Polish J. Chem., **76**, 1713–1720 (2002)

Hydrogen Peroxide Oxidation of N,N-Dimethylhydrazones Promoted by Selenium Compounds, Titanosilicalites or Acetonitrile

by M. Giurg, J. Młochowski[*] and A. Ambrożak

Institute of Organic Chemistry, Biochemistry and Biotechnology, Wrocław University of Technology,
Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

(Received August 20th, 2002; revised manuscript September 30th, 2002)

Hydrogen peroxide oxidation of N,N-dimethylhydrazones **1** promoted by title reagents has been investigated. Depending on the substrate nitrile **2** and/or amide **3** accompanied with carboxylic acid **4** and parent carbonyl compounds **5** were obtained. Formation of nitriles **2** with H_2O_2–acetonitrile system is limited for a few more active substrates. The mechanism of the reaction, based on generated *in situ* peroxyiminoacetic acid, is presented. A broad spectrum of aliphatic, unsaturated and aromatic nitriles **2** was obtained by oxidation of corresponding N,N-dimethylhydrazones **1** with hydrogen peroxide in the presence of poly(bis-9,10-anthracenyl) diselenide (PADS) (**7**) as catalyst.

Key words: oxidation, hydrogen peroxide, diselenides, hydrazones, nitriles, amides

Oxidation of organic compounds with hydrogen peroxide is a current problem of synthetic organic chemistry, because the oxidant is cheap, environmentally friendly and useful for large scale synthesis [1,2]. Unfortunately the activity of hydrogen peroxide toward many organic substrates is too low and numerous oxygen-transfer catalysts, making oxidation more effective, must be used. Among them, titanosilicalites, nitriles and selenium compounds have been reported as efficient hydrogen peroxide activators [3–7].

The broad spectrum of different compounds was oxidized by hydrogen peroxide in the presence of these promotors, among them N,N-dimethylhydrazones which produced nitriles. The conversion of azomethine group into cyano group is of particular interest in cases when other reactions are ineffective [8]. The mechanism of the reaction, although postulated previously [8–10], seems to be still disputable.

Our earlier works have shown that N,N-dimethylhydrazones were efficiently converted to nitriles by hydrogen peroxide oxidation in the presence of selenium compounds, such as 2-nitrobenzeneseleninic acid and 2-phenyl-1,2-benzisoselenazol-3(2H)-one (ebselen) [11,12]. Well known hydrogen peroxide containing reagent, the H_2O_2–acetonitrile or H_2O_2–benzonitrile system, although was applied for oxidation of different groups of organic substrates [7,13,14], to our knowledge has never been used for oxidation of N,N-dimethylhydrazones. Other extensively used

---

[*] Author for correspondence.

hydrogen peroxide oxidation catalysts – titanosilicalites [6,15] have also not been used for this purpose.

Extending our earlier works on the oxidative transformation of the carbonyl compounds and their azomethine derivatives [16–18], in this paper we report on our recent studies on the oxidation of aliphatic and aromatic N,N-dimethylhydrazones. Hydrogen peroxide was used as an stoichiometric oxidant in the presence of promotors such as titanosilicalites, acetonitrile and recently obtained in our laboratory organoselenium compounds. The reaction proceeded according to Scheme 1. Depending on the substrate used and the reaction conditions nitriles **2** and/or amides **3**, accompanied with carboxylic acids **4** and parent carbonyl compounds **5**, were produced.

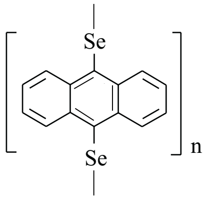
Scheme 1

$$\underset{\mathbf{1}}{\mathrm{RCH{=}N\text{-}NMe_2}} \xrightarrow{\text{oxidant}} \underset{\mathbf{2}}{\mathrm{RCN}} + \underset{\mathbf{3}}{\mathrm{RCONH_2}} + \underset{\mathbf{4}}{\mathrm{RCOOH}} + \underset{\mathbf{5}}{\mathrm{RCHO}}$$

oxidant: 30% H_2O_2/MeCN/Na_2CO_3 (Method A); 30% H_2O_2/MeCN (Method B); 30% H_2O_2/PADS (cat.) (Method C)

1-4	**R**	**1-4**	**R**	**1-4**	**R**
a	2-(5-NO_2furyl)-	**g**	3-CH_3O-C_6H_4-	**m**	$CH_3(CH_2)_6$-
b	4-$NO_2C_6H_4$-	**h**	4-CH_3O-C_6H_4-	**n**	$C_3H_7(CH_3)CH$-
c	4-$HOCOC_6H_4$-	**i**	4-$CH_3C_6H_4$-	**o**	$CH_3(CH_2)_8$-
d	4-$CH_3OCOC_6H_4$-	**j**	$C_6H_5CH{=}CH$-	**p**	4-NCC_6H_4-
e	4-BrC_6H_4-	**k**	$C_6H_5CH_2CH_2$-	**q**	4-$(Me_2NN{=}CH)C_6H_4$-
f	2,4-$Cl_2C_6H_3$-	**l**	cyclohexyl	**r**	2-$NaOSO_2C_6H_4$-

PADS =



Two titanosilicalites, prepared according to ref. [19] (non calcinated TS-1a and calcinated TS-1b), were used as the catalyst for oxidation of (4-bromophenyl)-N,N-dimethylhydrazone (**1e**) selected as a model substrate. The reaction was carried out in acetonitrile as a solvent for 6 h at temperature 65°C or for 48 h at room temperature. In these conditions nitrile **2e** was formed in 73–80% yield (based on the converted substrate **1e**) but conversion of hydrazone **1e** was low (29–42%). Surprisingly, similar results were obtained without catalyst (yield; 69–79%, conversion; 29–38%).

It can be explained according to postulated earlier mechanism where generated *in situ* peroxyiminoacetic acid (**6**) is an active oxygen donor [7,20]. Since it has been known that sodium carbonate as a base promotes formation of peroxyiminoacetic acid from acetonitrile [7,21], we used the mixture 30% H_2O_2 – MeCN (v/v 1:5) and Na_2CO_3 for oxidation of different N,N-dimethylhydrazones (**1a–o**). The products were nitriles **2d–o**, aromatic amides **3a–i**, carboxylic acids **4b–i**, **4k**, **4m–o** and parent aliphatic aldehydes **5k**, **5m–o** (Table 1). Oxidation of N,N-dimethylhydrazones derived from aliphatic **1k–o**, unsaturated **1j** and aromatic aldehydes having electron-donating **1g–i** or halogen substituents **1e** and **1f** in benzene ring gave nitriles **2e–o** as major products accompanied in some cases with amides **3** and acids **4**. When strong electron-withdrawing substituent was present in the aromatic ring, amides **3a–d** were the final products. Most probably during the long reaction period, the primary formed nitriles subsequently hydrolysed to amides. Six selected hydrazones **1a–e** and **1q** were also oxidized during 60 h without sodium carbonate. 4-Nitrobenzonitrile, 4-carboxybenzonitrile, 4-carboxymethylbenzonitrile, 4-bromobenzonitrile and 1,4-dicyanobenzene were formed in high selectivity from **1b–e**, **1q**, while conversion of **1a** was very low. It show that sodium carbonate not only promoted formation of peroxyiminoacetic acid, but also catalyzed nitrile hydrolysis. Moreover, when hydrazone derived from terephthaldehyde (**1q**) was oxidized with 30% hydrogen peroxide – urea adduct in acetonitrile without sodium carbonate the nitrile **2q** (oxidation only one azomethine group) was formed in good preparative yield.

Table 1. Oxidation of N,N-dimethylhydrazones **1**.

Hydrazone **1**	Reaction conditions		Products, yield[a], [%]				
	Method	Time [h]	Hydrazone **1**	Nitrile **2**	Amide **3**	Acid **4**	Aldehyde **5**
1	2	3	4	5	6	7	8
a	A	94	80	–	88[b,c]	–	–
	B	60	60	6[b,d]	–	–	–
	C	4	20	70	–	–	–
	C	18	–	70	–	–	–
b	A	72	–	–	70	21	–
	B	60	50	89[b,c]	–	–	–
	C	5	–	81	–	12	–
c	A	192	–	–	60[f]	40[f]	–
	B	60	–	85	–	–	–
	C	4	–	94	–	–	–
d	A	23	–	20	45	23	–
	B	60	–	95	–	–	–
	C	4	–	69	–	28	–

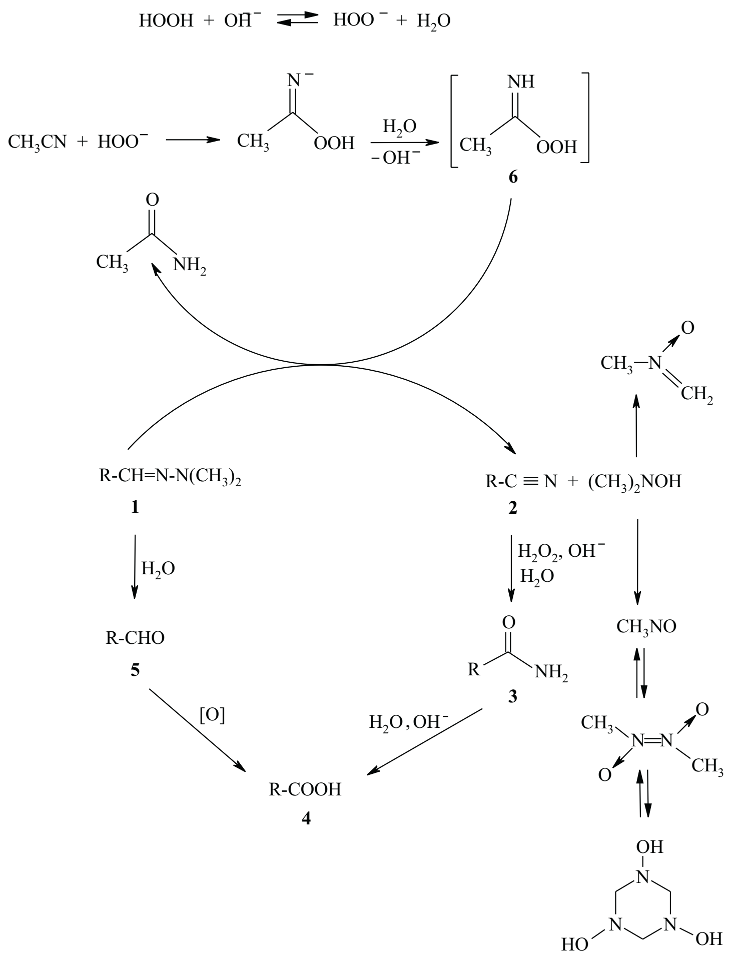
Table 1 (continuation)

e	A	42	–	35	40	15	–
	B	60	–	98	–	–	–
	C	8	–	91	–	–	–
f	A	23	–	57	19	19	–
	C	6	–	77	–	7.0	–
g	A	24	–	66	19	10	–
	C	1	–	90	–	–	–
h	A	16	–	70	15	7.0	–
	C	4	–	100	–	–	–
i	A	24	–	68	13	10	–
	C	7	–	89	–	4.0	–
j	A	20	–	85	–	–	–
	C	6	–	90	–	–	–
k	A	19	50	(66)[b,e]	–	(13)	(4.5)
	C	6	–	(60)	–	(21)	–
l	A	18	–	80	–	–	–
	C	7	–	(82)	–	(10)	(4.8)
m	A	25	–	(78)	–	(20)	(1.8)
	C	8	–	(63)	–	(23)	(3.7)
n	A	23	–	(98)	–	(1.6)	(2.0)
	C	6	–	(93)	–	(1.8)	(4.4)
o	A	24	–	(77)	–	(17)	(3.4)
	C	7	–	(55)	–	(27)	(8.0)
p	C	2.5	–	86	–	–	–
q	B	60	–	–[g]	–	–	–
	B	50[h]	–	63[i]	–	–	–
	C	2.5	–	–[j]	–	–	–
r	C	6	–	98	–	–	–

[a] Isolated yields. Data in parantheses are referred to yields determined by GC. [b] Yield of compound is referred to converted substrate. [c] Conversion of hydrazone **1a** is 17%. [d] Conversion of hydrazone **1a** is 36%. [e] Conversion of hydrazones **1b** and **1k** is 50%. [f] Mixture of products **3c** and **4c** was isolated. [g] 1,4-Dicyanobenzene was formed quantitatively. [h] Hydrogen peroxide – urea adduct was used (30%, 5.0 g, 50 mmol). [i] 1,4-Dicyanobenzene was isolated in 15% using silica gel column chromatography. [j] 1,4-Dicyanobenzene was isolated in 90% yield.

The results of our experiments suggest that the oxidation of N,N-dimethylhydrazone with H_2O_2–acetonitrile proceeds according to Scheme 2. Peroxyiminoacetic acid (**6**) formed from acetonitrile and hydrogen peroxide in basic conditions is an active oxidant of N,N-dimethylhydrazone to nitrile and unstable dimethylhydroxylamine which undergone subsequent transformation [8,10]. The nitrile **2** is subsequently hydrolysed to amide **3** and finally to carboxylic acid **4** [22]. Competetively, N,N-dimethylhydrazone **1** is hydrolysed to parent aldehyde **5** and subsequently oxidized to carboxylic acid **4**.

Scheme 2

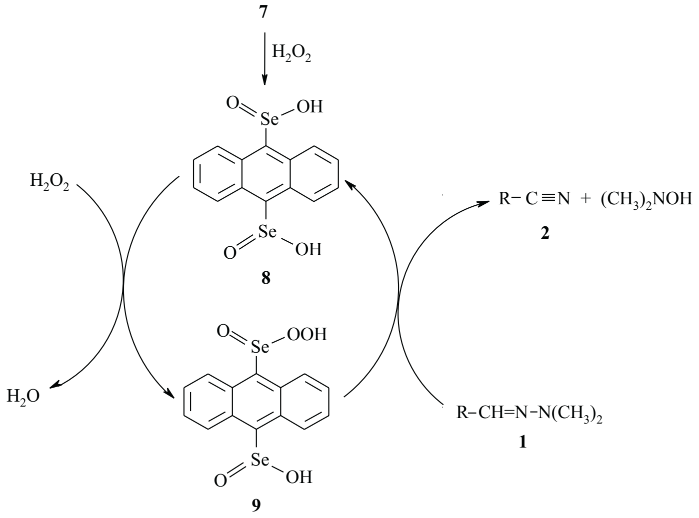


In other experiments N,N-dimethylhydrazone derived from 5-nitro-2-furaldehyde (**1a)** was taken as the model substrate, while hydrogen peroxide in the presence of different selenium compounds was used as an oxidant. The compounds **1a** was selected as a substrate because it had been resistant when treated with H_2O_2–acetonitrile. Products of its oxidation should be biologically important furane derivatives related to kojic acid [8]. Selenium dioxide and different organoselenium compounds such as 2-nitrobenzeneseleninic acid, 2-phenylbenzisoselenazol-3(2H)-one (ebselen), poly(bis-1,2-phenylene) diselenide and other diselenides such as 2-, 3-, and 4-pyridyl, 3,5-di(trifluoromethyl)phenyl and PADS (**7**) were used as oxidation catalysts. Desired nitrile **2a** was isolated in the up to 70% yield in the presence of poly(bis-9,10-anthracenyl) diselenide (**7**) (PADS). This result corresponds to the recently reported information that PADS effectively catalyzed hydrogen peroxide oxidation of cycloalkanones to cycloalkanecarboxylic acids [16].

The scope of H_2O_2–PADS oxidation was established for different aromatic, aliphatic and unsaturated N,N-dimethylhydrazones listed in Table 1. PADS was used in 5% mol amount (related to the substrate) and the reaction was carried out in *tert*-butanol in 55°C for a period given in Table 1. N,N-Dimethylhydrazones **1a–r** were converted to nitriles **2a–r** in good to excellent yields and their subsequent hydrolysis to amides **3** was not observed.

The mechanism of the oxidation with H_2O_2–PADS system can be explained according to the mechanisms postulated earlier for other aryldiselenides [3,23]. In our case PADS (**7**) oxidized with hydrogen peroxide produce areneseleninic acid **8**, which is subsequently oxidized to peroxyseleninic acid **9** being the active oxygen donor as it shown in Scheme 3.

Scheme 3



Concluding, we can say that for conversion of N,N-dimethylhydrazones to nitriles in H_2O_2–CH_3CN system may be used, but for practical purposes the reaction is limited to a few more active substrates. Better results are achieved when H_2O_2–PADS is an oxidant and various aliphatic, unsaturated and aromatic nitriles can be obtained in this way in good to excellent yields.

EXPERIMENTAL

The reaction products **2k–o**, **4k–o**, **5k–o**, presented in Table 1, were analyzed using Hewlett-Packard 5890 apparatus with capillary column HP-1 (25 m, 0.22 mm). All compounds were identified by comparison of their MS spectra (Hewlett-Packard 5971a) with data reported in the library NBS 49 K and 75 K and by their melting points (Digital Melting Point Apparatus Electrothermal IA 91100) as well as by their ^{1}H NMR data ($CDCl_3$ or CH_3OD, TMS, Bruker DRX 300 Spectrometer). Aldehydes, N,N-dimethylhydrazine, selenium dioxide, diphenyl diselenide and solvents were purchased from Aldrich and Fluka, silica gel (70–230 mesh) for column chromatography from Merck, and hydrogen peroxide, sodium chloride, sodium hydrogen carbonate and sodium carbonate from POCH (Polskie Odczynniki Chemiczne). N,N-Dimethylhadrazones **1a–r** were obtained by treating of aldehyde with N,N-dimethylhydrazine in methanol (**1a–l**, **1p**–**q**) or without solvent (**1m**,**o**) according to the procedure reported in ref. [11,22]. 2-Nitrobenzeneseleninic acid, 2-phenyl-1,2-benzisoselenazol-3(2H)one (ebselen) and diselenides tested as catalyst, such as 2-, 3-, and 4-pyridyl, poly(bis-1,2-phenylene) and poly(bis-9,10-anthracenyl) **6** (PADS) were synthesized according to the ref. [16,18,24,25]. The previously unknown compounds **1c**, **1d**, **1p**, **1r** were fully characterized.

4-Carboxybenzaldehyde N,N-dimethylhydrazone 1c: Pale yellow flakes; yield 83%, m.p. 192–194°C (ethyl acetate). IR (KBr): 3200–2000 cm^{-1} (COOH), 1675 cm^{-1} (C=O), 1608 and 1580 and 1548 cm^{-1} (C=N or C=C). ^{1}H NMR ($CDCl_3$): 11.0 (s, 1H, COOH), 8.05 (d, J = 8.3 Hz, 2H, H-3, H-5), 7.63 (d, J = 8.3 Hz, 2H, H-2, H-6), 7.17 (s, 1H, CH=N), 3.06 (s, 6H, NMe_2). Anal. calcd. for $C_{10}H_{12}N_2O_2$ (192.21): C, 62.48; H, 6.29; N, 14.58%. Found: C, 62.55; H, 6.38; N, 14.41%.

4-Carboxymethylbenzaldehyde N,N-dimethylhydrazone 1d: Colourless prisms; yield 91%, m.p. 62–63°C (*n*-hexane). IR (KBr): 1707 cm^{-1} (C=O), 1602 and 1575 and 1545 cm^{-1} (C=N or C=C). ^{1}H NMR ($CDCl_3$): 7.98 (d, J = 8.3 Hz, 2H, H-3, H-5), 7.60 (d, J = 8.3 Hz, 2H, H-2, H-6), 7.17 (s, 1H, CH=N), 3.90 (s, 3H, OCH_3), 3.04 (s, 6H, NMe_2). Anal. calcd. for $C_{11}H_{14}N_2O_2$ (206.24): C, 64.06; H, 6.84; N, 13.59%. Found: C, 64.10; H, 7.01; N, 13.50%.

4-Cyanobenzaldehyde N,N-dimethylhydrazone 1p: Colourless prisms; yield 94%, m.p. 139–140°C (methanol). IR (KBr): 2220 cm^{-1} (CN), 1601 and 1567 and 1539 cm^{-1} (C=N or C=C). ^{1}H NMR ($CDCl_3$): 7.60 (d, J = 8.5 Hz, 2H, ArH), 7.56 (d, J = 8.5 Hz, 2H, ArH), 7.08 (s, 1H, CH=N), 3.07 (s, 6H, CH_3). Anal. calcd. for $C_{10}H_{11}N_3$ (173.22): C, 69.34; H, 6.40; N, 24.26%. Found: C, 69.40; H, 6.58; N, 24.19%.

2-Formylbenzenesulfonic acid N,N-dimethylhydrazone sodium salt 1r: Colourless prisms; yield 88%, m.p. 340°C (decomposition) (methanol). IR (KBr): 2862 and 2794 cm^{-1} (Me), 1574 and 1545 cm^{-1} (C=N or C=C), 1229 and 1136 cm^{-1} (SO_3Na). ^{1}H NMR (CH_3OD): 8.20 (s, 1H, CH=N), 7.89 (d, J = 7.6 Hz, 1H, ArH), 7.85 (d, J = 7.6 Hz, 1H, ArH), 7.35 (t, J = 7.6 Hz, 1H, ArH), 7.22 (t, J = 7.6 Hz, 1H, ArH), 2.93 (s, 6H, NMe_2). Anal. calcd. for $C_9H_{11}N_2NaO_3S$ (250.26): C, 43.20; H, 4.43; N, 11.19%. Found: C, 43.35; H, 4.51; N, 10.90%.

Oxidation of N,N-dimethylhydrazones 1 with H_2O_2–acetonitrile

The mixture of corresponding N,N-dimethylhydrazones **1a**–**o**, **1q** (5 mmol) and powdered sodium carbonate (0.85 g, 8.0 mmol) in acetonitrile (30 ml) was treated under stirring with 30% aqueous hydrogen peroxide (6.0 ml, 60 mmol) in 55°C for 30 min. The reaction was monitored by TLC using dichloromethane as an eluent. After the reaction was finished, the mixture was treated with a pinch of Pt/C and then the solution of sodium hydrogen carbonate (2.5 g) and sodium chloride (7.5 g) in water (100 ml) was added. The mixture was shaken until the evolution of carbon dioxide and oxygen ceased. Organic products **2**, **3** and **5** were extracted with dichloromethane (50 ml and 3 × 20 ml), combined extracts were dried over anhydrous sodium sulfate, the solvent was removed *in vacuo* and nitrile was separated as first fraction on the column chromatography with silicagel (70–230 mesh) using chloroform (**2a**), dichloromethane (**2b**, **2e**–**j**) and (**2q**), dichloromethane–ethyl acetate (**2d**), and ethyl acetate (**2c**) as an eluent. Amide was separated as second fraction using dichloromethane (**3f**), dichloromethane–ethyl acetate (**3e**), ethyl acetate–methanol (**3a**, **3d**), and ethyl acetate (**3g**–**i**) as an eluent. 1,4-Dicyanobenzene (**2p**) was separated by sublimation and amide **3b** by recrystallization from *n*-hexane. Amides **3c** and carboxylic acids **4b**–**i** were isolated from the alkaline solution by acidification with concentrated hydrochloric acid (pH 1–2) and extraction with diethyl ether (**4b**, **4d**) or with chloroform (**4e**–**i**). The extract was dried over anhydrous sodium sulfate, solvent was removed *in vacuo* and the residue was a pure acid **2**. The mixture of amide **3c** and acid **4c** was filtered up, dried in air and it was analyzed by nitrogen elementary analysis.

Oxidation of N,N-dimethylhydrazones 1 with H_2O_2–PADS

The mixture of corresponding N,N-dimethylhydrazone **1a**–**r** (5.0 mmol) and poly(bis-9,10-anthracenyl) diselenide (**6**) (0.084 g, 0.25 mmol) in *tert*-butanol (30 ml) was treated under magnetic stirring with 30% aqueous hydrogen peroxide (2.5 ml, 25 mmol) in 55°C for 30 min. and the reaction was carried out in the same manner as with oxidation H_2O_2–acetonitrile. After the reaction finished, the nitriles **2a**–**o** and acid **4b**, **4d**, **4f**, **4i** were isolated in the same manner as described for oxidation with H_2O_2–acetonitrile. Dicyanobenzene (**2p**) was separated by sublimation.

2-Cyanobenzenesulfonic acid sodium salt 2r

To the solution of N,N-dimethylhydrazone **1r** (2.5 g, 10 mmol) in solution of methanol (50 ml) and *tert*-butanol (50 ml) and poly(bis-9,10-anthracenyl) diselenide (**7**) (0.17 g, 0.50 mmol) 30% aqueous hydrogen peroxide (5.0 ml, 50 mmol) was added and the reaction was continued at 55°C for 6 h. An excess of hydrogen peroxide was decomposed (Pt/C), the solvents were evaporated *in vacuo* and the crude nitrile **2r** was washed with hot dioxane, dissolved in hot methanol (250 ml), treated with charcoal and left to stand at room temperature for 3 days. The charcoal was filtered off and the solvent was removed *in vacuo*. Nitrile **2r**: yield 98% m.p > 350°C (methanol). IR (KBr): 2230 and 2247 cm^{-1} (CN), 2214 cm^{-1} (SO_3Na). ^1H NMR (CH_3OD): 7.98 (d, J = 7.5 Hz, 1H, ArH), 7.79 (d, J = 7.5 Hz, 1H, ArH), 7.68 (t, J = 7.5 Hz, 1H, ArH), 7.57 (t, J = 7.5 Hz, 1H, ArH). Anal. calcd. for $C_7H_4NNaO_3S$ (205.18): C, 40.98; H, 1.96; N, 6.83%. Found: C, 40.70; H, 2.11; N, 6.80 (lit. [26] N, 6.78%).

Acknowledgment

The authors thank Prof. Dr. Ludwik Syper for 3,5-di(trifluoromethyl)phenyl diselenide used in this work.

REFERENCES

1. Młochowski J. and Said S.B., *Polish J. Chem.,* **71**, 140 (1997).
2. Jones A.K. and Wilson T.E., in *Encyclopedia of Reagents for Organic Synthesis,* Paquette L.A. (ed), J. Wiley and Sons, Chichester 1995, p. 880.
3. Młochowski J., *Chem. Papers,* **52**, 45 (1998).
4. Młochowski J., *Phosphorus, Sulfur and Silicon*, **136–138**, 191 (1998).
5. Młochowski J., Brząszcz M., Giurg M. and Wójtowicz H., *Wiad. Chem.*, **55**, 9 (2001).
6. Kumar P., Kumar R. and Pandey B., *Synlett*, 289 (1995).
7. Payne G.B., *Tetrahedron*, **18**, 763 (1962).
8. Młochowski J., Giurg M., Uher M., Korenova A. and Vegh D., *J. prakt. Chem.*, **338**, 65 (1996).
9. Altamura A., D'Accotti L., Detomaso A., Dinoi A., Fiorentino M., Fusco C. and Curci R., *Tetrahedron Lett.*, **39**, 2009 (1998).
10. Rudler H., Denise B. and Masi S., *C. R. Acad. Sci. Paris, Serie IIc, Chimie/Chemistry*, **3**, 793 (2000).
11. Said S.B., Skarżewski J. and Młochowski J., *Synthesis*, 223 (1989).
12. Młochowski J., Giurg M., Kubicz E. and Said S.B., *Synth. Commun.*, **26**, 291 (1996).
13. Bachmann C., Gesson J.-P., Renoux B. and Tranoy I., *Tetrahedron Lett.*, **39**, 379 (1998).
14. Yamaguchi K., Mizugaki T., Ebitani K. and Kaneda K., *New J. Chem.*, **23**, 799 (1999).
15. Selvam T. and Ramaswamy A.V., *Chem. Commun.*, 1215 (1996).
16. Giurg M. and Młochowski J., *Synth. Commun.*, **29**, 2281 (1999).
17. Giurg M. and Młochowski J., *Polish J. Chem.*, **71**, 1093 (1997).
18. Giurg M., Said S.B., Syper L. and Młochowski J., *Synth. Commun.*, **31**, 3151 (2001).
19. Hoft E., Kosslick H., Fricke R. and Hamman H.-J., *J. prakt. Chem.*, **338**, 1 (1996).
20. Vacque V., Dupuy N., Sombret B., Huvenne J.P. and Legrant P., *J. Mol. Struct.*, **384**, 165 (1996).
21. Ogata Y. and Sawaki Y., *Tetrahedron*, **20**, 2065 (1964).
22. Młochowski J., Kloc K. and Kubicz E., *J. prakt. Chem.*, **336**, 467 (1994).
23. Ten Brink G.-J., Vis J.-M., Arends I.W.C.E. and Sheldon R.A., *Tetrahedron,* **58**, 3977 (2002).
24. Syper L. and Młochowski J., *Tetrahedron*, **44**, 6119 (1988).
25. Młochowski J., Kloc K., Syper L., Inglot A.D. and Piasecki E., *Liebigs Ann. Chem.,* 1239 (1993).
26. Cignarella G. and Toetino U., *J. Am. Chem. Soc.*, **22**, 1594 (1960).