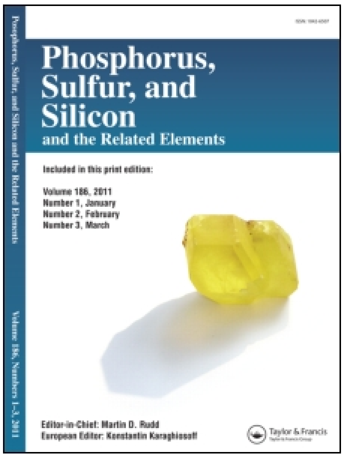

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Gamal A. Gohar[a]
[a] Chemistry Department, Faculty of Science, Alexandria University, Ibrahimia, Alexandria, Egypt

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SYNTHESIS, SPECTRAL STUDIES AND C—S BOND FISSION THROUGH PUMMERER REACTION OF SOME ALKYL[(SUBSTITUTED BENZYLIDENE)DITHIO]DIACETATES

GAMAL A. GOHAR

Chemistry Department, Faculty of Science, Alexandria University, P.O. 426, Ibrahimia, Alexandria 21321, Egypt

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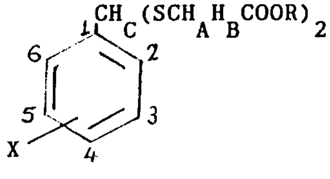
A series of methyl and ethyl[(substituted benzylidene)dithio]diacetates have been synthesized and their structures were identified. Correlation between δ-values of the benzylidene protons and σ-Hammett values has been found. The internal chemical shift Δν of the methylene protons was found to be correlated linearly with σ-Hammett constants indicating that the sulfur atom could transmit a polar effect to the substituent. Studies of H_2O_2 oxidation suggested that a competition between Pummerer and elimination reactions of the intermediate was involved.

Key words: Benzylidene dithio diacetates; ¹HNMR spectra; Pummerer reaction.

Benzylthio compounds and their derivatives have been the subject of several studies.[1–5] There is considerable interest in the reactions of benzylidene dithio compounds and their derivatives. The studies were directed to cyclization,[6] oxidation,[7] interchange[8] and cleavage by alkali[9] as well as studying their spectral behavior.[10]

Several interesting reports were noted on some of those compounds which exhibit stabilization effects on polyalkenes and halogen containing resins.[11] Some of them showed antimicrobial and/or antiprotozoal activity, in addition to their marked growth inhibition for Trichomonas Vaginalis.[12] They are useful as antifungal and antibacterial agents for fabric and biological applications[13] or they seem to be effective as the coprecusor of penicillin.[14] Accordingly, the present investigation was carried out in order to synthesize other derivatives of the basic structure with an ester group for chemical and biological studies. A series of alkyl[(substituted benzylidene)dithio]diacetates 1a–j and 2a–j have been synthesized to evaluate their activities.



(1) $R = CH_3$; (2) $R = C_2H_5$; (a), X = H; (b), $X = 4\text{-}CH_3$; (c), $X = 4\text{-}OCH_3$; (d), X = 4-OH; (e), X = 3-OH; (f), X = 4-Br; (g) X, = 2-Br; (h), X = 4-Cl; (i), $X = 4\text{-}NO_2$ and (j), $X = 2\text{-}NO_2$.

The synthetic routes are not the same as cited in the literature.[15] The physical properties, analysis and ¹HNMR data of 1a–j and 2a–j are listed in Tables I and II.

TABLE I

Physical properties, analysis, and 1HNMR spectra of methyl[substituted benzylidene)dithio]diacetates 1a-j

Cpd.	Yield %	m.p°c. n_D^{20}	λmax^i,nm (ϵ)x10^{-4}	CH_3 (ester)	1HNMR (δ ppm, CCl_4)					$\Delta\nu^{iv)}$ (H_z)	JAB (H_z)	Molecular formula	%calcd (% found)
					$H_{2,2'}$	$H_{3,3'}$	H_C	H_A	H_B				
1a	82	1.5940	226.0 (0.44)	3.60 (s,6H)	7.40-7.10 (m,5H)		5.27 (s,1H)	3.40 (d,2H)	3.07 (d,2H)	14.85	13.50	$C_{13}H_{16}O_4S_2$	C, 52.00; H, 5.30; S, 21.33 (C, 51.89; H, 5.21; S, 21.08)
b$^{(ii)}$	79	1.5880	229.0 (0.65)	3.62 (s,6H)	7.30 (d,2H)	7.05 (d,2H)	5.23 (s,1H)	3.38 (d,2H)	3.04 (d,2H)	15.30	13.50	$C_{14}H_{18}O_4S_2$	C, 53.50; H, 5.73; S, 20.38 (C, 53.39; H, 5.48; S, 19.98)
c$^{(iii)}$	74	1.5899	235.0 (0.77)	3.62 (s,6H)	7.31 (d,2H)	6.75 (d,2H)	5.24 (s,1H)	3.36 (d,2H)	3.02 (d,2H)	15.30	13.80	$C_{14}H_{18}O_5S_2$	C, 50.91; H, 5.46; S, 19.39 (C, 50.78; H, 5.28; S, 19.11)
d	81	semi solid	237.5 (0.45)	3.61 (s,6H)	7.32 (d,2H)	6.81 (d,2H)	5.21 (s,1H)	3.44 (d,2H)	3.09 (d,2H)	15.75	13.70	$C_{13}H_{16}O_5S_2$	C, 49.37; H, 5.06; S, 20.25 (C, 49.15; H, 4.85; S, 19.99)
e	72	semi solid	228.5 (0.64)	3.63 (s,6H)	7.35-6.75 (m,4H)		5.27 (s,1H)	3.48 (d,2H)	3.16 (d,2H)	14.40	13.20	$C_{13}H_{16}O_5S_2$	C, 49.37; H, 5.06; S, 20.25 (C, 49.01; H, 4.91; S, 20.03)
f	77	1.5952	239.0 (0.34)	3.67 (s,6H)	7.44 (d,2H)	7.27 (d,2H)	5.29 (s,1H)	3.36 (d,2H)	3.05 (d,2H)	14.00	13.40	$C_{13}H_{15}BrO_4S_2$	C, 41.16; H, 3.96; S, 16.89 (C, 40.91; H, 3.59; S, 16.64)
g	86	1.5970	226.5 (0.60)	3.68 (s,6H)	7.00-7.70 (m,4H)		5.78 (s,1H)	3.50 (d,2H)	3.22 (d,2H)	12.60	13.80	$C_{13}H_{15}BrO_4S_2$	C, 41.16; H, 3.96; S, 16.89 (C, 40.88; H, 3.78; S, 16.59)
h	89	1.5810	238.5 (0.46)	3.66 (s,6H)	7.42 (d,2H)	7.24 (d,2H)	5.30 (s,1H)	3.34 (d,2H)	3.03 (d,2H)	13.95	13.50	$C_{13}H_{15}CLO_4S_2$	C, 46.64; H, 4.48; S, 19.13 (C, 46.38; H, 4.17; S, 18.83)
i	83	52°	265.0 (0.75)	3.70 (s,6H)	8.25 (d,2H)	7.65 (d,2H)	5.38 (s,6H)	3.48 (d,2H)	3.19 (d,2H)	13.00	13.40	$C_{13}H_{15}NO_6S_2$	C, 45.22; H, 4.35; S, 18.55 (C, 44.40; H, 4.04; S, 18.29)
j	73	72°	226.0 (0.70)	3.71 (s,6H)	7.75-7.30 (m,4H)		6.06 (s,6H)	3.53 (d,2H)	3.25 (d,2H)	11.20	13.60	$C_{13}H_{15}NO_6S_2$	C, 45.22; H, 4.35; S, 18.55 (C, 44.19; H, 4.15; S, 18.31)

i) in methanol, ii) δCH_3 at 2.29 ppm (S,3H), iii) δOCH_3 at 3.58 ppm (S,3H). iv) $\Delta\nu = \nu_A - \nu_B$

TABLE II

Physical properties, analysis, and 1HNMR spectra of ethyl[substituted benzylidene)dithio]diacetates 2a-j

Cpd.	Yield %	m.p°c. n_D^{20}	λmax^{i},nm (ε)x10^{4}	CH_3 (ester)	CH_2 (ester)	1HNMR (δ ppm, CCl_4)					$^{iv)}$ Δν (H_z)	JAB (H_z)	Molecular formula	%calcd (% found)
						H_{ar}	H_{ar}	H_C	H_A	H_B				
2a	79	1.5885	221.0 (0.31)	1.26 (t,6H)	4.09 (q,4H)	7.47-7.20 (m,5H)		5.33 (s,1H)	3.39 (d,2H)	3.07 (d,2H)	14.40	13.50	$C_{15}H_{20}O_4S_2$	C, 54.88; H, 6.10; S, 19.51 (C, 54.65; H, 5.84; S, 19.24)
b^{ii}	80	1.5855	223.5 (0.76)	1.27 (t,6H)	4.07 (qwH)	7.29 (d,2H)	7.05 (d,2H)	5.30 (s,1H)	3.37 (d,2H)	3.04 (d,2H)	14.90	13.95	$C_{16}H_{22}O_4S_2$	C, 56.14; H, 6.43; S, 18.71 (C, 55.98; H, 6.31; S, 18.50)
c^{iii}	84	1.5975	224.4 (1.04)	1.24 (t,6H)	4.08 (q,4H)	7.33 (d,2H)	6.76 (d,2H)	5.31 (s,1H)	3.37 (d,2H)	3.03 (d,2H)	15.30	13.20	$C_{16}H_{22}O_5S_2$	C, 53.63; H, 6.15; S, 17.88 (C, 53.44; H, 5.91; S, 17.62)
d	75	semi solid	237.3 (0.72)	1.23 (t,6H)	4.07 (q,4H)	7.20 (d,2H)	6.67 (d,2H)	5.29 (s,1H)	3.36 (d,2H)	3.02 (d,2H)	15.30	13.92	$C_{15}H_{20}O_5S_2$	C, 52.32; H, 5.81; S, 18.60 (C, 52.25; H, 5.48; S, 18.49)
e	69	semi solid	265.5 (0.42)	1.26 (t,6H)	4.09 (q,4H)	7.33-6.72 (m,4H)		5.34 (s,1H)	3.39 (d,2H)	3.08 (d,2H)	13.95	13.80	$C_{15}H_{20}O_5S_2$	C, 52.32; H, 5.81; S, 18.60 (C, 52.11; H, 5.54; S, 18.46)
f	78	1.5895	224.7 (1.19)	1.30 (t,6H)	4.12 (q,4H)	7.42 (d,2H)	7.34 (d,2H)	5.34 (s,1H)	3.40 (d,2H)	3.10 (d,2H)	13.50	13.65	$C_{15}H_{19}BrO_4S_2$	C, 44.23; H, 4.67; S, 15.72 (C, 44.06; H, 4.39; S, 15.58)
g	81	1.5910	220.8 (0.79)	1.22 (t,6H)	4.05 (q,4H)	7.65-6.95 (m,4H)		5.72 (s,1H)	3.41 (d,2H)	3.13 (d,2H)	12.60	13.20	$C_{15}H_{19}BrO_4S_2$	C, 44.23; H, 4.67; S, 15.72 (C, 44.10; H, 4.59; S, 15.47)
h	89	1.5760	223.8 (0.89)	1.23 (t,6H)	4.09 (q,4H)	7.39 (d,2H)	7.27 (d,2H)	5.35 (s,1H)	3.38 (d,2H)	3.07 (d,2H)	13.95	13.80	$C_{15}H_{19}ClO_4S_2$	C, 49.66; H, 5.24; S, 17.66 (C, 49.49; H, 5.08; S, 17.53)
i	77	semi solid	260.4 (0.64)	1.26 (t,6H)	4.11 (q,4H)	8.22 (d,2H)	7.69 (d,2H)	5.41 (s,1H)	3.44 (d,2H)	3.16 (d,2H)	12.60	13.50	$C_{15}H_{19}NO_6S_2$	C, 48.26; H, 5.09; S, 17.16 (C, 48.07; H, 4.98; S, 16.88)
j	70	semi solid	220.2 (0.63)	1.20 (t,6H)	4.04 (q,4H)	7.78-7.30 (m,4H)		6.01 (s,1H)	3.42 (d,2H)	3.15 (d,2H)	12.20	13.74	$C_{15}H_{19}NO_6S_2$	C, 48.26; H, 5.09; S, 17.16 (C, 48.12; H, 4.87; S, 16.85)

i) in ethanol, ii) δCH_3 at 2.32 ppm (S.3H), iii) δOCH_3 at 3.68 ppm (S,3H). iv) $\Delta\nu = \nu_A - \nu_B$

Tables I and II showed that the chemical shifts of the benzylidene protons (H_c) varied from 5.21 to 6.06 ppm depending on the nature of substituent X and correlated nicely with σ-Hammett constants (Figure 1). This could be explained on the basis that the 3- or 4-substituent can affect the δ chemical shift of H_c by induction. ^{1}HNMR data of 1a–j and 2a–j also showed an AB spectrum centered at $(\delta_A + \delta_B)/2 = 3.19$–$3.39$ ppm, presumably due to the presence of two diastereotopic methylene protons, a behavior not observed for compounds containing one —SCH$_2$COOH moiety.[16,17] The nonequivalent magnetic properties of the methylene protons H_A and H_B, which are analogous to diethyl acetal derivatives,[18] could be attributed to the fact that, these protons can not be diposed symmetrically with the molecular symmetry plane containing the ArCH-group.

It has been reported that the internal chemical shifts ($\Delta\nu$) of the methylene protons of —SCH$_2$COOH showed solvent and constitution dependence, ($\Delta\nu = 10.8$–12.8 Hz),[19] however, these protons are apparently changed from 11.20 to 15.30 Hz in the titled compounds. This change may be ascribed to structural and applied field differences. The plotting of $K_{\Delta\nu} = \Delta\nu_{(\text{subs})} - \Delta\nu_{(\text{unsub})}$ of the methylene protons[20] in compounds 1 or 2 against σ-Hammett constants showed good correlations (Figure 2). This indicates that the internal chemical shifts of the methylene

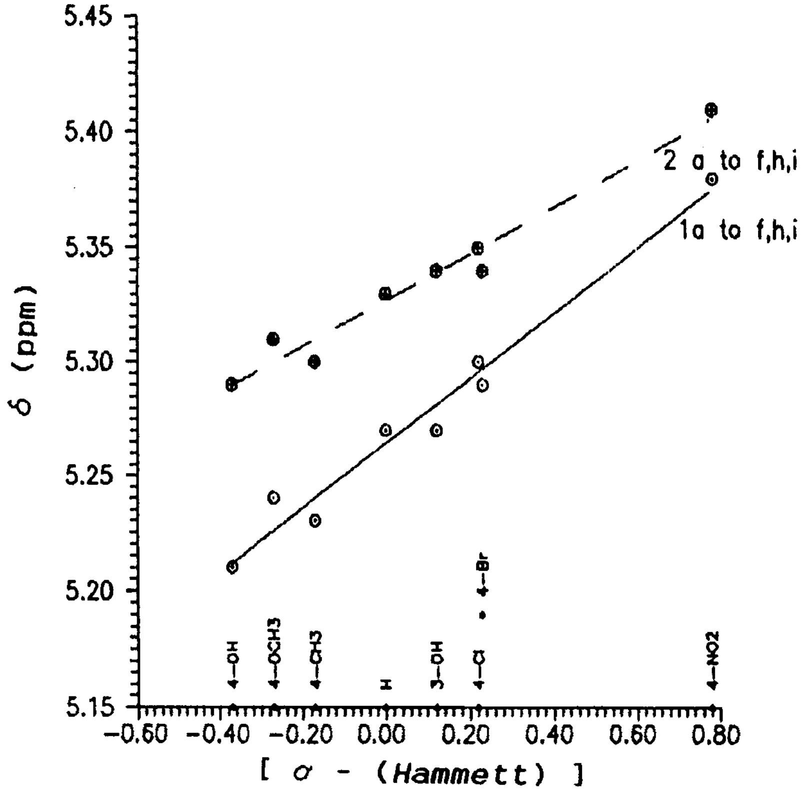


FIGURE 1 δ Values of benzylidene protons (H_c) of 1 a to f, h, i and 2 a to f, h, i against σ-Hammett values.

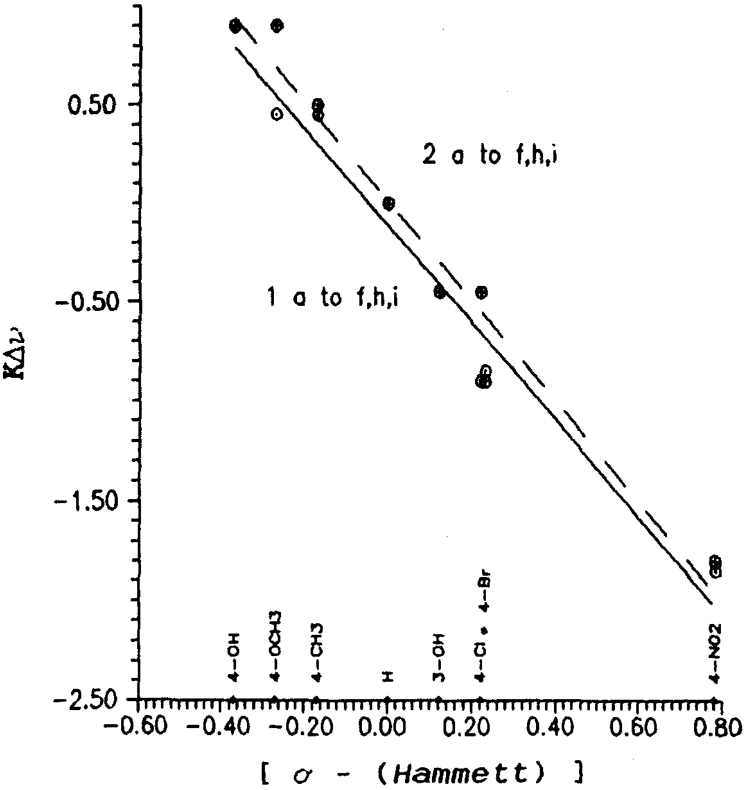


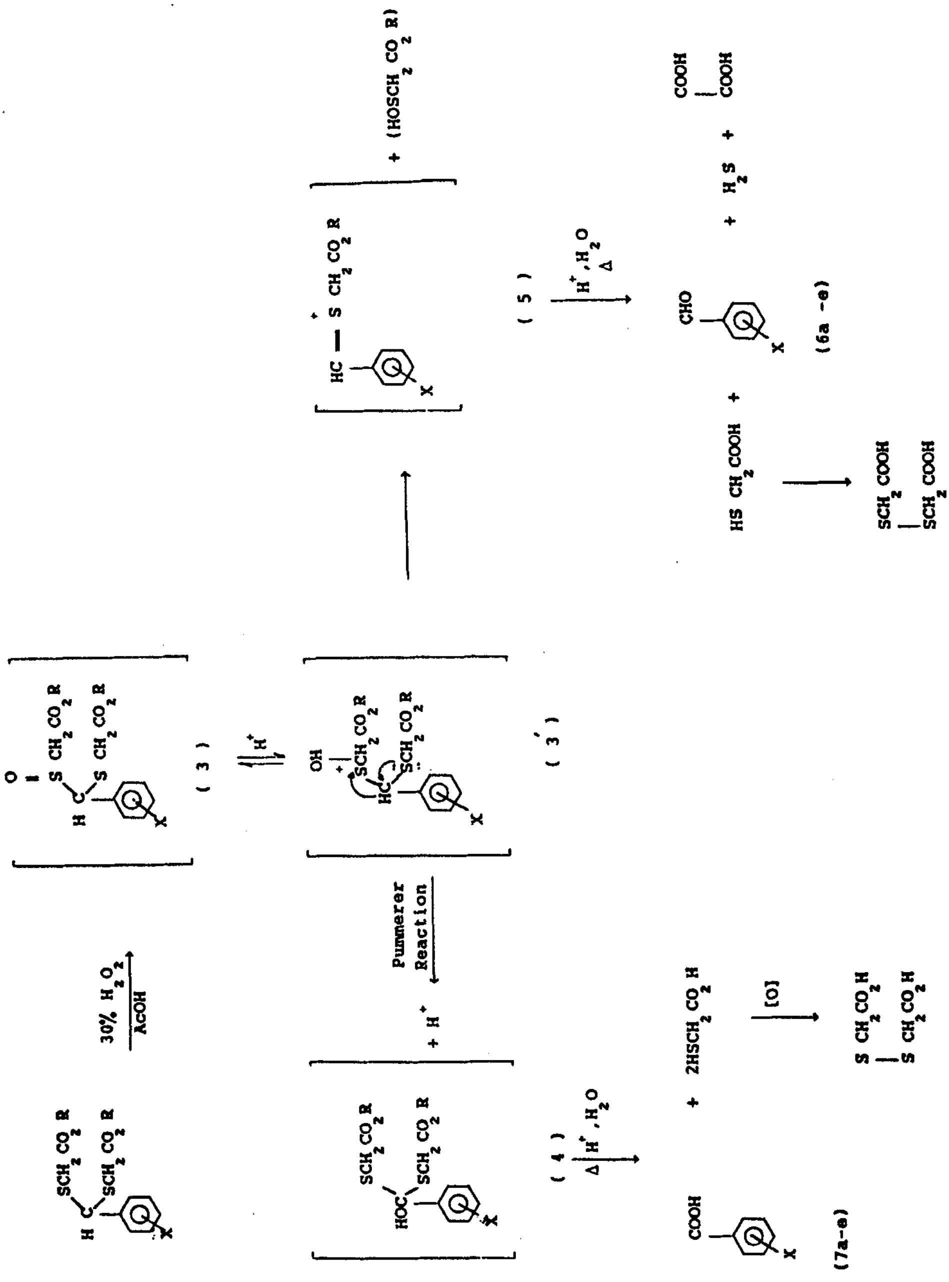
FIGURE 2 KΔν values of the methylene protons of 1 a to f, h, i and 2 a to f, h, i against σ-Hammett constants.

protons are influenced by the polar effects of the 3- and 4-substituents *X*, which could be transmitted through the sulfur atoms by induction.

The J_{AB} coupling constant values of the methylene protons were almost unchanged (13.20–13.95 Hz) and were lower than those of the corresponding thioglycollic acid compounds,[19,21] but they were nearly equal to those of thio-compounds in which the sulfur atom might be absent or replaced by SO or SO_2 groups.[22,23] This could be explained on the ground that the J_{AB} values are unaffected by either the electrical field of the adjacent sulfur atoms or the substitution on the aryl groups. However, they might be affected by the change in the constitution of —SCH_2COOR group.[24]

IR spectra[25] of the studied compounds showed sharp bands at 1710–1750 cm^{-1} (C=O), beside a characteristic stretching band at 710–730 cm^{-1} due to the (C—S) band.

The treatment of 1a–j with an excess 30% hydrogen peroxide in acetic acid-water mixture (60%:40% v/v), acidified to 3 M sulfuric acid and warming on a water-bath gave different products depending on the nature of substituent *X* (Scheme 1). Whereas compounds containing electron donating substituents 1a–e and 2a–e gave the corresponding aldehyde derivatives beside dithiodiacetic acid with liberation of hydrogen sulfide and oxalic acid, compounds containing electron with-



Scheme 1

drawing substituent X 1f–j and 2f–j gave the same dithiodiacetic acid in addition to the corresponding benzoic acid derivatives (Scheme 1).

It was observed that the oxidation of thioacetals, derived from aromatic aldehydes, did not produce the corresponding disulfones.[26] The isolation of 6a–e and 7a–e (Scheme 1) led to the suggestion that the oxidation of 1a–j and 2a–j proceeded via the Pummerer reaction[27] of the activated sulfoxide (3). This reacts under a variety of acidic conditions with reduction at sulfur, oxidation at the α-carbon and frequently, carbon-sulfur bond fission.[28] The reaction proceeds by the intramolecular rearrangement of O-protonated sulfoxides (3′) to the intermediate dithiohemiacetals (4)[29] leading to benzoic acid derivatives (7a–e) and thioacetic acid for compounds containing electron withdrawing substituents 1f–j and 2f–j. Thioacetic acid, formed under this reaction condition, could be oxidized to the corresponding disulfide. O-protonated sulfoxide (3′) might undergo cleavage of the thioether bond with liberation of sulfenic ester[30] and formation of a sulfur-stabilized carbenium ion[31] (5). This pathway may be facilitated due to the presence of electron donating substituents X, attached to the aryl group, which increase the stability of intermediate (5). This intermediate undergoes further cleavage to the corresponding aldehyde derivatives (6a–e) and thioacetic acid, Scheme 1. The latter compound oxidizes to dithioadiacetic acid while the sulfenic ester could be decomposed in an acidic medium to oxalic acid accompanied with evolution of hydrogen sulfide gas.[32]

EXPERIMENTAL

Melting points are uncorrected and were determined on a Thomas-Hoover Capillary apparatus, refractive index values were measured on PZO, RLi AAB refractometer, ^{1}HNMR spectra were obtained in CCl_4, using a BRUKER AM 300 L Spectrometer with Me_4Si as the internal standard. The IR spectra (KBr pellets or Nujol) were measured on a Pye Unicam Cambridge SP^3 200 instrument. UV spectra were measured on UV-Visible recording spectrophotometer 160-A Shimatzu. Analytical thin-layer chromatography (TLC) were carried out on Silica gel, using (1:9) ethylacetate: *n*-hexane. Elemental analyses were carried out in the Chemistry Department at the Faculty of Science, Cairo University, Egypt.

General procedure for synthesis of [(substituted benzylidene)dithio]diacetic acids. The synthetic routes of these acids are not the same as cited in the literature[15] to improve the yield of products.

To 5.0 g (0.03 mol) substituted benzaldehyde in 25 ml. glacial acetic acid, 6.09 g (0.07 mol) thioacetic acid was dropped with stirring at 60°C for 20 minutes, then, 1 ml of ethereal BF_3 solution was added. The reaction was left for 3 hours at 60°C. After cooling, it was poured into 200 g ice-water and a precipitate was formed. It has been purified by dissolving in 10% sodium carbonate solution, reprecipitated with 10% sulfuric acid and, finally, by recrystallization from aqueous ethanol in good quantitative yield.

General procedure for synthesis of alkyl-[(substituted benzylidene)dithio]diacetates 1a–j and 2a–j. Methyl-[(substituted benzylidene)dithio]diacetates 1a–j were synthesized by dropping a freshly prepared ethereal solution of diazomethane in a suspension of the corresponding acids in ether at 0°C with stirring for 3 hours. However, ethyl[(substituted benzylidene)dithio]diacetates 2a–j prepared by refluxing the corresponding acids in a mixture of absolute ethanol and a few drops of concentrated sulfuric acid. On distillation of solvents in both cases, sticky substances were obtained and upon washing with 10% sodium carbonate solution, either solids or oils were produced. The solids were purified by recrystallization from methanol or ethanol, however, oils were purified by flash column chromatography, using ethylacetate: *n*-hexane 1:9, respectively.

Oxidation of 1a–j and 2a–j compounds. With 1 equivalent or an excess 30% hydrogen peroxide in glacial acetic acid or in a mixture of 60% acetic acid and 40% water, acidified to 3M with sulfuric acid at room temperature for one week, render them unchanged. An alternate applicable procedure, involved warming the reaction mixtures of 1a–e and 2a–e compounds on a water-bath for 1 hour, hydrogen sulfide gas was liberated and a pale brown color developed. Distillation of solvents gave sticky substances which were washed with 10% sodium bicarbonate solution several times.

Acidification of the bicarbonate solutions gave a white precipitate which was identified as dithiodiacetic acid m.p. 107°C, (lit., 108-9)[33] (13–62%). The residues were identified as benzaldehyde, colourless oil, n_D^{20} 1.5447 (83–88%); *p*-talualdehyde, pale-yellow oil, n_D^{20} 1.5458 (89–91%). *p*-anisaldehyde, colourless oil, n_D^{20} 1.5734 (84–90%); *p*-hydroxybenzaldehyde, pale brown crystals m.p., 118°C (lit., 115–16)[34] (79–95%) and *m*-hydroxybenzaldehyde, pale brown powder, m.p. 106° (lit., 108)[35] (89–94%), respectively, (6a–e). Furthermore, 1f–j and 2f–j compounds, on warming for 48 hours under the previous conditions, cooling and extracting the reaction mixtures with ether, the TLC indicates the presence of two compounds in each case. Such compounds were separated by column chromatography, using silica gel (particle size 0.063–0.20 mm., 70-230 mesh ASTM) and (1:9) ethylacetate: *n*-hexane, respectively. The first compound separated was identified as dithiodiacetic acid, m.p. 107°C, (83–96%) while the second one in the mixture was identified as *p*-bromobenzoic acid, white crystals, m.p. 252°C (lit., 251-3°)[36] (80–91%); *o*-bromobenzoic acid, white crystals m.p. 152°C, (lit., 150)[37] (83–92%); *p*-chlorobenzoic acid, white crystals m.p. 240°C. (lit. 243°)[38] (87–93%); *p*-nitrobenzoic acid pale yellow crystals, m.p. 242°C (lit., 241.5)[39] (83–91%) and *o*-nitrobenzoic acid, pale yellow crystals m.p. 149°C (lit., 146-8°)[40] (79–88%), (7a–e), respectively. All these products were compared with a commercial specimen, (their refractive index, melting points, TLC and some ^{1}HNMR).

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