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Synthesis of fluorinated 2(3)-arylhydrazones of 1,2,3-tri(1,2,3,4-tetra)carbonyl compounds and their heterocyclization reactions

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Abstract

New fluorinated 2-arylhydrazones of 1,2,3-triketones, 2-arylhydrazone-1,2,3-diketo esters and 3-arylhydrazone-1,2,3,4-triketo esters have been prepared by the coupling of fluorine-containing 1,3-keto esters, 1,3-diketones, acyl(aroyl)pyruvic esters and their chelates with aryldiazonium chlorides. The arylhydrazones react with hydrazine hydrate, phenylhydrazine, thiosemicarbazide and hydroxylamine to form the corresponding pyrazole and isoxazole derivatives. Interaction of 3-arylhydrazone-1,2,3,4-diketo esters with *o*-phenylenediamine results in quinoxaline products. Intramolecular cyclization of the arylhydrazones with pentafluorophenyl substituents leads to cinnolone derivatives. © 1998 Published by Elsevier Science S.A.

Keywords: Coupling; Fluoroalkyl-containing 1,3-diketone; 1,3-keto ester; Acyl(aroyl)pyruvate; Arylhydrazone; Pyrazole; Isoxazole; Quinoxaline; Cinnolone

1. Introduction

It is known that 1,3-dicarbonyl compounds react with aryldiazonium salts to form the corresponding 2-arylhydrazone-1,2,3-tricarbonyl compounds [1]. Data on the coupling of fluorine-containing 1,3-dicarbonyl compounds are available only for the reactions of a few fluorinated 1,3-diketones [2,3], trifluoroacetoacetic [2] and pentafluorobenzoylacetic [4] esters. Information on the synthesis of arylhydrazones from fluorinated acyl(aroyl)pyruvic esters are absent (although their non-fluorinated analogues are known [5]).

In our view fluorine-containing 2-arylhydrazone-1,2,3-diketo esters, 2-arylhydrazones of 1,2,3-triketones, 3-arylhydrazone-1,2,3,4-triketo esters may serve as key precursors to a variety of novel heterocycles and react with dinucleophiles as non-substituted analogues [6–8].

This paper describes the synthesis of novel fluorinated 2-arylhydrazones of 1,2,3-triketones, 2-arylhydrazone-1,2,3-diketoesters, 3-arylhydrazone-1,2,3,4-triketoesters and their heterocyclization reaction products.

2. Experimental details

Melting points were measured in open capillaries and are reported uncorrected. Infrared spectra were measured on a Specord 75 IR spectrometer. ^{1}H-NMR spectra were recorded on a Tesla BS-567A instrument (^{1}H: 100 MHz) using TMS as an internal standard. ^{19}F-NMR spectra were recorded on a Tesla BS-587A instrument (^{19}F: 75 MHz) using $CFCl_3$ as an internal standard. Microanalyses were performed with a Carlo Erba CHNS-O EA 1108 elemental analyzer. Column chromatography was performed on silica gel L 100/250. Thin-layer chromatography was performed on 'Silufol-UV 254' plates.

2.1. Materials

Fluorinated keto esters **1a,b** and their copper (II) chelates **4d,e** were prepared by the method described previously [9,10]. Fluorinated diketones **2a,b** and copper (II) chelate **5a** were derived according to the literature methods [9,11]. Trifluoroacetopyruvic esters **3a,d** and copper (II) chelate **6a** were prepared by the method described previously [12]. Pentafluorobenzoylpyruvic ester **3e** and its copper **6e** and sodium **6h** chelates were prepared from pentafluorochlorobenzene via described procedures [13,14].

2.2. Synthesis of 2-arylhydrazone-1,2,3-tricarbonyl compounds

A solution of the appropriate arylamine (1.1 mmol) in a solution of 1 M HCl (50 ml) was diazotized at 0–5°C by

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addition of a saturated solution of $NaNO_2$ (1.1 mol) in 10 ml of water. The solution of aryldiazonium salt was added dropwise to a solution of the dicarbonyl compound (1 mmol) in 10 ml of methanol at 10–12°C. To the solution a saturated aqueous solution of NaOAc was added. The resulting precipitate was filtered off. Recrystallization from isopropyl alcohol gave compounds **7a–e, 8a–d, 9a–h** as yellow precipitates.

*2.2.1. Ethyl-2-(p-methoxyphenyl)hydrazone-4,4,4-trifluoro-2,3-dioxobutanoate (**7a**) (nc)*

Yield, 73%; m.p. 135–136°C; ^{1}H-NMR ($(CD_3)_2CO$) δ: 1.36 (3H, t, CH_3, $J_{(H-H)}$=7.1 Hz); 3.86 (3H, s, CH_3); 4.37 (2H, q, CH_2, $J_{(H-H)}$=7.1 Hz); 7.30 (4H, m, C_6H_4); 9.0 (1H, br.s, NH) ppm. ^{19}F-NMR ($(CD_3)_2CO$) δ: 93.72 (s, CF_3) ppm. IR: 3070, 1600 (NH); 1690 (CO_2Et); 1650 (C=O); 1580, 1520, 1510 (C=C, C=N) cm^{-1}. Analysis: Found: C, 49.05; H, 4.06; F, 17,97; N, 8.93. Calc. for $C_{13}H_{13}F_3N_2O_4$: C, 49.06; H, 4.12; F, 17,91; N, 8.80%.

*2.2.2. Ethyl-2-(p-methoxyphenyl)hydrazone-4,4,5,5,6,6,7,7,7-nonafluoro-2,3-dioxoheptanoate (**7b**) (nc)*

Yield, 81%; m.p. 77–78°C; ^{1}H-NMR ($(CD_3)_2CO$) δ: 1.36 (3H, t, CH_3, $J_{(H-H)}$=7.0 Hz); 3.86 (3H, s, CH_3); 4.38 (2H, q, CH_2, $J_{(H-H)}$=7.0 Hz); 7.30 (4H, m, C_6H_4); 13.43 (1H, br.s, NH) ppm. IR: 3090, 1615 (NH); 1685 (CO_2Et); 1660 (C=O); 1600, 1520, 1500 (C=C, C=N) cm^{-1}. Analysis: Found: C, 40.97; H, 3.13; F, 36.81; N, 5.95. Calc. for $C_{16}H_{13}F_9N_2O_4$: C, 41.04; H, 2.80; F, 36.51; N, 5.98%.

*2.2.3. Ethyl-2-(p-methylphenyl)hydrazone-4,4,5,5,6,6,7,7,7-nonafluoro-2,3-dioxoheptanoate (**7c**) (nc)*

Yield, 75%; m.p. 43–45°C; ^{1}H-NMR ($CDCl_3$) δ: 1.40 (3H, t, CH_3, $J_{(H-H)}$=7.1 Hz); 2.35 (3H, s, CH_3); 4.38 (2H, q, CH_2, $J_{(H-H)}$=7.1 Hz); 7.24 (4H, m, C_6H_4); 13.5 (1H, br.s, NH) ppm. ^{19}F-NMR ($CDCl_3$) δ: 36.84 (2F, m, CF_2); 41.26 (2F, m, CF_2); 50.44 (2F, m, CF_2); 81.10 (3F, s, CF_3) ppm. IR: 3100, 1600 (NH); 1690 (CO_2Et); 1660 (C=O); 1590, 1520, 1510 (C=C, C=N) cm^{-1}. Analysis: Found: C, 42.59; H, 3.29; F, 37.57; N, 6.16. Calc. for $C_{16}H_{13}F_9N_2O_3$: C, 42.49; H, 2.90; F, 37.81; N, 6.19%.

*2.2.4. Methyl-2-(p-methoxyphenyl)hydrazone-4,4,4-trifluoro-2,3-dioxobutanoate (**7d**) (nc)*

Yield, 72%; m.p. 142–144°C; ^{1}H-NMR ($CDCl_3$) δ: 3.86 (3H, s, CH_3); 3.94(3H, s, CH_3); 7.08 (4H, m, C_6H_4); 14.4 (1H, br.s, NH) ppm. ^{19}F-NMR ($CDCl_3$) δ: 96.72 (s, CF_3) ppm. IR: 3080, 1605 (NH); 1700 (CO_2Et); 1650 (C=O); 1590, 1520, 1500 (C=C, C=N) cm^{-1}. Analysis: Found: C, 47.31; H, 3.69; F, 18.62; N, 9.23. Calc. for $C_{12}H_{11}F_3N_2O_4$: C, 47.38; H, 3.64; F, 18.73; N, 9.21%.

*2.2.5. Methyl-2-(p-methoxyphenyl)hydrazone- 4,4,5,5,6,6,6-heptafluoro-2,3-dioxohexanoate (**7e**) (nc)*

Yield, 78%; m.p. 81–82°C; ^{1}H-NMR ($CDCl_3$) δ: 3.83 (3H, s, CH_3); 3.92 (3H, s, CH_3); 7.13 (4H, m, C_6H_4); 13.60 (1H, br.s, NH) ppm. ^{19}F-NMR ($CDCl_3$)) δ: 38.72 (2F, m, CF_2); 51.22 (2F, m, CF_2); 83.78 (3F, m, CF_3) ppm. IR: 2730, 1615 (NH); 1685 (CO_2Et), 1660 (C=O); 1600, 1520–1500 (C=C, C=N) cm^{-1}. Analysis: Found: C, 41.49; H, 2.79; F, 32.80; N, 6.76. Calc. for $C_{12}H_{11}F_3N_2O_4$: C, 41.60; H, 2.74; F, 32.90; N, 6.93%.

*2.2.6. 1,1,1-Trifluoro -2,3,4-pentanetrione 3-(p-methoxyphenyl)hydrazone (**8a**) (nc)*

Yield, 70%; m.p. 116–117°C; ^{1}H-NMR ($CDCl_3$) δ: 2.61 (3H, s, CH_3); 3.84 (3H, s, CH_3); 7.20 (4H, m, C_6H_4); 15.40 (1H, br.s, NH) ppm. ^{19}F-NMR ($CDCl_3$) δ: 91.66 (s, CF_3) ppm. IR: 2710, 1615 (NH); 1685 (C=O); 1590, 1500 (C=C, C=N) cm^{-1}. Analysis: Found: C, 50.07; H, 3.84; F, 19.83; N, 9.68. Calc. for $C_{12}H_{11}F_3N_2O_4$: C, 50.01; H, 3.85; F, 19.77; N, 9.72%.

From chelate **5a** (0.18 g, 1.0 mmol) compound **8a** (0.14 g, yield, 50%) was obtained. The physicochemical data were identical to those listed above.

*2.2.7. 1,1,2,2-Tetrafluoro-3,4,5-hexanetrione 4-(p-methoxyphenyl)hydrazone (**8b**) (nc)*

Yield, 85%; m.p. 130–131°C; ^{1}H-NMR ($(CD_3)_2CO$) δ: 2.56 (3H, s, CH_3); 3.87 (3H, s, CH_3); 6.71 (1H, t.t, $H(CF_2)_2$, $J_{(CF_2-H)}$=52.8, $J_{(CF_2-CHF_2)}$=7.3 Hz); 7.30 (4H, m, C_6H_4); 13.30 (1H, br.s, NH) ppm. ^{19}F-NMR ($(CD_3)_2CO$) δ: 26.65 (2F, d.t, HCF_2, $J_{(CF_2-H)}$=52.8, $J_{(CF_2-CHF_2)}$=7.3 Hz); 44.02 (2F, d.t, CF_2, $J_{(CF_2,CF_2)}$=7.3 Hz) ppm. IR: 2720, 1615 (NH); 1670 (C=O); 1590, 1580, 1500 (C=C, C=N) cm^{-1}. Analysis: Found: C, 48.53; H, 3.83; F, 24.09; N, 8.51. Calc. for $C_{12}H_{11}F_3N_2O_4$: C, 48.76; H, 3.78; F, 23.73; N, 8.75%.

*2.2.8. 1,1,2,2-Tetrafluoro-3,4,5-hexanetrione 4-(p-methylphenyl)hydrazone (**8c**) (nc)*

Yield, 80%; m.p. 90–91°C; ^{1}H-NMR ($CDCl_3$) δ: 2.39 (3H, s, CH_3); 3.61 (3H, s, CH_3); 6.35 (1H, t.t, $H(CF_2)_2$, $J_{(CF_2-H)}$=53.3, $J_{(CF_2-HCF_2)}$=6.7 Hz); 7.30 (4H, m, C_6H_4); 15.25 (1H, br.s, NH) ppm. ^{19}F-NMR ($CDCl_3$) δ: 25.06 (2F, d.t, HCF_2, $J_{(CF_2-H)}$=53.3, $J_{(CF_2-HCF_2)}$=7.3 Hz); 44.26 (2F, d.t, CF_2, $J_{(CF_2,CF_2)}$=6.7 Hz) ppm. IR: 3370, 1600 (NH); 1680 (C=O); 1580, 1510–1500 (C=C, C=N) cm^{-1}. Analysis: Found: C, 51.42; H, 3.93; F, 24.77; N, 9.29. Calc. for $C_{12}H_{11}F_3N_2O_4$: C, 51.32; H, 3.98; F, 24.98; N, 9.21%.

*2.2.9. 1,1,2,2-Tetrafluoro-3,4,5-hexanetrione 4-phenylhydrazone (**8d**) (nc)*

Yield, 74%; m.p. 125–126°C; ^{1}H-NMR ($CDCl_3$) δ: 2.62 (3H, s, CH_3); 6.35 (t.t, 1H, $H(CF_2)_2$, $J_{(CF_2-H)}$=53.2, $J_{(CF_2-HCF_2)}$=6.6 Hz); 7.44 (4H, m, C_6H_4); 15.20 (1H, br.s, NH) ppm. ^{19}F-NMR ($CDCl_3$) δ: 24.96 (2F, d.t, HCF_2, $J_{(CF_2-H)}$=53.2, $J_{(CF_2-HCF_2)}$=6.6 Hz); 44.26 (2F, d.t, CF_2, $J_{(CF_2,CF_2)}$=6.6 Hz) ppm. IR: 3380, 1610sh (NH); 1680 (C=O); 1580, 1500 (C=C, C=N) cm^{-1}. Analysis: Found: C, 49.88; H, 3.27; F, 25.70; N, 9.64. Calc. for $C_{12}H_{11}F_3N_2O_4$: C, 49.66; H, 3.47; F, 26.18; N, 9.65%.

*2.2.10. Ethyl-3-phenylhydrazone-5,5,5-trifluoro-2,3,4-trioxopentanoate (**9a**) (nc)*

Yield, 67%; m.p. 153–155°C; ^{1}H-NMR ($CDCl_3$) δ: 1.36 (3H, t, CH_3, $J_{(H–H)}$=7.1 Hz); 4.40 (2H, q, CH_2, $J_{(H–H)}$= 7.1 Hz); 7.68 (5H, m, C_6H_5); 14.80 (1H, br.s, NH) ppm. ^{19}F-NMR ($CDCl_3$) δ: 92.61 (s, CF_3) ppm. IR: 3070, 1585 (NH); 1730 (CO_2Et), 1695 (CF_3CO), 1625 (C=O); 1520 (C=C, C=N) cm^{-1}. Analysis: Found: C, 49.65; H, 3.53; F, 18.51; N, 8.85. Calc. for $C_{12}H_{11}F_3N_2O_4$: C, 49.38; H, 3.51; F, 18.02; N, 8.86%.

From chelate **6a** (2.43 g, 1.0 mmol) compound **9a** (1.52 g, yield, 44%) was obtained. The physicochemical data were identical to those listed above.

*2.2.11. Ethyl-3-(p-methylphenyl)hydrazone-5,5,5-trifluoro-2,3,4-trioxopentanoate (**9b**) (nc)*

Yield, 81%; m.p. 152–153°C; ^{1}H-NMR ($(CD_3)_2CO$) δ: 1.36 (3H, t, CH_3, $J_{(H–H)}$=7.1 Hz); 2.39 (3H, s, CH_3); 4.35 (2H, q, CH_2, $J_{(H–H)}$=7.1 Hz); 7.45 (4H, m, C_6H_4); 14.51 (1H, br.s, NH) ppm. ^{19}F-NMR ($CDCl_3$) δ: 92.72 (s, CF_3) ppm. IR: 3095, 1590 (NH); 1725 (CO_2Et), 1690 (CF_3CO), 1625 (C=O); 1525 (C=C, C=N) cm^{-1}. Analysis: Found: C, 51.15; H, 4.05; F, 17.67; N, 8.35. Calc. for $C_{14}H_{13}F_3N_2O_4$: C, 50.92; H, 3.97; F, 17.26; N, 8.48%.

*2.2.12. Ethyl-3-(p-methoxyphenyl)hydrazone-5,5,5-trifluoro-2,3,4-trioxopentanoate (**9c**) (nc)*

Yield, 69%; m.p. 131–133°C; ^{1}H-NMR ($(CD_3)_2CO$) δ: 1.34 (3H, t, CH_3, $J_{(H–H)}$=7.1 Hz); 3.87 (3H, s, OCH_3); 4.39 (2H, q, CH_2, $J_{(H–H)}$=7.1 Hz); 7.40 (4H, m, C_6H_4); 14.62 (1H, br.s, NH) ppm. ^{19}F-NMR ($CDCl_3$) δ: 92.73 (s, CF_3) ppm. IR: 3090, 1600 (NH); 1730 (CO_2Et), 1690 (CF_3CO), 1625 (C=O); 1525, 1500 (C=C, C=N) cm^{-1}. Analysis: Found: C, 48.82; H, 3.71; F, 16.29; N, 8.20. Calc. for $C_{14}H_{13}F_3N_2O_5$: C, 48.56; H, 3.78; F, 16.46; N, 8.09%.

*2.2.13. Methyl-3-(p-methoxyphenyl)hydrazone-5,5,5-trifluoro-2,3,4-trioxopentanoate (**9d**) (nc)*

Yield, 71%; m.p. 170–172°C; ^{1}H-NMR ($CDCl_3$) δ: 3.85, 3.96 (6H, s, $2CH_3$); 7.25 (4H, m, C_6H_4); 14.80 (1H, br.s, NH) ppm. ^{19}F-NMR ($CDCl_3$) δ: 90.42 (s, CF_3) ppm. IR: 3070, 1590 (NH); 1730 (CO_2Et, C=O); 1690 (CF_3CO); 1520, 1500 (C=C, C=N) cm^{-1}. Analysis: Found: C, 46.37; H, 3.36; F, 17.15; N, 8.44. Calc. for $C_{12}H_{11}F_3N_2O_4$: C, 46.99; H, 3.31; F, 17.17; N, 8.43%.

*2.2.14. Ethyl-3-phenylhydrazone-4-pentafluorophenyl-2,3,4-trioxobutanoate (**9e**) (nc)*

Yield, 91%; m.p. 123–125°C; ^{1}H-NMR ($CDCl_3$) δ: 1.45 (3H, t, CH_3, $J_{(H–H)}$=7.2 Hz); 4.42 (2H, q, CH_2, $J_{(H–H)}$= 7.2 Hz); 7.46 (5H, m, C_6H_5); 14.80 (1H, br.s, NH) ppm. ^{19}F-NMR ($CDCl_3$) δ: 1.27 (2F, m); 11.33 (1F, m); 22.73 (1F, m) ppm. IR: 3070, 1590 (NH); 1730 (CO_2Et, C=O); 1660 (C_6F_5CO); 1510, 1500 (C=C, C=N) cm^{-1}. Analysis: Found: C, 52.34; H, 2.85; F, 23.01; N, 6.34. Calc. for $C_{18}H_{11}F_5N_2O_4$: C, 52.19; H, 2.68; F, 22.93; N, 6.67%.

From chelate **6e** (3.41 g, 1.0 mmol) compound **9e** (1.37 g, yield, 40%) was obtained. The physicochemical data were identical to those listed above.

*2.2.15. Ethyl-3-(p-methylphenyl)hydrazone-4-pentafluorophenyl-2,3,4-trioxobutanoate (**9f**) (nc)*

Yield, 79%; m.p. 148–149°C; ^{1}H-NMR ($CDCl_3$) δ: 1.41 (3H, t, CH_3, $J_{(H–H)}$=7.1 Hz); 2.36 (3H, s, CH_3); 4.45 (2H, q, CH_2, $J_{(H–H)}$=7.1 Hz); 7.15 (5H, m, C_6H_5); 14.56 (1H, br.s, NH) ppm. ^{19}F-NMR ($CDCl_3$) δ: 0.92 (2F, m); 11.01 (1F, m); 22.71 (1F, m) ppm. IR: 3090, 1585 (NH); 1735 (CO_2Et); 1660 (C_6F_5CO); 1620 (C=O); 1525, 1510, 1500 (C=C, C=N) cm^{-1}. Analysis: Found: C, 53.08; H, 2.97; F, 22.17; N, 6.27. Calc. for $C_{19}H_{13}F_5N_2O_4$: C, 53.28; H, 3.06; F, 22.18; N, 6.54%.

*2.2.16. Ethyl-3-(p-methoxyphenyl)hydrazone-4-pentafluorophenyl-2,3,4-trioxobutanoate (**9g**) (nc)*

Yield, 84%; m.p. 153–155°C; ^{1}H-NMR ($CDCl_3$) δ: 1.42 (3H, t, CH_3, $J_{(H–H)}$=7.1 Hz); 4.46 (2H, q, CH_2, $J_{(H–H)}$= 7.1 Hz); 3.84 (3H, s, OCH_3); 7.15 (4H, m, C_6H_4); 14.80 (1H, br.s, NH) ppm. ^{19}F-NMR ($CDCl_3$) δ: 1.10 (2F, m); 11.73 (1F, m); 22.78 (1F, m) ppm. IR: 3080, 1585 (NH); 1730 (CO_2Et, C=O); 1665 (C_6F_5CO); 1530, 1515, 1500 (C=C, C=N) cm^{-1}. Analysis: Found: C, 51.35; H, 3.00; F, 21.21; N, 6.34. Calc. for $C_{19}H_{13}F_5N_2O_5$: C, 51.36; H, 2.95; F, 21.38; N, 6.31%.

*2.2.17. Methyl-3-phenylhydrazone-4-pentafluorophenyl-2,3,4-trioxobutanoate (**9h**) (nc)*

Yield, 91%; m.p. 123–125°C; ^{1}H-NMR ($CDCl_3$) δ: 1.45 (3H, t, CH_3, $J_{(H–H)}$=7.2 Hz); 4.42 (2H, q, CH_2, $J_{(H–H)}$= 7.2 Hz); 7.46 (5H, m, C_6H_5); 14.80 (1H, br.s, NH) ppm. ^{19}F-NMR ($CDCl_3$) δ: 1.27 (2F, m); 11.33 (1F, m); 22.73 (1F, m) ppm. IR: 3070, 1590 (NH); 1730 (CO_2Et, C=O); 1660 (C_6F_5CO); 1510, 1500 (C=C, C=N) cm^{-1}. Analysis: Found: C, 51.25; H, 2.58; F, 23.43; N, 6.79. Calc. for $C_{17}H_9F_5N_2O_4$: C, 51.01; H, 2.27; F, 23.73; N, 7.00%.

2.3. Reactions of 2-arylhydrazone-1,2,3-diketo esters with dinucleophiles

*2.3.1. 3-Nonafluorobuthyl-4-(p-methoxyphenyl) hydrazonepyrazolin-5-one (**10**) (nc)*

A solution of hydrazine hydrate (0.4 g, 8 mmol) in 10 ml of diethyl ether was added to a solution of compound **7b** (0.47 g, 1 mmol) in 20 ml of diethyl ether. The mixture was stirred at 20°C for 10 min. The solvent was removed. Recrystallization of residue from hexane gave **10** (0.35 g, 79%) as a yellow powder (m.p. 157–158°C). ^{1}H-NMR (CD_3Cl) δ: 3.85 (3H, s, OCH_3); 7.28 (4H, m, C_6H_4); 9.70, 15.3 (2H, br.s, 2NH) ppm. ^{19}F-NMR (CD_3Cl) δ: 36.52 (2F, m, CF_2); 38.92 (2F, m, CF_2); 49.66 (2F, m, CF_2); 80.92 (3F, m, CF_3) ppm. IR: 3260, 1600 (NH); 1660 (C=O); 1590, 1540, 1500 (C=N, C=C) cm^{-1}. Analy-

sis: Found: C, 38.40; H, 2.09; F, 39.02; N, 12.76. Calc. for $C_{14}H_9F_9N_4O_2$: C, 38.55; H, 2.08; F, 39.20; N, 12.84%.

2.3.2. 3-Trifluoromethyl-4-(p-methoxyphenyl) hydrazoneisoxazolin-5-one (**11**) (nc)

A mixture of compound **7a** (0.32 g, 1 mmol), hydroxylamine hydrocloride (0.28 g, 4 mmol) and NaOAc (0.2 g, 2.5 mmol) in 20 ml of methanol was refluxed for 3 h. 50 ml of water was added to the cooling mixture. The resulting precipitate was filtered off, washed with water. Recrystallization from benzene gave **11** (0.28 g, 80%) as a red powder (m.p. 140–141°C). ^{1}H-NMR ($CDCl_3$) δ: 3.87 (3H, s, OCH_3); 7.28 (4H, m, C_6H_4); 13.0 (1H, br.s, 1NH) ppm. ^{19}F-NMR ($CDCl_3$) δ: 96.52 (3F, s, CF_3) ppm. IR: 3190, 1590 (NH); 1730, 1720 (C=O); 1550, 1530, 1500 (C=N, C=C) cm^{-1}. Analysis: Found: C, 46.29; H, 2.79; F, 19.73; N, 14.68. Calc. for $C_{11}H_8F_3N_3O_3$: C, 46.00; H, 2.81; F, 19.84; N, 14.63%.

2.4. Reactions of 1,2,3-triketones arylhydrazones with dinucleophiles

2.4.1. 3-Tetrafluoroethyl-4-(p-methoxyphenyl)azo-5-methylpyrazole (**12a**)

A mixture of compound **8b** (0.32 g, 1 mmol), hydrazine hydrate (0.2 g, 4 mmol) in 10 ml of acetic acid was refluxed for 2.5 h. 50 ml of water was added to the cooled reaction mixture. The precipitate was filtered off, washed with water. Recrystallization from benzene gave **12a** (0.26 g, 83%) as a yellow powder (m.p. 182–183°C). ^{1}H-NMR ($CDCl_3$) δ: 2.64 (3H, s, CH_3); 3.88 (3H, s, OCH_3); 6.56 (1H, t.t, $H(CF_2)_2$, $J_{(H-CF_2)}$=53.7, $J_{(CF_2-HCF_2)}$=6.6 Hz); 7.44 (4H, m, C_6H_4); 12.2 (1H, br.s, 1NH) ppm. ^{19}F-NMR ($CDCl_3$) δ: 24.40 (2F, d.t, HCF_2, $J_{(H-CF_2)}$=53.7, $J_{(CF_2-HCF_2)}$=6.6 Hz); 46.25 (2F, d.t, CF_2, $J_{(CF_2-HCF_2)}$=6.6 Hz) ppm. IR: 3160, 3080, 1590 (NH); 1580, 1500, 1490 (C=N, C=C) cm^{-1}. Analysis: Found: C, 49.42; H, 3.77; F, 24.17; N, 17.74. Calc. for $C_{13}H_{12}F_4N_4O$: C, 49.41; H, 3.82; F, 24.03; N, 17.71%.

2.4.2. 3-Tetrafluoroethyl-4-phenylazo-5-methylpyrazole (**12b**) (nc)

A mixture of compound **8d** (0.3 g, 1 mmol), hydrazine hydrate (0.2 g, 4 mmol) in 10 ml of acetic acid was refluxed for 2.5 h. 50 ml of water was added to the cooled reaction mixture. The precipitate was filtered off and washed with water. Recrystallization from benzene gave **12b** (0.23 g, 81%) as a yellow powder (m.p. 180–181°C). ^{1}H-NMR ($CDCl_3$) δ: 2.65 (3H, s, CH_3); 6.54 (1H, t.t, $H(CF_2)_2$, $J_{(H-CF_2)}$=53.6, $J_{(CF_2-HCF_2)}$=5.5 Hz); 7.30 (5H, m, C_6H_5); 12.3 (1H, br.s, 1NH) ppm. IR: 3140, 3080, 1570 (NH); 1500, 1490 (C=N, C=C) cm^{-1}. Analysis: Found: C, 50.20; H, 3.33; F, 26.40; N, 19.43. Calc. for $C_{12}H_{10}F_4N_4$: C, 50.36; H, 3.52; F, 26.55; N, 19.57%.

2.4.3. 1-Phenyl-3-tetrafluoroethyl-4-(p-methoxyphenyl) azo-5-methylpyrazole (**13**) (nc)

A mixture of compound **8b** (0.32 g, 1 mmol), phenylhydrazine hydrochloride (0.58 g, 4 mmol) and NaOAc (0.21 g, 2.5 mmol) in 20 ml of methanol was refluxed for 2 h. 50 ml of water was added to the cooling reaction mixture. The precipitate was filtered off and washed with water. Recrystallization from acetic acid gave **13** (0.32 g, 82%) as a yellow powder (m.p. 115–116°C). ^{1}H-NMR ($CDCl_3$) δ: 2.63 (3H, s, CH_3); 3.88 (3H, s, OCH_3); 6.58 (1H, t.t, $H(CF_2)_2$, $J_{(H-CF_2)}$=53.5, $J_{(CF_2-HCF_2)}$=5.4 Hz); 7.46 (9H, m, C_6H_4, C_6H_5) ppm. IR: 1590, 1570, 1490 (C=N, CC, N=N) cm^{-1}. Analysis: Found: C, 58.14; H, 4.17; F, 19.23; N, 14.22. Calc. for $C_{19}H_{16}F_4N_4O$: C, 58.16; H, 4.11; F, 19.37; N, 14.28%.

2.4.4. 1-Thiocarbamoyl-3-tetrafluoroethyl-3-hydroxy-4-(p-methoxyphenyl)azo-5-methylpyrazoline (**14**) (nc)

A mixture of compound **8b** (0.32 g, 1 mmol), thiosemicarbazide (0.36 g, 4 mmol) in 20 ml of benzene: DMSO (3:1) was heated for 50 h. Benzene was removed. 50 ml of water was added to the residue. The precipitate was filtered off. Recrystallization from chloroform gave **14** (0.33 g, 84%) as a yellow powder (m.p. 125–126°C). ^{1}H-NMR ($(CD_3)_2CO$) δ: 2.22 (3H, s, CH_3); 3.79 (3H, s, OCH_3); 6.69 (1H, t.t, $H(CF_2)_2$, $J_{(H-CF_2)}$=51.7, $J_{(CF_2-HCF_2)}$=6.7 Hz); 6.7 Hz); 7.06 (4H, m, C_6H_4); 7.9, 8.6, 9.7 (4H, br.s, NH_2, NH, OH) ppm. IR: 3420, 3300, 1600 (NH); 3150 (OH); 1570, 1515, 1500 (C=N, C=C, N=N) cm^{-1}. Analysis: Found: C, 42.56; H, 3.91; F, 19.58; N, 17.54. Calc. for $C_{14}H_{15}F_4N_5O_2S$: C, 42.75; H, 3.84; F, 19.31; N, 17.88%.

2.4.5. Tetrafluoroethyl-3-hydroxy-4-(p-methylpheny)azo-5-methylisoxazoline (**15**) (nc)

A mixture of compound **8c** (0.32 g, 1 mmol), hydroxylamine hydrocloride (0.28 g, 4 mmol) and NaOAc (0.2 g, 2.5 mmol) in 20 ml of methanol was refluxed for 5 h. 50 ml of water was added to the mixture. The precipitate was filtered off. Recrystallization from chloroform gave **15** (0.25 g, 79%) as a yellow powder (m.p. 85–86°C). ^{1}H-NMR ($CDCl_3$) δ: 2.09 (3H, s, CH_3); 2.31 (3H, s, CH_3); 6.04 (1H, t.t, $H(CF_2)_2$, $J_{(H-CF_2)}$=52.7, $J_{(CF_2-HCF_2)}$= 6.2 Hz); 7.07 (4H, m, C_6H_4); 9.06 (2H, br.s, NH, OH) ppm. IR: 3350, 3120, 1600 (NH, OH); 1570, 1520, 1500 (C=N, C=C, N=N) cm^{-1}. Analysis: Found: C, 48.63; H, 4.33; F, 23.65; N, 12.88. Calc. for $C_{13}H_{13}F_4N_3O_2$: C, 48.91; H, 4.10; F, 23.80; N, 13.16%.

2.5. Heterocyclization of fluorinated 3-arylhydrazone-1,2,3,4-triketo esters

2.5.1. 3-Ethoxycarbonyl-4-phenylazo-5-trifluoromethylpyrazole (**16a**) (nc)

Hydrazine hydrate (0.2 g, 0.4 mmol) was added to a solution of compound **9a** (0.3 g, 0.1 mmol) in 10 ml of

acetic acid. The reaction mixture was refluxed for 4 h. 50 ml of water was added to the cooling mixture. The resulting precipitate was filtered off and washed with water. Reprecipitation from chloroform by hexane gave **16a** (0.21 g, 67%) as a red powder (m.p. 123–125°C). ^{1}H-NMR ($(CD_3)_2SO$) δ: 1.38 (3H, t, CH_3, $J_{(H-H)}$=7.1 Hz); 4.45 (2H, q, CH_2, $J_{(H-H)}$=7.1 Hz); 7.78 (5H, m, C_6H_5); 11.98 (1H, br.s, NH) ppm. ^{19}F-NMR ($(CD_3)_2SO$) δ: 102.3 (s, CF_3) ppm. IR: 3300, 3080, 1600 (NH); 1740 (CO_2Et) cm^{-1}. Analysis: Found: C, 50.26; H, 3.44; F, 18.04; N, 18,45. Calc. for $C_{13}H_{11}F_3N_4O_2$: C, 50.01; H, 3.55; F, 18.25; N, 17.94%.

2.5.2. 1-Phenyl-3-ethoxycarbonyl-4-(p-methoxyphenyl) azo-5-trifluoromethylpyrazole (**16b**) (nc)

Phenylhydrazine (0.12 g, 0.11 mmol) was added to a solution of compound **9c** (0.38 g, 0.11 mmol) in 30 ml of diethyl ether. The reaction mixture was refluxed for 20 h. The solvent was removed. The residue was washed with water. Recrystallization from isopropyl alcohol gave **16b** (0.34 g, 74%) as an orange powder (m.p. 114–116°C). ^{1}H-NMR ($(CD_3)_2SO$) δ: 1.13 (3H, t, CH_3, $J_{(H-H)}$=5.1 Hz); 4.29 (2H, q, CH_2, $J_{(H-H)}$=5.1 Hz); 3.87 (3H, s, OCH_3); 7.48 (5H, m, C_6H_5); 11.98 (1H, br.s, NH) ppm. ^{19}F-NMR($(CD_3)_2SO$) δ: 102.6 (s, CF_3) ppm. IR: 1725 (CO_2Et); 1595, 1580 (C=N, C=C) cm^{-1}. Analysis: Found: C, 50.26; H, 3.44; F, 18.04; N, 18,45. Calc. for $C_{13}H_{11}F_3N_4O_2$: C, 50.01; H, 3.55; F, 18.25; N, 17.94%.

2.5.3. 3-(1-Phenylhydrazone-1,2-di>xo-3,3,3-trifluoropropyl)-1,2-dihydroquinoxalin-2-one (**17a**) (nc)

A solution of *o*-phenylenediamine (0.11 g, 0.1 mmol) in 10 ml of methanol was added to a solution of compound **9a** (0.3 g, 0.1 mmol) in 15 ml of methanol. The reaction mixture was refluxed for 1 h. The resulting precipitate was filtered off. Crystallization from methanol gave **17a** (0.29 g, 85%) as an orange powder (m.p. 170–172°C). ^{1}H-NMR ($(CD_3)_2SO$) δ: 7.42 (9H, m, C_6H_5, C_6H_4); 11.72, 12.77 (2H, br.s, NH) ppm. ^{19}F-NMR ($(CD_3)_2SO$) δ: 93.23 (s, CF_3) ppm. IR: 3090, 2710, 1590 (NH); 1740 (CF_3CO); 1650 (C=O); 1530, 1510 (C=N, C=C) cm^{-1}. Analysis: Found: C, 56.70; H, 2.98; F, 15.44; N, 15.65. Calc. for $C_{17}H_{11}F_3N_4O_2$: C, 56.67; H, 3.08; F, 15.82; N, 15.55%.

2.5.4. 3-(1-Phenylhydrazone-1,2-dioxo-2-pentafluorophenylethyl)-1,2-dihydroquinoxalin-2-one (**17b**) (nc)

A solution of *o*-phenylenediamine (0.21 g, 0.05 mmol) in 15 ml of diethyl ether was added to a solution of compound **9e** (0.3 g, 0.1 mmol) in 15 ml of diethyl ether. The reaction mixture was refluxed for 1 h. The resulting precipitate was filtered off. Crystallization from methanol gave **17b** (0.2 g, 88%) as an orange powder (m.p. 280°C (decomposition)). ^{1}H-NMR ($(CD_3)_2SO$) δ: 7.44 (9H, m, C_6H_5, C_6H_4); 11.40, 12.63 (2H, br.s, NH) ppm. ^{19}F-NMR ($(CD_3)_2SO$) δ: 1.28 (2F, m); 10.43 (1F, m); 21.70 (2F, m) ppm. IR: 3100, 2710, 1590 (NH); 1685 (C_6F_5CO); 1660 (C=O); 1535, 1510 (C=N, C=C) cm^{-1}. Analysis: Found: C, 58.02; H, 2.53; F, 20.74; N, 12.02. Calc. for $C_{22}H_{11}F_5N_4O_2$: C, 57.65; H, 2.42; F, 20.73; N, 12.22%.

2.5.5. 1-(p-Methoxyphenyl)-3-ethoxalyl-5,6,7,8-tetrafluoro-1,4-dihydrocinnolin-4-one (**18a**) (nc)

Triethylamine (2.78 g, 2.75 mmol) was added to a solution of compound **9g** (2.45 g, 0.55 mmol) in 30 ml of chloroform. The reaction mixture was refluxed for 4 h. The precipitate of salt was filtered off. The filtrate was washed with 10 ml of dilute hydrochloric acid and water to pH∼7. The solvent was removed. The residue was crystallized from diethyl ether. Recrystallization from isopropyl alcohol gave **18a** (2.08 g, 89%) as a yellow powder (m.p. 74–76°C). ^{1}H-NMR ($(CD_3)_2SO$) δ: 1.26 (3H, t, CH_3, $J_{(H-H)}$=7.1 Hz); 4.33 (2H, q, CH_2, $J_{(H-H)}$=7.1 Hz); 3.86 (3H, s, OCH_3); 7.35 (4H, m, C_6H_4) ppm. ^{19}F-NMR ($(CD_3)_2SO$) δ: 5.23 (1F, m); 17.90 (1F, m); 19.79 (1F, m); 21.03 (1F, m) ppm. IR: 1740 (CO_2Et); 1710 (C=O); 1640 ($C{=}O_{cyclo}$) cm^{-1}. Analysis: Found: C, 53.51; H, 2.86; F, 18.06; N, 6.28. Calc. for $C_{19}H_{12}F_4N_2O_5$: C, 53.78; H, 2.85; F, 17.91; N, 6.60%.

2.5.6. 1-(p-Methylphenyl)-3-ethoxalyl-5,6,7,8-tetrafluoro-1,4-dihydrocinnolin-4-one (**18b**) (nc)

Triethylamine (1.01 g, 1.0 mmol) was added to a solution of compound **9h** (1.0 g, 0.25 mmol) in 15 ml of chloroform. The reaction mixture was refluxed for 1 h. The precipitate was filtered off. The filtrate was washed with 10 ml of dilute hydrochloric acid and water to pH∼7. The solvent was removed. The residue was crystallized from diethyl ether. Recrystallization from isopropyl alcohol gave **18b** (0.87 g, 93%) as a yellow powder (m.p. 109–110°C). ^{1}H-NMR ($(CD_3)_2CO$) δ: 1.30 (3H, t, CH_3, $J_{(H-H)}$=7.3 Hz); 4.35 (2H, q, CH_2, $J_{(H-H)}$=7.3 Hz); 2.47 (3H, s, CH_3); 7.51 (4H, m, C_6H_4) ppm. ^{19}F-NMR ($(CD_3)_2CO$) δ: 5.02 (1F, m); 17.24 (1F, m); 21.42 (1F, m); 22.55 (1F, m) ppm. IR: 1725 (CO_2Et); 1695 (C=O); 1640 ($C{=}O_{cyclo}$) cm^{-1}. Analysis: Found: C, 55.94; H, 2.95; F, 18.92; N, 6.81. Calc. for $C_{19}H_{12}F_4N_2O_4$: C, 55.89; H, 2.96; F, 18.61; N, 6.86%.

2.5.7. 1-Phenyl-3-(1,2-dihydroquinoxalinyl-2-one)-5,6,7,8-tetrafluoro-1,4-dihydrocinnolin-4-one (**18**) (nc)

Heating of compound **17b** (0.2 g, 0.04 mmol) at 280–290°C for 2 min gave compound **19** (0.19 g, ∼100%) as a white powder (m.p. >300°C). ^{1}H-NMR ($(CD_3)_2SO$) δ: 7.43 (9H, m, C_6H_4, C_6H_5); 12.74 (1H, br.s, NH) ppm. ^{19}F-NMR

($(CD_3)_2SO$) δ: 1.91 (1F, m); 15.80 (1F, m); 18.98 (1F,m); 20.0 (1F, m) ppm. IR: 2750, 1635 (NH); 1660 (C=O); 1500, 1490 (C=N, C=C) cm^{-1}. Analysis: Found: C, 59.84; H, 2.29; F, 17.95; N, 12.39. Calc. for $C_{22}H_{10}F_4N_4O_4$: C, 60.28; H, 2.38; F, 17.34; N, 12.78%.

3. Results and discussion

3.1. Synthesis of fluorinated 2-arylhydrazone-1,2,3-diketo esters, 2-arylhydrazones of 1,2,3-triketones and 3-arylhydrazone-1,2,3,4-triketo esters

In present work, it has been found that the fluorine-containing 1,3-keto esters **1a,b**, 1,3-diketones **2a,b** and acyl(aroyl)pyruvates **3a–g** react with aryldiazonium chlorides in water–methanol medium in presence of NaOAc to give the corresponding 2-arylhydrazone-1,2,3-diketo esters **7a–c**, 2-arylhydrazones of 1,2,3-triketones **8a–d** and 3-arylhydrazone-1,2,3,4-triketo esters **9a–h** (Scheme 1).

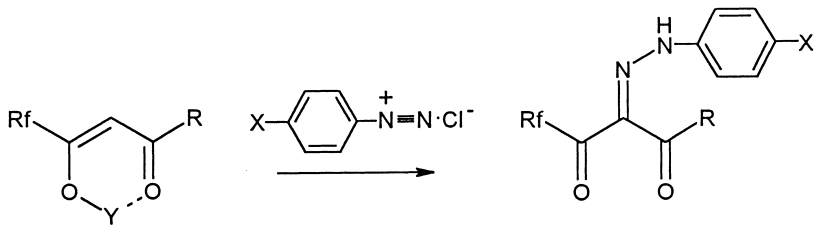
For the first time the 1,3-keto esterates of copper (II) **4d,e**, 1,3-diketonates of cooper (II) **5a**, acyl(aroyl)pyruvates of copper (II) **6a,e** and sodium **6h** were used as starting material in the coupling (Scheme 1). The use of the chelates forms the corresponding arylhydrazones with good yields, avoiding decomposition of chelates in the synthesis of free ligands.

It was proved by IR and ^{1}H-NMR spectroscopies that the obtained compounds **7a–e, 8a–d, 9a–h** exist in the hydrazo-form as their non-fluorinated analogues [1]. In the ^{1}H-NMR spectra of products **7a–e, 8a–d, 9a–e** the resonance signal of a methine proton was absent. The IR spectra of **7a–e, 8a–d, 9a–e** showed a C=O stretching absorption at 1695–1650 cm^{-1} from the keto groups of 1,3-dicarbonyl fragment. The low frequency of the C=O stretching absorption is probably the result of the conjugation of the C=N bond and participation of the C=O group in an intramolecular hydrogen bond with the aminogroup of arylhydrazone fragment.

3.2. Reactions of 2-arylhydrazone-1,3-diketo esters with dinucleophiles

Reaction of the arylhydrazone **7b** with hydrazine hydrate in diethyl ether leads to the substituted pyrazolinone **10**. Compound **7a** with hydroxylamine hydrochloride in methanol in the presence of NaOAc gives the substituted isoxazolinone **11** (Scheme 2).

Heterocycles **10, 11** may exist in azo- and hydrazoforms. Compound **10** may exist in amide- and oxyiminoforms also. The ^{19}F-NMR spectra of **10, 11** have single signals for CF_3 or C_4F_9 groups, indicating the presence of the only tautomer in each. IR data of compound **10** shows a preference for the amide form (the absorption band at 1660 cm^{-1} is typical for an amide group [15]). In the IR spectra of **10, 11**, the low frequency of the C=O stretching absorption is probably the

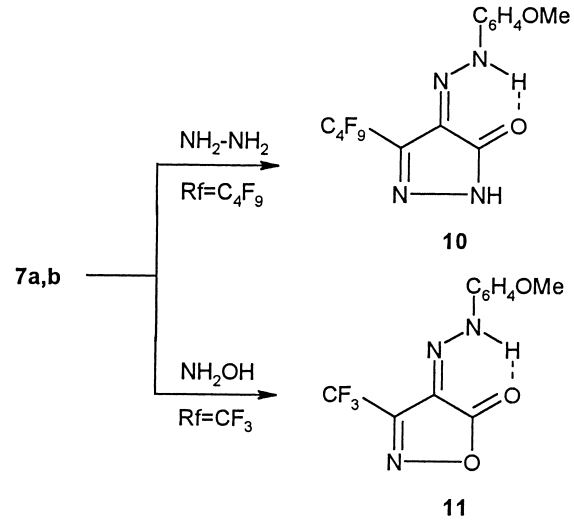


1a,b, 2a,b, 3a-g, 4d,e, 5a, 6a,e,h

7a-e, 8a-d, 9a-h

Y=H, R=OEt, Rf=CF_3, X=OMe (1a, 7a);
Rf=C_4F_9, X=OMe (1b, 7b); Me (7c);
R=Me, Rf=CF_3, X=OMe (2a, 8a);
Rf=$H(CF_2)_2$, X=OMe (2b, 8b), Me (8c), H (8d);
R=COOEt, Rf=CF_3, X=H (3a, 9a); Me (9b); OMe (9c);
R=COOMe, Rf=CF_3, X= OMe (3d, 9d);
R=COOEt, Rf=C_6F_5, X= H (3e, 9e); Me (9f); OMe (9g).
Y=$Cu/_2$, R=OMe, Rf=CF_3, X=OMe (4d, 7d);
Rf=C_3F_7, X=OMe (4e, 7e);
R=Me, Rf=CF_3, X=OMe (5a, 8a);
R=COOEt, Rf=CF_3, X=H (6a, 9a);
Rf=C_6F_5, X=H (6e, 9e);
Y=Na, R=COOMe, Rf=C_6F_5, X=H (6h, 9h).

Scheme 1.

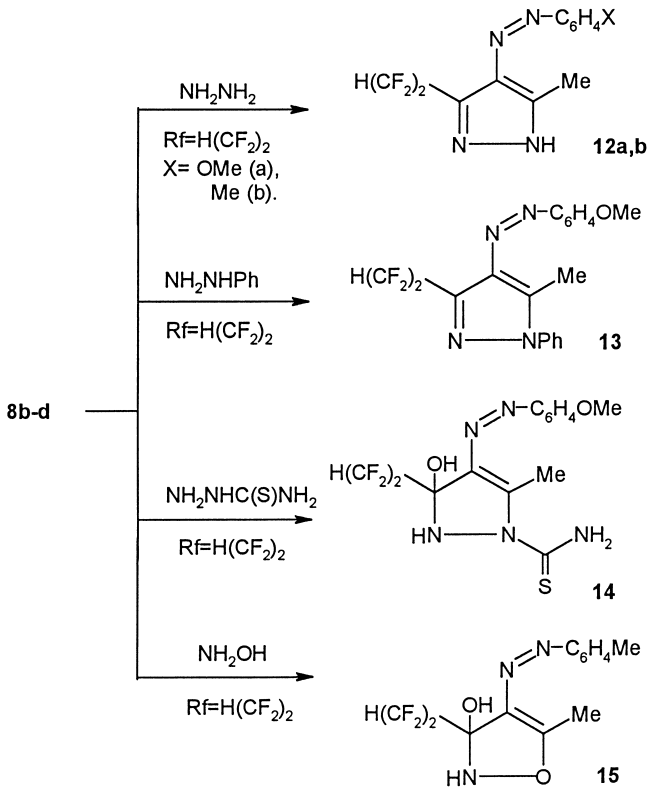


Scheme 2.

result of participation of C=O in an intramolecular hydrogen bond with the aminogroup, that is possible only in the hydrazoform.

3.3. Reactions of 1,2,3-triketones arylhydrazones with dinucleophiles

It was found that arylhydrazones **8b,c** react with hydrazine hydrate in acetic acid to form the substituted pyrazoles **12a,b** (Scheme 3). The compounds **12a,b** may exist in azo- and hydrazoforms. The ^{19}F-NMR spectrum of **12a** has one $H(CF_2)_2$ group signal, indicating the presence of the only tautomer. The IR and NMR data could be assigned to either azo- or hydrazo isomers.



Scheme 3.

Reaction of **8b** with phenylhydrazide hydrochloride in methanol in the presence of NaOAc yields the corresponding pyrazole **13**. Heating **8b** with thiosemicarbazide in DMSO: benzene leads to the substituted pyrazoline **14**. Interaction of **8c** with hydroxylamine hydrochloride in the presence of NaOAc in methanol results in the formation of isoxazoline **15** (Scheme 3).

Products **14, 15** are stable to dehydration. It is well known that the formation of hydrated heterocycles in the reactions with diamines is typical for 2-substituted fluorine-containing 1,3-dicarbonyl compounds [16,17].

3.4. Heterocyclization of fluorinated 3-arylhydrazone-1,3,2,4-triketo esters

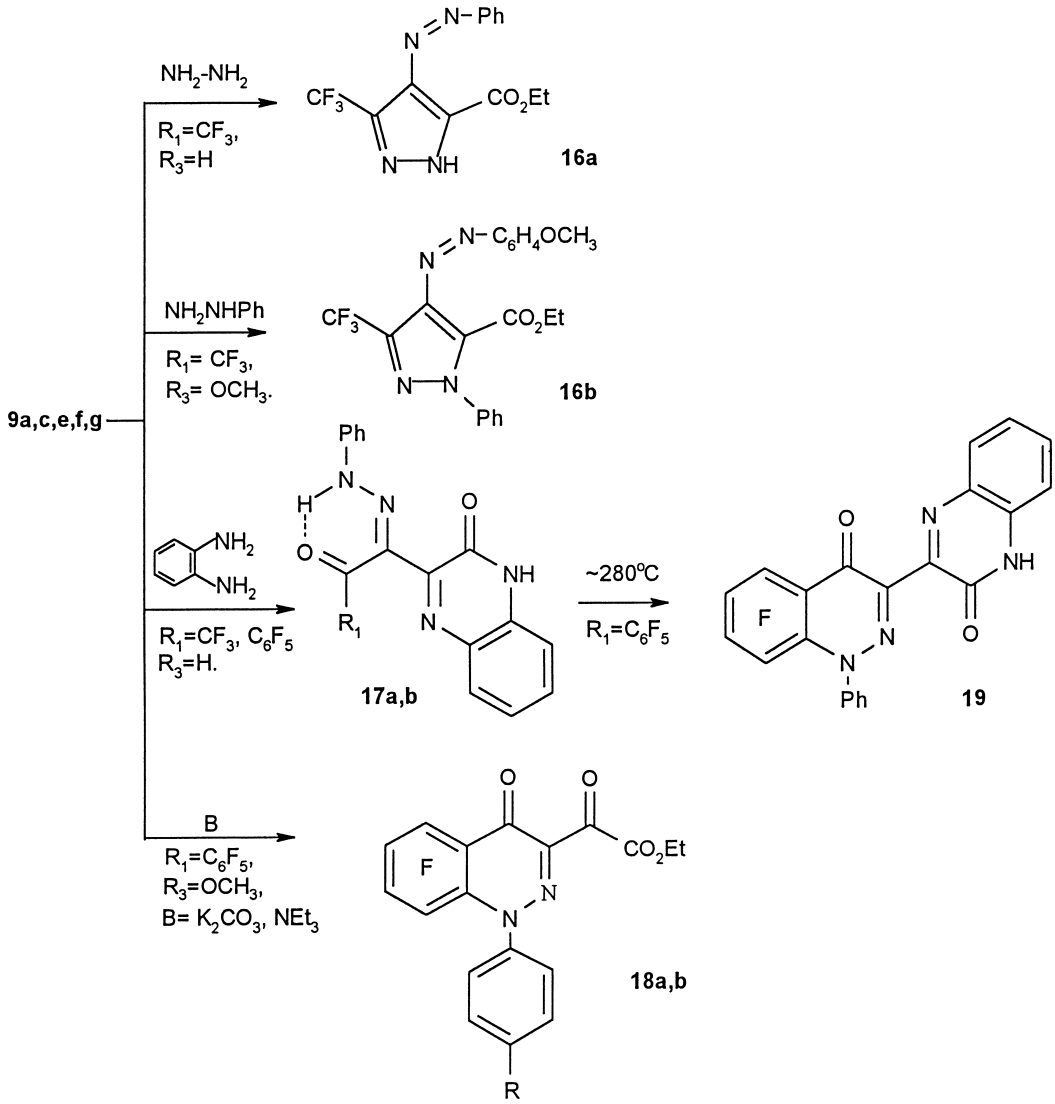
The arylhydrazones **9a–h** were used as precursors for synthesis of heterocycles. Compound **9a** reacts with hydrazine hydrate on boiling acetic acid to yield the substituted pyrazole **16a**, unlike the pentafluorophenylsubstituted analogue **9e**. A similar reaction of the latter gives a mixture of products that is difficult to separate. Interaction of **9c** with phenylhydrazine on boiling in diethyl ether for 20 h leads to pyrazole **16b**. Arylhydrazones **9a,e** react with *o*-phenylenediamine on boiling in diethyl ether to give quinoxaline derivatives **17a,b** (Scheme 4).

It is known that the arylhydrazones derived from benzoylacetic esters with *o*-fluorines [4,18] undergo intramolecular cyclization through the nucleophilic displacement of *o*-fluorine atom to give the cinnolone structure. We have found that arylhydrazones of pentafluorobenzoylpyruvic ester **9f,g** on heating at 100°C in DMSO in presence of K_2CO_3 and dibenzo-18-crown-6 or boiling in $CHCl_3$ with an excess of triethylamine form the substituted cinnolones **18a,b** (Scheme 4).

Compound **17b** undergoes also intramolecular cyclization to yield the cinnolone derivative **19**. Interestingly, that compound **19** was also obtained in the reaction of arylhydrazone **9e** with *o*-phenylenediamine on boiling in methanol as a by-product. Only under mild conditions (on boiling in diethyl ether), the formation of **19** was avoided. Compound **17b** completely converted into product **19** without decomposition on heating to ~280 (Scheme 4).

The structures of compounds **18a,b, 19** were assigned on the basis of their IR, ^{1}H and ^{19}F-NMR spectra. In the ^{19}F-NMR spectra of heterocycles **18a,b, 19**, four signals in the expected ratio were attributed to the fluorine atom of the C_6F_4 group.

In conclusion, the reactions described demonstrate the preparation of 2(3)-arylhydrazones of tri- and tetracarbonyl compounds. Interaction of these arylhydrazones with dinucleophiles is established by the behavior of the correspond-



Scheme 4.

ing di- or tricarbonyl compound and by the nucleophilic mobility of the *o*-fluorine atom of C_6F_5-substitutent.

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