(m, 5 H), 1.28 (t, J = 7.2 Hz, 3 H); MS, m/z 304 (M^+).

Reaction of 1 with 27. To a stirred solution of 1 (150 mg, 0.64 mmol) in 10 mL of dry toluene at −78 °C was added 1 equiv of $BF_3{\cdot}Et_2O$ (0.08 mL, 0.64 mmol) under Ar, and the reaction mixture was stirred at −78 °C. After 30 min, **27** (200 mg, 0.64 mmol) was added to the reaction mixture, which was stirred for 30 min. The reaction mixture was quenched with 5 mL of H_2O, extracted with AcOEt, washed with brine, dried over Na_2SO_4, and evaporated to dryness. The residual solids were chromatographed on silica gel eluting with n-hexane/AcOEt (9:1) to give **32** (89 mg, 29%) as red crystals: mp 180–181 °C (CH_2Cl_2–n-hexane); IR ($CHCl_3$) 1715, 1620, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 13.54 (s, 1 H), 12.94 (s, 1 H), 8.36–8.22, 7.90–7.69 (m, 4 H), 7.05 (s, 1 H), 6.94 (s, 1 H), 4.32 (s, 2 H), 4.14 (q, J = 7.2 Hz, 2 H), 2.72–2.65 (m, 4 H), 2.08–1.89 (m, 2 H), 1.66 (s, 3 H), 1.24 (t, J = 7.2 Hz, 3 H); MS, m/z 484 (M^+). Anal. Calcd for $C_{25}H_{24}O_6S_2$: C, 61.97; H, 4.99. Found: C, 61.78; H, 4.97.

Hydrolysis of the Thioketal of 32. To a solution of **32** (20 mg, 0.04 mmol) in 3 mL of THF was added $Hg(ClO_4)_2$ (73 mg, 0.16 mmol), and the reaction mixture was stirred at room temperature. After 30 min, the mixture was filtered. The filtrate was diluted with AcOEt, washed with H_2O and brine, dried over Na_2SO_4, and evaporated to dryness. The residual solids were chromatographed on silica gel eluting with n-hexane/AcOEt (9:1) to give **33** (12 mg, 75%): mp 149–150 °C; IR ($CHCl_3$) 1720, 1685, 1620, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 13.44 (s, 1 H), 12.89 (s, 1 H), 8.41–8.20, 7.95–7.73 (m, 4 H), 7.00 (s, 1 H), 6.82 (s, 4 H), 4.26 (s, 2 H), 4.25 (q, J = 7.2 Hz, 2 H), 2.43 (s, 3 H), 1.29 (t, J = 7.2 Hz, 3 H); MS, m/z 394 (M^+). Anal. Calcd for $C_{22}H_{18}O_7$: C, 67.00; H, 4.60. Found: C, 67.01; H, 4.59.

2-(2′-(Carbethoxymethyl)-3′-oxobutyl)-1,4-dihydroxyanthraquinone (35). A mixture of 50 mg (0.13 mmol) of **33**, 51 mg (0.78 mmol) of zinc dust, and 2 mL of acetic acid was stirred at room temperature. After 1 h, the reaction mixture was diluted with 5 mL of CH_2Cl_2 and filtered. The filtrate was washed with saturated $NaHCO_3$, H_2O, brine, dried over Na_2SO_4, and evaporated to dryness. The residual solids were dissolved in 2 mL of DMF and the solution was treated with TMSCl (0.1 mL, 0.78 mmol) and imidazole (70 mg, 1.04 mmol). After this stirred at room temperature under Ar for 1 h, 5 mL of saturated NaF was added. The mixture was stirred for 15 min, extracted with AcOEt, washed with H_2O and brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residual solids were chromatographed on silica gel eluting with n-hexane/AcOEt (4:1) to give **35** (30 mg, 60%) as red crystals: mp 82–84 °C; IR ($CHCl_3$) 1720, 1620, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 13.35 (s, 1 H), 12.80 (s, 1 H), 8.40–8.18, 7.96–7.74 (m, 4 H), 7.10 (s, 1 H), 4.09 (q, J = 7.2 Hz, 2 H), 3.64–2.45 (m, 5 H), 2.29 (s, 3 H), 1.21 (t, J = 7.2 Hz, 3 H); MS, m/z 396 (M^+). Anal. Calcd for $C_{22}H_{20}O_7$: C, 66.66; H, 5.09. Found: C, 66.49; H, 5.26.

2-(2′-(Carbomethoxymethyl)-3′-oxobutyl)-1,4-dihydroxyanthraquinone (36). A mixture of 50 mg (0.13 mmol) of **35**, 2 drops of H_2SO_4, and 30 mL of MeOH was stirred for 24 hr. The mixture was diluted with CH_2Cl_2, washed with saturated $NaHCO_3$, H_2O, brine, dried over Na_2SO_4, and evaporated to dryness. The residual solids were chromatographed on silica gel eluting with n-hexane/AcOEt (4:1) to give **36** as red crystals: mp 182–184 °C (lit.[27] mp 170–180 °C) (CH_2Cl_2–n-hexane); IR ($CHCl_3$) 1720, 1620, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 13.38 (s, 1 H), 12.83 (s, 1 H), 8.41–8.21, 7.96–7.75 (m, 4 H), 7.10 (s, 1 H), 3.63 (s, 3 H), 3.49–2.45 (m, 5 H), 2.29 (s, 3 H); MS, m/z 382 (M^+). Anal. Calcd for $C_{21}H_{18}O_7$: C, 65.97; H, 4.74. Found: C, 65.78; H, 4.75.

Reaction of Lithium Enolates with Carbon Disulfide: Synthesis of *O*-(1-Alkoxy-2,2-dialkylvinyl) *S*-Alkyl Dithiocarbonates

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The reaction of lithium enolates **5**, generated from esters **4** having only one α-hydrogen atom, with carbon disulfide at −78 °C followed by alkylation with alkyl halide afforded *O*-(1-alkoxy-2,2-dialkylvinyl) *S*-alkyl dithiocarbonates (**7**) in excellent yields (84–95%). An unambiguous structural assignment was made with the help of spectral and microanalytical data. A plausible mechanism has been proposed, in light of available literature, that explains the results of the reaction of enolates with carbon disulfide. The transformation is significant from both the synthetic and mechanistic points of view. These products have not previously been reported, and compound **8** was reported to be the primary product of the reaction of lithium enolate with carbon disulfide. This report represents the first example of the formation of a C–O bond between the oxygen of an enolate and the carbon disulfide.

Lithium enolates have played a major role in the development of modern organic chemistry. They are generated by the deprotonation of carbonyl compounds with amide bases, such as lithium diisopropylamide (LDA),[1] lithium tetramethylpiperidide (LTMP),[2] and lithium hexamethyldisilazanide (LHMDS),[3] in THF in the presence of a cosolvent or of a complexing agent and preferably at low temperature. The reactions involving enolates were described until recently by drawing a negative charge on the carbon atom, even though it was realized that the negative charge is located on the more electronegative oxygen, but pragmatically this was done because that is where they react. Recent studies[4] on the structure and reactivity of enolates, in solution and in the crystalline state, by X-ray, spectroscopic, and physicochemical methods have now established that Li and Na enolates exist as aggregates in nonpolar solvents and that these aggregates,[5] probably, are the product-forming species. These studies have certainly helped in a better understanding of the reaction of lithium enolates, but there still exist gaps in our knowledge.

The reaction of enolates with carbon disulfide has been well studied.[6-8] A typical course of the reaction of carbonyl

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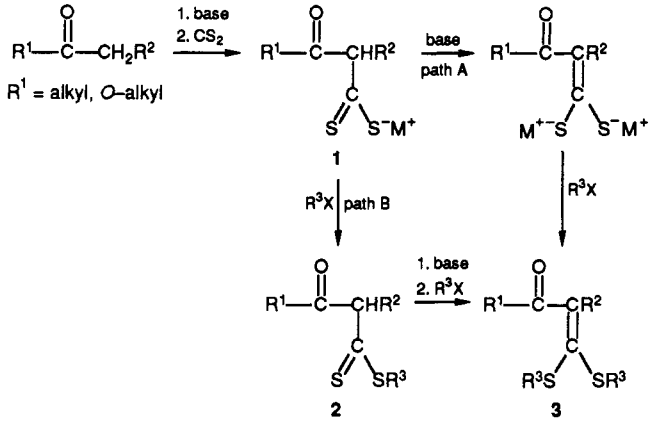
0022-3263/89/1954-5603$01.50/0

Scheme I

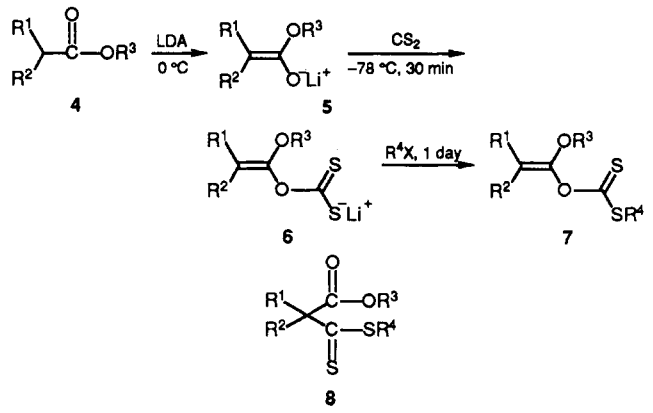


compounds with carbon disulfide in the presence of a base is outlined in Scheme I. The reaction of enolates with carbon disulfide is reported to result initially in the formation of an intermediate (**1**) that is then converted, either by a one-step (path A) or a two-step (path B) process, to α-oxo ketene dithioacetals (**3**), which are versatile synthetic intermediates.[9] The conversion of ketones to α-oxo ketene dithioacetals can easily be performed by the use of a variety of bases.[6-8] There are also a few reports on the preparation of α-oxo ketene dithioacetals from simple esters.[10] In no case, however, has the formation of xanthate been observed. The preparation of **3** from a lactone and an α,β-unsaturated ester is reported by the use of amide bases; high yields of the product were obtained with LHMDS, but a significant amount of condensation product and low yields of the desired product were obtained when LDA was used.[8]

We have investigated the reaction of several lithium enolates of carboxylic esters having only one α-hydrogen atom with carbon disulfide to gain an insight into the mechanism of the reaction for designing strategy for the preparation of α-oxo ketene dithioacetals from simple esters. Thus, lithium enolates **5** (Scheme II) were generated from carboxylic esters **4** by LDA at 0 °C in THF–hexane and treated with carbon disulfide at −78 °C for 30 min followed by alkylation with alkyl halides. The workup of the reaction after 24 h provided crude products which were distilled to furnish pure, hitherto unknown, *O*-(1-alkoxy-2,2-dialkylvinyl) *S*-alkyl dithiocarbonates (**7**) in excellent yields (84–95%). The results have been summarized in Table I. The possibility of isomeric structure **8** for these products was ruled out on the basis of comparative NMR spectral data and mass fragmentation pattern of **7**. Though 1 equiv of both carbon disulfide and alkyl halide was required, better yields were obtained when 3 equiv was used.

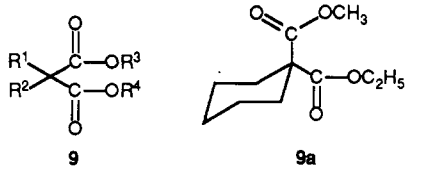
The microanalyses data for all the products were found satisfactory. The IR spectra of these products displayed strong bands in the region 1732–1740 cm^{-1}, which were ascribed to C=C stretching. The olefinic stretching bands

Scheme II



in the IR spectra of *O*-trimethylsilyl ketene acetals appear around 1710 cm^{-1} as strong bands.[11] The IR spectral data did not help in eliminating the other possible structure (**8**). The structure of these products could be established, unambiguously, with the help of ^1H NMR and ^{13}C NMR spectral data and the mass fragmentation pattern of **7**.

The ^1H NMR spectral data of **7** proved highly fruitful in the structural elucidation. The most significant signals in the ^1H NMR spectra of these products were those assigned to allylic protons. These signals are too low for the β-protons of **8**. The ^1H NMR data for **8** are not available but can be compared, to some extent, to those of malonic ester derivatives **9**.[12] The chemical shift values for the



β-protons of **9** are about 0.2 ppm higher than those of allylic protons in the corresponding **7**. A comparison of the ^1H NMR data of **9a** with those of **7i** and **7j** proved a decisive factor in the elimination of structure **8**. The signals for the axial and equatorial allylic protons were observed at δ 1.9 (t) and 2.5 (d) in the cases of **7i** and **7j**, while both β-protons appear together as a triplet at δ 1.95 in the case of **9a**. The possibility of structure **8** for these products, therefore, can be ruled out.

The assignment of ^{13}C NMR spectral data of **7** was made by comparison with that of related compounds. The signal for C=S carbon could not be observed in all of the cases. The signals for the olefinic carbon atoms were seen in the region 62–73 and 170–174 ppm. The chemical shifts of the olefinic carbon atoms in the ^{13}C NMR spectrum of enolate **10** are reported as 62.1 and 171.4 ppm,[13] while the calculated chemical shift values for the olefinic carbon atoms of **11** are 68.8 and 167.5 ppm.[14] The signals for the olefinic carbon atoms in **7** can be expected in this range.

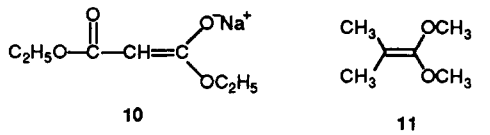


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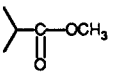
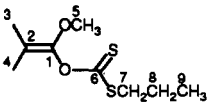
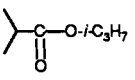
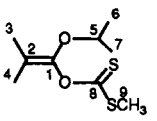
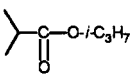
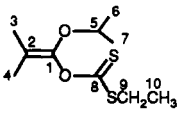
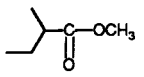
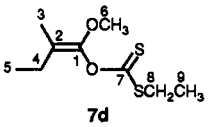
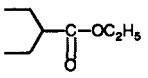
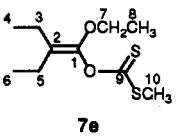
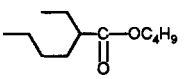
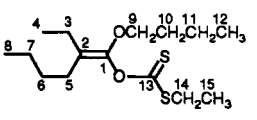
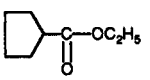
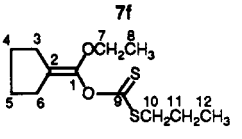
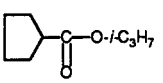
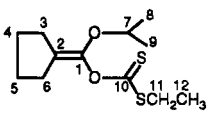
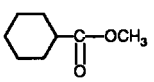
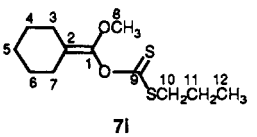
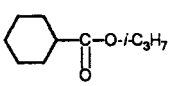
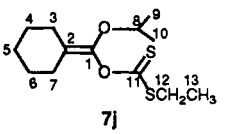
Table I. Preparation of *O*-(1-Alkoxy-2,2-dialkylvinyl) *S*-Alkyl Dithiocarbonates (7)

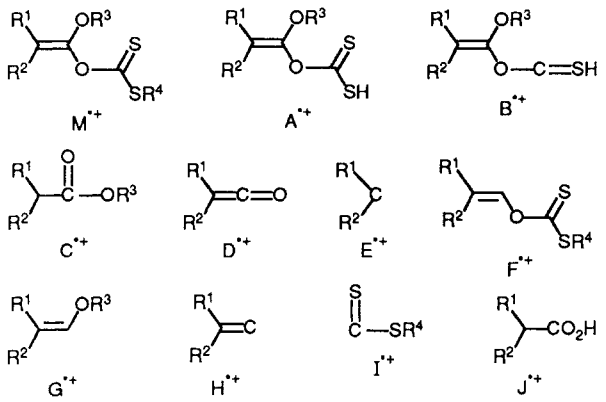
run	ester	alkyl halide	product	yield,[a] %
1	 **4a**	C_3H_7Br	 **7a**	84
2	 **4b**	CH_3I	 **7b**	91
3	 **4c**	C_2H_5Br	 **7c**	87
4	 **4d**	C_2H_5Br	 **7d**	89
5	 **4e**	CH_3I	 **7e**	86
6	 **4f**	C_2H_5Br	 **7f**	93
7	 **4g**	C_3H_7Br	 **7g**	92
8	 **4h**	C_2H_5Br	 **7h**	90
9	 **4i**	C_3H_7Br	 **7i**	88
10	 **4j**	C_2H_5Br	 **7j**	95

[a] Pure isolated product.

An examination of the mass fragmentation pattern of these products also helped in the structural elucidation. Some of the important fragments are depicted in Chart I. The molecular ion peaks were intense in all cases. The peaks corresponding to fragments A, B, and C were the most intense. The major fragmentation path led to the formation of ketene D which gave rise to ion E by the loss of carbon monoxide. The peaks for these fragments were also intense. The fragment F, formed by the loss of alkoxy group from the molecular ion, was present as a less intense peak. The peaks corresponding to fragments G and H were found only in some cases. An intense peak for the ion I was present in mose cases. The most diagnostic feature of the mass spectra was the absence of an ion formed by the loss of R^3 from the molecular ion. This fragment would be expected by the McLafferty rearrangement in the cases where R^3 = Et or Pr had there been a $COOR^3$ group in the molecule. The peaks corresponding to fragment J, formed from the fragment C, were intense in all the cases.

The fact that xanthate carbonyl signal could not be observed in the ^{13}C NMR spectra is a bit troubling, but the spectral and analytical data, particularly the presence of molecular ion peaks in the mass spectra and elemental analysis, leave no ambiguity in the assignment of structure **7** to these products. Another important factor that served as a chemical probe for the assignment of structure **7** instead of **8** was the instability of these products even in the

Chart I

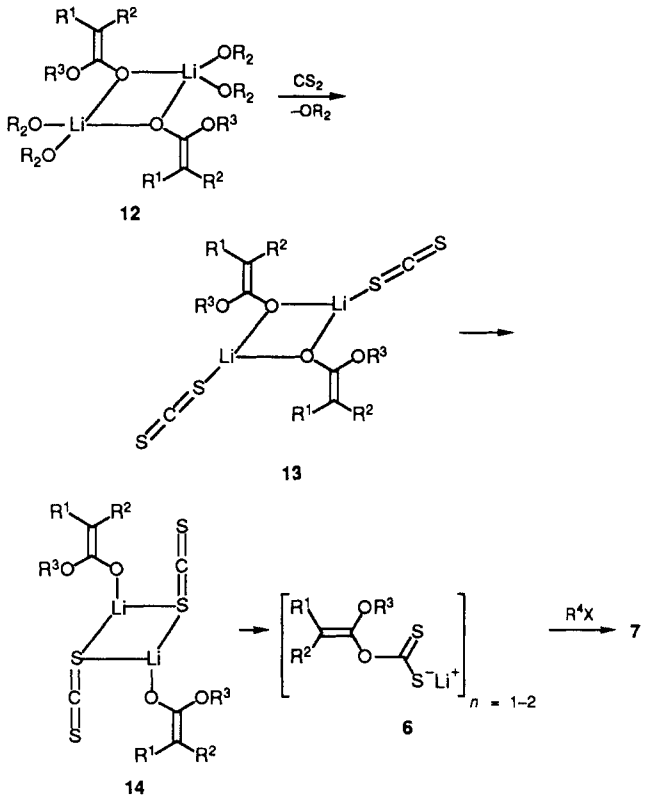


presence of a trace of acid. These products decomposed when treated with methanolic HCl, the chemical reactivity being consistent with the structure proposed on the basis of spectral and analytical data.

Though the formation of **7** can be simply explained by the attack of oxygen of ester enolate on the carbon disulfide followed by alkylation, a mechanism involving lithium enolate aggregate seems more probable since it is now believed that lithium enolates exist as aggregates.[4,5] The exact nature of lithium ester enolates **5**, i.e., dimeric, tetrameric, or hexameric, is not clear, but the formation of **7** can best be explained, in light of the available literature, by assuming a dimeric structure[15] of **5**, as being parallel to the mechanism proposed for the formation of the -ate complex[16] by the addition of HMPT to a lithium enolate in which the oxygen of HMPT initially replaces THF coordinated to Li in the aggregate and then becomes part of the aggregate nucleus. The proposed mechanism is outlined in Scheme III. The enolate unit in **12** can attain increased charge density through complexation of the Li with a carbon disulfide sulfur (**13**), the enolate oxygen being still neutralized by two Li^+. Through reorganization, S may become part of the aggregate nucleus (**14**), the enolate oxygen outside being neutralized only by one Li^+, which should increase the nucleophilicity. An interaction between the O of the enolate and C of carbon disulfide may give **6**, which is then alkylated with alkyl halide.

We propose on the basis of these results that intermediate **6** is, probably, the primary product of the reaction of lithium enolate with carbon disulfide. The intermediate **6** is stable at −78 °C but decomposes above −20 °C in solution. In one experiment, we allowed the reaction mixture, after addition of carbon disulfide at −78 °C and stirring for 30 min, to warm to −20 °C and stir for 1 h. The contents were again cooled to −78 °C followed by addition of alkyl halide and stirring overnight. The ^1H NMR spectrum of the residue obtained after the usual workup revealed the presence of a large amount of condensation products and the absence of **7**. It is quite probable that intermediate **6**, from ketones, may convert to **1**, intra- or intermolecularly, when the contents are allowed to warm to 0 °C.[8] In the case of esters, however, there is another possible path leading to ketene that can give rise to condensation products. The decomposition of the lithium enolate of *tert*-butyl propionate to ketene is indicated even in the crystalline state.[17] The investigations on the esters

Scheme III[a]



[a] R_2O = THF.

with an α-methylene group are in progress in this laboratory and will be published at a later stage. The results in hand[18] strongly support the proposal that the course of the reaction may be a function of temperature.

In conclusion, the preparation of **7** by the reaction of lithium enolate **5** generated from carboxylic esters **4**, having only one α-hydrogen atom, with carbon disulfide at −78 °C followed by alkylation is described. These products have not been previously reported, and the reaction has never been observed before in the extensive work on the carbon disulfide alkylation of ketone and ester enolates. The results give an insight into the mechanism of reaction of lithium enolates with carbon disulfide.

Experimental Section

All the reactions were performed under nitrogen atmosphere. The boiling points were determined by ordinary distillation. Infrared spectra were obtained on a JASCO IR-810 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-200 spectrometer. All the NMR spectra were recorded in $CDCl_3$ and are reported in parts per million (ppm) relative to TMS (δ = 0.0). The mass spectral data were obtained on a JEOL JMS-DX-300 instrument. The microanalyses were determined by using a Yanaco MT-3 instrument.

General Procedure for the Preparation of *O*-(1-Alkoxy-2,2-dialkylvinyl) *S*-Alkyl Dithiocarbonates (7). A 250-mL round-bottom flask was equipped with an addition funnel and a magnetic stirrer. The system was swept with dry nitrogen, and a solution of diisopropylamine (3 g, 0.03 mol) in THF (25 mL) was added. After cooling in an ice bath, a hexane solution of *n*-butyllithium (18.75 mL of 1.6 M solution) was added during 15 min, and the mixture was stirred for an additional 15 min. To this solution was added 0.03 mol of ester **4** over 15 min, and the stirred solution was maintained at 0 °C for 30–40 min. The

(15) Bauer, W.; Laube, T.; Seebach, D. *Chem. Ber.* **1985**, *118*, 764.
(16) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624.
(17) Seebach, D.; Amstutz, R.; Laube, T.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5403. Häver, R.; Laube, T.; Seebach, D. *J. Am. Chem. Soc.* **1985**, *107*, 5396.

(18) The esters with an α-methylene group when subjected to these conditions furnish α-oxo ketene dithioacetals as the major product, and the corresponding xanthate has also been obtained in a large amount in a few cases.

constants were then cooled to −78 °C in a dry ice–acetone bath, and carbon disulfide (6.84 g, 0.09 mol) was added over 30 min. The temperature of the mixture was not allowed to rise above −70 °C during addition. An immediate color change was observed, and the mixture turned orange–red after addition of carbon disulfide. The solution was clear in some cases, while a solid precipitated in a few cases. Alkyl halide (0.09 mol) was then added, and the contents were stirred for 30 min at −78 °C. The contents were then allowed to warm to room temperature and left stirring overnight. The reaction was worked up by adding water and extracting with ethyl acetate, washed several times with water, and dried over Na_2SO_4. The evaporation of the solvent furnished crude products in all cases which were distilled to yield pure products as orange liquids.

***O*-(1-Methoxy-2,2-dimethylvinyl) *S*-Propyl Dithiocarbonate (7a)**: bp 96–100 °C (3 mmHg); ^{1}H NMR δ 0.98 (t, 3 H, J = 7.4 Hz, H-9), 1.62 (s, 6 H, H-3, 4), 1.57–1.77 (m, 2 H, H-8), 3.15 (t, 2 H, J = 7.4 Hz, H-7), 3.65 (s, 3 H, H-5); ^{13}C NMR δ 13.60 (C-9), 20.47 (C-8), 27.34 (C-3, 4), 38.47 (C-7), 52.43 (C-5), 62.34 (C-2), 173.81 (C-1); IR (neat) ν 2967, 2934, 2875, 1738, 1462, 1265, 1148, 1095, 945 cm^{-1}; MS, m/z (rel intensity) 222 (2), 221 (3), 220 (M$^{\bullet+}$, 24), 189 (4), 178 (15), 177 (7), 157 (7), 146 (33), 144 (6), 119 (16), 117 (22), 102 (32), 97 (21), 96 (19), 85 (32), 73 (33), 69 (27), 59 (25), 57 (17), 55 (18), 45 (27), 43 (51), 41 (80), 27 (49), 16 (100). Anal. Calcd for $C_9H_{16}O_2S_2$: C, 49.05; H, 7.32. Found: C, 49.04; H, 7.62.

***O*-(1-Isopropoxy-2,2-dimethylvinyl) *S*-Methyl Dithiocarbonate (7b)**: bp 89–92 °C (3 mmHg); ^{1}H NMR δ 1.16 (d, 6 H, J = 6.2 Hz, H-6, 7), 1.63 (s, 6 H, H-3, 4), 2.58 (s, 3 H, H-9), 4.88–5.10 (m, 1 H, J = 6.2 Hz, H-5); ^{13}C NMR δ 19.99 (C-9), 21.31 (C-6, 7), 27.39 (C-3, 4), 62.13 (C-2), 68.65 (C-5), 172.74 (C-1); IR (neat) ν 2985, 2922, 2875, 1736, 1464, 1385, 1263, 1155, 1110, 1095, 930 cm^{-1}; MS, m/z (rel intensity) 222 (4), 221 (4), 220 (M$^{\bullet+}$, 40), 173 (2), 161 (12), 160 (6), 133 (13), 131 (27), 129 (5), 103 (13), 91 (69), 87 (23), 86 (24), 85 (31), 71 (14), 59 (8), 45 (19), 43 (100), 41 (32), 32 (42). Anal. Calcd for $C_9H_{16}O_2S_2$: C, 49.05; H, 7.32. Found: C, 48.99; H, 7.38.

***O*-(1-Isopropoxy-2,2-dimethylvinyl) *S*-Ethyl Dithiocarbonate (7c)**: bp 100–105 °C (3 mmHg); ^{1}H NMR δ 1.13 (d, 6 H, J = 6.2 Hz, H-6, 7), 1.26 (t, 3 H, J = 7.4 Hz, H-10), 1.58 (s, 6 H, H-3, 4), 3.15 (q, 2 H, J = 7.4 Hz, H-9), 4.85–5.05 (m, 1 H, J = 6.2 Hz, H-5); ^{13}C NMR δ 11.83 (C-10), 21.31 (C-6, 7), 27.30 (C-3, 4), 30.73 (C-9), 62.11 (C-2), 68.56 (C-5), 172.75 (C-1); IR (neat) ν 2982, 2930, 2875, 1736, 1462, 1384, 1261, 1154, 1104, 1096, 930 cm^{-1}; MS, m/z (rel intensity) 236 (3), 235 (4), 234 (M$^{\bullet+}$, 31), 206 (1), 175 (9), 164 (7), 147 (10), 146 (8), 131 (22), 129 (6), 105 (74), 87 (23), 86 (25), 85 (32), 77 (20), 71 (12), 59 (10), 45 (16), 43 (100), 41 (42), 29 (39), 27 (30). Anal. Calcd for $C_{10}H_{18}O_2S_2$: C, 51.24; H, 7.74. Found: C, 50.98; H, 7.74.

***O*-(1-Methoxy-2-ethyl-2-methylvinyl) *S*-Ethyl Dithiocarbonate (7d)**: bp 97–101 °C (3 mmHg); ^{1}H NMR δ 0.87 (t, 3 H, J = 7.4 Hz, H-5), 1.32 (t, 3 H, J = 7.4 Hz, H-9), 1.61 (s, 3 H, H-3), 2.17 (q, 2 H, J = 7.4 Hz, H-4), 3.21 (q, 2 H, J = 7.4 Hz, H-8), 3.69 (s, 3 H, H-6); ^{13}C NMR δ 8.99 (C-5), 11.80 (C-9), 23.62 (C-3), 30.81 (C-8), 32.55 (C-4), 52.38 (C-6), 66.52 (C-2), 173.35 (C-1); IR (neat) ν 2977, 2938, 2874, 1740, 1456, 1374, 1305, 1238, 1142, 1098, 938 cm^{-1}; MS, m/z (rel intensity) 222 (2), 221 (4), 220 (M$^{\bullet+}$, 23), 205 (9), 191 (4), 189 (5), 187 (3), 177 (2), 160 (7), 159 (14), 149 (5), 143 (4), 131 (20), 127 (6), 125 (6), 115 (34), 105 (63), 102 (12), 100 (16), 99 (35), 85 (1), 83 (12), 77 (32), 75 (17), 71 (13), 69 (14), 59 (41), 55 (25), 45 (25), 43 (44), 41 (51), 39 (28), 32 (100). Anal. Calcd for $C_9H_{16}O_2S_2$: C, 49.05; H, 7.32. Found: C, 48.86; H, 7.15.

***O*-(1-Ethoxy-2,2-diethylvinyl) *S*-Methyl Dithiocarbonate (7e)**: bp 113–118 °C (3 mmHg); ^{1}H NMR δ 0.76 (t, 6 H, J = 7.2 Hz, H-4, 6), 1.17 (t, 3 H, J = 7.0 Hz, H-8), 2.11–2.35 (m, 4 H, H-3, 5), 2.59 (s, 3 H, H-10), 4.10 (q, 2 H, J = 7.0 Hz, H-7); ^{13}C NMR δ 8.34 (C-4, 6), 13.86 (C-8), 19.94 (C-10), 27.97 (C-3, 5), 61.06 (C-7), 69.97 (C-2), 172.22 (C-1); IR (neat) ν 2980, 2945, 2882, 1738, 1462, 1300, 1222, 1180, 1137, 1098, 1035, 980, 930 cm^{-1}; MS, m/z (rel intensity) 234 (M$^{\bullet+}$, 11), 219 (8), 161 (9), 159 (11), 143 (18), 131 (8), 120 (23), 115 (14), 113 (21), 105 (8), 97 (11), 91 (36), 77 (11), 75 (14), 73 (17), 69 (21), 57 (19), 55 (17), 45 (17), 43 (19), 41 (50), 27 (24), 18 (100). Anal. Calcd for $C_{10}H_{18}O_2S_2$: C, 51.24; H, 7.74. Found: C, 51.33; H, 7.70.

***O*-(1-Butoxy-2-butyl-2-ethylvinyl) *S*-Ethyl Dithiocarbonate (7f)**: bp 142–147 °C (3 mmHg); ^{1}H NMR δ 0.77 (t, 3 H, J = 7.6 Hz, H-8), 0.86 (t, 6 H, J = 7.0 Hz, H-4, 12), 1.05–1.41 (m, 9 H, H-7, 10, 11, 15), 1.46–1.62 (m, 2 H, H-6), 2.05–2.21 (m, 4 H, H-3, 5), 3.20 (q, 2 H, J = 7.6 Hz, H-14), 4.05 (t, 2 H, J = 6.6 Hz, H-9); ^{13}C NMR δ 8.38 (C-4), 11.83 (C-15), 13.57 (C-8), 13.88 (C-12), 19.11 (C-6), 23.07 (C-11), 26.07 (C-7), 28.52 (C-3), 30.36 (C-10), 30.63 (C-14), 34.60 (C-5), 64.93 (C-9), 69.68 (C-2), 172.50 (C-1); IR (neat) ν 2955, 2926, 2871, 1733, 1448, 1380, 1240, 1208, 1137, 1100, 946 cm^{-1}; MS, m/z (rel intensity) 306 (4), 305 (8), 304 (M$^{\bullet+}$, 44), 276 (6), 275 (43), 243 (23), 231 (7), 215 (6), 203 (8), 201 (25), 199 (14), 187 (22), 186 (16), 174 (12), 173 (27), 162 (18), 159 (11), 149 (13), 143 (52), 141 (50), 135 (37), 125 (10), 105 (61), 99 (21), 77 (24), 57 (42), 55 (47), 41 (57), 29 (100). Anal. Calcd for $C_{15}H_{28}O_2S_2$: C, 59.16; H, 9.27. Found: C, 58.89; H, 9.22.

***O*-(Ethoxycyclopentylidenemethyl) *S*-Propyl Dithiocarbonate (7g)**: bp 126–132 °C (3 mmHg); ^{1}H NMR δ 0.99 (t, 3 H, J = 7.4 Hz, H-12), 1.16 (t, 3 H, J = 7.2 Hz, H-8), 1.56–1.76 (m, 6 H, H-4, 5, 11), 2.12–2.40 (m, 4 H, H-3, 6), 3.14 (t, 2 H, J = 7.4 Hz, H-10), 4.11 (q, 2 H, J = 7.2 Hz, H-7); ^{13}C NMR δ 13.58 (C-12), 13.83 (C-8), 20.56 (C-11), 24.53 (C-4, 5), 38.19 (C-10), 38.48 (C-3, 6), 61.39 (C-7), 73.88 (C-2), 172.02 (C-1); IR (neat) ν 2961, 2935, 2868, 1736, 1451, 1362, 1234, 1185, 1050, 1024 cm^{-1}; MS, m/z (rel. intensity) 261 (2), 260 (M$^{\bullet+}$, 12), 237 (7), 218 (6), 187 (10), 185 (7), 172 (21), 169 (5), 157 (4), 144 (10), 142 (21), 141 (22), 113 (14), 112 (15), 111 (33), 97 (22), 96 (22), 95 (21), 79 (7), 69 (100), 67 (50), 55 (10), 43 (34), 41 (52), 29 (33). Anal. Calcd for $C_{12}H_{20}O_2S_2$: C, 55.34; H, 7.75. Found: C, 55.11; H, 7.68.

***O*-(Isopropoxycyclopentylidenemethyl) *S*-Ethyl Dithiocarbonate (7h)**: bp 114–118 °C (3 mmHg); ^{1}H NMR δ 1.15 (d, 6 H, J = 6.2 Hz, H-8, 9), 1.27 (t, 3 H, J = 7.4 Hz, H-12), 1.57–1.75 (m, 4 H, H-4, 5), 2.21–2.37 (m, 2 H, H_a-3, 6), 2.38–2.54 (m, 2 H, H_b-3, 6), 3.18 (q, 2 H, J = 7.4 Hz, H-11), 4.90–5.10 (m, 1 H, J = 6.2 Hz, H-7); ^{13}C NMR δ 11.92 (C-12), 21.25 (C-8, 9), 24.47 (C-4, 5), 30.71 (C-11), 38.04 (C-3, 6), 68.55 (C-7), 73.81 (C-2), 171.87 (C-1); IR (neat) ν 2977, 2938, 2874, 1732, 1454, 1372, 1234, 1190, 1103, 1060, 984 cm^{-1}; MS, m/z (rel intensity) 260 (M$^{\bullet+}$, 19), 234 (7), 205 (6), 203 (5), 201 (5), 198 (6), 189 (4), 173 (11), 172 (4), 157 (11), 156 (11), 155 (8), 145 (6), 143 (4), 129 (5), 114 (4), 113 (39), 111 (24), 105 (20), 95 (12), 85 (7), 79 (8), 77 (11), 71 (8), 69 (8), 67 (16), 55 (6), 45 (12), 43 (25), 41 (20), 32 (71), 18 (100). Anal. Calcd for $C_{12}H_{20}O_2S_2$: C, 55.34; H, 7.75. Found: C, 55.39; H, 7.76.

***O*-(Methoxycyclohexylidenemethyl) *S*-Propyl Dithiocarbonate (7i)**: bp 142–145 °C (3 mmHg); ^{1}H NMR δ 0.99 (t, 3 H, J = 7.4 Hz, H-12), 1.30–1.50 and 1.60–1.78 (m, 4 H each, H-4, 5, 6, 11), 1.96 (t, 2 H, J = 15.0 Hz, H_{ax}-3, 7), 2.48 (d, 2 H, J = 15.0 Hz, H_{eq}-3, 7), 3.15 (t, 2 H, J = 7.4 Hz, H-10), 3.69 (s, 3 H, H-8); ^{13}C NMR δ 13.65 (C-12), 20.43 (C-11), 23.57 (C-4, 6), 25.21 (C-5), 36.20 (C-3, 7), 38.36 (C-10), 52.39 (C-8), 67.79 (C-2), 172.21 (C-1); IR (neat) ν 2962, 2935, 2858, 1736, 1450, 1432, 1300, 1218, 1122, 1038, 997, 960, 900 cm^{-1}; MS, m/z (rel intensity) 262 (5), 261 (8), 260 (M$^{\bullet+}$, 52), 229 (9), 227 (8), 220 (10), 219 (17), 218 (93), 217 (54), 202 (12), 201 (8), 188 (24), 187 (33), 186 (100), 185 (92), 167 (6), 159 (14), 158 (57), 157 (71), 153 (31), 142 (39), 141 (95), 129 (17), 127 (19), 126 (27), 125 (100), 121 (16), 119 (56), 110 (44), 109 (36), 97 (28), 91 (58), 81 (90), 67 (47), 58 (59). Anal. Calcd for $C_{12}H_{20}O_2S_2$: C, 55.34; H, 7.75. Found: C, 55.08; H, 7.66.

***O*-(Isopropoxycyclohexylidenemethyl) *S*-Ethyl Dithiocarbonate (7j)**: bp 134–139 °C (3 mmHg); ^{1}H NMR δ 1.20 (d, 6 H, J = 6.4 Hz, H-9, 10), 1.29 (t, 3 H, J = 7.6 Hz, H-13), 1.44–1.74 (m, 6 H, H-4, 5, 6), 1.95 (t, 2 H, J = 13.4 Hz, H_{ax}-3, 7), 2.50 (d, 2 H, J = 13.4 Hz, H_{eq}-3, 7), 3.18 (q, 2 H, J = 7.6 Hz, H-12), 4.90–5.12 (m, 1 H, J = 6.4 Hz, H-8); ^{13}C NMR δ 11.78 (C-13), 21.36 (C-9, 10), 23.49 (C-4, 6), 25.25 (C-5), 30.55 (C-12), 36.08 (C-3, 7), 67.28 (C-2), 68.35 (C-8), 170.82 (C-1); IR (neat) ν 2980, 2935, 2855, 1734, 1450, 1368, 1298, 1217, 1104, 1032, 950 cm^{-1}; MS, m/z (rel intensity) 275 (9), 274 (M$^{\bullet+}$, 21), 245 (10), 203 (8), 185 (11), 171 (14), 170 (12), 169 (15), 149 (6), 127 (27), 125 (18), 109 (10), 105 (26), 104 (10), 91 (22), 81 (16), 77 (20), 69 (13), 67 (18), 45 (22), 43 (38), 41 (56), 27 (45), 18 (100). Anal. Calcd for $C_{13}H_{22}O_2S_2$: C, 56.89; H, 8.08. Found: C, 56.70; H, 8.02.

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