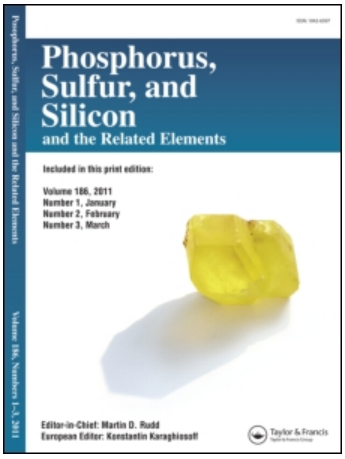

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Thiocarbonyl Photochemistry: The Photoreactions of Pyrimidine-2-thione Derivative with Alkynes and Alkenes

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*The photocycloaddition of pyrimidine-2-thione derivative **1** to alkynes **2a–c** and alkenes **7** and **11** are studied. Irradiation of a dioxane solution of **1** in the presence of alkynes **2a–c** produced the thiol derivatives **3a–c** through ring cleavage of thietene **5**. Irradiation of **1** in the presence of alkenes **7** and **11** under the same conditions produced the corresponding photoproducts **10** and **13**, respectively. The structure of all products was confirmed by analytical and spectral data.*

Keywords alkenes; alkynes; high pressure mercury lamp; photocycloaddition; Thiocarbonyl

INTRODUCTION

The photochemistry of thiocarbonyl compounds has extensively received high attention.[1–4] The observed photoreaction of thiocarbonyl compounds often follow a different course from those analogous carbonyl compounds. A majority of those reported involving thioketenes undergo [2 + 2] cycloaddition to alkenes, alkynes, imines, inter-and intramolecular H-abstraction, and photooxidation.[3–6] Some reports dealt with the photochemical reactions involving the C=S group of thioamides.[7]

In particular, they gave, by [2 + 2] photocycloaddition with alkenes or alkynes, thietanes as primary products,[8] which are often unstable and transformed into fragmentation products. This may be ascribed to the participation of the lone-pair electrons of the N-atom, which facilitate

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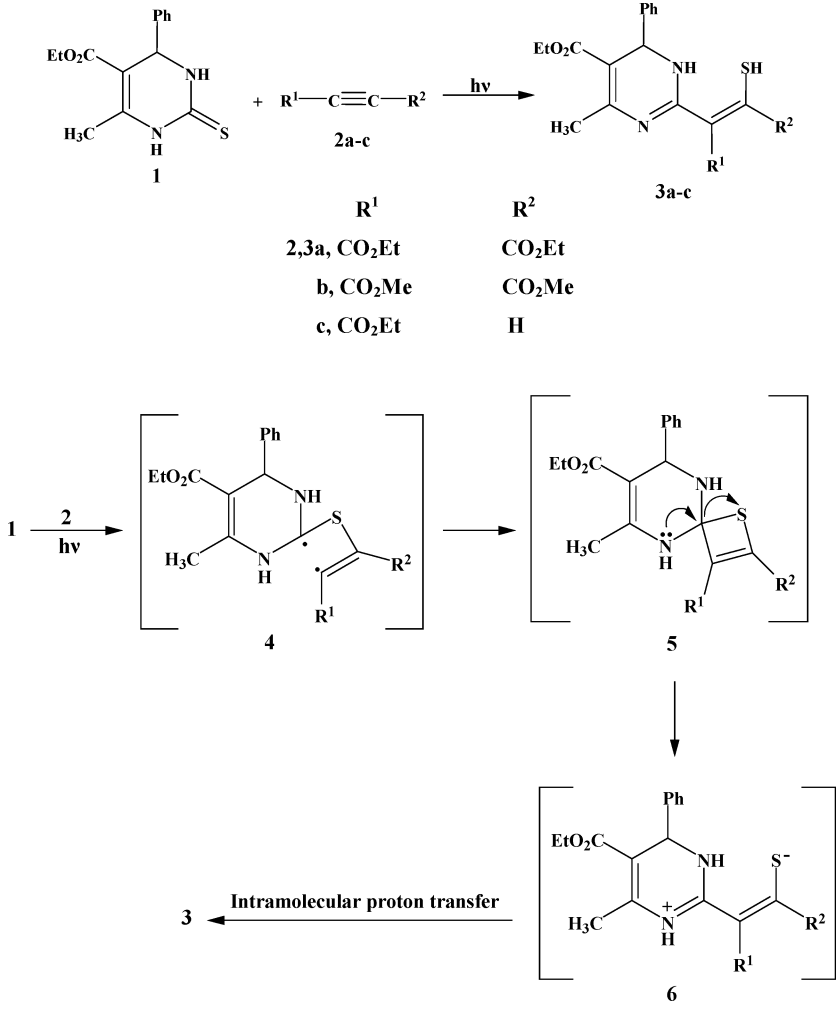
the C—S bond cleavage of the thietane ring.[9] In this article we would like to study the photocycloaddition reactions of ethyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **1**[10] with different alkynes and alkenes to furnish the corresponding thiol, sulphide, and vinyl derivatives that showed a great activity as antioxidant[11] and antinematode.[12]

RESULTS AND DISCUSSION

Irradiation of a dioxane solution of **1** with a high pressure Mercury lamp through a Pyrex filter under Nitrogen in the presence of alkynes **2a–c** furnished the corresponding thiol derivatives **3a–c**. The formation of 2-(2-mercaptoalkyl) pyrimidine **3** can be best explained by the intermediacy of the spirocyclic thietene **5**. The latter is formed regioselectively by photochemical [2 + 2] cycloaddition of the C=S of the pyrimidine-2-thione **1** and the C ≡ C of the alkynes **2** via the more stable biradical intermediate **4**.[13–15] Compound **5** undergoes ring cleavage for the presence of the lone-pair electrons of the N-atom to afford the Zwitter ion **6**. Finally, the intramolecular proton transfer occurs to form the final isolated product **3** (Scheme 1).

The structure of the new photoproducts was elucidated on the basis of their spectral and analytical data. As an example the ^{1}H-NMR spectrum of **3a** revealed the characteristic signal of the SH group at $\delta = 1.30$ ppm; the doublet signal for pyrimidine H-4 at $\delta = 6.18$ ppm, (J = 3 Hz), in addition to the doublet signal for the pyrimidine NH at $\delta = 8.02$ ppm, (J = 3 Hz). The IR spectrum exhibited the characteristic thiol absorption band at 2550 cm^{-1}. The UV spectra of **3a** revealed $\lambda_{max} = 313.252$ at 5 A^0, that establish the conjugated structure (c.f., Experimental section).

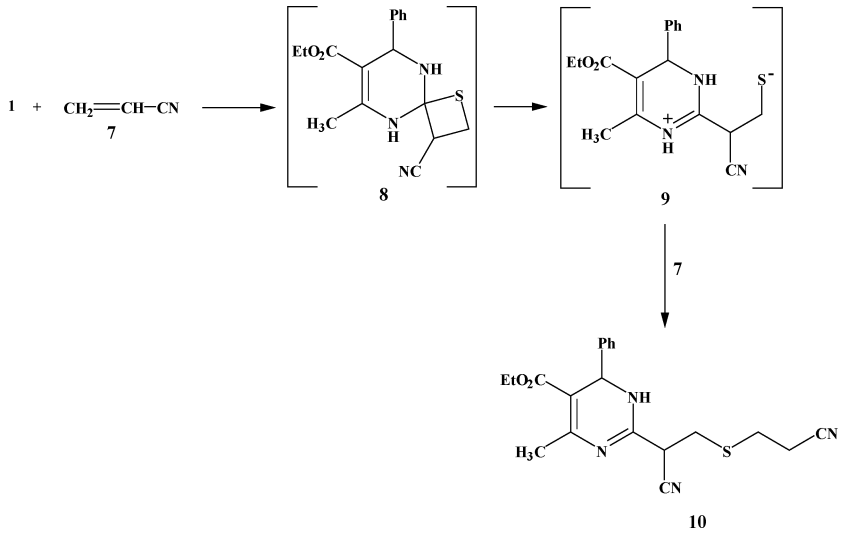
Next, the photocycloaddition reactions of **1** with electron-deficient alkenes like acrylonitile and *trans*-stilbine are studied. Irradiation of a dioxane solution of **1** in the presence of excess of acrylonitrile **7** under the same previously explained conditions led to the formation of the product **10**. In spite of, the presence of two regioisomeric modes of cycladdition of a thione with acrylonitrile. Compound **10**, in the present work, is the only isolable isomer that could be obtained and identified. Similar sulphide adduct was previously detected and identified as a product from the photoreaction of benzothiazole-2-thione with dimethylethylene (DME).[16] The presence of additional products in the reaction of **1** with acrylonitrile **7** could also be detected (column chromatography). However, these minor unspecified products could not be isolated. Further studies are now under investigation to isolate and to



SCHEME 1

identify these products. Formation of compound **10** could be explained by assuming that the Zwitter ion **9** formed at first via the thietane intermediate **8**;[1] then reacted with another molecule of **7** to furnish the corresponding photoadduct **10** (Scheme 2).

The mass spectrum revealed the molecular ion peaks [M^+] at m/z= 382 for the correct molecular weight of **10**. The IR and ^{1}H-NMR spectra revealed the disappearance of the characteristic signal of the SH group.

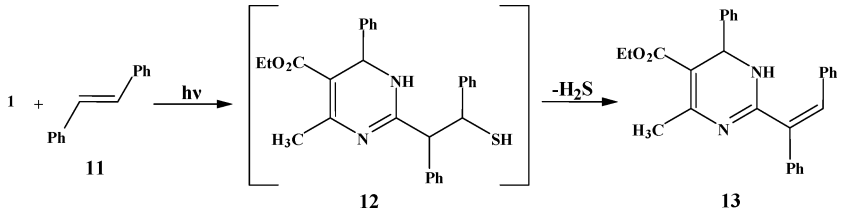


SCHEME 2

All the spectroscopic and microanalytical data were in accordance with the suggested structure (c.f., Experimental section).

Carrying out the previously explained reaction by the use of *trans*-stilbine **11** yielded the photoproduct **13**. We believe that the reaction occurred via [2+2] cycloaddition pathway to afford the adduct **12**. The latter was converted to 2-(1,2-Diphenyl-vinyl)pyrimidine **13** via elimination of H_2S (Scheme 3).

The structure of **13** is assigned from its molecular ion peak (m/z = 422, M^+). The IR and ^{1}H-NMR spectra showed the disappearance of the characteristic signal of SH group. The ^{13}C-NMR spectrum shows the characteristic carbon signals of vinyl group at $\delta = 126.30$ (C_α vinyl), 126.37 (C_β vinyl) respectively, (c.f., Experimental section).



SCHEME 3

EXPERIMENTAL

The IR spectra expressed in cm^{-1} and recorded on Nexus 670 FTIR spectrophotometer, the sample was prepared as a thin film on a KBr disc. ^{1}H-NMR, ^{13}C-NMR spectra were obtained on a Varian EM-390 300 MHz spectrometer in CD_3Cl as solvent and TMS as an internal reference. Chemical shifts (δ) are expressed in ppm. Mass spectra were recorded on Kartos (75 eV) MS equipment. UV spectra determined on Shimadzu 2401 PC UV spectrophotometer. Elemental analyses were carried out by the microanalytical unit at the National Research Center, Giza, Egypt.

The Photoreactions of Pyrimidine-2-thione 1 with Alkynes 2a–c and Different Alkenes 7 and 11—General Procedure

A solution of **1** (2.76 g, 0.01 mol) in dioxane (300 ml) in the presence of excess of alkynes **2a–c** or alkenes **7** and **13** in a Pyrex vessel under N_2 was irradiated with a high pressure mercury lamp (HP, Philips, 125 W), until completion of the reaction at room temperature. The reactions were monitored by thin layer chromatography (TLC) using aluminum sheets with silica gel 60 F254 (Merck). After removal of the solvent, the residue was chromatographed (silica gel, 60 mesh) with suitable solvent to yield the photoproducts **3a–c**, **10,** and **13**.

Diethyl 2-(5-Ethoxycarbonyl-4-methyl-6-phenyl-1,6-dihydro-pyrimidin-2-yl)-3-mercapto-but-2-enedioate, 3a

Irradiation time 20 h, eluent (ethyl acetate: petroleum ether 40–60^{0}C, 8:2), oil; Yield 4.10 g (92%); IR (film, cm^{-1}): 3448 (NH), 2981, 2907, 2862 (CH_3), 2550 (SH), 1733 (CO), 1656 (CO); UV, λ_{max} = 313.252 nm at 5 A^0; ^{1}H-NMR (CD_3Cl): δ (ppm) = 1.21–1.26 (m, 9H, $3CH_3$), 1.30 (s, 1H, SH), 2.55 (s, 3H, CH_3), 4.19–4.23 (m, 6H, $3CH_2$), 6.18 (d, 1H, H-4 pyrimidine, J = 3 Hz), 7.30-7.80 (m, 5H, aromatic protons), 8.02 (d, 1H, NH, J= 3 Hz); ^{13}C-NMR (CD_3Cl): δ (ppm) = 13.48, 13.77, 14.70, 17.82, 57.84, 60.78, 61.49, 62.30, 121.84, 126.26, 128.39, 129.55 129.78, 132.24, 137.21, 144.07, 164.57, 164.77, 165.09, 165.81; MS (m/z) = 446 (M^+, 14%). Anal. Calcd. for $C_{22}H_{26}N_2O_6S$: C 59.18%, H 5.87%, N 6.27%, S 7.18%. Found: C 59.02%, H 5.56%, N 6.13%, S 7.01%.

Dimethyl 2-(5-Ethoxycarbonyl-4-methyl-6-phenyl-1,6-dihydro-pyrimidin-2-yl)-3-mercapto-but-2-enedioate, 3b

Irradiation time 20 h, eluent (ethyl acetate: petroleum ether 40–60°C, 7:3), oil; Yield 3.67 g (88%); UV, λ_{max} = 320.196 nm at 5 A^0; IR (film, cm^{-1}): 3447 (NH), 2981, 2937, 2907 (CH_3), 2553 (SH), 1733 (CO),

1655 (CO); ^{1}H-NMR (CD_3Cl): δ (ppm) = 1.07 (t, 3H, CH_3, J = 7.5 Hz), 1.26 (s, 1H, SH), 2.56 (s, 3H, CH_3), 3.73 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 4.06 (q, 2H, CH_2, J = 7.5 Hz), 6.26 (d, 1H, H-4 pyrimidine, J = 3 Hz), 7.31–7.45 (m, 5H, aromatic protons), 8.06 (d, 1H, NH, J= 3 Hz); MS (m/z) = 418 (M^+, 8%). Anal. Calcd. for $C_{20}H_{22}N_2O_6S$: C 57.40%, H 5.30%, N 6.69%, S 7.66%. Found: C 57.22%, H 5.13%, N 6.48%, S 7.58%.

Ethyl 2-(1-Ethoxycarbonyl-2-mercapto-vinyl)-4-methyl-6-phenyl-1,6-dihydro-pyrimidine-5-carboxylate, 3c

Irradiation time 15 h, eluent (ethyl acetate: petroleum ether 40–60^{0}C, 8:2), oil; Yield 3.21 g (86%); IR (film, cm^{-1}): 3453 (NH), 2955, 2907, 2891 (CH_3), 2556 (SH), 1731 (CO), 1651 (CO); ^{1}H-NMR (CD_3Cl): δ (ppm) = 0.9–1.02 (m, 6H, $2CH_3$), 1.21 (s, 1H, SH), 2.55 (s, 3H, CH_3), 4.09-4.11 (m, 4H, $2CH_2$), 6.03 (d, 1H, H-4 pyrimidine, J = 3 Hz), 6.66 (s, 1H, CH olefinic), 7.38–7.98 (m, 5H, aromatic protons), 8.69 (d, 1H, NH, J = 3 Hz); MS (m/z) = 374 (M^+, 3%). Anal. Calcd. for $C_{19}H_{22}N_2O_4S$: C 60.94%, H 5.92%, N 7.48%, S 8.56%. Found: C 60.62%, H 5.86%, N 7.27%, S 8.43%.

Ethyl 2-[1-Cyano-2-(2-cyano-ethylsulfanyl)-ethyl]-4-methyl-6-phenyl-1,6-dihydro-pyrimidine-5-carboxylate, 10

Irradiation time 4 h, eluent (MeOH), oil; Yield 2.82 g (74%); IR (film, cm^{-1}): 3421 (NH), 2935 (CH_3), 2242 (CN), 1723 (CO); ^{1}H-NMR (CD_3Cl): δ (ppm) = 1.02 (t, 3H, CH_3, J = 7.5 Hz), 2.36 (t, 2H. CH_2, J = 6.0 Hz), 2.55 (s, 3H, CH_3), 2.62 (d, 2H, CH_2, J = 8 Hz), 3.64 (t, 2H, CH_2, J = 6.0 Hz), 4.15 (q, 2H, CH_2, J = 7.5 Hz), 4.97 (t, 1H, CH, J = 8.0 Hz), 5.83 (d, 1H, H-4 pyrimidine, J = 3.2 Hz), 7.30–7.59 (m, 5H, aromatic protons), 8.55 (d, 1H, NH, J = 3.2 Hz); MS (m/z) = 382 (M^+, 3%). Anal. Calcd. for $C_{20}H_{22}N_4O_2S$: C 62.80%, H 5.80%, N 14.65%, S 8.38%. Found: C 62.74%, H 5.62%, N 14.45%, S 8.21%.

Ethyl 2-(1,2-Diphenyl-vinyl)-4-methyl-6-phenyl-1,6-dihydro-pyrimidine-5-carboxylate, 13

Irradiation time 8 h, eluent (ethyl acetate: petroleum ether 40–60°C, 9:1), oil; Yield 2.99 g (71%); IR (film, cm^{-1}): 3396 (NH), 2976, 2928 (CH_3), 1714 (CO); ^{1}H-NMR (CD_3Cl): δ (ppm) = 1.13 (t, 3H, CH_3, J = 7.5 Hz), 2.32 (s, 3H, CH_3), 4.05 (q, 2H, CH_2, J = 7.5 Hz), 5.36 (s, 1H, CH olefinic), 6.02 (d, 1H, H-4 pyrimidine, J = 3.5 Hz), 7.09–7.24 (m, 5H, aromatic protons), 7.34–7.50 (m, 10H, aromatic protons), 8.68 (d, 1H, NH, J = 3.5 Hz);^{13}C-NMR (CD_3Cl): δ (ppm) = 13.42, 13.89, 55.41, 60.24, 122.45, 126.30, 126.37, 126.45, 126.58, 126.72, 127.43, 127.73, 127.90, 128.00, 128.49, 128.66, 129.84, 131.82, 137.09, 144.78, 164.71,

165.03; MS (m/z) = 422 (M^+, 2%). Anal. Calcd. for $C_{28}H_{26}N_2O_2$: C 79.59%, H 6.20%, N 6.63%. Found: C 79.37%, H 6.03%, N 6.39%.

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