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Nucleophilic Sulfanylation of 1,5-Disubstituted Pent-2-en-4-yn-1-ones

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Abstract—Regioselectivity of nucleophilic addition of benzenethiols and phenylmethanethiol to 1,5-diarylpent-2-en-4-yn-1-ones in ethanol in the presence of triethylamine at 0–30°C is determined by the nucleophile nature. Phenylmethanethiol adds to the double bond, whereas benzenethiols add to the triple bond. The addition products, 1,5-diaryl-3-benzylsulfanylpent-4-yn-1-ones and 1,5-diaryl-5-(4-arylsulfanyl)penta-2,4-dien-1-ones, respectively, were isolated in 43–89% yield. Substituents in the aryl rings of the substrates did not affect the reaction direction.

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Nucleophilic sulfanylation of activated α,β-unsaturated compounds provides a simple and efficient synthetic route to sulfides [1–4] and sulfur-containing heterocyclic compounds [5–7]. This reaction smoothly occurs in polar solvents in the presence of bases, such as amines, alkoxides, and alkalies. Thiols add especially readily to α,β-unsaturated [8] and acetylenic ketones [5, 9]. In all cases, nucleophilic attack by the reagent is directed at the β-carbon atom of the multiple bond (1,4-addition), and the yields of addition products attain 80–90%. Acetylenic ketones are more reactive than their vinyl analogs [10] in nucleophilic sulfanylation.

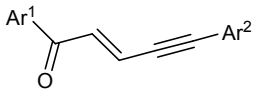
Sulfanylation of acetylenic ketones is characterized by some stereochemical peculiarities. Thermodynamically controlled reaction of 1,3-diarylprop-2-yn-1-ones with benzenethiols in the presence of trialkylamines, regardless of the reactant nature, leads to the formation of a mixture of *E*- and *Z*-isomeric 1-aryl-3-arylsulfanylprop-2-en-1-ones [11], the *Z* isomer appreciably prevailing. The *E*/*Z*-isomer ratio under kinetic control is determined mainly by the active reagent species (whether it acts as amine–thiol H-complex, ion pair, or free Et_3NH^+ and ArS^- ions), as well as by the solvent nature and substituent in arenethiol. Analogous conclusions were drawn while studying the reaction kinetics [12, 13].

Addition of thiols to activated vinylacetylenes was studied to a considerably lesser extent. It is known that nucleophilic sulfanylation of enynoic acids and enyne ketones may involve both double and triple bonds therein, depending on the substrate structure, reagent and catalyst nature, and reaction conditions. Ketones with the general formula R′CH=CHC(O)C≡CR″ in the presence of bases at room temperature in alcohol take up benzenethiols and ethanethiol primarily at the triple bond [10, 14], whereas mixtures of several further sulfanylation products are formed when excess reagent is used [10]. Sodium hydrogen sulfide reacts at both multiple bonds of such ketones, yielding 2,3-dihydropyran-4-ones [7].

Benzenethiol and ethanethiol add only to the double bond of enynes XCH=CHC≡CR (X = CO_2Me, CN, COMe) in the presence of sodium ethoxide to afford acetylenic sulfides which undergo rearrangement into dienic ketones on prolonged storage (24–72 h) in the presence of EtONa [15]. The transformation of acetylenic sulfanylation products into dienes is interpreted as reversible addition–elimination of thiol to the double bond and irreversible addition to the triple bond.

Taking into account that some unsaturated sulfides exhibit anticarcinogenic activity and may also be used as antibiotics and coenzymes [16], development of convenient procedures for their synthesis from ac-

tivated vinylacetylenic compounds is an important problem. In the present work we studied regio- and stereoselectivity of sulfanylation of 1,5-diarylpent-2-en-4-yn-1-ones **Ia**–**Ig** and the structure of the sulfanylation products.



Ia–Ig

Ar^1 = Ph (**a**, **g**), 4-MeC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**), 4-ClC_6H_4 (**d**), 4-BrC_6H_4 (**e**), furan-2-yl (**f**); Ar^2 = Ph (**a**–**f**), 4-BrC_6H_4 (**g**).

Compounds **Ia**–**Ig** were selected as substrates due to the possibility for easy variation of electron density in the enyne fragment via introduction of electron-donating or electron-withdrawing substituents into the Ar^1 and Ar^2 aryl rings [17]. According to the IR, ^{1}H NMR, and X-ray diffraction data, vinylacetylenic ketones described by us previously [18] have *E* configuration in the crystalline state and in solution.

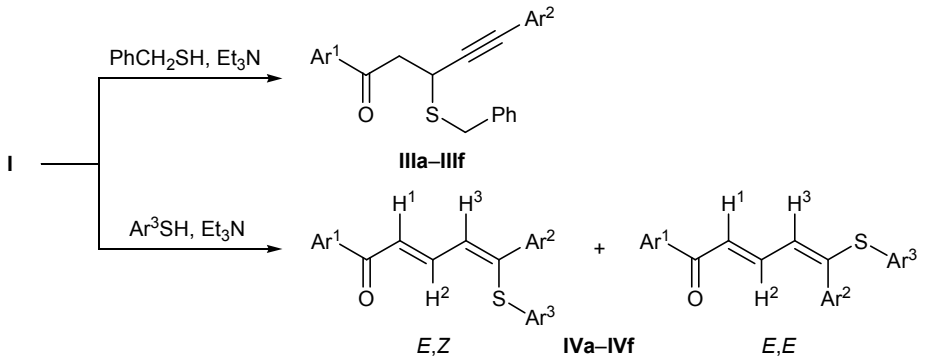
As sulfanylating agents we used phenylmethanethiol (**IIa**), and benzenethiols **IIb**–**IId** (Ar^3 = Ph, 4-MeC_6H_4, 4-BrC_6H_4). Preliminarily, we found that no sulfanylation of ketones **I** occurred in the absence of a catalyst. Addition of a catalytic amount of triethylamine ensured smooth sulfanylation in ethanol even at room temperature. Thiol **IIa** adds to the double bond of **Ia**, leading to the formation of 1,5-diaryl-3-benzylsulfanylpent-4-yn-1-ones **III** with high regioselectivity in the temperature range from 0 to 30°C (Scheme 1). The highest yields (89–90%) were obtained in the sulfanylation of ketones **Id** and **Ie** containing a halogen atom in the *para* position of the Ar^1 ring. Substituents in Ar^1 and Ar^2 in the initial ketones did not affect the direction of the addition of thiol **IIa**.

Acetylenic keto sulfides **IIIa**–**IIIf** were isolated as colorless crystalline substances. Their structure was confirmed by spectral data, as well as by X-ray analysis. The ^{1}H NMR spectra of **III** contained two doublets of doublets at δ 3.43–3.62 (J = 16.8–17.4, 7.8–8.0 Hz) and 3.25–3.48 ppm (J = 16.9, 6.2–6.3 Hz) due to diastereotopic protons 2-H_A and 2-H_B (Fig. 1). The 3-H proton appeared as a doublet of doublets at δ 4.18–4.35 ppm (J = 7.6–7.7, 6.3–6.4 Hz), and the benzylic protons (18-H_A and 18-H_B) gave two doublets at δ 4.03–4.08 (J = 13.3–13.7 Hz) and 3.99–4.02 ppm (J = 13.3 Hz). In the ^{13}C NMR spectra of **IIIa**–**IIIf**, signals from the triple-bonded carbon atoms were located at δ_C 87.8–89.5 (C^4) and 84.1–88.6 ppm (C^5), the carbonyl carbon signal was observed at δ_C 185.0–195.9 ppm (C^1), and signals at δ_C 43.9–44.2, 30.5–30.6, and 35.3–36.1 ppm were assigned to alkyl carbon atoms (C^2, C^3, and C^{18}, respectively).

The IR spectra of **IIIa**–**IIIf** lacked absorption bands assignable to stretching vibrations of diene (1650, 1600 cm^{-1}) or allene bond system (1950–1930 cm^{-1}). The carbonyl group gives rise to a strong narrow peak at 1690–1676 cm^{-1}, which suggests its conjugation only with aryl ring. The C≡C stretching vibration band (~2230 cm^{-1}) is characterized by a low intensity and is observed only at a high sample concentration, presumably due to high pseudosymmetry. The structure of **IIIa**–**IIIe** was proved by X-ray analysis.

Ketones **I** reacted with benzenethiols **IIb**–**IId** under analogous conditions, but thiols **II** added to the triple bond of **I**, affording dienic keto sulfides **IV** (Scheme 1). The best yields (82–83%) were obtained in the sulfanylation of ketone **Id**. Donor substituents in the aryl rings of ketones **I** (Ar^1, Ar^2) and benzenethiols **II** (Ar^3) reduced the yield to 43–66%.

Scheme 1.



III, Ar^1 = Ph (**a**, **f**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**), 4-BrC_6H_4 (**d**), furan-2-yl (**e**); Ar^2 = Ph (**a**–**e**), 4-BrC_6H_4 (**f**); **IV**, Ar^1 = Ar^2 = Ph, Ar^3 = 4-BrC_6H_4 (**a**); Ar^1 = 4-MeC_6H_4, Ar^2 = Ph, Ar^3 = 4-BrC_6H_4 (**b**); Ar^1 = 4-$MeOC_6H_4$, Ar^2 = Ph, Ar^3 = 4-BrC_6H_4 (**c**); Ar^1 = 4-ClC_6H_4, Ar^2 = Ar^3 = Ph (**d**); Ar^1 = 4-ClC_6H_4, Ar^2 = Ph, Ar^3 = 4-MeC_6H_4 (**e**); Ar^1 = 4-ClC_6H_4, Ar^2 = Ph, Ar^3 = 4-BrC_6H_4 (**f**).

Ketones **IVa–IVf** were isolated as bright yellow crystalline substances which are stable on storage. According to the ^{1}H NMR data, adducts **IV** are mixtures of *E*,*E* and *E*,*Z* isomers. The major *E*,*Z* isomer is represented in the ^{1}H NMR spectra by two doublets at δ 6.97–7.05 (J = 11.2–11.5 Hz) and 7.05–7.10 ppm (J = 11.2–11.5 Hz) from 3-H and 1-H and by a doublet of doublets at δ 8.20–8.29 ppm (J = 11.2–11.5, 14.9–14.4 Hz) from 2-H. The latter signal is displaced appreciably downfield relative to the 3-H and 1-H signals, which may be due to deshielding effect of the Ar[3] ring. In the ^{1}H NMR spectra of the *E*,*E* isomers, the doublets at δ 6.19–6.29 (J = 11.7 Hz) and 6.74–6.88 ppm (J = 14.7–14.9 Hz) with the coupling constants typical of *trans* configuration correspond to 1-H and 3-H, respectively. The 2-H signal is overlapped by those belonging to aromatic protons. The *E*,*E*/*E*,*Z* ratio in $CDCl_3$ ranges from 1:1.5 to 1:2.7; compounds **IVc** and **IVe** in solution were pure *E*,*Z* isomers. In the ^{13}C NMR spectra of **IVa**, **IVb**, and **IVd–IVf** we observed two signals in the region δ_C 180–190 ppm, which belong to the carbonyl carbon atoms of the two isomers.

The IR spectra of compounds **IV** in CCl_4 contained two poorly resolved carbonyl stretching vibration bands. The high-frequency band (1657–1660 cm^{-1}) corresponds to the *E*,*Z* isomer, and the shoulder at 1645–1637 cm^{-1}, to the *E*,*E* isomer. The assignment of these bands to C=O stretching vibrations is confirmed by their low-frequency shift by 5–6 cm^{-1} in going from carbon tetrachloride to more polar methylene chloride [19]. The IR spectra of crystalline samples (in KBr) displayed only one carbonyl band (1653–1648 cm^{-1}), indicating that compounds **IV** in crystal are likely to exist as a single isomer.

Thus, as with 1,3-diarylprop-2-yn-1-ones, the addition of benzenethiols to ketones **I** in the presence of triethylamine gives mixtures of two stereoisomers, the *Z* isomer prevailing.

It is known that in the sulfanylation of α,β-unsaturated ketones in polar solvents (alcohols, acetonitrile)

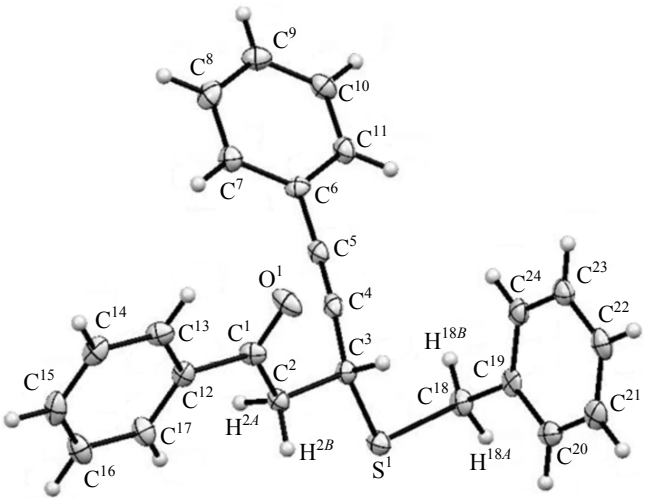


Fig. 1. Structure of the molecule of 1,5-diphenyl-3-benzylsulfanylpent-4-yn-1-one (**IIIa**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

under catalysis by tertiary amines the nucleophilic species is benzenethiolate ion, both free and in a solvent-separated ion pair ($RC_6H_4S^-||HN^+Et_3$) [20, 21]. Quantum chemical calculations [17] showed that electrophilic centers in ketones **I** may be the C^1, C^3, and C^5 atoms; however, the double bond is more polarizable and is more sensitive than the triple bond to the activating effect of the carbonyl group. Therefore, the double bond is more reactive toward such soft bases as thiols. Presumably, all thiols **IIa–IId** initially add to the double bond of **I** (kinetically controlled process). Due to fairly high resonance stability of benzenethiolate ions, the reaction with benzenethiols **IIb–IId** is reversible [22]. Benzenethiolate ion occurring in equilibrium with acetylenic keto sulfide **V** slowly adds to the triple bond of **I**, yielding adduct **IV** (thermodynamically controlled process; Scheme 2).

Unlike benzenethiolate ion, resonance stabilization of $PhCH_2S^-$ is impossible. Therefore, the addition of phenylmethanethiol to vinylacetylenic ketones **I** is almost irreversible, and no subsequent transformation of acetylenic keto sulfides **III** into dienes is observed.

Scheme 2.

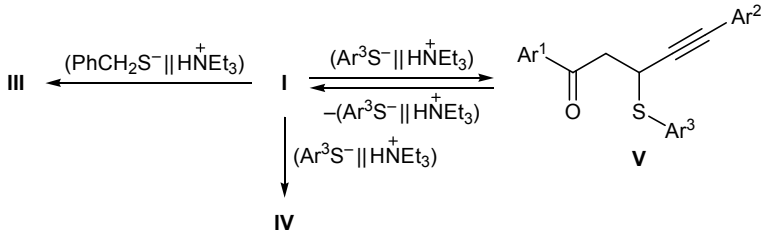


Table 1. Some bond lengths (Å) in molecules **IIIa**–**IIIe**

Bond	**IIIa**	**IIIb**	**IIIc**	**IIId**	**IIIe**
C^1–O^1	1.218(4)	1.217(2)	1.219(1)	1.216(2)	1.216(4)
C^1–C^2	1.517(4)	1.519(2)	1.516(2)	1.516(2)	1.512(4)
C^2–C^3	1.522(4)	1.533(3)	1.526(2)	1.530(2)	1.538(4)
C^3–C^4	1.467(4)	1.461(2)	1.465(2)	1.463(2)	1.464(4)
C^4–C^5	1.199(4)	1.198(2)	1.195(2)	1.196(2)	1.201(4)
C^3–S^1	1.829(3)	1.836(1)	1.834(1)	1.835(2)	1.824(3)
S^1–C^{18}	1.821(3)	1.821(2)	1.821(1)	1.823(2)	1.815(4)

Table 2. Some bond and torsion angles (deg) in molecules **IIIa**–**IIIe**

Angle	**IIIa**	**IIIb**	**IIIc**	**IIId**	**IIIe**
$O^1C^1C^2$	121.7(3)	121.4(2)	121.6(1)	121.7(1)	122.2(3)
$C^1C^2C^3$	113.2(3)	113.7(1)	114.0(1)	113.1(1)	111.8(3)
$C^4C^3C^2$	111.6(3)	112.1(1)	112.1(1)	111.7(1)	111.5(3)
$C^3C^4C^5$	176.2(3)	178.1(1)	177.7(1)	177.5(1)	176.1(3)
$C^{18}S^1C^3$	100.6(2)	100.5(1)	100.8(1)	100.5(1)	100.6(2)
$O^1C^1C^{12}C^{13}$	1.3	1.9	0.2	3.6	2.2[a]

[a] $O^1C^1C^{12}O^2$.

In order to confirm the proposed mechanism, we tried to detect kinetically controlled adduct **V** in the reaction mixtures. In the IR spectrum of the reaction mixtures, recorded in 15 min after addition of triethylamine, we observed two absorption bands in the carbonyl stretching vibration region, at 1687–1676 and 1655–1649 cm^{-1}. In some cases, the high-frequency band appeared as a shoulder. The absorption band at ~1685 cm^{-1} corresponds to the adduct in which the carbonyl group is conjugated only with the aryl ring, i.e., to the kinetically controlled product (**V**). The low-frequency band arises from the C=O group of dienic keto sulfides **IV**. After 18 h, the high-frequency band disappears almost completely from the IR spectrum, whereas the intensity of the low-frequency band appreciably increases. Kinetically controlled adduct **V** was also detected in the reaction mixture by capillary GLC. In all cases, the chromatograms of samples withdrawn from the reaction mixture in the initial moment contained an additional peak with a retention time matching neither initial reactants nor dienone **IV**; after 18–25 h, that peak was no longer detected.

Thus, the mechanism proposed previously for the sulfanylation of activated vinylacetylenic compounds XCH=CHC≡CR, where X is an electron-withdrawing group [15], is likely to be general. Taking into account our present data on the steric structure of compounds **IV**, we can state that the addition reactions of benzenethiols to vinylacetylenic ketones **I** and 1,3-diarylprop-2-yn-1-ones are analogous from the stereochemical viewpoint.

Substituents in the aryl rings of vinylacetylenic ketones **I** do not affect the direction of nucleophilic attack by thiol but only the yield of adducts. Therefore, the selectivity of the addition is determined mainly by the chemical nature of the reagent. The proposed scheme makes it possible to rationalize the regioselectivity of reactions with different thiols. Undoubtedly, further more detailed studies of nucleophilic reactions with activated enyne systems are necessary to confirm the proposed mechanism.

The X-ray diffraction data for compounds **III** showed that rupture of conjugation leads to extension of not only C^2–C^3 bond (Fig. 1; Tables 1, 2) where thiol adds but also of the neighboring C^3–C^4 and (to a lesser extent) C^1–C^2 bonds and that the triple C^4–C^5 bond slightly shortens [18]. The fact that in all cases the S^1–C^{18} bond is shorter than S^1–C^3 indicates electron density transfer from the phenyl group of the benzyl fragment. This also follows from the formation of characteristic intermolecular contacts (see below). Unlike initial ketones **I** [18], the Ar^1 ring lies almost in the plane passing through the C^{12}, C^1, O^1, and C^2 atoms. Insofar as rotation of the Ar^1 ring about the ordinary C^1–C^{12} bond should not be hindered, its coplanar arrangement is likely to be determined by intermolecular contacts. In fact, molecules **IIIa**–**IIId** in crystal are linked to form dimers via C^2–$H^{2B}\cdots\pi(Ar^1)$ interactions; the dimers formed by compounds **IIIb**, **IIId**, and **IIIe** are additionally stabilized by C^3–H···H(Me) or C^3–H···Hlg interactions. Here, the distance between the coplanar $ArCOCH_2$ fragments (through inversion center) is 3.19(1)–3.53(1) Å. The presence in molecule **IIIe** of an electron-acceptor furan oxygen atom makes H···O(Ar^1) interactions more favorable than H···$\pi(Ar^1)$. The identity of the substituents on C^5 and C^1 in compounds **IIIa**–**IIId** enables analogous contacts (C=O···H) with participation of hydrogen atoms in the *meta* positions of different phenyl groups (Ar^2 and benzylic phenyl group), since displacement of the electron density toward the triple bond and sulfur atom should result in localization of partial positive charge just on the above atoms. Analogous contact with hydrogen atom of the benzylic fragment was also detected for compound **IIIe** and initial ketones **I** (Ar^2 = Ph). If $Ar^2 \neq$ Ph, electron density redistribution and steric hindrances hamper this

Table 3. Principal crystallographic data and parameters of X-ray diffraction experiments for compounds **IIIa**–**IIIe**

Parameter	**IIIa**	**IIIb**	**IIIc**	**IIId**	**IIIe**
CCDC entry no.	933440	933441	933442	933443	933444
Molecular weight	356.46	370.49	390.90	435.36	346.42
Crystal dimensions, mm	0.36×0.30×0.25	0.41×0.36×0.28	0.43×0.37×0.21	0.36×0.22×0.19	0.26×0.15×0.13
a, Å	9.150(7)	9.2932(5)	9.3431(14)	9.4997(13)	11.5354(3)
b, Å	9.686(7)	10.1093(5)	10.0112(12)	10.2173(12)	9.2601(3)
c, Å	11.084(8)	11.2485(6)	11.2636(14)	11.0080(12)	33.3338(8)
α, deg	102.66	105.343(1)	105.734(4)	104.673(3)	90
β, deg	103.404	102.112(2)	102.194(3)	102.339(6)	90
γ, deg	90.475	95.263(9)	95.255(4)	95.837(6)	90
V, Å^3	930.5(12)	984.20(9)	978.7(2)	995.9(2)	3560.7(2)
d_{calc}, g/cm^3	1.272	1.250	1.326	1.452	1.292
μ, mm^{-1}	0.183	0.176	0.313	2.179	1.700
Number of independent reflections (R_{int})	3627 (0.083)	5198 (0.028)	5154 (0.014)	5801 (0.018)	2875 (0.051)
Number of observed reflections/parameters	2275 / 235	3978 / 245	4385 / 244	5071 / 244	2232 / 226
R, % [$I > 2\sigma(I)$]	0.058	0.041	0.032	0.028	0.057
R_w, %	0.121	0.098	0.091	0.081	0.143
Goodness of fit *S*	1.02	1.01	1.01	1.01	1.05

interaction, which leads to change of the crystal packing. Thus, compounds **IIIa**–**IIId** in crystal (i.e., in the absence of solvent molecules) are characterized by similar intermolecular interactions which determine not only similarity of their geometries (Fig. 2) but also isotypy of their unit cells in crystal (Table 3). In all cases, similar C=O···H contacts with participation of *meta*-hydrogen atoms in the phenyl group are observed for compounds **III** with Ar^2 = Ph. Electron density redistribution in keto sulfide **IIIe** changes the topology of intermolecular bonds and hence molecular geometry (the Ar^2 plane is turned through a considerable angle with respect to the C^5–C^6 bond, Fig. 2), so that isotypy in the series of the examined compounds is violated (Table 3).

EXPERIMENTAL

The IR spectra were recorded on an FSM-1201 instrument. The NMR spectra were obtained on Bruker AM-300 and Jeol ECX-400A instruments using tetramethylsilane as internal standard.

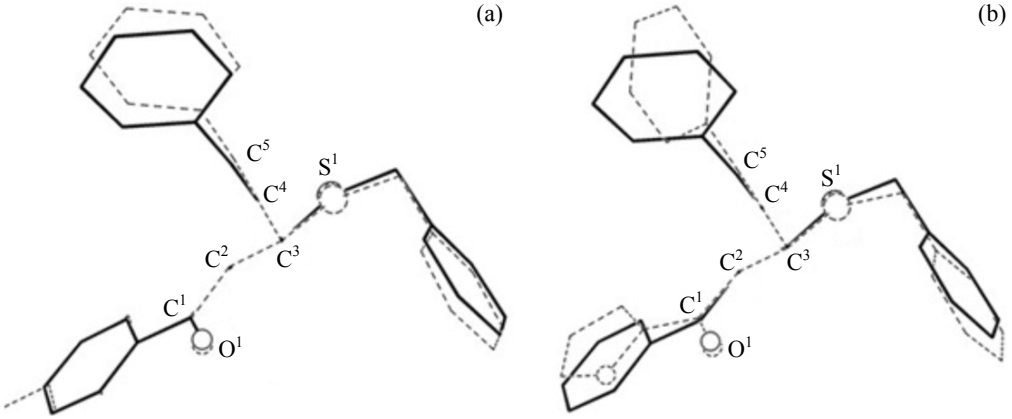


Fig. 2. Superpositions of (a) molecules **IIIa** and **IIIb** and (b) **IIIa** and **IIIe**. The positions of O^1, C^1, C^2, and C^3 coincide in pairs.

The progress of reactions and the purity of products were monitored by TLC on Sorbfil plates (ethyl acetate–hexane, 1:2), as well as by GLC on a Kristall 4000M chromatograph equipped with a flame ionization detector (ZB-1 capillary column, 50 m×0.25 mm, stationary phase 100% polydimethylsiloxane, film thickness 0.5 μm; oven temperature 230°C, injector and detector temperature 315°C).

(*E*)-1,5-Diarylpent-2-en-4-yn-1-ones **Ia**–**Ig** were synthesized according to [18].

3-Benzylsulfanyl-1,5-diphenylpent-4-yn-1-one (IIIa). Five drops of triethylamine were added to a suspension of 1020 mg (4.4 mmol) of ketone **Ia** and 550 mg (4.4 mmol) of thiol **IIa** in 10 mL of 95% ethanol, and the mixture was stirred and left to stand for 10 h. An oily material separated and was ground with a glass rod to induce crystallization. The precipitate was filtered off, washed with 50% ethanol, and dried in air. Yield 890 mg (57%), mp 44–45°C (from CH_2Cl_2–C_6H_{14}). IR spectrum (KBr), ν, cm^{-1}: 2851 (SCH_2), 1690 (C=O). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 3.28–3.54 m (2H, CH_2), 4.00–4.09 m (2H, SCH_2), 4.35 t (1H, CH, *J* = 7.0 Hz), 7.24–7.34 m (6H, H_{arom}), 7.40–7.42 m (4H, H_{arom}), 7.46 d (2H, H_{arom}, *J* = 7.8 Hz), 7.57 t (1H, H_{arom}, *J* = 7.3 Hz), 7.89 d (2H, H_{arom}, *J* = 7.6 Hz). Found, %: C 81.19; H 6.06; S 8.62. $C_{24}H_{20}OS$. Calculated, %: C 80.85; H 5.67; S 9.00.

Compounds **IIIb**–**IIIf** and **IVa**–**IVf** were synthesized in a similar way.

3-Benzylsulfanyl-1-(4-methylphenyl)-5-phenylpent-4-yn-1-one (IIIb). Yield 75%, mp 55–56°C (from Me_2CO–H_2O). IR spectrum (KBr), ν, cm^{-1}: 2854 (SCH_2), 1682 (C=O). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 2.41 s (3H, CH_3), 3.27–3.53 m (2H, CH_2), 4.02–4.11 m (2H, SCH_2), 4.38 d.d (1H, CH, *J* = 7.56, 6.4 Hz), 7.24–7.36 m (8H, H_{arom}), 7.42–7.45 m (4H, H_{arom}), 7.81 d (2H, H_{arom}, *J* = 8.2 Hz). ^{13}C NMR spectrum (100 MHz, DMSO-d_6), δ_C, ppm: 21.8 (CH_3), 30.6 (CH), 36.1 (SCH_2), 44.1 (CH_2), 84.1 and 88.4 (C≡C); 123.0, 127.3, 128.4, 128.5, 128.8, 129.2, 129.5, 131.9, 134.2, 138.2, 144.4 (C_{arom}); 195.7 (C=O). Found, %: C 81.06; H 6.36; S 8.31. $C_{25}H_{22}OS$. Calculated, %: C 81.05; H 6.00; S 8.64.

3-Benzylsulfanyl-1-(4-chlorophenyl)-5-phenylpent-4-yn-1-one (IIIc). Yield 89%, mp 77–78°C (from Me_2CO–H_2O). IR spectrum (KBr), ν, cm^{-1}: 2852 (SCH_2), 1689 (C=O). ^1H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 3.45–3.65 m (2H, CH_2), 3.97–4.04 m (2H, SCH_2), 4.18 t (1H, CH, *J* = 7.7, 6.3 Hz), 7.22–7.35 m (10H, H_{arom}), 7.55 d (2H, H_{arom}, *J* = 8.5 Hz), 7.94 d (2H, H_{arom}, *J* = 8.7 Hz). ^{13}C NMR spectrum (100 MHz, DMSO-d_6), δ_C, ppm: 30.5 (CH), 35.3 (SCH_2), 44.2 (CH_2), 84.1 and 89.3 (C≡C); 122.7, 127.6, 129.1, 129.2, 129.4, 129.5, 130.6, 131.9, 135.4, 138.4, 139.0 (C_{arom}); 195.9 (C=O). Found, %: C 73.50; H 4.95; S 8.11. $C_{24}H_{19}ClOS$. Calculated, %: C 73.73; H 4.91; S 8.19.

3-Benzylsulfanyl-1-(4-bromophenyl)-5-phenylpent-4-yn-1-one (IIId). Yield 90%, mp 81–82°C (from Me_2CO–H_2O). IR spectrum (KBr), ν, cm^{-1}: 2853 (SCH_2), 1688 (C=O). ^1H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 3.22–3.45 m (2H, CH_2), 3.99–4.06 m (2H, SCH_2), 4.30 t (1H, CH, *J* = 7.0, 6.3 Hz), 7.24–7.41 m (10H, H_{arom}), 7.58 d (2H, H_{arom}, *J* = 8.5 Hz), 7.72 d (2H, H_{arom}, *J* = 8.5 Hz). Found, %: C 66.24; H 4.74; S 7.07. $C_{24}H_{19}BrOS$. Calculated, %: C 66.21; H 4.41; S 7.35.

3-Benzylsulfanyl-1-(furan-2-yl)-5-phenylpent-4-yn-1-one (IIIe). Yield 81%, colorless crystals, mp 85–86°C (from Me_2CO–H_2O). IR spectrum (KBr), ν, cm^{-1}: 2852 (SCH_2), 1676 (C=O). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 3.16–3.37 m (2H, CH_2), 3.98–4.07 m (2H, SCH_2), 4.28–4.32 m (1H, CH), 6.52 d.d (1H, furan, *J* = 3.4, 1.6 Hz), 7.16 d (1H, furan, *J* = 3.7 Hz), 7.23–7.41 m (10H, H_{arom}). 7.58 s (1H, furan). ^{13}C NMR spectrum (100 MHz, DMSO-d_6), δ_C, ppm: 30.5 (CH), 36.0 (SCH_2), 43.9 (CH_2), 84.9 and 87.8 (C≡C); 112.5, 118.0, 122.9, 127.3, 128.4, 128.4, 128.7, 129.2, 131.9, 138.0, 147.0, 152.5 (C_{arom}); 185.0 (C=O). Found, %: C 75.95; H 5.45; S 9.01. $C_{22}H_{18}OS$. Calculated, %: C 76.28; H 5.25; S 9.24.

3-Benzylsulfanyl-5-(4-bromophenyl)-1-phenylpent-4-yn-1-one (IIIf). Yield 78%, mp 150–151°C (from Me_2CO–H_2O). IR spectrum (KBr): ν 1681 cm^{-1} (C=O). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 3.27–3.52 m (2H, CH_2), 3.97–4.06 m (2H, SCH_2), 4.31 d.d (1H, CH, *J* = 7.7, 6.3 Hz), 7.23–7.47 m (11H, H_{arom}), 7.57 t (1H, H_{arom}, *J* = 7.3 Hz), 7.89 d (2H, H_{arom}, *J* = 7.6 Hz). ^{13}C NMR spectrum (100 MHz, DMSO-d_6), δ_C, ppm: 30.6 (CH), 36.1 (SCH_2), 44.0 (CH_2), 88.6 and 89.5 (C≡C); 121.9, 122.6, 127.4, 128.3, 128.8, 129.1, 131.6, 133.3, 133.6, 136.5, 138.0 (C_{arom}); 195.9 (C=O). Found, %: C 65.97; H 4.35. $C_{24}H_{19}BrOS$. Calculated, %: C 66.21; H 4.41.

(*E*,*E*)- and (*E*,*Z*)-5-(4-Bromophenylsulfanyl)-1,5-diphenylpenta-2,4-dien-1-one (IVa, isomer mixture, 1:1.5**).** Yield 63%, mp 75–76°C (from Me_2CO–H_2O). IR spectrum (CCl_4), ν, cm^{-1}: 1660 (C=O, *E*,*Z*), 1645

(C=O, *E*,*E*). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 6.28 d (3-H, *E*,*E*, *J* = 11.7 Hz), 6.84 d (1-H, *E*,*E*, *J* = 14.9 Hz), 8.23 d.d (2-H, *E*,*Z*, *J* = 11.2, 15.1 Hz). Found, %: C 65.71; H 4.07. $C_{23}H_{17}BrOS$. Calculated, %: C 65.68; H 4.08.

(*E*,*E*)- and (*E*,*Z*)-5-(4-Bromophenylsulfanyl)-1-(4-methylphenyl)-5-phenylpenta-2,4-dien-1-one (IVb, isomer mixture, 1:2.7**).** Yield 82%, mp 119–120°C (from Me_2CO–H_2O). IR spectrum (CCl_4), ν, cm^{-1}: 1660 (C=O, *E*,*Z*), 1643 (C=O, *E*,*E*). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 6.29 d (3-H, *E*,*E*, *J* = 11.7 Hz), 6.88 d (1-H, *E*,*E*, *J* = 14.9 Hz), 7.04 d (3-H, *E*,*Z*, *J* = 11.7 Hz), 7.20 d (1-H, *E*,*Z*, *J* = 14.9 Hz), 8.22 d.d (2-H, *E*,*Z*, *J* = 11.1, 15.0 Hz). Found, %: C 66.52; H 4.52. $C_{24}H_{19}BrOS$. Calculated, %: C 66.21; H 4.41.

(*E*,*Z*)-5-(4-Bromophenylsulfanyl)-1-(4-methoxyphenyl)-5-phenylpenta-2,4-dien-1-one (IVc). Yield 43%, mp 99–100°C (from Me_2CO–H_2O). IR spectrum (CCl_4): ν 1657 cm^{-1} (C=O). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 3.88 s (3H, CH_3O), 6.96 d (2H, H_{arom}, *J* = 8.7 Hz), 7.01 d (2H, H_{arom}, *J* = 8.5 Hz), 7.05 d (1H, 2-H, *J* = 11.5 Hz), 7.21 d (1H, 1-H, *J* = 14.4 Hz), 7.22–7.28 m (6H, H_{arom}, *J* = 8.2 Hz), 7.59 d (2H, H_{arom}), 7.98 d (2H, H_{arom}, *J* = 7.8 Hz), 8.20 d.d (1H, 3-H, *J* = 11.5, 14.4 Hz). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ_C, ppm: 55.6 (CH_3O); 113.9, 120.5, 128.2, 128.3, 128.6, 129.3, 130.9, 131.1, 131.3, 132, 133.4, 133.9, 138.7, 139.9, 144.9, 163.5 (C_{arom}, C^2, C^3, C^4, C^5); 188.9 (C=O). Found, %: C 63.76; H 4.30. $C_{24}H_{19}BrO_2S$. Calculated, %: C 63.86; H 4.25.

(*E*,*E*)- and (*E*,*Z*)-1-(4-Chlorophenyl)-5-phenyl-5-phenylsulfanylpenta-2,4-dien-1-one (IVd, isomer mixture, 1:2.4**).** Yield 82%, mp 91–93°C (from Me_2CO–H_2O). IR spectrum (CCl_4), ν, cm^{-1}: 1660 (C=O, *E*,*Z*), 1637 (C=O, *E*,*E*). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 6.19 d (3-H, *E*,*E*, *J* = 11.7 Hz), 6.74 d (1-H, *E*,*E*, *J* = 14.7 Hz), 7.02 d (3-H, *E*,*Z*, *J* = 11.2 Hz), 7.12 d (1-H, *E*,*Z*, *J* = 14.9 Hz), 8.27 d.d (2-H, *E*,*Z*, *J* = 11.2, 15.0 Hz). Found, %: C 73.33; H 4.67. $C_{23}H_{17}ClOS$. Calculated, %: C 73.29; H 4.56.

(*E*,*Z*)-1-(4-Chlorophenyl)-5-(4-methylphenylsulfanyl)-5-phenylpenta-2,4-dien-1-one (IVe). Yield 66%, mp 121–122°C (from Me_2CO–H_2O). IR spectrum (CCl_4): ν 1660 cm^{-1} (C=O). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 2.19 s (3H, CH_3), 6.92 d (2H, H_{arom}, *J* = 7.8 Hz), 6.97 d (1H, 2-H, *J* = 11.2 Hz), 7.06 d (2H, H_{arom}, *J* = 8.0 Hz), 7.10 d (1H, 1-H, *J* = 15.3 Hz), 7.22–7.25 m (3H, H_{arom}), 7.44 d (2H, H_{arom}, *J* = 8.2 Hz), 7.59 d (2H, H_{arom}), 7.90 d (2H, H_{arom}, *J* = 8.2 Hz), 8.29 d.d (1H, 3-H, *J* = 11.2, 14.9 Hz). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ_C, ppm: 21.1 (CH_3); 127.0, 128.5, 129.0, 129.3, 129.8, 130.0, 130.5, 130.6, 131.8, 136.7, 136.8, 139.0, 139.1, 141.6, 148.1 (C_{arom}, C^2, C^3, C^4, C^5); 189.5 (C=O). Found, %: C 73.84; H 4.87. $C_{24}H_{19}ClOS$. Calculated, %: C 73.73; H 4.91.

(*E*,*E*)- and (*E*,*Z*)-5-(4-Bromophenylsulfanyl)-1-(4-chlorophenyl)-5-phenylpenta-2,4-dien-1-one (IVf, isomer mixture, 1:2.2**).** Yield 83%, mp 123–125°C (from Me_2CO–H_2O). IR spectrum, ν, cm^{-1}: 1661 (C=O, *E*,*Z*), 1638 (C=O, *E*,*E*). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 6.24 d (3-H, *E*,*E*, *J* = 11.7 Hz), 6.81 d (1-H, *E*,*E*, *J* = 14.7 Hz), 7.14 d (1-H, *E*,*Z*, *J* = 15.1 Hz), 8.23 d.d (2-H, *E*,*Z*, *J* = 11.1, 15.0 Hz). Found, %: C 61.04; H 3.63. $C_{23}H_{16}BrClOS$. Calculated, %: C 60.60; H 3.55.

Detection of kinetically controlled adduct V. One drop of triethylamine was added at room temperature to a solution of 0.1 mmol of ketone **I** and 0.1 mmol of benzenethiol **IIb**–**IId** in 1 mL of 95% ethanol. The mixture was stirred, and two drops were withdrawn from the mixture using a pipette at definite time intervals. The solvent was evaporated from the sample, and the oily residue was pelleted with KBr and analyzed by IR spectroscopy (2300–1600 cm^{-1}). A sample for GLC analysis was withdrawn using a microsyringe and was directly injected into the chromatograph.

X-Ray analysis of compounds IIIa–IIIe. Single crystals of **IIIa**–**IIIe** were obtained by crystallization from chloroform–hexane. Compounds **IIIa**–**IIId** crystallized in triclinic crystal system (at 100 K), and compound **IIIe**, in rhombic. Reflection intensities were measured on a Bruker APEX II diffractometer at 100 K [λMoK_α 0.71073 Å for compounds **IIIa**–**IIId**, λCuK_α 1.54178 Å for **IIIe**]. Space group *P*-$\bar{1}$ (**IIIa**–**IIId**), *Pbca* (**IIIe**). The structures were solved by the direct methods. All non-hydrogen atoms were localized by difference syntheses of electron density, and their positions were refined against F^2_{hkl} in anisotropic approximation. Hydrogen atoms on carbon atoms were visualized geometrically and were refined in isotropic approximation according to the rigid body model: U_{iso}(H) = 1.5U_{eq}(C_i) for methyl groups and U_{iso}(H) =1.2U_{eq}(C_{ii}) for other carbon atoms, where U_{eq}(C) is the equivalent temperature factor of the carbon atom to which the given hydrogen atom is attached. All calculations were performed with the aid of SHELXTL 5.10

software package [23]. The principal crystallographic data and refinement parameters are given in Table 3.

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