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Synthesis of Novel Thiazole and Pyrrolothiadiazine Derivatives from Aldehyde Thiosemicarbazones

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ABSTRACT: *Substituted thiosemicarbazones* **7a–e** *reacted with ethenetetracarbonitrile (TCNE) in ethyl acetate with formation of 5-amino-3-(substituted benzylidene-amino)-2-phenylimino-2,3-dihydrothiazole-4-carbonitrile* **8a–e** *2-amino-6-phenyl-imino-1,6-dihydropyrrolo[1,3,4]thiadiazine-3-carbonitrile* **9**, *and phenyl-(5-{substituted phenyl}-3H-[1,3,4]thiadiazole-2-ylidene)amines* **10a–e**. *Rationales for the observed conversations are presented.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:261–266, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20198

INTRODUCTION

Heterocyclic compounds as 1,2,4-triazole, 1,3,4-oxadiazole, and 1,3,4-thiadiazole derivatives can be obtained by oxidative cyclization of suitable open chain molecules such as semicarbazones and thiosemicarbazones [1–5]. Oxidative cyclization of substituted aldehyde thiosemicarbazones, induced by different metallic salts, led to 1,2,4-triazoline derivatives [2–6]. Cyclization of 1,4-disubstituted thiosemicarbazides may be achieved under various conditions [7–11]. For example, 4-substituted 1-phenylacetylthiosemicarbazides undergo cyclization to yield 3-benzyl-Δ^2-1,2,4-triazoline-5-thiones and 2-amino-5-benzyl-1,3,4-thiadiazole, respectively, in the presence of either acid or alkali. The cyclization of suitable open chain organic molecules is a classical and very popular approach to the synthesis of heterocyclic derivatives, owing to both the large variety of heterocycles accessible through this way, and the large variety of conditions under which the reaction can be performed [12–14]. Noticeably, when more than one product can be obtained at the same time in a particular reaction, good to excellent selectivities can often be achieved by means of a suitable choice of the cyclizing agent and conditions [15,16]. Frequently, such cyclization reactions are induced by acidic media or electrophilic reagents [15,17–20]. On other occasions, the cyclization mechanism involves a plain oxidation step—electron abstraction or dehydrogenation—prior to the actual ring closure step [21–23]. On the other hand, the interaction of thiosemicarbazide derivatives with some π-acceptors such as ethenetetracarbonitrile (TCNE), (1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile and benzoquinones as well as naphthoquinones afforded thiazole, thiazine, thiadiazole, thiadiazine, thiadiazepine, oxathiadiazole, and indazole as well as pyridazine derivatives [22–26].

Recently, we have demonstrated that 4-substituted thiosemicarbazides **1a–c** and 1,4-disubstituted thiosemicarbazides **2a–c** reacted with TCNE in ethyl acetate with admission of air to give products **3** and **4** (with **1a–c**) and **5** and **6**, in addition to the thiadiazole derivatives (with **2a–c**) (Chart 1) [27,28].

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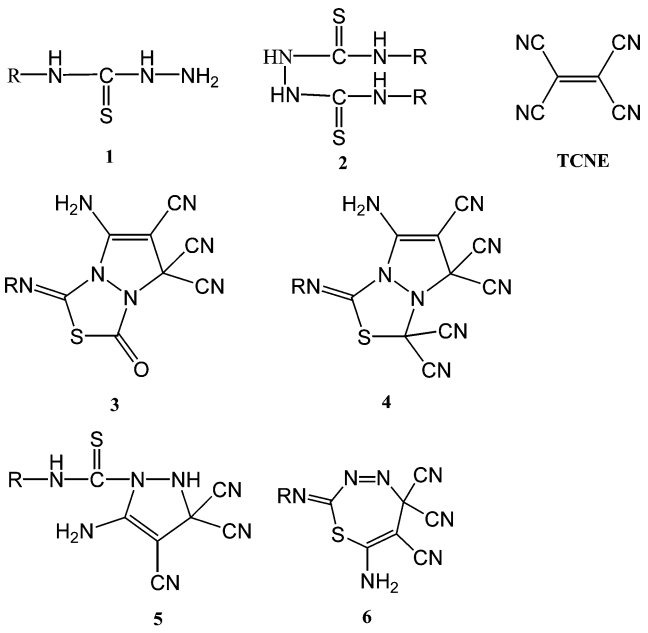
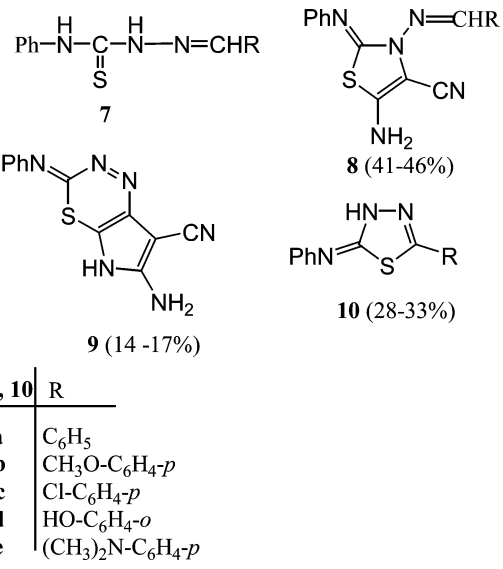


1-6: **a**, R = Ph; **b**, R = $PhCH_2$; **c**, R = allyl

CHART 1



7, 8, 10	R
a	C_6H_5
b	CH_3O-C_6H_4-*p*
c	Cl-C_6H_4-*p*
d	HO-C_6H_4-*o*
e	$(CH_3)_2N$-C_6H_4-*p*

CHART 2

Aldehyde semi- and thiosemicarbazones are polyfunctionalyzed compounds which easily cyclized by action of bases [7,8], acids [9], or oxidants [2–6]; therefore, they are useful and versatile synthons for the preparation of five- or six-membered heterocyclic compounds.

As will be outlined in detail below in this paper, we report several heterocyclization of substituted aldehyde thiosemicarbazones **7a–e** using TCNE either as a reaction mediator or a building block.

Ethenetetracarbonitrile is the simplest of percyanoalkenes (cyanocarbons) [29]. The general chemistry of TCNE has been reviewed with emphasis on molecular complexes, reactions with ketones and amines, tricyanovinylation reactions [29], additions [29], and cycloaddition reactions [30] as well as synthesis of heterocycles [29–34].

RESULTS AND DISCUSSION

Treatment of **7a–e** with two molar equivalents of TCNE in ethyl acetate as solvent at room temperature resulted in a pink coloration of the solution which quickly turned into brown. This behavior may be explained as due to initial formation of unstable charge-transfer (CT) complexes followed by chemical reaction.

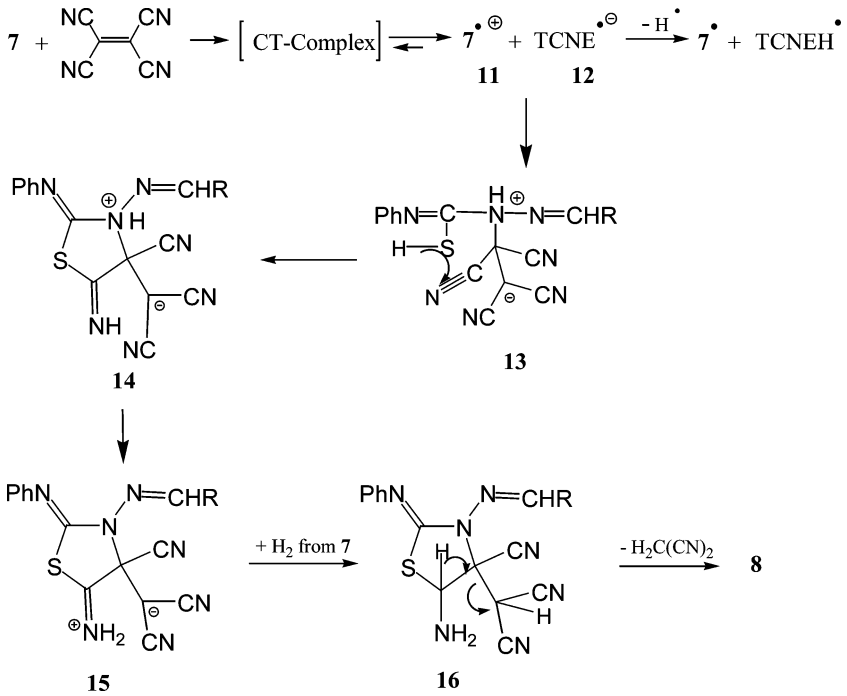
Monitoring of the reaction by visible spectroscopy failed, since the reaction is fast and also at lower concentration no significant color changes were observed any more. The reaction mixture was concentrated to dryness, and the residue was subjected to vacuum sublimation to remove any unreacted TCNE. Chromatographic separation of the residue in each case gave numerous zones, from which products **8–10** could be isolated (Chart 2). 5-Amino-3-(benzylideneamino)-2-phenylimino-2,3-dihydrothiazole-4-carbonitrile **8a** was obtained as characteristically colorless crystals. Its molecular structure is supported by the following findings:

The gross formula $C_{17}H_{13}N_5S$ represents a product from one molecule of **7a** and one molecule of TCNE with loss of $C(CN)_2$ unit probably in the form of $H_2C(CN)_2$.

Both NH_2 ($\delta_H = 6.88$ ppm) and low-field CH=N group ($\delta_H = 8.15$ ppm) are present.

In its ^{13}C NMR spectrum, thiazole C-2, C-4, and C-5 resonate at $\delta = 164.34$, 50.93, and 153.77 ppm, respectively, are in accordance with the observed trends in the δ values for C-atoms in push–pull alkenes [35,36]. Further peaks at 117.70 ppm (CN) and 154.36 ppm (CH=N) besides the aromatic carbons support the assigned structure. The presence of CH=N group is also evident from the ^{13}C DEPT NMR spectrum exhibiting positive signals at $\delta = 154.36$ ppm. The absence of a ^{13}C C=S signal and the presence of C=N signal as well as only one CN resonance at 117.70 ppm support structure **8a**.

The combination of the radicals **11** and **12** form tetracyanoethylated product **13** (Scheme 1). Instead of expelling one molecule of hydrogen cyanide, however, the adduct **15** was observed which abstract



SCHEME 1

a molecule of hydrogen from **7** [22,23] with successive release a molecule of malononitrile to give **8**.

The decoupled carbon spectrum of **9** showed signals at $\delta = 165.04$, 120.28, 118.49, 61.91, and 154.87 assigned to C-6, C-7′, C-3′, C-3, and C-2, respectively. The ^{1}H NMR of **9** showed two broad singlets with the ratio 2:1 centered at 7.22 and 10.95 ppm due to exocyclic NH_2 and pyrazole —NH, in addition to five aromatic protons.

The alternative structures **17–19** (Chart 3) could be ruled out on the basis of ^{1}H NMR, ^{13}C NMR, and the fragment ions in the mass spectrum of **9**.

Nucleophilic attack of the active nitrogen atom of the imino group of **7** on TCNE followed by the loss of HCN from **21** and hydrolysis form the tricyanovinylation product **22** which cyclized to give product **9** (Scheme 2).

The structure of thiadiazoles **10a–e** was confirmed by comparison with authentic samples [37–39].

In a fairly complex and multistep process, two types of cyanoheterocyclic products are formed from various substituted thiosemicarbazones **7a–e** and

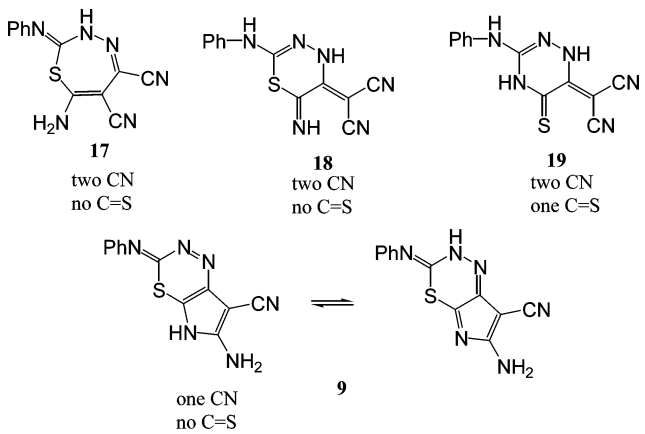
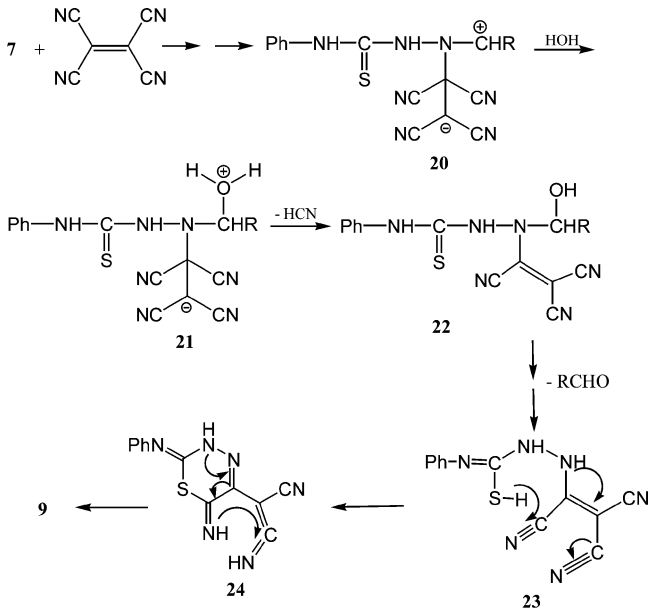


CHART 3



SCHEME 2

TCNE. The latter has a dual functioning role as a dehydrogenating agent and as a source of a dicyanomethylene units. Since the reactions reported very likely require numerous steps, moderate yields (based throughout on the amount of starting materials) have to be regarded as acceptable.

CONCLUSION

In this study three kinds of ring forming reactions of substituted thiosemicarbazones **7a–e** with TCNE have been observed: (i) cyclization of **7a–e** to **8a–e** by tetracyanoethylation of secondary amino function with loss of malononitrile (Scheme 1); (ii) the nucleophilic attack of the active nitrogen atom of the imino group on the TCNE followed by loss of HCN and hydrolysis to give the tricyanovinylation which cyclized to form the product **9** (Scheme 2); and (iii) dehydrogenation and cyclization of **7** using TCNE as dehydrogenating agent. Thus, TCNE may act either as mediator or as a building block in heterocyclization of thiosemicarbazone derivatives.

EXPERIMENTAL

Melting points have been determined using open glass capillaries on a Gallenkamp melting point apparatus and are uncorrected. The IR spectra were recorded with a Shimadzu 408 instrument using potassium bromide pellets. ^{1}H NMR (300 MHz), and ^{13}C NMR (75 MHz) spectra were obtained on a Bruker WM 300 instrument. Mass spectra have been obtained with an AMD 604 doubly focusing instrument using electron impact ionization (70 eV). Elemental analyses were determined by Microanalytical Center, Cairo University. Preparative layer chromatography (PLC) was made using 48 cm × 20 cm glass plates covered with a 1 mm layer of Merck silica gel PF_{254}, from applied slurry and air dried. Zones were detected by indicator fluorescence quenching upon 254 nm excitation, removed from plates and extracted with cold acetone.

Starting Materials

All thiosemicarbazones **7a–e** were synthesized by reaction of 4-phenylthio-semicarbazide and the proper aldehyde according to the published procedures **7a** [40], **7b** [41], **7c** [42], **7d** [43], and **7e** [44]. Ethentetracarbonitrile (TCNE, Merck) was purified by crystallization from chlorobenzene and sublimed.

Preparation of Thiazole, Pyrrolothiadiazine, and Thiadiazole Derivatives **8–10**. To a stirred solution of 256 mg (2.0 mmol) of TCNE in 10 mL of ethyl acetate, a solution of 1.0 mmol of **7a–e** was added dropwise, which caused a spontaneous change of color from pink to brown. The mixture was stirred for 5 h and left standing for 48 h at room temperature. After concentration to dryness, the residues were sublimed at 80°C under vacuum to remove unreacted TCNE and then subjected to PLC using cyclohexane/ethyl acetate (5:1) as eluent to give numerous zones, three of which (with high intensity) were removed and extracted. The fastest moving zone ($R_f = 0.54$) contained the pyrrolothiadiazine derivative **9** (14–17%), the second zone ($R_f = 0.46$) contained the thiadiazole derivatives **10 a–e** (28–33%), while the slowest moving zone ($R_f = 0.34$) contained the thiazole derivatives **8a–e** (41–46%). Extraction of the zones with acetone and concentration gave residues, which were rechromatographed to improve purification and then recrystallized.

5-Amino-3-(benzylideneamino)-2-phenylimino-2,3-dihydrothiazole-4-carbo-nitrile **8a**. Yield (137 mg, 43%), mp 220°C, IR (KBr) ν_{max} 3430 (NH_2), 2220 (CN), 1640 (C=N), 1595 (Ar-C=C) cm^{-1}. ^{1}H NMR (300.13 MHz, DMSO-d_6) δ 6.88 (s, br, 2H, NH_2), 7.39–7.67 (m, 10H, Ar-H), 8.15 (s, 1H, CH=N). ^{13}C NMR (75.47 MHz, DMSO-d_6) 164.34 (C-2), 154.36 (CH=N), 134.63, 134.15, 130.35, 130.18, 129.94, 129.19, 128.92, 127.49, 126.50 (Ar-C), 117.70 (CN), 50.93 (C-4), 153.77 (C-5). MS (EI, 70 eV), *m/z* (%) 319 (M^+, 100), 253 (45), 148 (21), 118 (27), 90 (40), 77 (56). $C_{17}H_{13}N_5S$ (319.39); Calcd C, 63.93; H, 4.10; N, 21.93; S, 10.04%; Found: C, 64.11; H, 4.01; N, 22.09; S, 9.88%.

5-Amino-3-[4-(methoxybenzylidene)amino]-2-phenylimino-2,3-dihydro-thiazole-4-carbonitrile **8b**. Yield (161 mg, 46%), mp 236°C. IR (KBr) ν_{max} 3425 (NH_2), 2980 (Ali-CH), 2215 (CN), 1635 (C=N), 1600 (Ar-C=C) cm^{-1}. ^{1}H NMR (300.13 MHz, DMSO-d_6) δ 3.86 (s, 3H, OCH_3), 6.94 (s, br, 2H, NH_2), 7.36–7.65 (m, 9H, Ar-H), 8.18 (s, 1H, CH=N). ^{13}C NMR (75.47 MHz, DMSO-d_6) 164.22 (C-2), 154.71 (CH=N), 140.11, 133.97, 129.87, 129.16, 128.91, 128.66, 126.14, 125.18 (Ar-C), 118.18 (CN), 51.11 (C-4), 54.69 (OCH_3), 152.86 (C-5). MS (EI, 70 eV), *m/z* (%) 349 (M^+, 100), 318 (37), 283 (44), 148 (31), 90 (28), 77 (54). $C_{18}H_{15}N_5SO$ (349.42); Calcd C, 61.87; H, 4.33; N, 20.04; S, 9.18%; Found: C, 61.98; H, 4.18; N, 20.19; S, 9.04%;

5-Amino-3-[4-(chlorobenzylidene)amino]-2-phenylimino-2,3-dihydrothiazole-4-carbonitrile **8c**. Yield (145 mg, 41%), mp 213°C. IR (KBr) ν_{max} 3440 (NH_2), 2210 (CN), 1630 (C=N), 1590 (Ar-C=C) cm^{-1}. ^{1}H NMR (300.13 MHz, DMSO-d_6) δ 6.91 (s, br, 2H,

NH_2), 7.13–7.59 (m, 9H, Ar-H), 8.17 (s, 1H, CH=N). MS (EI, 70 eV), *m/z* (%) 355/353 (M^+, 76), 318 (36), 287 (38), 182 (24), 90 (41), 77 (100). $C_{17}H_{12}ClN_5S$ (353.83); Calcd C, 57.71; H, 3.42; N, 19.79; S, 9.06%; Found: C, 57.89; H, 3.29; N, 19. 94; S, 8.88%.

5-Amino-3-[2-(hydroxybenzylidene)amino]-2-phenylimino-2,3-dihydro-thiazole-4-carbonitrile **8d**. Yield (147 mg, 44%), mp 208°C. IR (KBr) ν_{max} 3480–3375 (OH, NH_2), 2220 (CN), 1635 (C=N), 1600 (Ar-C=C) cm^{-1}. ^1H NMR (300.13 MHz, DMSO-d_6) δ 6.92 (s, br, 2H, NH_2), 7.29–7.74 (m, 9H, Ar-H), 8.15 (s, 1H, CH=N), 10.39 (s, br, 1H, OH). MS (EI, 70 eV): *m/z* (%) 335 (M^+, 100), 319 (32), 269 (47), 163 (19), 90 (64), 77 (52). $C_{17}H_{13}N_5SO$ (335.39); Calcd C, 60.88; H, 3.91; N, 20.88; S, 9.56%; Found: C, 61.06; H, 4.08; N, 20.71; S, 9.38%.

5-Amino-3-[(4-N,N-dimethylaminobenzylidene)-amino]-2-phenylimino-2,3-dihydro-thiazole-4-carbonitrile **8e**. Yield (152 mg, 42%), mp 256°C. IR (KBr) ν_{max} 3430 (NH_2), 2980–2965 (Ali-CH), 2210 (CN), 1630 (C=N), 1580 (Ar-C=C) cm^{-1}. ^1H NMR (300.13 MHz, DMSO-d_6) δ 2.97 (s, 6H, Me_2N), 6.84 (s, br, 2H, NH_2), 7.31–7.69 (m, 9H, Ar-H), 8.18 (s, 1H, CH=N). MS (EI, 70 eV), *m/z* (%) 362 (M^+, 84), 332 (22), 296 (53), 191 (34), 90 (55), 77 (100). $C_{19}H_{18}N_6S$ (362.47); Calcd C, 62.96; H, 5.00; N, 23.19; S, 8.85%; Found: C, 63.12; H, 5.11; N, 23.02; S, 9.03%.

2-Amino-6-phenylimino-1,6-dihydropyrrolo- [1,3,4]thiadiazine-3-carbonitrile **9**. Yield (as from the following starts; **7a**: 40 mg, 15%; **7b**: 46 mg, 17%; **7c**: 38 mg, 14%; **7d**: 43 mg, 16%; and **7e**: 40 mg, 15%), mp 244°C. IR (KBr) ν_{max} 3380, 3340 (NH, NH_2), 2220 (CN), 1630 (C=N), 1600 (Ar-C=C) cm^{-1}. ^1H NMR (300.13 MHz, DMSO-d_6) δ 7.22 (s, br, 2H, NH_2), 7.29–7.91 (m, 5H, Ar-H), 10.95 (s, br, 1H, pyrrole–NH). ^{13}C NMR (75.47 MHz, DMSO-d_6) 165.04 (C-6), 143.13, 129.49, 127.14, 124.29 (Ar-C), 120.28 (C-7′), 118.49 (C-3′), 117.74 (CN), 61.91 (C-3), 154.87 (C-2). MS (EI, 70 eV), *m/z* (%) 268 (M^+, 43), 202 (15), 187 (10), 135 (49), 91 (92), 77 (100). $C_{12}H_8N_6S$ (268.30); Found: C, 53.87; H, 2.89; N, 31.21; S, 12.14%, Calcd C, 53.72; H, 3.01; N, 31.32; S, 11.95%.

Phenyl-(5-phenyl-3H-[1,3,4]thiadiazole-2-ylidene)-amine **10a**. Yield (76 mg, 30%), mp 138°C, lit. 139°C [37,38].

Phenyl-(5-{4-methoxyphenyl}-3H-[1,3,4]thiadiazole 2-ylidene)amine **10b**. Yield (83 mg, 33%), mp 143°C, lit. 141°C [38].

Phenyl-(5-{4-chlorophenyl}-3H-[1,3,4]thiadiazole-2-ylidene)amine **10c**. Yield (71 mg, 28%), mp 175°C, lit. 175 [38].

Phenyl-(5-{2-hydroxyphenyl}-3H-[1,3,4]thiadiazole-2-ylidene)amine **10d**. Yield (78 mg, 31%), mp 203°C, lit. 205°C [39].

Phenyl-(5-{4-N,N-dimethylaminophenyl}-3H-[1,3,4]thiadiazole-2-ylidene)amine **10e**. Yield (76 mg, 30%), mp 140°C, lit. 142°C [38].

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