, 49.78 (49.51); H, 2.58 (2.60); F, 15.00 (14.68); N, 10.61 (10.82)%.

5j: m.p., 149–150 °C. ^{19}F NMR: δ −59.74 ppm. IR (Nujol): 1540; 1350; 1145 cm^{-1}. Mass spectrum *m/z* (%): 368 (M^+, 3); 340 ($M^+ - N_2$, 5); 294 ($M^+ - N_2 - NO_2$, 7); 259 (10); 225 (4); 190 (8); 168 (10); 76 (100). Analysis, found (calc.): C, 49.17 (48.86); H, 2.28 (2.19); F, 15.18 (15.46); N, 15.00 (15.20)%.

6j: m.p., 120–122 °C. ^{19}F NMR: δ −54.99 ppm. IR (Nujol): 1540; 1355; 1130 cm^{-1}. Mass spectrum *m/z* (%): 340 ($M^+ - N_2$, 38); 323 ($M^+ - NO_2$, 6); 294 (42); 259 (29); 239 (21); 225 (26); 207 (62); 190 (53); 123 (43); 76 (100). Analysis, found (calc.): C, 49.11 (48.86); H, 2.16 (2.19); F, 15.22 (15.46); N, 15.23 (15.20)%.

Results and discussion

1-Aryl-3,3,3-trifluoro-1-propynes (**3**) are prepared in two steps from alcohols **1** via the known alkene intermediates **2** [7] (Scheme 1). We, and other authors, have previously described the synthesis of **3** from **2** in a reaction system containing sodium amide and t-butyl alcohol in benzene or toluene [7, 11]. However, this method has the disadvantage of employing an expensive base, a mixture of anhydrous solvents and an inert atmosphere.



1,2,3	Ar^1
a	4-ClC_6H_4
b	2-ClC_6H_4
c	4-$O_2NC_6H_4$
d	4-$CH_3OC_6H_4$
e	4-$H_2NC_6H_4$
f	3-pyridyl
g	2,4-$Cl_2C_6H_3$
h	3,4-$CH_3OC_6H_3$

Scheme 1.

TABLE 1

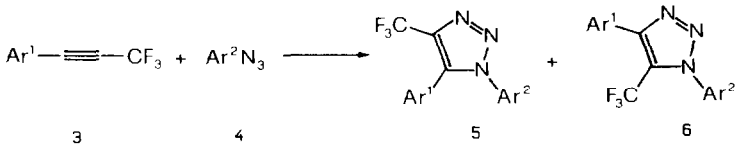
Variations of compound **3** prepared together with relevant analytical data

Compound	Yield[a] (%)	M.p. (°C) or b.p. (°C/mbar)	IR (cm^{-1})
3a	83	67/20	2250; 1170[b]
3b	89	73/20	2260; 1150[b]
3c[d]	–	71–72	2250; 1535[c] 1350; 1155
3d	93	87/20	2250; 1150[c]
3e	89	60–61	3200; 3300[c] 2240; 1140
3f	92	48–50	2260; 1170[c]
3g	86	91/20	2270; 1155[c]
3h	95	110/20	2250; 1130[c]

[a]Yield of isolated pure products **3** based on **2**.
[b]Liquid film.
[c]Nujol
[d]A complex mixture of products was obtained. Compound **3c** was prepared as described in ref. 7.

We have now found that the dehydrochlorination of the alkenes **2** can be carried out more readily with sodium or potassium hydroxide in commercial dimethyl sulphoxide at room temperature. The yields are in some cases better than those obtained by the previous method. In addition, this method allows reactions which involve alkenes which are insoluble in hydrocarbon solvents to be performed (Table 1).

1,3-Dipolar cycloaddition between alkynes and azides is a well-known method for the synthesis of triazoles [12–14]. The reaction is carried out by heating the reagents for several hours in a high boiling aromatic solvent. The regioselectivity of these reactions depends on the nature of the substituents present on the dipole and on the dipolarophile [15]. In our case the cycloadditions involving fluorinated alkynes **3** and azides **4** led to the triazoles **5** and **6** in a ratio of *ca.* 4:1 (Scheme 2). The results obtained are summarized in Table 2.



3 4 5 6

5,6	Ar^1	Ar^2
a	4-ClC_6H_4	C_6H_5
b	2-ClC_6H_4	C_6H_5
c	4-$O_2NC_6H_4$	C_6H_5
d	4-$CH_3OC_6H_4$	C_6H_5
e	4-$H_2NC_6H_4$	C_6H_5
f	4-ClC_6H_4	2,6-$Cl_2C_6H_3$
g	2-ClC_6H_4	2,6-$Cl_2C_6H_3$
h	4-$O_2NC_6H_4$	2,6-$Cl_2C_6H_3$
i	4-$CH_3OC_6H_4$	2,6-$Cl_2C_6H_3$
j	4-ClC_6H_4	4-$O_2NC_6H_4$

Scheme 2.

TABLE 2

Yields and regioselectivity obtained in the reaction **3 + 4 → 5 + 6**

Product	Yield[a] (%)	Reaction time (h)	Ratio[b] **5/6**
5a/6a	85	12	82:18
5b/6b	87	12	93:7
5c/6c	97	12	72:28
5d/6d	78	12	80:20
5e/6e	80[c]	12	88:12
5f/6f	83	24	78:22
5g/6g	64	24	80:20
5h/6h	95	24	71:29
5i/6i	75	24	79:21
5j/6j	65	30	80:20

[a]Yield of isolated pure products (**5 + 6**) after chromatography.
[b]The ratios **5:6** of isolated pure products were the same as estimated by ^{19}F NMR spectroscopic analyses of the crude reaction mixtures.
[c]Compounds **5e** and **6e** were converted to their more stable acetyl derivatives **5e ac** and **6e ac** and characterized.

According to Houk's model [16–18] the regioselectivity obtained in these cycloaddition reactions can be explained in terms of HOMO–LUMO interactions between the reacting species. The presence of the electron-withdrawing group CF_3 lowers the HOMO and LUMO energy of dipolarophiles so that the reaction is HOMO/dipole–LUMO/dipolarophile controlled.

The preferred regioisomeric transition state will be the one in which the nitrogen atom bearing the aryl group (larger atomic orbital coefficient in the HOMO of the azide) interacts with the carbon atom bearing the aryl group (larger atomic orbital coefficient in the LUMO of the dipolarophile) and the unsubstituted nitrogen atom of the azide interacts with the carbon atom bearing the CF_3 group of the dipolarophile. The regioselectivity observed may also be explained by considering the Coulombic or dipole–dipole interactions in the perturbation equation [19]. In this case the favoured interaction will be the one between the N_α of the azides $Ar^2-\overset{-}{N}_\alpha-\overset{+}{N}=N$ and the carbon atom bearing the aryl group of the polarized alkynes $Ar^1-\overset{\delta+}{C}\equiv\overset{\delta-}{C}-CF_3$. It should be noted that the nature of the substituent on the aryl moiety of the alkynes has some effect on the regioselectivity (small increase with electron-releasing group).

Steric effects seem to have little relevance to the regioselectivity except in the case of **3b**. However, steric hindrance decreases the reaction rate so that longer reaction times are required when 2,6-dichloro-phenylazide is employed. A much longer reaction time is necessary in the reaction involving 4-nitro-phenylazide, although the regioselectivity remains unaffected (**5j** and **6j**). The presence of the electron-withdrawing group NO_2 in the aryl moiety of the azide lowers its HOMO level, increasing the gap to the alkyne LUMO and thus lowering the reaction rate.

A similar behaviour was observed in the reaction between phenylazide and methyl 3-phenyl-propynoate or methyl 2-butynoate, which leads to the formation of 4- and 5-methoxycarbonyl-substituted triazoles in a 66:34 and a 70:30 ratio respectively [5]. An even more distinctive regioselectivity is obtained in reactions between alkynes **3** and nitrile oxides [7]. The exclusive formation of the 1,5-diphenyl-substituted triazole in the reaction of phenylazide with $C_6F_{13}-C\equiv C-C_6H_5$ has been reported [20].

Spectra

^{19}F NMR spectra

In the ^{19}F NMR spectra the signals of the trifluoromethyl groups in the 4-position of the triazole ring (products **5**) resonate at higher fields (2–4 ppm) than those in the 5-position (products **6**). This behaviour is in agreement with previously reported data for perfluoroalkylated triazoles [21, 22].

Mass spectra

Mass spectra distinguish between compounds **5** and **6**. Thus, the M^+ peak of compound **5** is more abundant than that of **6**; in particular in the case of **6b**, **6f**, **6g**, **6h** and **6i** the M^+ peak is absent from the spectrum. The most common fragmentation pathway for both **5** and **6** is the loss of

N_2, and for **6a**, **6c**, **6d** and **5f** the base peak is due to the ion $[M-N_2]^+$. In contrast, in compounds **5a**, **5b**, **5c** and **5d** the base peak is due to the ion $[Ar^2]^+$.

This result may be explained by taking into account the fragmentation that leads to the loss of N_2. In the case of compound **6** the two bonds which ruptured during the elimination of a nitrogen molecule are both α to a phenyl group while compound **5** has only one nitrogen atom in such a position. This reflects the difference in activation energy for the transition state relative to the fragmentation of **5** and **6** [23].

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