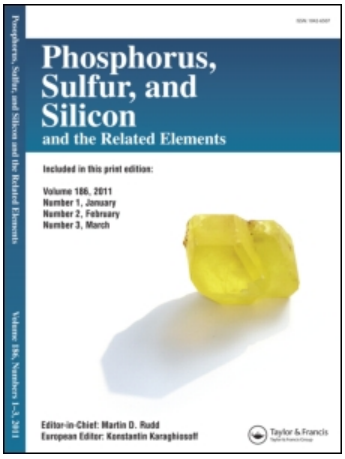


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Synthesis of New Thiosubstituted Compounds with Butadienyl and Butenynyl Groups

Cemil İbis[a]; Sibel Şahinler Ayla[a]
[a] Faculty of Engineering, Department of Chemistry, Istanbul University, Avcilar-Istanbul, Turkey

Online publication date: 13 January 2011

To cite this Article İbis, Cemil and Ayla, Sibel Şahinler(2011) 'The Synthesis of New Thiosubstituted Compounds with Butadienyl and Butenynyl Groups', Phosphorus, Sulfur, and Silicon and the Related Elements, 186: 1, 58 — 66
To link to this Article: DOI: 10.1080/10426501003781624
URL: http://dx.doi.org/10.1080/10426501003781624

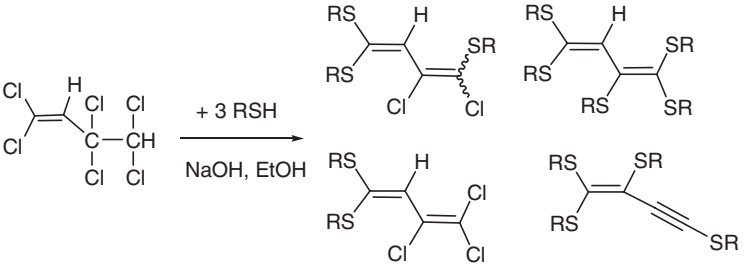
Phosphorus, Sulfur, and Silicon, 186:58–66, 2011

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426501003781624

THE SYNTHESIS OF NEW THIOSUBSTITUTED COMPOUNDS WITH BUTADIENYL AND BUTENYNYL GROUPS

Cemil İbis and Sibel Şahinler Ayla
Faculty of Engineering, Department of Chemistry, Istanbul University, Avcilar-Istanbul, Turkey

GRAPHICAL ABSTRACT



Abstract *Mono(thio)substituted butadiene **3a**, tetrakis(thio)substituted butadiene **4b**, and bis(thio)substituted butadiene **10j** were synthesized from 1,1,3,3,4,4-hexachloro butene and aromatic thiols in dimethylformamide at room temperature in the presence of triethylamine. Thiosubstituted butenyne compounds **5c**, **6a**, **7a**,**h**, and **11i** and butadiene compounds **3f**,**g**, **4d**, **8g**, **9d**, **and 10i** were synthesized from 1,1,3,3,4,4-hexachloro butene and different thiols in EtOH with NaOH solution. The thiosubstituted butadienes **13e** and **14f** were obtained from the reactions of 2H-1,1,3,4,-tetrachloro-4-bromo-butadiene and thiols in EtOH/H_2O solution of NaOH. The structures of the new compounds were determined by microanalysis, FT-IR, UV/Vis, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, MS, and fluorescence spectrophotometry.*

Keywords Coumarin; fluorescence property; spectroscopy; thioethers; thiosubstituted butadiene and butenyne compounds

INTRODUCTION

Reactions of butadiene compounds are important from both practical and theorical points of view. The ethylenic bond activates the functional group, with the result that the compounds undergo replacement reactions much more readily than analogous saturated compounds.[1] Dihalo-1,3-butadienes are useful for organic synthesis because of the vinyl-halide moiety and the butadienyl skeleton.[2–4] The other importance of butadiene structures refers to their biological properties.[5] Bis-, tris-, tetrakis(thio)subsituted diene, triene, and

Received 24 November 2009; accepted 15 March 2010.
We thank the Research Fund of the University of Istanbul for financial support of this work.
Address correspondence to Cemil İbis, Faculty of Engineering, Department of Chemistry, Istanbul University, 34320 Avcilar-Istanbul, Turkey. E-mail: ibiscml@istanbul.edu.tr

butenyne compounds were synthesized by nucleophlilic substitution of butadiene compounds.[6–10]

Because of their widespread occurence in nature, coumarins have received increased attention in chemistry, acting as antioxidants, enzyme inhibitors, and precursors of toxic substances.[11] The chemical and biological proporties of coumarin derivatives depend upon the type of substituents.[12,13] Their fluorescence properties have also been used as an advantage for the biochemical assay of enzymes.[14] The biological activities of coumarins and mercaptobenzoazoles are well known and include antiviral, anticonvulsant, antimicrobial, antibacterial, anticancer, and anti-HIV properties.[15,16]

The aim of this study is the synthesis and characterization of novel thiosubstituted butadiene and butenyne compounds with different types of substituents including the coumarin and benzoazole moieties.

RESULTS AND DISCUSSION

The mono(thio)substituted compound **3a**, tetrakis(thio) substituted compound **4b**, and bis(thio)substituted butadiene **10j** were synthesized by the reaction between the halobutene **1** and **2a**, **2b**, and **2j** in the presence of DMF and triethylamine, respectively. The new butenynes **5c**, **6a**, **7a**,**h**, and **11i** and the thiosubstituted butadienes **3f**,**g**, **4d**, **8g**, **9d**, and **10i** were obtained from the reaction of halobutenes **1** and the corresponding thiols (Scheme 1) in the presence of an EtOH/H_2O solution of NaOH. The thiosubstituted butadienes **13e** and **14f** were prepared by the reaction of *2H*-1,1,3,4,-tetrachloro-4-bromo-butadiene and respective thiols in an EtOH/H_2O solution of NaOH.

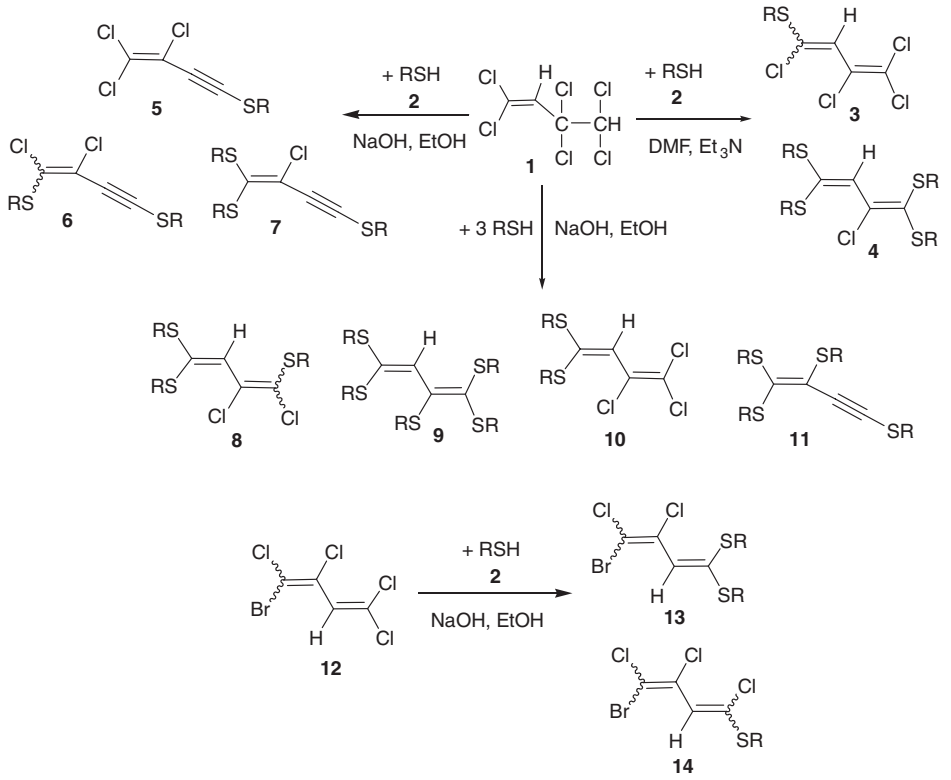
The ^{1}H NMR spectrum of compound **3a** exhibited the presence of a vinyl proton at 6.27 ppm. The IR spectrum of compounds **3g** and **8g** showed sharp peaks at 1720 and 1731 cm^{-1}, indicative for the C = O stretching. The fluorescence properties of the two thiosubstituted butadienes **3g** and **8g** containing a coumarin group are presented in Table 1. The excitation and emission spectra for these compounds are shown in Figure 1.

Regarding the reaction mechanism, it is possible that 2*H*-pentachlorobutadiene ($Cl_2C{=}CH{-}CCl{=}CCl_2$), formed by elimination of HCl from halobutene **1**, undergoes a second elimination of HCl leading to perchlorobutenyne ($Cl_2C{=}CCl{-}C{\equiv}C{-}Cl$). The new butenynes **5c**, **6a**, **7a**, and **7h** are obtained by substitution at this perchlorobutenyne compound.[6] In the IR spectra of **6a** and **7a**, characteristic bands at 2144 and 2153 cm^{-1} for the (C≡C) streching were observed, respectively. The IR spectra of compound **5c** also showed a characteristic band for the carbonyl group at 1671 cm^{-1} as a result of conjugated group effect. The mass spectrum of **3f** in the positive ion mode for ESI confirms the proposed structure; the protonated molecular peak was identified at m/z (%) 341 (100) $[M+H]^+$ (Figure 2). The fragmantation of the molecular peak gave a fragment ion corresponding to the cleavage of a chlorine atom at m/z (%) 304 (100).

The ^{19}F NMR spectrum of compound **4b** shows the presence of fluorine atoms in meta, para, and ortho positions on the phenyl rings (−137.36, −158.23, −158.60 ppm),

Table 1 Excitation and emission maximum wavelengths

Compound	Solvent	$\lambda_{ex.}$(max.)	$\lambda_{em.}$(max.)
3g	$CHCl_3$	326.00	396.00
8g	$CHCl_3$	327.07	393.07



R		Product	R		Product
a	OCH_3, OCH_3	3a, 6a, 7a	**f**		3f, 14f
b	F, F, F, F, F	4b	**g**	CH_3, O, O	3g, 8g
c	COOH	5c	**h**	$HO-(CH_2)_3-$	7h
d	CF_3-CH_2-	4d, 9d	**i**		10i, 11i
e	$HO-(CH_2)_6-$	13e	**j**	NO_2	10j

Scheme 1 Synthesis of novel butadiene and butenyne compounds.

respectively.[17,18] The IR spectra of compounds **7h** and **13e** show broad bands at 3344 and 3341 cm^{-1} for the −OH streching. In the ^1H NMR spectrum of compounds **4d** and **14f**, the vinyl protons are detected at 6.90 and 6.23 ppm, respectively.

The ^{19}F NMR spectrum of compound **9d** displays the presence of five different CF_3CH_2-groups resonating at −68.41, −68.48, −68.54, −68.52, and −68.68 ppm.[19] The pentakis(thio)substituted compound **9d** is formed by the addition of one thiol molecule to the butatriene or butenyne compound **11**.[20] The mass spectrum of **10j** in the positive ion mode for ESI confirms the proposed structure; the molecular peak was identified at m/z

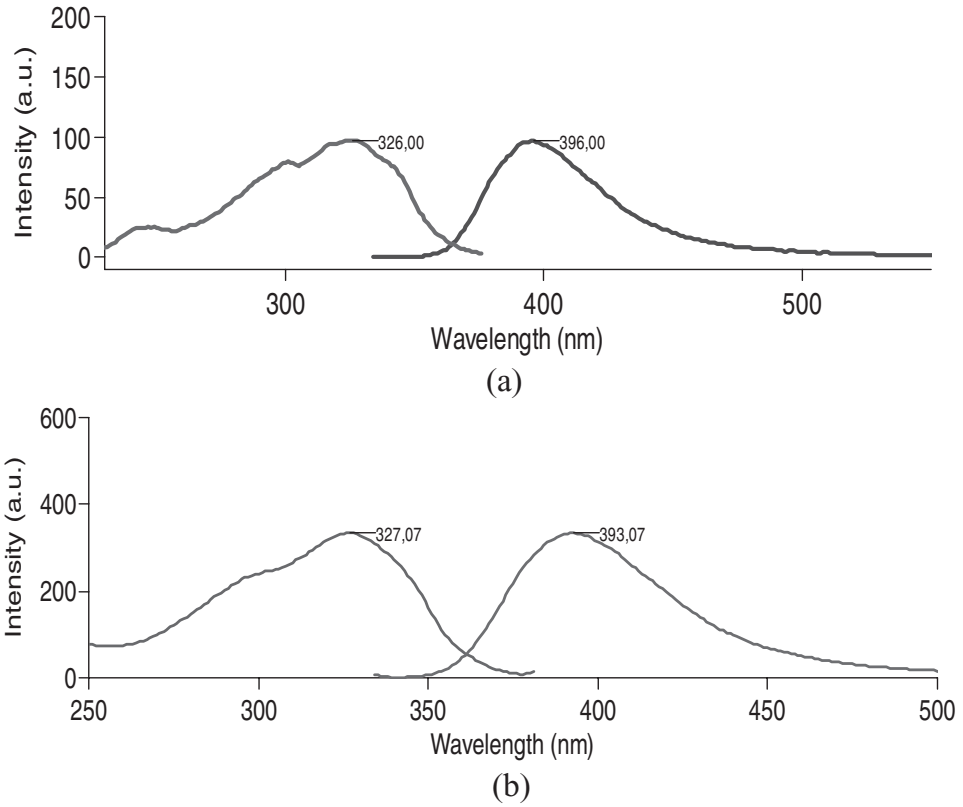


Figure 1 Excitation and emission spectra measured for 10^{-4} M solutions for (a) compound **3g** and (b) compound **8g** in $CHCl_3$. Excitation and emission slit widths were set at 5 nm.

(%) 486 (38) $[M+Na]^+$. The fragmentation of the molecular peak gives a fragment ion at m/z (%) 452 (100) corresponding to the cleavage of one chlorine atom from the molecule.

The new butadiene **10i** and new butenyne **11i** are obtained from the reaction of the halobutene **1** and cyclopentyl mercaptan (**2i**). These two compounds show different patterns in the IR spectrum. For compound **11i**, a characteristic sharp peak at 2150 cm^{-1} is observed, indicating the presence of a triple bond in the molecule, while compound **10i** does not show any peak in this area of IR. Regarding the reaction mechanism, it is possible that the tetrakisbutatriene is formed first and subsequently isomerizes to the butenyne **11i**.[20,21]

Results from the spectroscopic characterization of all compounds are reported in the Experimental section.

EXPERIMENTAL

Melting points were measured using a Büchi B-540 melting point apparatus and are uncorrected. Microanalyses were performed on a Thermo Finnigan Flash EA 1112 series elemental analyser. Infrared (IR) spectra were recorded in KBr pellets or in Nujol mulls on a Perkin Elmer Precise Spectrum One FTIR spectrometer. UV spectra were recorded on a Perkin Elmer Precise Lambda 35 UV-Vıs spectrometer. Fluorescence spectra were run

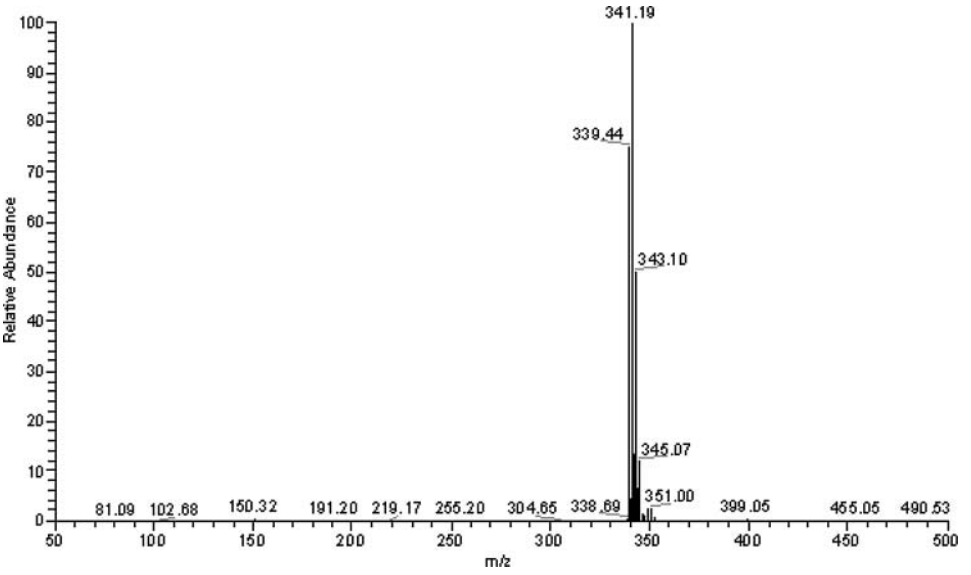


Figure 2 Full-MS spectrum of compound **3f** in the positive mode of ESI.

on a Varian Cary Eclipse Fluorescence spectrophotometer. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 with a Varian Unıty INOVA spectrometer. In the case of the ^{1}H NMR spectra, the FIDs were obtained at a sweep width of 8 KHz for a digital resolution of 0.49 Hz/point. Chemical shifts δ are given in ppm, coupling constants in Hz. Internal standards used: TMS for ^{1}H and ^{13}C and $CFCl_3$ for ^{19}F.

Mass spectra were obtained on a Thermo Finnigan LCQ Advantage MAX LC/MS/MS spectrometer using ion-trap mass analyzer for ESI source. Products were isolated by column chromatography on silica gel (Fluka silica gel 60, particle size 63–200 μm). Thin-layer chromatography was performed on Merck silica gel plates ($60F_{254}$), and detection was carried out with ultraviolet light (254 nm). All reagents and solvents were of reagent grade, obtained from commercial suppliers, and used without further purification.

General Procedure 1

1,1,3,3,4,4-Hexachloro butene (1.0 g, 3.8 mmol) and the aromatic thiol (15.2 mmol) were stirred in a mixture of DMF (30 mL) and triethylamine (3 mL) for 2 h at room temperature. Chloroform was added to the reaction mixture to separate the organic layer. The organic layer was washed with water (4 $\times$ 30 mL) and dried with Na_2SO_4. After filtering, the solvent was evaporated, and the residue was purified by column choromatography on silica gel.

General Procedure 2

1,1,3,3,4,4-Hexachloro butene (1.0 g, 3.8 mmol) and different amounts of the respective thiol were stirred in a mixture of EtOH (30 mL) and aqueous solution of NaOH (1.2 g NaOH and 8 mL of water) for 2 h at room temperature. Chloroform was added to the reaction mixture to separate the organic layer. The organic layer was washed with water

(4 × 30 mL) and dried with Na_2SO_4. The solvent was evaporated, and the residue was purified by column choromatography on silica gel.

General Procedure 3

Equimolar amounts of *2H*-1,1,3,4-tetrachloro-4-bromo-butadiene (1.0 g, 3.7 mmol) and the respective thiol (3.7 mmol) were stirred in a mixture of EtOH (30 mL) and an aqueous solution of NaOH (1.2 g NaOH and 8 mL of water) for 2 h at room temperature. Chloroform was added to the reaction mixture to separate the organic layer. The organic layer was washed with water (4 × 30 mL) and dried with Na_2SO_4. The solvent was evaporated, and the residue was purified by column choromatography on silica gel.

1,1,2,4-Tetrachloro-4-(3-4-dimethoxyphenylthio)-1,3-butadiene (3a). Yield 0.22 g (16%); oil, $R_f = 0.3$ with $CHCl_3$ as an eluent; IR (KBr, cm^{-1}): 2933, 1398 (C—H), 1584 (C=C); UV-VIS ($CHCl_3$) λ_{max} (nm) (log ε): 292 (3.60), 240 (3.84); ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 3.80 (s, 3H, $-OCH_3$), 3.81 (s, 3H, $-OCH_3$), 6.27 (s, 1H, >C=C*H*), 6.6–7.1 (m, 3H, arom-H); ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 55.0 ($-OCH_3$), 118.2, 118.4, 117.7 (**C**H$_{arom}$), 148.7, 148.4, 132.8 (**C**$_{arom}$), 114.1, 123.8, 128.5, 132.9 (C$_{butad}$); MS (—ESI): m/z 359 $(M-H)^-$; $C_{12}H_{10}SCl_4$ (M, 360.08). Calcd. C, 40.03; H, 2.80; S, 8.90. Found. C, 40.10; H, 2.90; S, 8.54%.

1,1,2,4-Tetrachloro-4-(benzo-1,3-imidazolyl-(2)-thio)-1,3-butadiene (3f). Yield 1.09 g (85%); white solid, mp: 175–177°C; $R_f = 0.35$ with $CHCl_3$ as eluent; IR (KBr, cm^{-1}): 3042 (Ar—H), 2961, 2880 (C—H), 3074 (N—H), 1515 (C=C); UV-VIS ($CHCl_3$) λ_{max} (nm) (log ε): 286 (3.65), 264 (3.63), 239 (3.60); ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 5.57 (s, 1H, —NH), 6.6 (s, 1H, >C=C*H*), 7.1–7.8 (m, 4H, arom-H); ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 147.1 (S—C=N), 116.6, 118.0, 122.4, 122.5 (CH$_{arom}$), 131.8, 141.1, 142.2 (C$_{arom}$), 120.7, 123.3, 126.5, 131.4 (C$_{butad}$); MS (+ESI): m/z 341 $(M+H)^+$, 304 (M—Cl); $C_{11}H_6Cl_4N_2S$ (M, 340.06). Calcd. C, 38.85; H, 1.78; S, 9.43. Found C, 38,70; H, 1.62; S, 9.35%.

1,1,2,4-Tetrachloro-4-(7-mercapto-4-methyl-coumarinyl)-1,3-butadiene (3g). Yield 1.2 g (83%); yellow solid; mp: 125–127°C; R_f = 0.45 with EtAc as an eluent; IR (KBr, cm^{-1}): 3059, 1385 (C—H), 1733 (C=O), 1599 (C=C); UV-VIS ($CHCl_3$) λ_{max}(logε) (nm): 330 (4.19), 283 (4.10), 240 (4.18); fluorescence: ($CHCl_3$) λ_{max}(ex): 326, λ_{max}(em): 396 nm; ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 2.36 (s, 3H, CH_3), 6.26 (s, 1H, >C=C*H*), 6.70 (s, 1H, >C=C*H*), 7.30–7.50 (m, 3H, arom-H); ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 17.6 (CH_3), 120.7, 122.4, 124.1, 125.6 (**C**H$_{arom}$), 122.8, 135.3, 153.0, 158.9 (**C**$_{arom}$), 113.3, 124.4, 128.1, 134.0 (C$_{butad}$), 159.0 (C=O); MS (+ESI): m/z 383 $(M+H)^+$, 347 (M—Cl); $C_{14}H_8Cl_4O_2S$ (M, 382,09). Calcd. C, 44.21; H, 2.11; S, 8.39. Found C, 43.89; H, 2.20; S, 8.25%.

2-Chloro-1,1,4,4-(pentafluorophenylthio)-1,3-butadiene (4b). Yield 0.30 g (9%); oil, $R_f = 0.4$ with $CHCl_3$:EtAc (2:1) as eluent; IR (KBr, cm^{-1}): 2936, 1390 (C—H), 1483 (C—F), 1601 (C=C); UV-VIS ($CHCl_3$) λ_{max} (nm) (log ε): 267 (3.44), 240 (3.45), 231 (3.25); ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 6.59 (s, 1H, >C=C*H*); ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 147.3, 145.4, 141.3, 141.1, 139.4, 139.2, 135.6 (**C**$_{arom}$), 101.8, 121.8, 123.3, 135.3 (C$_{butad}$); ^{19}F NMR (470.22 MHz, $CDCl_3$, CCl_3F) $\delta = -137.36$ (*m*-F), −158.23 (*p*-F), −158.60 (*o*-F), MS (—ESI): m/z 880 $(M-H)^-$; $C_{28}HClF_{20}S_4$ (M, 880.99). Calcd. C, 38.17; H, 0.11; S, 14.56. Found C, 38.29; H, 0.10; S, 14.30%.

2-Chloro-1,1,4,4-(2,2,2-trifluoroethylsulfanyl)-1,3-butadiene (4d). Yield 0.1 g (5%); oil, R_f = 0.25 with $CHCl_3$ as eluent; IR (KBr, cm^{-1}): 3000, 2950 (C—H);

1083, 1309 (C—F); UV-VIS ($CHCl_3$) λ_{max} (nm) (log ε): 315 (3.30), 267 (3.20), 238 (3.25); ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 3.35, 3.37, 3.38, 3.40 (s, 8H, —S—C*H*$_2$), 6.9 (s, 1H, >C=C*H*);^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 34.0, 34.2, 34.6, 34.8 (—S—*C*H$_2$), 122.5, 124.8, 133.1, 141.6 (C_{butad}), 132.7, 132.8, 135.6, 135.8 (—CF_3); ^{19}F NMR (470.22 MHz, $CDCl_3$, CCl_3F) δ = −68.53, −68.55, −68.85, −69.00 (—C*F*$_3$); MS (—ESI): m/z 579 $(M+Cl)^-$; $C_{12}H_9ClF_{12}S_4$ (M, 544.84). Calcd. C, 26.45; H, 1.66; S, 23.54. Found C, 26.20; H, 1.59; S, 23.50%.

1,1,2-Trichloro-4-(2-carboxy-phenyl-thio)-1-buten-3-in (5c). Yield 0.4 g (34%); oil, R_f = 0.2 with EtAc as an eluent; IR (KBr, cm^{-1}): 2159 (C≡C), 1671 (C=O), 3444 (—OH); UV-VIS (DMF) λ_{max} (nm) (log ε): 302 (3.70), 270 (3.47), 240 (3.65); ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 7.81 (d, J = 7.8 Hz, 1H, arom-H), 8.20 (t, J = 7.8 Hz, 2H, arom-H), 7.25 (t, J = 6.8 Hz, 1H, arom-H); ^{13}C NMR (125.66 MHz, DMSO): δ = 90.8, 92.3 (C≡C), 131.8, 134.8 (C_{arom}), 124.6, 129.2, 131.8, 134.8 (CH_{arom}), 112.5, 127.6 (C=C), 167.9 (C=O); $C_{11}H_5Cl_3O_2S$ (M, 307.58). Calcd. C, 42.95; H, 1.64; S, 10.42. Found C, 42.70; H, 1.60; S, 10.55%.

1,2-Dichloro-1,4-(3,4-dimethoxyphenylthio)-1-buten-3-in (6a). Yield 0.3 g (17%); oil, R_f = 0.3 with $CHCl_3$ as eluent; IR (KBr, cm^{-1}): 2957, 1339 (C—H), 2153 (C≡C), 1585 (C=C); UV-VIS ($CHCl_3$) λ_{max} (nm) (log ε): 289 (3.52), 239 (3.72); ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 3.79 (s, 3H, —OCH_3), 3.82 (s, 3H, —OCH_3), 6.7–7.1 (m, 6H, arom-H); ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 86.1, 88.4 (C≡C), 55.1 (—OCH_3), 116.8, 125.9, 127.4 (**C**H$_{arom}$), 134.8, 148.3, 149.4 (**C**$_{arom}$), MS (+ESI): m/z 458 $(M+H)^+$, 422 (M—Cl); $C_{20}H_{18}Cl_2O_4S_2$ (M, 457.39). Calcd. C, 52.52; H, 3.97; S, 14.02. Found C, 52.48; H, 3.90; S, 14.10%.

2-Chloro-1,1,4-(3,4-dimethoxyphenylthio)-1-buten-3-in (7a). Yield 0.2 g (10%); oil, R_f = 0.3 with $CHCl_3$ as eluent; IR (KBr, cm^{-1}): 2932, 1398 (C—H), 2144 (C≡C), 1584 (C=C); UV-VIS ($CHCl_3$) λ_{max} (nm) (log ε): 256 (4.30), 242 (4.29), 209 (4.69); ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 3.80 (s, 3H, —OCH_3), 3.81 (s, 3H, —OCH_3), 6.7–7.1 (m, 6H, arom-H); ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 88.3, 89.1 (C≡C), 55.1 (—OCH_3), 116.0, 116.2, 118.1, 123.3, 123.4, 123.5, 124.0 (**C**H$_{arom}$), 126.1, 126.5, 127.0, 138.4, 148.2, 148.7, 149.4, 149.8 (**C**$_{arom}$); MS (+ESI): m/z 591 $(M)^+$; $C_{28}H_{27}ClO_6S_3$ (M, 591.16). Calcd. C, 56.89; H, 4.60; S, 16.27. Found C, 56.48; H, 4.48; S, 15.90%.

2-Chloro-1,1,4,4-(1-propanol-3-sulfanyl)-1-buten-3-yne (7h). Yield 0.45 g (34%); oil, R_f = 0.45 with EtAc: $CHCl_3$ (1:1) as eluent; IR (KBr, cm^{-1}): 3344 (—OH), 2934 (C—H), 2151 (C≡C); UV-VIS ($CHCl_3$) λ_{max} (log ε) (nm): 288 (3.78), 277 (3.83), 240 (4.01); ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 1.2–1.8 (m, 6H, —S—CH_2—C*H*$_2$), 2.81 (t, J = 6.8 Hz, 6H, —S—CH_2); 3.83 (t, J = 7.3 Hz, 6H, —O—CH_2); 4.1 (s, 3H, —OH),^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 85.1, 91.9 (C≡C); 24.3, 26.9, 28.3 (—CH_2), 31.5, 31.6, 34.9 (—S—CH_2), 59.3, 61.8, 61.9 (—O—CH_2), 166.2 (C—S); $C_{13}H_{21}ClO_3S_3$ (M, 356,03). Calcd. C, 43.74; H, 5.93; S, 26.95. Found C, 43.45; H, 5.82; S, 26.45%.

1,2-Dichloro-1,4,4-(7-mercapto-4-methyl-coumarinyl)-1,3-butadiene (8g). Yield 0.3 g (10%); yellow solid, mp: 130–132°C; R_f = 0.35 with $CHCl_3$ as eluent; IR (KBr, cm^{-1}): 2924, 1385 (C—H), 1731 (C=O), 1600 (C=C); UV-VIS ($CHCl_3$) λ_{max} (log ε) (nm): 332 (3.56), 284 (3.34), 239 (3.59); Fluorescence: ($CHCl_3$) λ_{max}(ex): 327.07, λ_{max}(em): 393.07 nm; ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 2.34 (s, 9H, CH_3), 6.21 (s, 1H, >C=C*H*), 6.23 (s, 1H, >C=C*H*), 6.24 (s, 1H, >C = C*H*), 6.68 (s, 1H, >C=C*H*), 7.33 (d, J = 8.3 Hz, 6H, arom-H); 7.46 (d, J = 8.2 Hz, 3H, arom-H); ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 17.6 (—CH_3), 121.1, 123.5, 124.3, 124.4 (**C**H$_{arom}$), 129.3, 136.4, 139.9, 152.3, 152.8 (C_{arom}), 113.4, 126.1, 142.4 (C_{butad}), 159.1, 153.1, 150.8 (C=O); MS

(+ESI): m/z 716 $(M+Na)^+$; $C_{34}H_{22}Cl_2O_6S_3$ (M, 693,64). Calcd. C, 58.87; H, 3.20; S, 13.87. Found C, 58.60; H, 3.07; S, 13.40%.

2-Chloro-1,1,3,4,4-(2,2,2-trifluoro-ethyl-sulfanyl)-1,3-butadiene (9d). Yield 0.4 g (17%); oil, $R_f = 0.25$ with $CHCl_3$ as eluent; IR (KBr, cm^{-1}): 3002, 2950 (C—H); 1083, 1308 (C—F); UV-VIS ($CHCl_3$) λ_{max} (nm) (log ε): 312 (3.96), 239 (3.84); ^{1}H NMR (499.74 MHz, $CDCl_3$): $\delta = 3.35, 3.37, 3.38, 3.40, 3.41$ (s, 10H, —S—CH_2), 6.75 (s, 1H, >C=CH); ^{13}C NMR (125.66 MHz, $CDCl_3$): $\delta = 33.9, 34.3, 34.6, 34.7, 34.9$ (—S—CH$_2$), 127.6, 124.7, 122.7, 141.8 (C_{butad}), 132.7, 132.8, 135.4, 135.8 (CF_3); ^{19}F NMR (470.22 MHz, $CDCl_3$, CCl_3F): $\delta = -68.41, -68.48, -68.54, -68.52, -68.68$ (CF_3); MS (—ESI): m/z 660 $(M+Cl)^-$; $C_{14}H_{11}F_{15}S_5$ (M, 624.54). Calcd. C, 26.92; H, 1.78; S, 25.67. Found C, 26.72; H, 1.72; S, 25.32%.

1,1,2-Trichloro-4,4-(cyclopentil-sulfanyl)-1,3-butadiene (10i). Yield 0.3 g (22%); oil, $R_f = 0.35$ with $CHCl_3$ as eluent; IR (KBr, cm^{-1}): 2957 (C—H), 1546 (C=C); UV-VIS ($CHCl_3$) λ_{max} (log ε) (nm): 306 (4.05), 239 (4.07), 280 (3.99); ^{1}H NMR (499.74 MHz, $CDCl_3$): $\delta = 1.8–2.1$ (m, 8H, —CH_2), 3.45–3.55 (m, 8H, —CH_2), 3.6–3.7 (m, 2H, >CH—S), 6.87 (d, $J = 6.3$, 1H, >C=CH); ^{13}C NMR (125.66 MHz, $CDCl_3$): $\delta = 49.4$, 49.3 (>C—S), 32.3, 32.2, 32.1, 31.8, 23.8, 23.8, 23.7, 23.60 (—CH_2), 143.9, 132.0, 120.9, 126.1 (C_{butad}); MS (+ESI): m/z 358 $(M+H)^+$, 288 (M—2Cl); $C_{14}H_{19}S_2Cl_3$ (M, 359.79). Calcd. C, 47.0; H, 5.35; S, 17.92. Found C, 46.87; H, 5.15; S, 17.23%.

1,1,3-Trichloro-4,4-(4-nitrophenyltiyo)-1,3-butadiene (10j). Yield 0.3 g (17%); oil, $R_f = 0.3$ with $CHCl_3$ as eluent; IR (KBr, cm^{-1}): 3039 (C—H), 1341 (Ar—NO_2), 1519 (C=C); UV-VIS ($CHCl_3$) λ_{max} (log ε) (nm): 334 (3.65), 241 (3.64), 230 (3.61); ^{1}H NMR (499.74 MHz, $CDCl_3$): $\delta = 6.89$ (s, 1H, >C=CH), 7.1–7.9 (m, 4H, arom-H); ^{13}C NMR (125.66 MHz, $CDCl_3$): $\delta = 119.7, 122.7, 123.3, 130.0$ (C_{butad}), 125.5, 128.0, 128.6, 129.8, 131.5 (CH_{arom}), 140.9, 144.5, 146.1 (C_{arom}); MS (+ESI): m/z 486 $(M+Na)^+$, 452 (M—Cl); $C_{16}H_9Cl_3N_2O_4S_2$ (M, 463.74). Calcd. C, 41.44; H, 1.96; S, 13.83. Found C, 41.33; H, 1.85; S, 13.75%.

1,1,2,4-(Cyclopentil-sulfanyl)-1-buten-3-yne (11i). Yield 0.15 g (9%); oil, $R_f = 0.4$ with $CHCl_3$ as eluent; IR (KBr, cm^{-1}): 2951 (C—H), 2150 (C≡C); UV-VIS ($CHCl_3$) λ_{max} (log ε) (nm): 240 (3.33), 235 (3.08), 231 (3.05); ^{1}H NMR (499.74 MHz, $CDCl_3$): $\delta = 1.71–2.00$ (m, 16H, —CH_2), 3.42–3.55 (m, 16H, —CH_2), 3.65–3.68 (m, 4H, >CH—S); ^{13}C NMR (125.66 MHz, $CDCl_3$): $\delta = 49.1, 48.9, 46.9, 42.2$ (>C—S), 33.6, 33.5, 33.4, 33.0, 32.1, 29.9, 29.8, 29.6, 25.1, 25.0, 24.9, 24.8, 24.91, 24.89 (—CH_2), 86.7, 93.3 (C≡C); MS (+ESI): m/z 478 $(M+Na)^+$; $C_{24}H_{36}S_4$ (M, 452.80). Calcd. C, 63.66; H, 8.01; S, 28.33. Found C, 63.41; H, 7.98; S, 28.24%.

1-Bromo-1,2-dichloro-4,4-(1-propanol-3-sulfanyl)-1,3-butadiene (13e). Yield 0.2 g (11%); oil, $R_f = 0.2$ with $CHCl_3$ as eluent; IR (KBr, cm^{-1}): 3341 (—OH), 2930, 2857 (C—H), 1542 (C=C); UV-VIS ($CHCl_3$) λ_{max} (log ε) (nm): 290 (4.27), 278 (3.54), 240 (3.81); ^{1}H NMR (500 MHz): $\delta = 1.2–1.4$ (m, 12H, (CH_2)$_3$), 1.8–2.2 (m, 4H, —S—CH_2—CH_2), 2.90 (t, $J = 6.8$ Hz, 4H, —S—CH_2); 3.82 (t, $J = 7.3$ Hz, 6H, —O—CH_2), 5.2 (s, 2H, —OH), 6.44 (s, 1H, >C=CH); ^{13}C NMR (125.66 MHz, $CDCl_3$): $\delta = 18.1, 20.9, 21.2, 28.7$ (—CH_2), 36.6, 39.5 (—S—CH_2), 59.3, 60.5, 65.7 (—O—CH_2), 167.5 (C—S), 137.0, 125.9, 123.1, 121.4 (C_{butad}); MS (+ESI): m/z 467 $(M+H)^+$; $C_{16}H_{27}Cl_2O_2S_2Br$ (M, 466.32). Calcd. C, 41.21; H, 5.84; S, 13.75. Found C, 41.18; H, 5.45; S, 13.63%.

1-Bromo-1,2,4-Trichloro-4-(benzo-1,3-imidazolyl-(2)-thio)-1,3-butadiene (14f). Yield 0.3 g (21%); oil; $R_f = 0.3$ with $CHCl_3$ as eluent; IR (KBr, cm^{-1}): 2980 (Ar—H), 2961, 2855 (C—H), 3071 (N—H), 1563 (C=C); UV-VIS ($CHCl_3$) λ_{max} (nm) (log ε): 290 (3.45), 270 (2.98), 240 (3.54); ^{1}H NMR (499.74 MHz, $CDCl_3$): $\delta = 5.5$ (s, 1H,

−NH), 6.23 (s, 1H, >C=C*H)*, 7.1–7.8 (m, 4H, arom-H); ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 144.5 (S−C=N), 115.5, 123.6, 123.5 (CH_{arom}), 138.5, 140.5 (C_{arom}), 119.4, 124.6, 138.5, 138.7 (C_{butad}); MS (+ESI): m/z 407 $(M+Na)^+$; $C_{11}H_6BrCl_3N_2S$ (M, 384.51). Calcd. C, 34.37; H, 1.57; S, 8.34. Found C, 34,32; H, 1.30; S, 8.56%.

REFERENCES

1. DeWolfe, R. H.; Young, W. G. *Chem. Rev.* **1956**, *56*, 753.
2. Block, E.; Tries, F.; He, C.; Guo, C.; Thiruvazhi, M.; Toscano, P. J. *Org Lett.* **2003**, *5*, 1325.
3. Xi, C.; Huo, S.; Afifi, T. H.; Hara, R.; Takahashi, T. *Tetrahedron Lett*. **1997**, *38*, 4099.
4. Liu, P.; Li, L.; Webb, J. A.; Zhang, Y.; Goroff, N. S. *Org. Lett.* **2004**, *6*, 2082.
5. Diamond Alkali Company (Erf. H. Bluestone), U.S. Patent 3021370 (February 13, 1962).
6. Roedig, A.; Ibis, C.; Zaby, G. *Chem. Ber.* **1981**, *114*, 684.
7. Roedig, A.; Zaby, G. *Tetrahedron Lett*. **1977**, *21*, 1771.
8. İbis, C. *Liebigs Ann. Chem.* **1984**, 1873.
9. İbis, C. *Liebigs Ann. Chem.* **1987**, 1009.
10. İbis, C.; Bal, T. *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, *178*, 431.
11. Carpenter, I.; McGarry, E. J.; Scheimann, F. *Tetrahedron Lett.* **1970**, *46*, 3983.
12. Kamelia, M.; Amin, M. D. E.; Doaa, E.; Abdel, R.; Yasmin, A. A. *Bioorg. Med. Chem.* **2008**, *16*, 5377.
13. İbis, C.; Şahinler Ayla, S. *Arkivoc* **2008**, **>xvi**, 29.
14. Zhao, W. W.; Bian, W. S. *J. Mol. Struct. THEOCHEM* **2008**, *859*, 73.
15. Zimmerman, M.; Yurewicz, E.; Patel, G. *Anal. Biochem.* **1976**, *70*, 258.
16. Hays, S. J.; Rice, M. J.; Ortwine, D. F.; Johnson, G.; Schwarz, R. D.; Boyd, D. K.; Copeland, L. F.; Vartanian, M. G.; Boxer, P. A. *J. Pharm. Sci.* **1994**, *83*, 1425.
17. Shaikh, T. A.; Bakus, R. C.; Parkin, S.; Atwood, D. A. *J. Organomet. Chem.* **2004**, *691*, 1825.
18. Peach, M. E. *Can. J. Chem.* **1968**, *46*, 211.
19. Large-Radix, S.; Billard, T.; Langlois, B. *J. Fluorine Chem.* **2006**, *124*, 147.
20. Roedig, A.; Zaby, G. *Liebigs Ann. Chem.* **1979**, 1626.
21. Liu, P. H.; Li, L.; Web, J. A.; Zhang, Y.; Goroff, N. S. *Org. Lett.* **2004**, *6*, 2081.