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Ahmad S. Shawali[a]; Abdelwahed R. Sayed[a]; Mohie M. Zayed[a]
[a] Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

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Site selectivity in reactions of hydrazonoyl halides with ketene-*N*,*S*-acetals

Ahmad S. Shawali*, Abdelwahed R. Sayed and Mohie M. Zayed

Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

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Ketene-*N*,*S*-acetal **7** reacts with hydrazonoyl chloride **1** to afford 1,2,4-triazoles **9**. The formation of **9** indicates that **7** behaves mostly as *N*-nucleophile rather than 1,3-dipolarophile.

Keywords: Ketene-*N*,*S*-acetrals; hydrazonoyl halides; nucleophilicity; nitrilimines; dipolarophilicity

1. Introduction

Literature reports indicate that reactions of nitrilimines **2**, generated *in situ* from the respective hydrazonoyl halides **1**, with acyclic ketene aminals and the related heterocyclic ketene aminals proceeded in totally different fashions (*1*). For example, reaction of 1,1-dimorpholinoethene 3 with nitrilimines proceeded via 1,3-dipolar cycloaddition followed by deaminative aromatization to produce 5-(substituted amino)pyrazoles **5** (*2*). In contrast, reactions of cyclic ketene aminals **4** bearing a secondary amino group with nitrilimines proceeded via a nucleophilic addition followed by intramolecular condensation to give the corresponding 4-heteroarylpyrazole derivatives **6** (Scheme 1) (*2*). Interest in this intriguing cycloaddition reactions and in continuation of our research in the chemistry of hydrazonoyl halides (*3–9*) encouraged us to study the reactions of ketene-*N*,*S*-acetal, namely 2-cyano-3-methylthio-3-phenylaminoacrylonitrile **7**, with the hydrazonoyl chlorides **1a-v** to explore the site selectivity in such reactions. The present paper, as shown below, highlights the behavior of ketene-*N*,*S*-acetal, **7** as N-nucleophile rather than C-nucleophile or as dipolarophile in the studied reactions (Scheme 2).

2. Results and discussion

Refluxing of ketene-*N*,*S*-acetal **7** with each of the hydrazonoyl halides **1a-v** in ethanol in the presence of triethylamine for 1.0–1.5 h and working up the reaction mixture gave, in each case,

*Corresponding author. Email: as_shawali@yahoo.com

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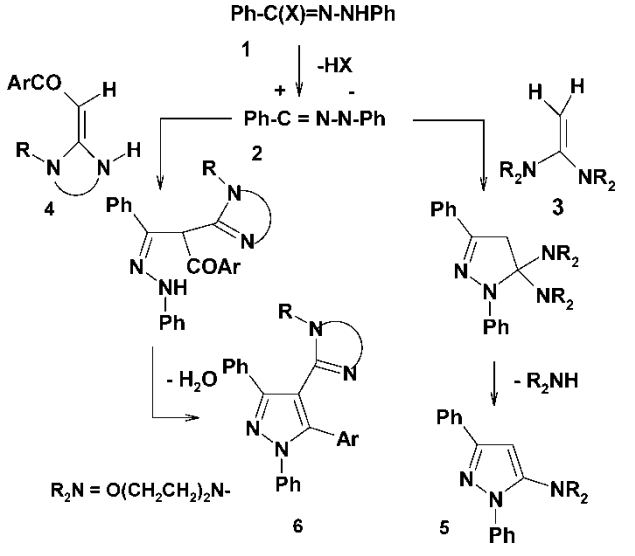
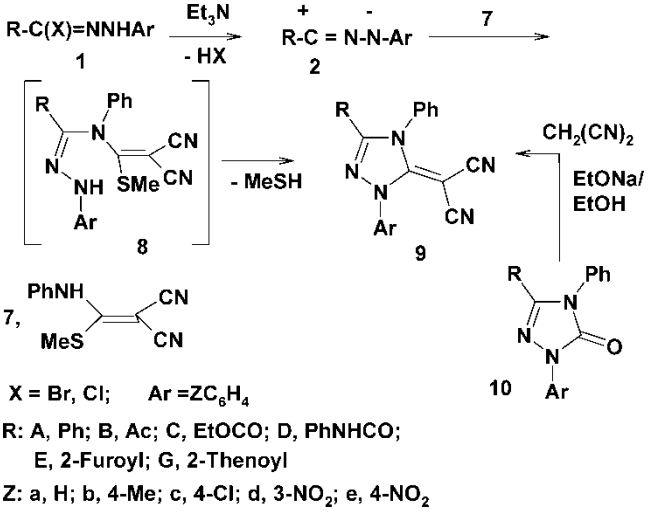


Scheme 1.



Scheme 2.

one product as evidenced by tlc analysis. On the basis of the microanalysis and spectral (MS, ^{1}H NMR, and IR) data, the isolated products were assigned the triazole structure **9** (Scheme 2). For example, their mass spectra and elemental analyses revealed the absence of sulfur. The mass spectra showed peaks of *m/z* corresponding to [RCNNAr], [PhNCC(CN)$_2$], [PhN], [R], and [Ar] ionic species in addition to the molecular ion peaks M^+ and $M^+ + 1$. Their IR spectra showed, in each case, two nitrile absorption bands in the regions 2208-2197 and 2176-2160 cm^{-1}. The assigned structure was further confirmed by alternate synthesis of **9a** as a typical example of the series prepared. Thus, the reaction of 1,3,4-triphenyl-5(4H)-1,2,4-triazole **10** (*9*) with malonitrile in ethanol in the presence of ethoxide under reflux afforded a product identical in all respects to **9a**, which was isolated above from the reaction of **1a** with **7**. On the basis of this finding, the other possible isomeric structure **11** (Scheme 2) was discarded.

To account for the formation of products **9**, it is suggested, as depicted in Scheme 2, that the studied reactions started with 1,3-addition of **7** to nitrilimine **2**, generated *in situ* via base catalyzed dehydrohalogenation of **1**, to give the respective amidrazone intermediate **8**. The latter underwent *in situ* intramolecular cyclization with concurrent elimination of methanethiol to form the corresponding 1,2,4-triazole derivative **9** as end product. The formation of **9** rather than **11** indicates that ketene-*N*,*S*-acetal **7** behaves as nucleophile rather than 1,3-dipolarophile. Furthermore, although *N*,*S*-acetal **7** is a kind of ambident nucleophile, the involvement of amidrazone intermediates **8** in the studied reactions indicates that it behaves as an N-nucleophile rather than a C-nucleophile or as dipolarophile.

3. Experimental

Melting points were measured using an electrothermal Gallenkamp melting point apparatus and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 with tetramethylsilane as an internal standard using 300 MHz Varian Gemini spectrometer. The IR spectra were measured on a Fourier transform and Pye Unicam Infrared spectrophotometers using potassium bromide wafer. Mass spectra were recorded on a GCMS-QP 1000 EX spectrometer at an ionizing potential of 70 eV. Elemental analyses were carried out at the Microanalytical Laboratory of Cairo University, Giza, Egypt. The identification of compounds from different experiments were secured by mixed m.p. and superimposable IR spectra. The hydrazonoyl halides **1a-v** (*10–16*) and 2-cyano-3-methylthio-3-phenylaminoacrylonitrile **7** (*17*) were prepared as described previously.

3.1. *Synthesis of 1,4-diaryl-3-substituted-5-dicyanomethylene-1,2,4-triazoles (9)*

General method – To an equimolar mixture of the appropriate hydrazonoyl halide **1** and ketene-*N*,*S*-acetal **7** (0.005 mole each) in ethanol (40 ml) was added triethylamine (0.7 ml, 0.005 mole) and the mixture was refluxed till methanethiol ceased to evolve (1.0–1.5 h). The solid, which precipitated, was filtered and crystallized from the DMF-EtOH mixture to give the respective **9**. The physical constants of the compounds prepared are listed below.

3.1.1. *1,3,4-Triphenyl-5-dicyanomethylene-1,2,4-triazole (9Aa)*

Pale yellow solid (1.08 g, 60%), mp >300°C. IR (KBr) ν2196 cm^{-1}. ^{1}H NMR δ 7.34–7.33 (m). MS *m*/*z* (%) 362 (M$^+$+1, 26), 361 (M$^+$, 100), 194 (3), 167 (2), 116 (10), 103 (10), 91 (32), 77 (41). Anal. found (calcd) for $C_{23}H_{15}N_5$ (361.4): C, 76.42 (76.44); H, 4.17 (4.18), N, 19.39 (19.38)%.

3.1.2. *1-(p-Nitrophenyl)-3,4-triphenyl-5-dicyanomethylene-1,2,4-triazole (9Ae)*

Dark yellow solid (1.12 g, 55%), mp 295°C. IR (KBr) ν 2201, 2171 cm^{-1}. ^{1}H NMR δ 7.38–7.71 (m, 10H), 8.05 (d, J = 9 Hz, 2H), 8.50 (d, J = 9 Hz, 2H). MS *m*/*z* (%) 407 (M$^+$+1, 27), 406 (M$^+$, 100), 239 (1), 167 (2), 136 (2), 91 (32), 77 (37). Anal. found (calcd) for $C_{23}H_{14}N_6O_2$ (406.4): C, 67.97 (67.98); H, 3.45 (3.47), N, 20.69 (20.68)%.

3.1.3. *3-Acetyl-1,4-diphenyl-5-dicyanomethylene-1,2,4-triazole (9Ba)*

Yellow solid (0.85 g, 52%), mp 288°C. IR (KBr) ν 2201, 2173, 1710 cm^{-1}. ^{1}H NMR δ 3.33 (s, 3H), 7.49–7.72 (m, 10H). MS *m*/*z* (%) 328 (M$^+$+1, 23), 327 (M$^+$, 100), 312 (11), 284 (15), 259 (11),

167 (5), 118 (22), 91 (22), 77 (75). Anal. found (calcd) for $C_{19}H_{13}N_5O$ (327.3): C, 69.95 (69.72); H, 4.01 (4.00), N, 21.40 (21.39)%.

3.1.4. *3-Acetyl-1-(p-tolyl)-4-phenyl-5-dicyanomethylene-1,2,4-triazole (9Bb)*

Yellow solid (0.94 g, 55%), mp 305°C. IR (KBr) ν 2202, 2176, 1709 cm^{-1}. ^1H NMR δ 2.52 (s, 3H), 3.40 (s, 3H), 7.26–7.61 (m, 9H). MS m/z (%) 342 (M^++1, 25), 341 (M^+, 100), 298 (23), 271 (10), 182 (18), 167 (1), 130 (20), 91 (89), 77 (51). Anal. found (calcd) for $C_{20}H_{15}N_5O$ (341.3): C, 69.95 (70.39); H, 4.14 (4.43), N, 21.40 (20.52)%.

3.1.5. *3-Acetyl-1-(p-chlorophenyl)-4-phenyl-5-dicyanomethylene-1,2,4-triazole (9Bc)*

Yellow solid (0.94 g, 55%), mp 294°C. IR (KBr) ν 2202, 2176, 1711 cm^{-1}. ^1H NMR δ 3.58 (s, 3H), 7.26–7.59 (m, 5H), 7.71 (d, J = 12 Hz, 2H), 7.75 (d, J = 12 Hz, 2H). MS m/z (%) 363 (M^++2, 26), 362 (M^++1, 18), 361 (M^+, 80), 318 (16), 201 (8), 177 (10), 167 (1), 150 (17), 117 (12), 91 (29), 77 (82). Anal. found (calcd) for $C_{19}H_{12}ClN_5O$ (361.8): C, 63.07 (63.08); H, 3.32 (3.34), N, 19.35 (19.36)%.

3.1.6. *3-Acetyl-1-(3-nitrophenyl)-4-phenyl-5-dicyanomethylene-1,2,4-triazole (9Bd)*

Yellowish solid (1.2 g, 61%), mp >310°C. IR (KBr) ν 2208, 2182, 1711 cm^{-1}. ^1H NMR δ 2.60 (s, 3H), 7.52–7.69 (m, 9H). MS m/z (%) 373 (M^++1, 26), 372 (M^+, 100), 329 (6), 283 (10), 167 (3), 118 (24), 91 (91), 77 (79). Anal. found (calcd) for $C_{19}H_{12}N_6O_3$ (372.3): C, 61.25 (61.29); H, 3.23 (3.25), N, 22.54 (22.57)%.

3.1.7. *3-Ethoxycarbonyl-1,4-diphenyl-5-dicyanomethylene-1,2,4-triazole (9Ca)*

Pale yellow solid (1.11 g, 62%), mp 250°C. IR (KBr) ν 2208, 2172, 1741 cm^{-1}. ^1H NMR δ 1.26 (t, J = 7 Hz, 3H), 4.24 (q, J = 7 Hz, 2H), 7.56–8.13 (m, 10H). MS m/z (%) 358 (M^++1, 27), 357 (M^+, 100), 329 (17), 284 (9), 257 (3), 225 (2), 167 (8), 118 (33), 91 (18), 77 (93). Anal. found (calcd) for $C_{20}H_{15}N_5O_2$ (357.3): C, 67.21 (67.22); H, 4.22 (4.23), N, 19.69 (19.60)%.

3.1.8. *3-Ethoxycarbonyl-1-(p-tolyl)-4-phenyl-5-dicyanomethylene-1,2,4-triazole (9Cb)*

White solid (1.11 g, 60%), mp 250°C. IR (KBr) ν 2203, 2172, 1747 cm^{-1}. ^1H NMR δ 1.26 (t, J = 7 Hz, 3H), 2.5 (s, 3H), 4.24 (q, J = 7 Hz, 2H), 7.26–7.593 (m, 10H). MS m/z (%) 372 (M^++1, 27), 371 (M^+, 98), 181 (23), 156 (17), 130 (18), 91 (100), 77 (59). Anal. found (calcd) for $C_{21}H_{17}N_5O_2$ (371.4): C, 67.92 (67.91); H, 4.62 (4.61), N, 18.85 (18.86)%.

3.1.9. *3-Ethoxycarbonyl-1-(p-chlorophenyl)-4-phenyl-5-dicyanome-thylene-1,2,4-triazole (9Cc)*

White solid (1.19 g, 61%), mp 273°C. IR (KBr) ν 2203, 2172, 1751 cm^{-1}. ^1H NMR δ 1.26 (t, J = 7 Hz, 3H), 4.24 (q, J = 7 Hz, 2H), 7.26–7.59 (m, 5H), 7.71 (d, J = 12 Hz, 2H), 7.75 (d, J = 12 Hz, 2H). MS m/z (%) 393 (M^++2, 36), 392 (M^++1, 23), 391 (M^+, 94), 363 (18), 201 (16), 167 (13), 158 (19), 125 (79), 118 (79), 91 (22), 77 (100). Anal. found (calcd) for $C_{20}H_{14}ClN_5O_2$ (391.8): C, 61.32 (61.31); H, 3.58 (3.60), N, 17.81 (17.87)%.

3.1.10. *3-Phenylaminocarbonyl-1,4-diphenyl-5-dicyanomethylene-1,2,4-triazole (9Da)*

Yellow solid (1.31 g, 65%), mp 290°C. IR (KBr) ν 2380, 2203, 2168, 1696 cm^{-1}. ^1H NMR δ 7.23–7.66 (m, 15H), 10.96 (s, 1H). MS m/z (%) 405 (M^++1, 28), 404 (M^+, 100), 284 (15), 259 (8), 167 (6), 118 (21), 91 (21), 77 (73). Anal. found (calcd) for $C_{24}H_{16}N_6O$ (404.4): C, 71.23 (71.28); H, 3.97 (3.99), N, 20.75 (20.78)%.

3.1.11. *3-Phenylaminocarbonyl-1-(p-tolyl)-4-phenyl-5-dicyanome-thylene-1,2,4-triazole (9Db)*

White solid (1.4 g, 67%), mp >300°C. IR (KBr) ν 3390, 2203, 2186, 1697 cm^{-1}. ^1H NMR δ 2.5 (s, 3H), 7.30–7.60 (m, 14H), 10.97 (s, 1H). MS m/z (%)419 (M^++1, 31), 418 (M^+, 100), 298 (12), 273 (6), 181 (8),119 (9), 91 (45), 77 (33). Anal. found (calcd) for $C_{25}H_{18}N_6O$ (418.4): C, 71.75 (71.76); H, 4.32 (4.34), N, 20.01 (20.08)%.

3.1.12. *3-Phenylaminocarbonyl-1-(p-chlorophenyl)-4-phenyl-5-dicyanomethylene-1,2,4-triazole (9Dc)*

White solid (1.53 g, 70%), mp >300°C. IR (KBr) ν 3378, 2204, 2177, 1690 cm^{-1}. ^1H NMR δ 7.26–7.59 (m, 10H), 7.71 (d, J = 12 Hz, 2H), 7.75 (d, J = 12 Hz, 2H), 10.96 (s, 1H). MS m/z (%) 440 (M^++2, 12), 439 (M^++1, 13), 438 (M^+, 49), 318 (9), 201 (6), 167 (8), 152 (14), 118 (42), 91 (37), 77 (100). Anal. found (calcd) for $C_{24}H_{15}ClN_6O$ (438.5): C, 65.70 (65.68); H, 3.46 (3.45), N, 19.17 (19.15)%.

3.1.13. *3-Benzoyl-1,4-diphenyl-5-dicyanomethylene-1,2,4-triazole (9Ea)*

Yellow solid (1.07 g, 55%), mp 290°C. IR (KBr) ν 2205, 2175, 1702 cm^{-1}. ^1H NMR δ 7.56–8.13 (m). MS m/z (%) 390 (M^++1, 19), 389 (M^+, 65), 312 (11), 105 (94), 91 (2), 77 (100). Anal. found (calcd) for $C_{24}H_{15}N_5O$ (389.4): C, 73.90 (74.02); H, 3.81 (3.88), N, 18.13 (17.98)%.

3.1.14. *3-Benzoyl-1-(p-chlorophenyl)-4-phenyl-5-dicyanomethylene-1,2,4-triazole (9Ec)*

Pale brown solid (1.27 g, 60%), mp 205°C. IR (KBr) ν 2202, 2176, 1709 cm^{-1}. ^1H NMR δ 7.29–7.59 (m, 9H), 7.71 (d, J = 12 Hz, 2H), 7.75 (d, J = 12 Hz, 2H). MS m/z (%) 425 (M^++2, 8), 424 (M^++1, 6), 423 (M^+, 26), 361 (80), 201 (2), 166 (3), 105 (100), 77 (81). Anal. found (calcd) for $C_{24}H_{14}Cl\ N_5O$ (423.8): C, 68.27 (68.01); H, 3.60 (3.33), N, 16.50 (16.52)%.

3.1.15. *3-(2-Furoyl)-1,4-diphenyl-5-dicyanomethylene-1,2,4-triazole (9Fa)*

Yellow solid (1.04 g, 55%), mp 255°C. IR (KBr) ν 2203, 2173, 1660 cm^{-1}. ^1H NMR δ 6.82–8.20 (m). MS m/z (%) 380 (M^++1, 3), 379 (M^+, 2), 253 (100), 167 (2), 91 (10), 77 (21). Anal. found (calcd) for $C_{22}H_{13}N_5O_2$ (379.3): C, 69.51 (69.65); H, 3.69 (3.45), N, 18.47 (18.46)%.

3.1.16. *3-(2-Furoyl)-1-(p-tolyl)-4-phenyl-5-dicyanomethylene-1,2,4-triazole (9Fb)*

Yellow solid (1.08 g, 55%), mp 245°C. IR (KBr) ν 2202, 2180, 1662 cm^{-1}. ^1H NMR δ 2.53 (s, 3H), 7.23-7.66 (m, 12H). MS m/z (%) 394 (M^++1, 5), 393 (M^+, 25), 264 (6), 182 (3), 168 (2), 95 (100), 91 (15), 77 (11). Anal. found (calcd) for $C_{23}H_{15}N_5O_2$ (393.4): C, 70.17 (70.22); H, 3.60 (3.84), N, 18.03 (17.80)%.

3.1.17. *3-(2-Furoyl)-1-(p-chlorophenyl)-4-phenyl-5-dicyanome-thylene-1,2,4-triazole (9Fc)*

Yellow solid (1.24 g, 60%), mp 290°C. IR (KBr) ν 2204, 2175, 1667 cm^{-1}. ^1H NMR δ 7.26–7.59 (m, 8H), 7.71 (d, $J = 12$ Hz, 2H), 7.75 (d, $J = 12$ Hz, 2H). MS m/z (%) 415 (M^++2, 6), 414 (M^++1, 5), 413 (M^+, 18), 111 (7), 96 (100), 77 (8). Anal. found (calcd) for $C_{22}H_{12}ClN_5O_2$ (413.8): C, 63.63 (63.85); H, 2.80 (2.92), N, 16.87 (16.92)%.

3.1.18. *3-(2-Thenoyl)-1,4-diphenyl-5-dicyanomethylene-1,2,4-triazole (9Ga)*

Yellow solid (0.99 g, 50%), mp 195°C. IR (KBr) ν 2201, 2173, 1710 cm^{-1}. ^1H NMR δ 6.82–8.20 (m). MS m/z (%) 396 (M^++1, 7), 395 (M^+, 27), 167 (3), 111 (100), 91 (12), 77 (29). Anal. found (calcd) for $C_{22}H_{13}N_5OS$ (395.4): C, 66.76 (66.82); H, 3.43 (3.31), N, 17.91 (17.71)%.

3.1.19. *3-(2-Thenoyl)-1-(p-tolyl)-4-phenyl-5-dicyanomethylene-1,2,4-triazole (9Gb)*

Yellow solid (1.0 g, 49%), mp 275°C. IR (KBr) ν 2203, 2199, 1696 cm^{-1}. ^1H NMR δ 2.5 (s, 3H), 7.17–8.52 (m, 12H). MS m/z (%) 410 (M^++1, 9), 409 (M^+, 32), 380 (3), 111 (100), 91 (15), 77 (7). Anal. found (calcd) for $C_{23}H_{15}N_5OS$ (409.4): C, 67.03 (67.47); H, 3.77 (3.69), N, 17.13 (17.10)%.

3.1.20. *3-(2-Thenoyl)-1-(p-chlorophenyl)-4-phenyl-5-dicyanome-thylene-1,2,4-triazole (9Gc)*

Dark yellow solid (1.09 g, 60%), mp 245°C. IR (KBr) ν 2199, 2173, 1776 cm^{-1}. ^1H NMR δ 7.23–7.60 (m, 8H), 7.71 (d, $J = 12$ Hz, 2H), 7.75 (d, $J = 12$ Hz, 2H). MS m/z (%) 431 (M^++2, 9), 430 (M^++1, 6), 429 (M^+, 23), 202 (1), 111 (100), 77 (3). Anal. found (calcd) for $C_{22}H_{12}ClN_5OS$ (429.89): C, 61.48 (61.47); H, 2.79 (2.81), N, 16.27 (16.29)%.

3.2. *Alternate synthesis of 9Aa*

To a stirred solution of sodium ethoxide, prepared by dissolving sodium metal (0.23 g, 0.01 gmole) in absolute ethanol (50 ml), was added malononitrile (0.66 g, 0.01 mole) and the mixture was stirred for 5 min. To the resulting mixture was added 1,3,4-triphenyl-5(4H)-1,2,4-triazole **10** (3.13 g, 0.01 mole) and the mixture was refluxed for 3 h, cooled, and then acidified with hydrochloric acid. The solid, which precipitated, was filtered and crystallized from DMF-EtOH to give the product that proved identical in all respects (m.p., mixed m.p., and IR) to the product **9Aa**, prepared from **7** and **1Aa**.

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