JOC*Note*

Fluorinated Heterocyclic Compounds. An Expedient Route to 5-Perfluoroalkyl-1,2,4-triazoles via an Unusual Hydrazinolysis of 5-Perfluoroalkyl-1,2,4-oxadiazoles: First Examples of an ANRORC-Like Reaction in 1,2,4-Oxadiazole Derivatives

Silvestre Buscemi, Andrea Pace, Ivana Pibiri, and Nicolò Vivona*

Dipartimento di Chimica Organica "E. Paternò", Università degli Studi di Palermo, Viale delle Scienze − Parco d'Orleans II, I-90128 Palermo, Italy

Domenico Spinelli

Dipartimento di Chimica Organica "A. Mangini", Università degli Studi di Bologna, Via S. Donato 15, I-40127 Bologna, Italy

nvivona@unipa.it

Received August 2, 2002

Abstract: The hydrazinolysis reaction of 5-perfluoroalkyl-1,2,4-oxadiazoles has been investigated. Nucleophilic addition of the reagent to the C(5)−N(4) double bond of the oxadiazole ring, followed by ring-opening and then ring-closure involving the β-nitrogen atom of the hydrazino moiety and the C(3) of the oxadiazole ring, explains the formation of 5-perfluoroalkyl-1,2,4-triazoles as final products. Useful applications in synthesis of this uncommon hydrazinolysis can be claimed.

Because of the wide application of fluorinated heterocyclic compounds in medicinal and agricultural fields as well as in new material sciences and fluorine chemistry, a growing interest is devoted to pointing out more convenient synthetic procedures for target molecules.[1] In this respect, besides the direct introduction of fluorine or a fluorinated group into a given heterocycle, the construction of a heterocyclic ring from fluorinated noncyclic precursors through conventional heterocyclization reactions appears to be a widely exploitable procedure.[1]

In our opinion, a promising strategy could be found among the enormous variety of ring interconversion reactions[2,3] which can be promoted thermally or photochemically.[4] This means that an easily accessible fluorinated heterocycle can be used as a fluorinated synton or precursor and then converted into a different one that could be otherwise constructed with difficulty. In this regard, we have recently emphasized a photochemical approach that consists of a photoinduced ring opening (through an O−N bond cleavage) of fluorinated 1,2,5-oxadiazoles (furazans) in the presence of reagents able to form intermediates that will develop into different heterocyclic structures.[5]

Among ring-to-ring interconversion reactions, it appears noteworthy to consider processes that require addition of a nucleophile, followed by ring-opening and ring-closure steps (a ANRORC-like pattern).[3] These reactions, which are well documented in the azine series[3,6] due to their large π-deficiency, appear to be less exploited in the case of five-membered ring derivatives. Some interesting examples include 1,3,4-oxadiazoles,[7] 1,3,4-thiadiazoles,[8] or nitroimidazoles,[3,9] which are highly susceptible to nucleophilic attack. With regard to possible applications of these reactions for the synthesis of fluorinated five-membered heterocycles, an interesting example can be recognized in the aminolysis or hydrazinolysis of fluorinated 1,3,4-oxadiazoles leading to fluorinated 1,2,4-triazoles directly or through subsequent heterocyclization of intermediates.[10]

As concerns the 1,2,4-oxadiazole ring, despite its extensive use in the Boulton−Katritzky-type rearrangements[2b−f,11] or photoinduced rearrangements,[12] scanty information has been reported on the use of this heterocycle for ring-opening/ring-closure processes by means of nucleophilic reagents. As a matter of fact notwithstanding their low aromaticity 1,2,4-oxadiazoles are considered hydrolysis-resistant isosteres of an ester or of an amide functionality.[13,14] On the other hand 5-trifluoromethyl-

(1) (a) Chambers, R. D.; Sargent, C. R. *Adv. Heterocycl. Chem*. **1981**, *28*, 1−71. (b) Silvester, M. J. *Adv. Heterocycl. Chem*. **1994**, *59*, 1−38. (c) Burger, K.; Wucherpfennig, U.; Brunner, E. *Adv. Heterocycl. Chem*. **1994**, *60*, 1−64. (d) Furin, G. G. *Targets in Heterocyclic Systems*; Attanasi, O. A., Spinelli, D., Eds.; Societa Chimica Italiana: Roma, 1998; Vol. 2, pp 355−441.

(2) For heterocyclic rearrangements, see: (a) Van der Plas, H. C. *Ring Transformations of Heterocycles*; Academic: New York, 1973; Vols. 1 and 2. (b) Boulton, A. J.; Katritzky, A. R.; Hamid, A. M. *J. Chem. Soc. C* **1967**, 2005−2007. (c) Afridi, A. S.; Katritzky, A. R.; Ramsden, C. A. *J. Chem. Soc., Perkin Trans. 1* **1976**, 315−320. (d) Ruccia, M.; Vivona, N.; Spinelli, D. *Adv. Heterocycl. Chem*. **1981**, *29*, 141−169. (e) L'abbé, G. *J. Heterocycl. Chem*. **1984**, *21*, 627−638. (f) Vivona, N.; Buscemi, S.; Frenna, V.; Cusmano, G. *Adv. Heterocycl. Chem*. **1993**, *56*, 49−154.

(3) Van der Plas, H. C. *Adv. Heterocycl. Chem*. **1999**, *74*, 1−253.

(4) For photoinduced rearrangements of five-membered heterocycles, see: (a) Padwa, A. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 501−547. (b) D'Auria, M. *Heterocycles* **1999**, *50*, 1115−1135. (c) D'Auria, M. In *Targets in Heterocyclic Systems*; Attanasi, O. A., Spinelli, D., Eds.; Società Chimica Italiana: Roma, 1999; Vol. 2, pp 233−279. (d) D'Auria, M. *Adv. Heterocycl. Chem*. **2001**, *79*, 41−88.

(5) (a) Buscemi, S.; Pace, A.; Vivona, N. *Tetrahedron Lett*. **2000**, *41*, 7977−7981. (b) Buscemi, S.; Pace, A.; Calabrese, R.; Vivona, N.; Metrangolo P. *Tetrahedron* **2001**, *57*, 5865−5871.

(6) Inter alia, see: (a) Dickinson, R. G.; Jacobsen, N. W. *Aust. J. Chem*. **1975**, *28*, 2435−2446. (b) Rykowski, A.; Wolinska, E. *Tetrahedron Lett*. **1996**, *37*, 5795−5796. (c) Rykowski, A.; Branowska, D. *Heterocycles* **1996**, *43*, 2095−2098. (d) Chupakhin, O. N.; Kozhevnikov, V. N.; Kozhevnikov, D. N.; Rusinov, V. L. *Tetrahedron Lett*. **1999**, *40*, 6099−6100. (e) Chupakhin, O. N.; Kozhevnikov, V. N.; Prokhorov, A. M.; Kozhevnikov, D. N.; Rusinov, V. L. *Tetrahedron Lett*. **2000**, *41*, 7379−7382.

(7) (a) Hetzheim, A.; Mockel, K. *Adv. Heterocycl. Chem*. **1966**, *7*, 183−224. (b) Reid, J. R.; Heindel, N. D. *J. Heterocycl. Chem*. **1976**, *13*, 925−926.

(8) Sandstrom, J. *Adv. Heterocycl. Chem*. **1968**, *9*, 165−209.

(9) Suwinski, J.; Pawlus, W.; Salwinska, E.; Swierczek, K. *Heterocycles* **1994**, *37*, 1511−1520.

(10) (a) Reitz, D. B.; Finkes, M. J. *J. Heterocycl. Chem*. **1989**, *26*, 225−230. (b) Reitz, D. B.; Finkes, M. J. *J. Org. Chem*. **1989**, *54*, 1760−1762. (c) Critchley, J. P.; Pippett, J. S. *J. Fluorine Chem*. **1973**, *2*, 137−156.

(11) For mechanistic studies on azole-to-azole interconversion reactions of the Boulton−Katritzky-type, see: Cosimelli, B.; Guernelli, S.; Spinelli, D.; Buscemi, S.; Frenna, V.; Macaluso, G. *J. Org. Chem*. **2001**, *66*, 6124−6129 and references therein for several papers on this series from the Spinelli research group.

10.1021/jo0262762 CCC: $25.00
Published on Web 12/07/2002

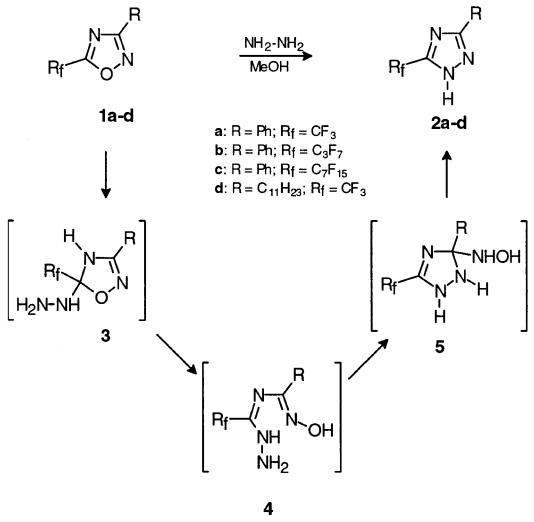
1,2,4-oxadiazoles are hydrolyzed to amidoximes by the action of ammonia at room temperature through a nucleophilic addition at the C(5) of the ring.[15,16] The occurrence of this nucleophilic attach at C(5) is strictly linked to the strong electron-withdrawing effect of the trifluoromethyl group (σ_I +0.40),[17] which makes C(5) electron-deficient and thus prone to nucleophilic attack. By contrast, for the 5-perfluoropropyl-3-phenyl-1,2,4-oxadiazoles the failure of the aminolysis reaction (with methylamine) is reported.[10c]

For this reason, in the course of our studies[5,18] on fluorinated five-membered heterocycles aimed at pointing out new methodologies for their synthesis, we have now investigated the hydrazinolysis reaction of the 5-perfluoroalkyl-1,2,4-oxadiazoles **1a**−**d**, which can be easily obtained by the reaction of the proper amidoxime with a fluorinated acylating reagent.

The reaction of compounds **1a**−**d** with hydrazine in methanol at room temperature allowed us to directly isolate triazoles **2a**−**d** (Scheme 1). Their identity was confirmed by analytical and spectroscopic evidences, as well as by comparison with an authentic sample of **2a**.[19] Yields of isolated products (44−88%) were not optimized, and their variation depends on the nature of the perfluoroalkyl group, which exerts its effect both on the nucleophilic attack of the reagent and on the subsequent reaction of the resulting intermediates. Interestingly, the reaction was markedly favored (both in reactivty and yields of isolated products) when carried out in DMF as a solvent at room temperature (see Experimental Section). In a representative experiment, yields of **2b** increased from 58% (in methanol, after 48 h) to 74% (in DMF, after just 1 h). In our opinion, this result assumes great significance in a preparative-scale application of the reaction.

The formation of triazoles **2a**−**d** clearly indicates that (i) the 5-perfluoroalkyl-1,2,4-oxadiazoles easily undergo

SCHEME 1



hydrazinolysis due to the presence of the fluorinated group at C(5) of the ring. In regard to this, it is worth noting that in our hands neither the 3,5-diphenyloxadiazole nor the 5-methyl-3-phenyloxadiazole and the fluorinated regioisomer of **1c** 3-perfluoroheptyl-5-phenyl-1,2,4-oxadiazole react with hydrazine under the above experimental conditions. (ii) After the initial nucleophilic addition to C(5)−N(4) double bond of the oxadiazole followed by the ring-opening, a subsequent ring-closure step involves the C(3) of the starting oxadiazole ring and the β nitrogen atom of the reagent, which acts as a bidentate nucleophile. The final product will then arise through displacement of the hydroxylamine component from the supposed intermediate **5**. On the whole, the driving force of the reaction could be found in the ability of the key species **4** to develop through a new heterocyclization giving rise to very stable 1,2,4-triazole derivatives.[11] The observed marked solvent effect can be ascribed both to the enhanced nucleophilic character of the reagent in the first step of the reaction and to the fact that DMF could favor to some extent subsequent steps. Because of its properties,[20] DMF is a better solvent than methanol for reactions occurring through a nucleophilic attack, especially when neutral nucleophiles are involved. The values of its relative permittivity (relative dielectric constant, $\epsilon_r = 36.71$),[20,21] donicity (an estimate of electron-donor ability; normalized donor number, $DN^N = 0.69$),[20,22] and hydrogen-bond donor character (normalized constant, $E_T^N = 0.404$)[20,23] represent a combination able to make this aprotic dipolar solvent an "excellent" medium for all the nucleophilic reactions (addition as well as substitution). On the other hand, the use of this aprotic solvent would minimize unproductive hydrolysis of open chain intermediates.[24]

(12) (a) Vivona, N.; Buscemi, S. *Heterocycles* **1995**, *41*, 2095−2116 and references therein. (b) Buscemi, S.; Vivona, N.; Caronna, T. *J. Org. Chem*. **1995**, *60*, 4096−4101. (c) Buscemi, S.; Vivona, N.; Caronna, T. *J. Org. Chem*. **1996**, *61*, 8397−8401. (d) Vivona, N.; Buscemi, S.; Asta, S.; Caronna, T. *Tetrahedron* **1997**, *53*, 12629−12636. (e) Buscemi, S.; Pace, A.; Vivona, N.; Caronna, T.; Galia, A. *J. Org. Chem*. **1999**, *64*, 7028−7033. (f) Buscemi, S.; Pace, A.; Vivona, N.; Caronna, T. *J. Heterocycl. Chem*. **2001**, *38*, 777−780. (g) Buscemi, S.; Pace, A.; Pibiri, I.; Vivona, N. *J. Org. Chem*. **2002**, *67*, 6253−6255.

(13) Jochims, J. C. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds; Pergamon: Elsevier Science, 1996; Vol. 4, pp 179−228.

(14) Differently from 3,5-disubstituted 1,2,4-oxadiazoles, monosubstituted derivatives are markedly less stable under hydrolytic conditions.[13]

(15) (a) Andrianov, V. G.; Eremev, A. V.; Sheremet, Yu. B. *Chem. Heterocycl. Compd. (Engl. Transl.)* **1988**, *24*, 707. (b) Andrianov, V. G.; Semenikhina, V. G.; Eremev, A. V. *Chem. Heterocycl. Compd. (Engl. Transl.)* **1991**, *27*, 651−656.

(16) Differently from 5-trichloromethyl-1,2,4-oxadiazoles, for which displacement of the trichloromethyl group has been observed under the influence of nucleophiles,[13] bis(5-trifluoromethyl-1,2,4-oxadiazol-3-yl) reacts with alcoholic potassium or sodium hydroxide furnishing stable anionic σ-adducts [Andrianov, V. G.; Eremev, A. V. *Chem. Heterocycl. Compd. (Engl. Transl.)* **1990**, *26*, 714].

(17) Exner, O. *Correlation Analysis of Chemical Data*; Plenum Press: New York, 1988.

(18) (a) Buscemi, S.; Pace, A.; Frenna, V.; Vivona, N. *Heterocycles* **2002**, *57*, 811−823. (b) Buscemi, S.; Pace, A.; Pibiri, I.; Vivona, N. *Heterocycles* **2002**, *57*, 1891−1896.

(19) Funabiki, K.; Noma, N.; Kuzuya, G.; Matsui, M.; Shibata, K. *J. Chem. Res., Synop.* **1999**, 300−301; *J. Chem. Res., Miniprint* **1999**, 1301−1308 and references therein for recent literature on fluorinated 1,2,4-triazoles.

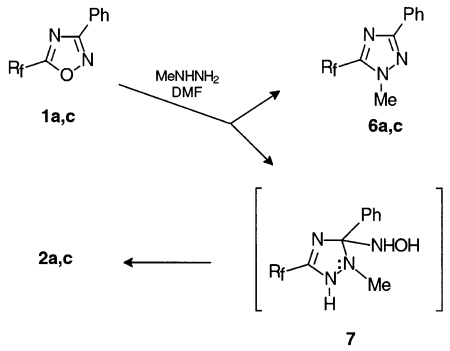
(20) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, Germany, 1988.

(21) (a) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. Organic Solvents. In *Techniques of Chemistry*, 4th ed.; Weissberger, A., Ed.; Wiley−Interscience: New York, 1986; Vol. 2. (b) Maryott, A. A.; Smith, E. R. *Table of Dielectric Constants of Pure Liquids*; NBS Circular 514; National Bureau of Standards: Washington, DC, 1951.

(22) (a) Schmid, R. *J. Sol. Chem*. **1983**, *12*, 135−152. (b) Marcus, Y. *J. Sol. Chem*. **1984**, *13*, 599−624.

(23) Reichardt, C.; Harbusch-Görnert, E. *Liebigs Ann. Chem*. **1983**, 721−743.

SCHEME 2



We then considered the reaction of representative 5-perfluoroalkyl-1,2,4-oxadiazoles **1a** and **1c** with methylhydrazine, from which two different triazole regioisomers could be expected, and for these experiments we chose the highly favorable DMF conditions. Interestingly, the reaction of **1c** with methylhydrazine gave the 1-methyltriazole regioisomer **6c** (49%) and the unexpected demethylated triazole **2c** (22%). The structure of **6c** (between the two possible regioisomers) has been confirmed both by the low-field chemical shift of the *N*-methyl signal and by analysis of the mass spectrum showing the [$PhCNH^+$] fragment. The formation of **6c**, in which the more nucleophilic methyl-substituted nitrogen of the reagent is involved, follows a reaction pathway strictly similar to that reported in Scheme 1 for **2a**−**d**. Since the isolated **6c** does not give demethylation at all in DMF under reaction conditions, an intriguing hypothesis to explain the formation of **2c** from **1c** and methylhydrazine could consider an intramolecularly assisted demethylation of the possible intermediate **7** (formed when the unsubstituted nitrogen of the reagent acts as a nucleophile during the first step). Obviously, when one considers the formation of **7** and its aromatization into the final triazole **2c**, the choice between a concerted or multistep mechanism for the involved processes as well as the role of the solvent remains an open question. However, the proposed pathway well fit with structure **6c** assigned to the isolated *N*-methyltriazole regioisomer.

As expected, regioselectivity of the nucleophilic attack by one of the two centers of methylhydrazine on the oxadiazole ring will depend on the steric effects of the C(5) fluorinated group. In fact, the reaction of the 5-trifluoromethyl derivative **1a** and methylhydrazine in DMF essentially gave the 1-methyl triazole regioisomer **6a** (70%), whereas only a small percent of the corresponding **2a** was detected. A deeper investigation on this aspect of the reactivity will follow.

On the whole, these results interestingly show that 5-perfluoroalkyl-1,2,4-oxadiazoles can really be considered useful synthons for the synthesis of 5-perfluoroalkyl-1,2,4-triazoles.[19] Work currently in progress aims to generalize this useful synthetic approach by exploiting different bidentate nucleophiles.

(24) In the hydrazinolysis reaction carried out in DMF, significant competition of the formed hydroxylamine (as a bidentate nucleophile) towards the attack at C(5) of the starting oxadiazole was observed to some extent, depending on the substrate and on the molar ratio of the reagents. This peculiar aspect of the reactivity will be investigated elsewhere.

Experimental Section

Materials and Methods. For instruments and general procedures, see our previous papers.[12,18] IR spectra were recorded from Nujol mulls. ^{1}H NMR spectra (250 MHz) were taken with TMS as an internal standard. Flash chromatography was performed by eluting with mixtures of light petroleum (fraction boiling in the range of 40−60 °C) and ethyl acetate in varying ratios.

Compounds **1a**,[25] **1b**,[10c] and **1c**,[10c] were prepared as reported. Compound **1d** was prepared by a similar procedure.

5-Trifluoromethyl-3-undecyl-1,2,4-oxadiazole (1d). A mixture of dodecanamidoxime[26] (2 g; 9.4 mmol) and trifluoroacetic anhydride (1.5 mL; 10.6 mmol) in anhydrous toluene (100 mL) was refluxed for 8 h. After removal of the solvent, the residue was treated with water and then extracted with EtOAc. The organic layers were dried over Na_2SO_4 and evaporated. Chromatography of the residue gave 5-trifluoromethyl-3-undecyl-1,2,4-oxadiazole (**1d**) (1.5 g, 54%), oil: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7 Hz, 3H), 1.20−1.40 (m, 16H), 1.73−1.84 (m, 2H), 2.64 (t, J = 7 Hz, 2H); MS m/z 292 (M^+, 100), 192 (10), 178 (11), 81 (9). Anal. Calcd for $C_{14}H_{23}F_3N_2O$: C, 57.52; H, 7.93; N, 9.58. Found: C, 57.30; H, 8.10; N, 9.40.

General Procedure for Hydrazinolysis of 3-Phenyl-5-perfluoroalkyl-1,2,4-oxadiazoles (1a−d) in Methanol. To a sample of **1a**−**d** (1.5 mmol) in dry methanol (50 mL) was added an excess of 99% hydrazine monohydrate (7.5 mmol), and the mixture was left at room temperature for 48 h. After removal of the solvent under reduced pressure, the residue was worked-up with water. In the case of **1c**, filtration of insoluble material gave **2c**. In the cases of **1a**, **1b**, or **1d** the mixture was extracted with EtOAc, which was dried over Na_2SO_4 and evaporated and the residue chromatographed.

Hydrazinolysis of the Oxadiazole 1a. Hydrazinolysis of **1a** gave 3-phenyl-5-trifluoromethyl-1,2,4-triazole (**2a**) (0.14 g; 44%), mp 160−162°C (from water) [lit.[19] 147.6−147.9 °C (from hexanes−Et_2O)]. In our hands, a sample of **2a** prepared by the method previously reported[19] had a mp = 158−160 °C (from water).

Hydrazinolysis of the Oxadiazole 1b. Hydrazinolysis of **1b** gave 3-phenyl-5-perfluoropropyl-1,2,4-triazole (**2b**) (0.27 g; 58%), mp 125 °C (from water); IR 3140, 3070 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.62−7,65 (m, 3H), 8.09−8.12 (m, 2H), 15.46 (br s, 1H); MS m/z 313 (M^+, 27), 312 (100), 193 (70), 103 (33), 76 (21), 68 (14). Anal. Calcd for $C_{11}H_6F_7N_3$: C, 42.19; H, 1.93; N, 13.42. Found: C, 42.30; H, 2.10; N, 13.20.

Hydrazinolysis of the Oxadiazole 1c. Hydrazinolysis of **1c** gave 3-phenyl-5-perfluorohepthyl-1,2,4-triazole (**2c**) (0.68 g, 88%), mp 127 °C (from water); IR 3130, 3090 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.62−7.64 (m, 3H), 8.07−8.11 (m, 2H), 15.40 (br s, 1H); MS m/z 513 (M^+, 45), 193 (100), 103 (32), 68 (27). Anal. Calcd for $C_{15}H_6F_{15}N_3$: C, 35.11; H, 1.18; N, 8.19. Found: C, 35.30; H, 1.40; N, 8.00.

Hydrazinolysis of the Oxadiazole 1d. Hydrazinolysis of **1d** gave 5-trifluoromethyl-3-undecyl-1,2,4-triazole (**2d**) (0.30 g; 68%), oil: IR 3140 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 0.91 (t, J = 7 Hz, 3H), 1.20−1.40 (m, 16H), 1.70−1.85 (m, 2H), 2.62 (t, J = 7 Hz, 2H), 14.48 (br s, 1H); MS m/z 291 (M^+, 100), 261 (19), 219 (15), 150 (23). Anal. Calcd for $C_{14}H_{24}F_3N_3$: C, 57.71; H, 8.30; N, 14.42. Found: C, 57.50; H, 8.10; N, 14.20.

Hydrazinolysis of 3-Phenyl-5-perfluoroalkyl-1,2,4-oxadiazoles (1a−d) in DMF. To a sample of compounds **1a**−**d** (1.5 mmol) in dry DMF (2 mL) was added an excess of 99% hydrazine monohydrate (7.5 mmol), and the mixture was left at room temperature for 1 h (for **1a**,**b**,**d**) or 10 h (for **1c**). After dilution with water, the mixture was extracted with EtOAc, which was

(25) Durden, J. A.; Heywood, D. L. *J. Org. Chem*. **1971**, *36*, 1306−1307.

(26) Japanese Kokai, Tokyo, 1984; *Chem. Abstr*. **1985**, *102*, 135675.

dried and then evaporated. Chromatography of the residue gave **2a** (0.22 g; 70%), **2b** (0.35 g; 74%), **2c** (0.70 g; 91%), or **2d** (0.31 g; 70%), respectively.

Hydrazinolysis of 3-Phenyl-5-perfluoroalkyl-1,2,4-oxadiazoles (1a and 1c) with Methylhydrazine in DMF. To a sample of **1a** or **1c** (1.5 mmol) in dry DMF (2 mL) was added an excess of methylhydrazine (7.5 mmol), and the mixture was left at room temperature for 1 h (for **1a**) or 10 h (for **1c**). After dilution with water, the mixture was extracted with EtOAc, which was dried and evaporated and the residue chromatographed.

Hydrazinolysis of the Oxadiazole 1a with Methylhydrazine. Hydrazinolysis of **1a** gave 1-methyl-3-phenyl-5-trifluoromethyl-1,2,4-triazole (**6a**)[27] (0.24 g; 70%) and **2a** (0.020 g; 6%). Compound **6a**, oil: ^{1}H NMR ($CDCl_3$) δ 4.07 (s, 3H), 7.52−7.58 (m, 3H), 7.70−7.73 (m, 2H); MS *m*/*z* 227 (M^+, 100), 103 ($PhCN^+$, 12), 63(3). Anal. Calcd for $C_{10}H_8F_3N_3$: C, 52.87; H, 3.55; N, 18.50. Found: C, 52.70; H, 3.50; N, 18.30.

Hydrazinolysis of the Oxadiazole 1c with Methylhydrazine. Hydrazinolysis of **1c** gave 1-methyl-3-phenyl-5-perfluoroheptyl-1,2,4-triazole (**6c**) (0.39 g; 49%) and **2c** (0.17 g; 22%). Compound **6c** had a mp = 52 °C (from light petroleum): ^{1}H NMR ($CDCl_3$) δ 4.09 (s, 3H), 7.55−7.59 (m, 3H), 7.70−7.74 (m, 2H); MS *m*/*z* 527 (M^+, 100), 508 (10), 208 (55), 104 ($PhCNH^+$, 25), 68 (18). Anal. Calcd for $C_{16}H_8F_{15}N_3$: C, 36.45; H, 1.53; N, 7.97. Found: C, 36.30; H, 1.40; N, 7.80.

Acknowledgment. Financial support from Italian MIUR within the National Research Project "Fluorinated Compounds: New Materials for Advanced Applications" is gratefully acknowledged.

JO0262762

(27) Burger, K.; Thomas, K. *Chem. Ztg.* **1988**, *112*, 109−111; *Chem. Abstr.* **1989**, *110*, 23805.