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Spectral Studies and Configurational Assignments of Some 2-Propenone Derivatives

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SPECTRAL STUDIES AND CONFIGURATIONAL ASSIGNMENTS OF SOME 2-PROPENONE DERIVATIVES

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3-(4-Substitutedphenyl)-1-phenyl-2-phenylthio-2-propen-1-ones (1–5) (1, R = H; 2, R = 4-OCH₃; 3, R = 4-Cl; 4, R = 4-Br; 5, R = 4-NO₂) have been synthesized by the condensation of 4-substituted benzaldehyde and phenacyl sulfide in presence of base. The structure and configuration of these compounds were determined by UV, IR and NMR spectroscopy. The DEPT, 2DNMR, NOE and ³J_{CH} in the coupled ¹³C-NMR spectra indicated that compounds 1–5 belong to the E-configuration.

Keywords: Configuration; trisubstituted ethylene; UV; IR and NMR spectra

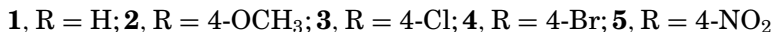
INTRODUCTION

Structural proof and configurational assignments of trisubstituted ethylenes were based on ¹HNMR data^{1–4} and the theoretical shifts obtained by applying the NMR rule of the additivity principle.^{5,6} It was found that the vinylic carbon atom was shielded due to the electron-withdrawing abilities of the attached groups and deshielded owing to the electron-attracting group at the α -position.⁷ A good evidence to assign the configuration of trisubstituted ethylene is the long-range (³J_{CH}) values which indicated *E* or *Z* isomers.^{8,9}

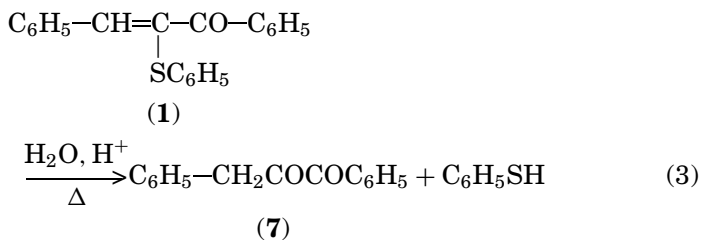
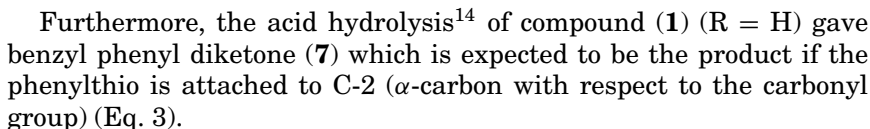
This investigation forms a part of a study undertaken to establish the configurational assignment of 3-(4-substituted phenyl)-1-phenyl-2-phenylthio-2-propen-1-ones **1–5** utilizing their spectroscopic data. In these compounds, the phenylthio and benzoyl groups are bulky and cross-conjugated with the –CH=CHAr. It would be of interest to know which of them is *cis* and which is *trans* to the aryl group.

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The treatment of phenyl phenacyl sulfide¹⁰ with 4-substituted benzaldehydes in the presence of a catalytic amount of piperidine afforded condensation products¹¹ **1–5** according to a mechanism analogous to that of Knoevenagel condensation (Eq. 1). The Knoevenagel reaction



Elemental analyses, UV, IR and NMR spectroscopy indicated the formation of 3-(4-substituted phenyl)-1-phenyl-2-phenylthio-2-propen-1-ones **1–5** (Eq. 1). An initial determination of the structure of compounds **1–5** could be suggested from the spectral data of 3-(4-nitrophenyl)-1-phenyl-3-phenylthio-2-propen-1-one (**6**), which is different from that of compound **5** (R = 4-NO₂). This indicates evidence for the presence of a phenylthio moiety at the C-3 rather than at the 3-one in compound **5**. Compound **6** was obtained by the addition of sodium thiophenoxide to 3-(4-nitrophenyl)-1-phenyl-2-propyn-1-one (Eq. 2).¹³

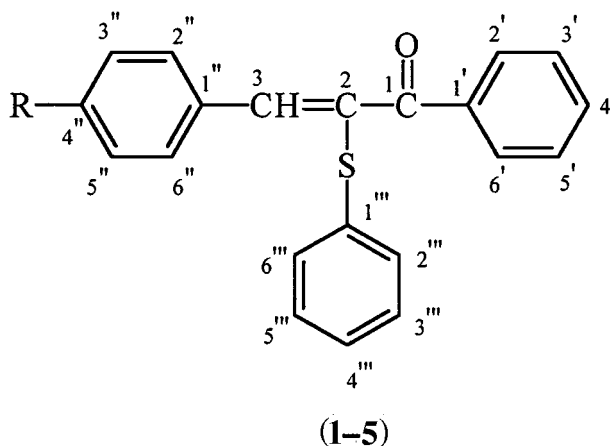


Structural Proof and Configurational Assignment of Compounds (1–5)

Though compounds **1–5** can exist as *E*- and *Z*-configurational isomers, only one form of compounds **1–5** was obtained. The more stable form, whether the benzoyl should be *trans* or the phenylthio should be *trans* to the aryl cannot be decided on steric grounds. This is because in either case there are bulky groups in the *cis* position that gave rise to considerable nonbonding interactions. The dipole moments revealed that *E*-isomer was the likely structure of these compounds.¹⁵ However, a study of their spectral data would be of a valuable aid in gaining further information about their configuration.

Nuclear Magnetic Resonance

The configurational assignment of compounds **1–5** were based on NMR analysis. Typical ¹H and ¹³CNMR chemical shifts are given in Tables I and II.



The two doublets in the ¹H-NMR spectra at δ 8.28–7.43 (H-2'',6'') and 7.91–6.95 ppm (H-3'',5'') strongly suggest the presence of para-substituted aromatic ring. The two triplets at δ 7.39–7.37 (H-3',5') and 7.51–7.49 ppm (H-4') and a doublet at δ 8.29–7.72 ppm (H-2',6') with five hydrogens suggest the presence of monosubstituted aromatic ring attached to carbonyl group. Also, the doublet at δ 7.24–7.19 (H-2''',6''') and a multiplet at δ 7.13 ppm (H-3''', 4''',5''') with five hydrogens indicate the presence of monosubstituted aromatic ring bonded to sulfur atom. The signal at δ 194.69–193.53 ppm in the ¹³C-NMR spectra and the peak at frequency ($\bar{\nu}$) at 1662–1656 cm⁻¹ in the IR spectra is in the region

TABLE I ^1H -NMR Spectral Data of 3-aryl-1-phenyl-2-phenylthio-2-propen-1-ones (**1-5**) (δ ppm, CDCl_3)

Nucleus ^1H	1 (R=H)	2 (R=OCH $_3$) ^a	3 (R=Cl)	4 (R=Br)	5 (R=NO $_2$)
H-2',6'	7.74 (d) (J = 8.50 Hz)	7.65 (d) (J = 8.72)	8.29 (d) (J = 8.80)	7.80 (d) (J = 7.45)	7.72 (d) (J = 7.72)
H-2'',6''	7.71 (d) (J = 7.94)	7.52 (d) (J = 7.27)	7.72 (d) (J = 7.29)	7.43 (d) (J = 7.50)	8.28 (d) (J = 8.78)
H-4'	7.49 (t) (J = 7.42)	7.49 (t) (J = 7.36)	7.51 (t) (J = 7.43)	7.48 (t) (J = 7.58)	7.51 (t) (J = 7.40)
H-3',5'	7.39 (t) (J = 7.36)	7.37 (t) (J = 7.72)	7.38 (t) (J = 7.69)	7.37 (t) (J = 7.67)	7.37 (t) (J = 7.79)
H-3'',5''	7.36 (m)+H-4''	6.95 (d) (J = 8.78)	7.91 (d) (J = 8.73)	7.73 (d) (J = 7.49)	7.91 (d) (J = 8.70)
H-2''',6'''	7.19 (m)	7.24 (d) (J = 8.53)	7.23 (d) (J = 7.60)	7.22 (d) (J = 7.34)	7.19 (d) (J = 7.25)
H-3''',5''',4''' =CH	7.13 (m) 7.29(s)	7.13 (m) 7.25 (s)	7.13 (m) 7.26 (s)	7.13 (m) 7.25 (s)	7.13 (m) 7.26 (s)

^a4-OCH $_3$ protons appear at δ 3.85 ppm.

of carbonyl group of conjugated ketones.⁸ The ^{13}C -NMR spectra of the vinylic carbon that bears phenylthio group displays signal at δ 133.85–133.05 ppm which agrees with the reported value for vinylic carbon bearing an electron-withdrawing substituent.^{7,16,17} The low intensity of such signal could be expected for carbon bearing no hydrogens.

TABLE II ^{13}C NMR Spectral Data of 3-aryl-1-phenyl-2-phenylthio-2-propen-1-ones (**1-5**) (δ ppm, CDCl_3)

Nucleus ^{13}C	1 (R=H)	2 (R=OCH $_3$) ^a	3 (R=Cl)	4 (R=Br)	5 (R=NO $_2$)
C-2',6'	131.55	132.54	132.55	130.37	129.29
C-2'',6''	129.29	128.89	129.29	128.42	130.64
C-4'	132.55	132.12	133.05	132.44	132.54
C-3',5'	128.67	129.29	128.24	128.06	128.25
C-3'',5''	128.09	113.89	130.64	129.39	123.79
C-4''	128.09	160.76	147.24	133.04	147.22
C-2''',6'''	131.41	130.32	129.11	131.24	129.29
C-3''',5'''	127.54	128.02	123.68	128.91	132.71
C-4'''	127.54	126.89	128.31	127.33	131.64
C-1'	137.11	137.79	141.36	135.53	141.07
C-1''	136.28	165.64	144.33	137.33	140.94
C-1'''	135.16	127.64	136.51	134.59	136.51
C-3	137.82	142.00	133.32	139.41	134.31
C-2	133.05	133.85	133.29	133.49	133.31
C-1	194.14	194.69	193.55	194.38	193.33

^a4-OCH $_3$ carbon-13 appears at δ 55.35 ppm.

The DEPT technique^{8,9} shows the disappearance of quaternary carbons at δ 194.69–193.53 (C-1), 133.85–133.05 (C-2), 141.36–137.11 (C-1'), 165.64–134.31 (C-1''), and 136.51–135.16 (C-1''') (Tables I and II). The CH COSY^{8,9} technique (2DNMR, HETCOR spectrum) is attractive because it is efficient and indicates which carbons are bonded to which hydrogens. The resulting counter plots (e.g., (R = H), Figure 1), confirm the tentative ^1H and ^{13}C shift assignments (Tables I and II).

The configurational assignments of compounds **1–5** could be determined by applying the ^1H -NMR additivity increment scheme.^{5,6,8} The calculated chemical shifts of the vinylic protons in compounds **1–5** are δ 7.31 ppm for the *E*-configuration and δ 7.57 ppm for the corresponding *Z*-isomer (Figure 2). These values indicate a small difference in the chemical shift of the vinylic hydrogens for *E*- and *Z*-isomers.

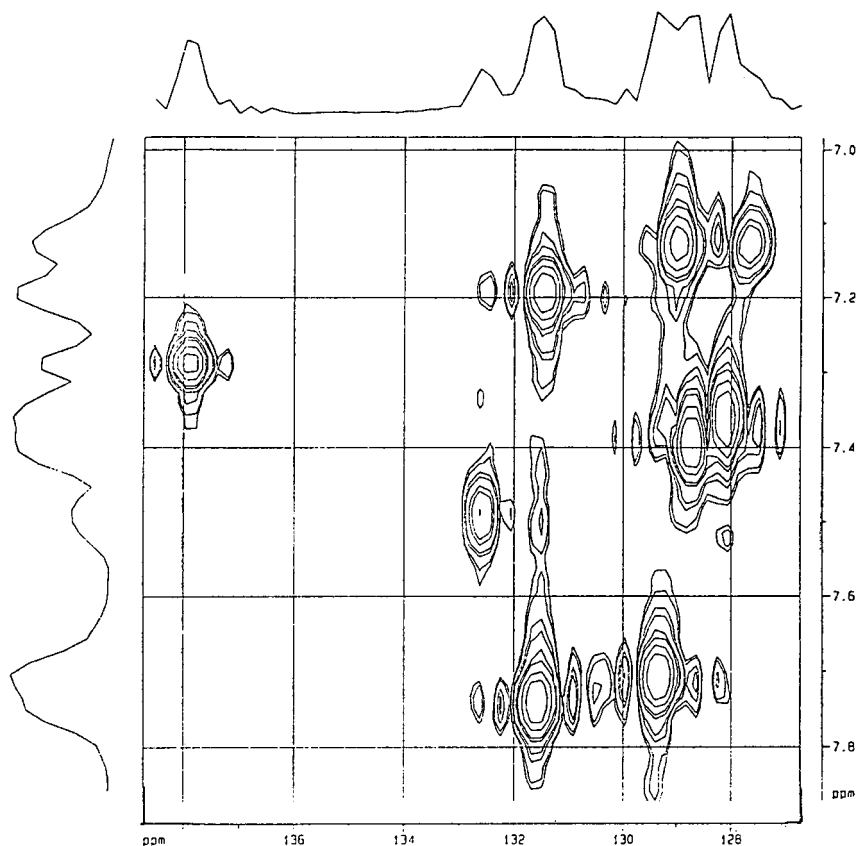


FIGURE 1 The HETCOR spectrum of 1,3-diphenyl-2-propen-1-one **1** in CDCl_3 at 400 MHz ^1H and 100 MHz for ^{13}C .

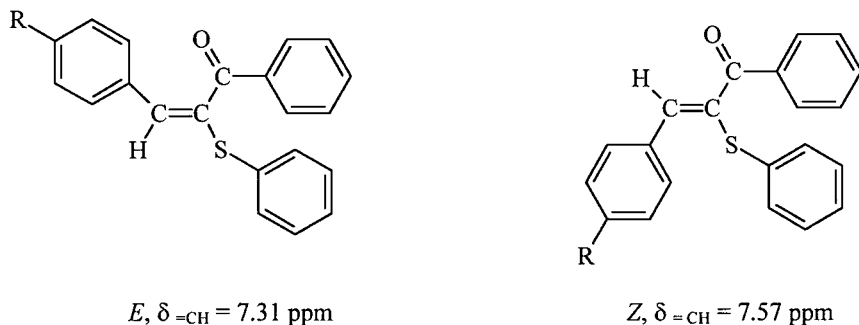


FIGURE 2 The calculated chemical shifts of the vinylic proton of *E* and *Z* of **1–5**.

Therefore, the conclusion from the additivity calculation is unreliable. This may be due to the fact that the calculations are using a single value for the aryl groups regardless of its substitution and the Ar-C=C dihedral angle.

Since the olefinic C=C double bond in (**1–5**) is trisubstituted, the relative configuration cannot be obtained on the basis of the *cis* and *trans* couplings of vicinal alkene proton in the ^1H -NMR spectrum. However, the relative configuration at the 2,3-double bond in compounds (**1–5**) can be derived from NOE difference spectra of (**3**) (R = 4-Cl) (Figure 3a) an enhancement of a signal when a nearby resonance is irradiated, ^1H ^1H through space interaction. The irradiation of H-2', 6' indicates that H-3',5', H-3'',5'' and H-2'',6'' are definitely enhanced (Figure 3b). Irradiation of H-3'',5'' with strongly enhances H-2',6', H-3',5' and H-2'',6'' (Figure 3c). The results are supported by irradiation of H-2'',6'' and H-3'',5'' strong effect on H-2'',6'' and H-3',5' (Figure 3d), while irradiation of H-3',5' greatly enhances H-2',6', H-3'',5'' and H-2'',6'' (Figure 3e). These observations indicate that the phenyl ring attached to the carbonyl group and 4-chlorophenyl ring are on the same side of the 2,3-double bond suggesting the *E*-configuration of compound **3** (R = 4-Cl). This result is confirmed from $^3J_{\text{CH}}$ of the carbonyl carbon (C-1) ^{13}C signal at 194.69–193.53 ppm in the coupled ^{13}C -NMR spectrum. This technique gives conclusive information concerning the relative configuration of C and H in tri-substituted alkenes.^{8,9} As a result, a doublet ($J = 16.9 \text{ Hz}$) and multiplet were observed for compound **3** (R = 4-Cl). The $^3J_{\text{CH}}$ value = 16.9 Hz coupling points to a *trans* configuration^{8,9} of carbonyl carbon (C-1) and olefinic H-3. Consequently, the benzoyl and aryl groups are therefore occupying *cis*-position. Similarly, compounds **1**, **2**, **4**, and **5** belong to the *E*-configuration.

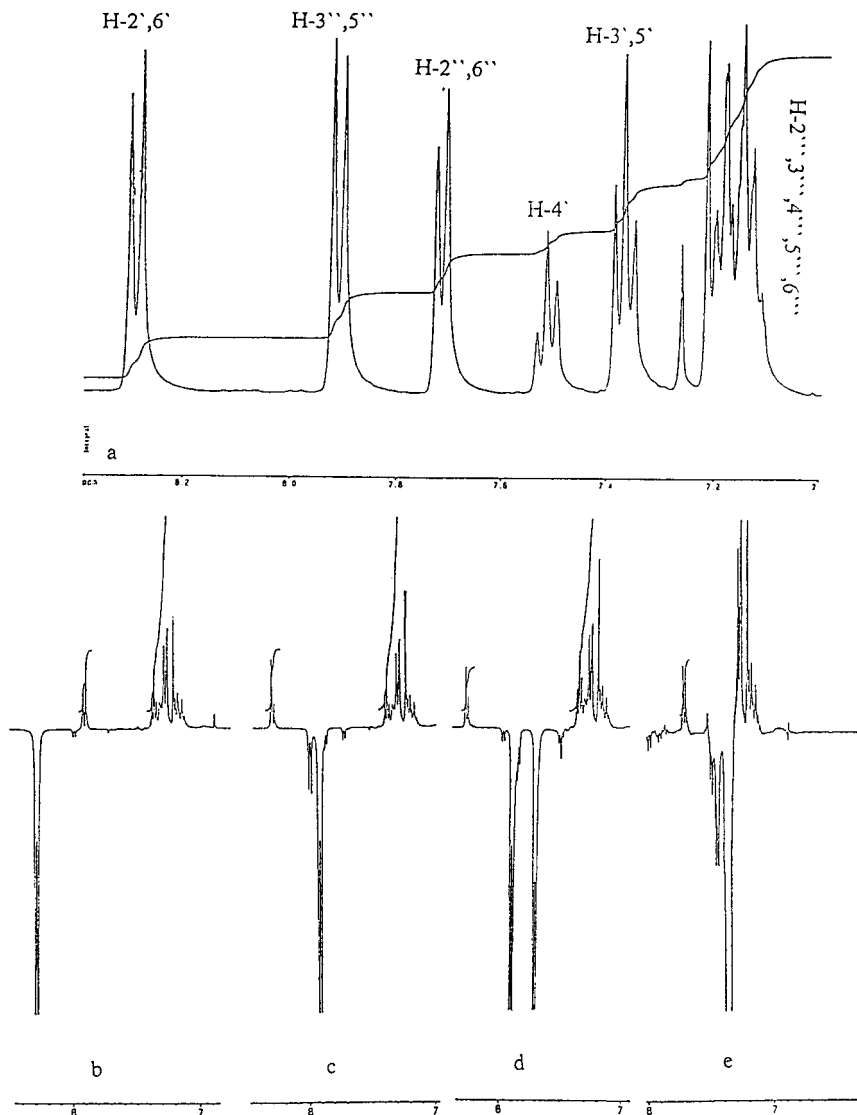


FIGURE 3 (a) ^1H NMR of **3** (R = 4-Cl); (b) Irradiation of H-2',6', (c) Irradiation of H-3'',5'', (d) Irradiation of H-2'',6'' and H-3'',5'', (e) Irradiation of H-3',5'.

Infrared Spectral Study

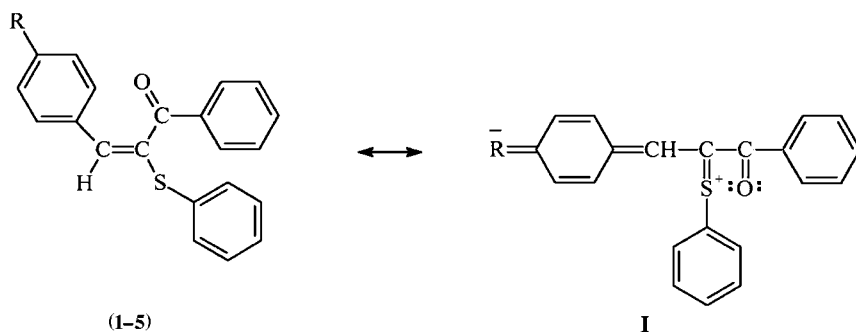
The infrared spectra of **1-5** can be used to confirm their *E*-configuration. The C-H stretching and deformation vibrations are not used to investigate the configuration. However, it may be determined by examining

TABLE III UV and IR Spectral Data of 3-aryl-1-phenyl-2-phenylthio-2-propen-1-ones (**1–5**) and 1-phenyl 3-(4-nitrophenyl)-3-phenylthio-2-propen-1-one (**6**)

Cpd.	R	λ nm (log ϵ)			$\bar{\nu}$ cm ⁻¹	
					C=O	C=C
1	H	203 (4.06)	268 (3.91)	345 (3.49)	1661	1582
2	4-OCH ₃	211 (4.29)	253 (4.27)	285 (4.28)	340 (4.15)	1657
3	4-Cl	206 (4.20)	260 (4.11)	365 (3.93)	1659	1599
4	4-Br	214 (4.32)	255 (4.39)	342 (3.95)	1662	1561
5	4-NO ₂	204 (4.11)	260 (3.93)	365 (3.74)	1656	1513
6	4-NO ₂	207 (4.21)	265 (4.06)	243 (4.09)	337 (4.10)	1631

the characteristic vibrational frequencies of the C=O and C=C and the influence of substituent on them.

It was observed that the presence of a substituent in the 4-position of the aryl group (at C-3) does not have any significant effect on the frequency of the C=O (C-1) stretching vibrations in compounds **1–5** (Table III). This is consistent with the deconjugation of the carbonyl and aryl groups in the *Z*-isomer of α -phenyl chalcone.¹⁸ In contrast, the frequency of C=C is changed by varying the nature of the 4-substituents. Table III shows that $\bar{\nu}_{\text{C=C}}$ in compound **5** (R = 4-NO₂) is differing by ca 69 and 61 cm⁻¹ respectively than **1**

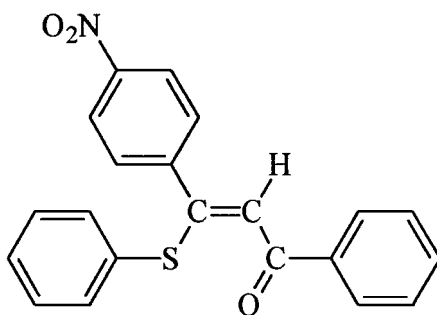
**FIGURE 4** Conjugative interaction between lone pair of sulfur atom and 4-substituent.

(R = H) and **2** (R = 4-OCH₃). Therefore, there is an appreciable conjugative interaction between the lone pair of electrons on the sulfur atom of the phenylthio moiety and the 4-substituent on the aryl at C-3 through the double bond (structure I; Figure 4). Consequently the configuration of compounds **1–5** could exist in the *E*-configuration where the benzoyl group is situated *cis* to the aryl ring.

Ultraviolet Spectral Studies

The electronic spectra of compounds **1–5** show three bands at λ 203–214, 253–268, and 345–365 nm except compound **2** (R = 4-OCH₃) which exhibited a fourth band at λ 285 nm. The bands at λ 345–365 nm are presumably due to the stability of the quinoid resonance structure I (Figure 4) via the electrostatic attraction between the electron density on the oxygen atom of the carbonyl group and the developed positive charge on the sulfur atom.

The high extinction coefficient and the lower wavelength of compound **5** (R = 4-NO₂; λ = 365 nm, $\log \epsilon$ = 3.74) compared to compound **6** 3-(4-nitrophenyl)-3-phenylthio-1-phenyl-2-propene-1-one, (λ = 337 nm), $\log \epsilon$ = 4.10) (Table III) indicate a direct conjugation between the 4-NO₂ substituent and the carbonyl group in the latter. However, the lower wavelength of **6** than that of **5** indicates that the former subsist mainly in the *Z*-configuration (Figure 5). This is confirmed from the difference in the frequency of C=O and C=C for compounds **6** ($\bar{\nu}_{\text{C=O}}$ 1631, $\bar{\nu}_{\text{C=C}}$ 1536 cm⁻¹) and **5** ($\bar{\nu}_{\text{C=O}}$ 1656, $\bar{\nu}_{\text{C=C}}$ 1513 cm⁻¹), which have



(**Z-6**)

4-NO₂ substituent. These electronic spectral data indicate the presence of the phenylthio group at C-2 *trans* to the aryl group and compounds **1–5** belong to the *E*-configuration.

EXPERIMENTAL

Melting points were uncorrected. Microanalyses were performed by the microanalysis unit, Faculty of Science, King Abdulaziz University, Jeddah. Infrared spectra (KBr pellets) were measured on Perkin-Elmer 1430 recording spectrophotometer and the electronic spectra were recorded in absolute ethanol on UV-VIS Shimadzu 160-A spectrometer. The ^1H and ^{13}C -NMR spectra were recorded at 400 and 100 MHz respectively (DRX 400 FTNMR Bruker). All the ^1H -NMR spectra were obtained for approximately 0.03 M solutions in CDCl_3 with TMS as internal reference and broadband and off-resonance decoupled ^{13}C NMR spectra were obtained for approximately 0.5 M solutions in CDCl_3 with TMS as internal reference. 2D C/H shift correlated spectra were obtained using the standard Bruker program. The ^1H and ^{13}C chemical shifts of the titled compounds are presented in Tables I and II.

Preparation of Phenacyl Aryl Sulfide¹¹

Thiophenol (2.65 g, 0.024 mol) and 5.60 g (0.24 g atm) of finely divided sodium metal were allowed to react in 300 ml of anhydrous diethylether for 16 h. The suspension was cooled to -5°C and the mixture was stirred while 4.80 g (0.024 mol) of phenacyl bromide was added during 45 min. The temperature was held at 0°C throughout the addition, then the mixture was allowed to warm to room temperature during a further two and one half hour period. Dry ether (250 ml) was then added, the sodium bromide filtered off, and the product was crystallized from methanol after removal of ether, yield 4.31 g (77%) of phenyl phenacyl sulfide, m.p. 62° . Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{OS}$: C, 73.68; H, 5.26; S, 14.09. Found: C, 73.18; H, 5.53; S, 14.36.

Synthesis of 3-aryl-1-phenyl-1-phenylthio-2-propen-1-ones^{11,19} (1–5) General Method

A mixture of phenacyl phenyl sulfide (0.05 mol), freshly distilled benzaldehyde or pure substituted benzaldehyde (0.05 mol), glacial acetic acid (30 ml), ammonium acetate (0.05 mol) and piperidine (2 ml) were heated under reflux for 40 h. The solution was cooled, mixed with ether (200 ml) as successively washed with dil HCl, aqueous sodium carbonate (20%), a saturated aqueous solution of sodium bisulfite and water. After drying and removal of ether, the residue was crystallized from methanol-water. TLC (ethylacetate: petroleum ether 1:9) showed that only one product was obtained.

1,3-diphenyl-2-phenylthio-2-propen-1-one (1). Pale yellow crystals, yield 78%, m.p. 83°C. Anal. Calcd. for $C_{21}H_{16}OS$; C, 79.75; H, 5.06; S, 10.13. Found: C, 79.45; H, 5.26; S, 10.56.

1-phenyl-3-(4-methoxyphenyl)-2-phenylthio-2-propen-1-one (2). Pale yellow crystals, yield 70%, m.p. 106°C. Anal. Calcd. for $C_{22}H_{18}O_2S$; C, 76.30; H, 5.20; S, 9.25. Found: C, 76.42; H, 5.55; S, 8.94.

1-phenyl-3-(4-chlorophenyl)-2-phenylthio-2-propen-1-one (3). Deep yellow crystals, yield 75%, m.p. 133°C. Anal. Calcd. for $C_{21}H_{15}ClOS$; C, 71.90; H, 4.28; S, 9.13. Found: C, 72.32; H, 4.61; S, 9.62.

1-phenyl-3-(4-bromophenyl)-2-phenylthio-2-propen-1-one (4). Beige crystals, yield 75%, m.p. 132°C. Anal. Calcd. for $C_{21}H_{15}BrOS$; C, 63.80; H, 3.80; S, 8.10. Found: C, 64.03; H, 4.03; S, 8.66.

1-phenyl-3-(4-nitrophenyl)-2-phenylthio-2-propen-1-one (5). Deep yellow crystals, yield 82%, m.p. 133°C. Anal. Calcd. for $C_{21}H_{15}NO_3S$; C, 69.81; H, 4.16; N, 3.88; S, 8.86. Found: C, 70.37; H, 4.53; N, 4.08; S, 8.71.

Synthesis of 1-phenyl-3-(4-nitrophenyl)-3-phenylthio-2-propen-1-one (6)

The synthesis of 3-aryl-1-phenyl-2-propyn-1-ones has been reported earlier.¹³ 1-Phenyl-3-(4-nitrophenyl)-propynone (0.5 g, 0.01 mol) was dissolved in absolute methanol and a solution of equivalent amounts of sodium and thiophenol (0.5 g, 0.01 mol) in absolute methanol were added. A precipitate was formed, filtered off, washed with 1% sodium hydroxide, then crystallized from methanol as yellow needles, 0.68 g (94%), m.p. 125°C. 1H -NMR δ ppm ($CDCl_3$); 7.67 (d, H-2',6', $J = 8.46$), 8.04 (d, H-2'',6'', $J = 8.54$), 7.64 (t, H-4', $J = 7.89$), 7.57 (t, H-3',5', $J = 7.72$), 8.16 (d, H-3'',5'', $J = 8.26$), 7.31 (m, H-2''',6'''), 7.15 (m, H-3''',4''',5''') and 7.52 (s, Z=CH). Anal. Calc. for $C_{21}H_{15}NO_3S$; C, 69.81; H, 4.16; N, 3.88; S, 8.86. Found: C, 69.43; H, 4.33; N, 3.58; S, 9.04.

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