## Interaction Between the Carbonyl Group and an $\alpha$ -Sulphur Atom. Part I. Infrared and Ultraviolet Spectra of Some $\alpha$ -(Alkylthio)Thioesters

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Some  $\alpha$ -(alkylthio)thioesters exhibit a shift of the carbonyl stretching frequency to lower frequencies in comparison with the unsubstituted thioesters, and a strong u.v. absorption maximum at *ca*. 285 nm, which is absent from the spectra of the unsubstituted thioesters. The similarity of the spectroscopic data for the  $\alpha$ -(alkylthio)-ketones and -esters is discussed.

THE decrease in the normal carbonyl stretching frequencies reported for some  $\alpha$ -(alkylthio)-ketones<sup>1</sup> and -esters<sup>2</sup> has been attributed<sup>1</sup> to a change in the force constant of the carbonyl group due to the influence of the sulphur atom.

Evidence for the interaction between the non-bonded sulphur atom and the carbonyl group in the excited state has been presented <sup>1,3</sup> for a larger number of  $\alpha$ -(alkyl-thio)-ketones and -esters, which showed strong u.v. absorption bands at 300 and 250 nm (log  $\epsilon$  2.5) respectively.

We report here i.r. and u.v. evidence for interaction in the ground and excited states, respectively, between the carbonyl group and the  $\alpha$ -sulphur atom in some  $\alpha$ -(alkylthio) thioesters.

## RESULTS AND DISCUSSION

The i.r. spectra of the  $\alpha$ -(alkylthio)thioesters (IV)—(X) showed a significant shift (*ca.* 15 cm<sup>-1</sup>) of the carbonyl stretching band toward lower frequencies in comparison with unsubstituted thioesters (I)—(III) (Table 1). This

TABLE 1

Carbonyl stretching vibrations of thioesters $[R^1C(:O)\cdot SR^2]$ in $CCl_4^{a}$					
	$\mathbb{R}^{1}$	$R^2$	v/cm⁻¹		
(I)	Me	$\mathbf{Et}$	1694		
(ÌI)	Et	$\mathbf{Et}$	1694		
(ÌII)	Me	CH,Ph	1696		
(IV)	EtS·CH <sub>2</sub>	Et	1678		
) (V)	PhCH <sub>2</sub> ·S·CH <sub>2</sub>	Et	1679		
(VI)	EtS·CHMe	Et	1672		
(VII)	PhCH <sub>2</sub> ·S·CHMe	Et	1671		
(VIII)	EtS·C(Me),	Et	1671		
(IX)	EtS·CH <sub>2</sub>	$CH_{2}Ph$	1681		
(X)	PhCH, S·CH,	CH,Ph	1682		
(XI)	$PhCH_2 \cdot S(CH_2)_2$	$CH_2Ph$	1691		
	a 3-6% solutions i	n 0.1 mm cell.			

shift is similar to that for  $\alpha$ -(alkylthio)ketones,<sup>1</sup> but larger than that for  $\alpha$ -(alkylthio)esters (*ca.* 10 cm<sup>-1</sup>).<sup>2</sup> However, no shift was observed for the  $\beta$ -(alkylthio)-thioester (XI).

Comparison of the i.r. absorption of S-ethyl  $\alpha$ -(ethyl-thio)thioacetate with that of S-ethyl thioacetate in different solvents (Table 2) showed that the shift of the carbonyl stretching frequency is still present. This indicates that the frequency shift does not originate in

differences in solvation, but it is caused by a change in the force constant of the carbonyl group.

U.v. spectra of some thioesters are shown in Table 3.

TABLE	<b>2</b>
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Carbonyl stretching vibrations  $(\nu/cm^{-1})$  of unsubstituted and  $\alpha$ -(alkylthio)-thioesters in various solvents <sup>a</sup>

	Solvent					
Thioester	n- C <sub>6</sub> H <sub>14</sub>	CCl4	Me <sub>2</sub> SO	CHCl <sub>3</sub>	Abs. EtOH	Pure liquid
MeC(:O)·SEt	1701	1694	1683	1686	1696, 1675	1692
EtS·CH <sub>2</sub> ·C(:O)·SEt	1684	1678	1669	1673	1681, 1653	1677
<sup>a</sup> $3-5\%$ solutions in 0.1 mm cell.						

The unsubstituted thioesters (I)—(III) exhibit a strong band at 231 nm. This, in the  $\alpha$ -(alkylthio)thioesters (IV)—(X), is slightly shifted to the visible (236 nm) and, in addition, a new broad band at 284—285 nm (log  $\varepsilon$ 2·6—2·7) appears. The absence of the latter for  $\beta$ -(alkylthio)- (XI) and  $\alpha$ -alkoxy- (XII) thioesters and the similarity in position and intensity to the u.v. absorption bands of  $\alpha$ -(alkylthio)ketones and esters <sup>1,3</sup> (respectively

TABLE 3						
U.v. absorption spectra of thioesters [R <sup>1</sup> C(:O)·SR <sup>2</sup> ]						
	in n-	hexan	e			
Compound *	Compound * $\lambda_{max}/nm$			log ε		
(I)	231		3.58			
(II)	231		3.58			
(III)	230		3.78			
(IV)	236	286	3.54	2.59		
(V)	236	<b>285</b>	3.74	2.65		
(VI)	236	284	3.50	2.70		
(VII)	236	284	3.66	2.74		
(VIII)	236	<b>284</b>	3.42	2.73		
(IX)	233	284	3.71	2.70		
$(\mathbf{X})$	234	286	3.83	2.75		
(XI)	234		3.74			
(XII) a	234		3.87			
(XIII) b	$241$ $^{\circ}$		3.70			
* For substituents	in com	pounds	(I)—(XI) :	see Table 1.		

<sup>*a*</sup>  $\mathbb{R}^1 = \text{EtO}\cdot\text{CH}_2$ ;  $\mathbb{R}^2 = \text{CH}_2\text{Ph}$ . <sup>*b*</sup>  $\mathbb{R}^1 = \text{EtSO}_2\cdot\text{CH}_2$ ;  $\mathbb{R}^2 = \text{Et.}$  <sup>*a*</sup> In absolute ethanol.

299 and 250 nm;  $\log \epsilon 2.5$ ) suggests that they have the same origin.

Several different interpretations have been given for electronic spectra of  $\alpha$ -(alkylthio)-ketones and -esters. Fehnel and Carmack<sup>3</sup> suggested the non-bonding hyper-conjugation and the three-membered ring polarized

<sup>3</sup> E. Fehnel and M. J. Carmack, J. Amer. Chem. Soc., 1949, 71, 84.

<sup>&</sup>lt;sup>1</sup> G. Bergson and A. L. Delin, Arkiv Kemi, 1962, 18, 489.

<sup>&</sup>lt;sup>2</sup> A. Chauveau and R. Mathis-Noel, Ann. Fac. Sci. Univ. Toulouse, 1963, 147 (Chem. Abs., 1964, 60, 11,885).

structures (A) and (B). Price and Oae<sup>4</sup> suggested that a 'biradical-like' singlet structure (C), involving expansion of the sulphur valence shell, was responsible for the u.v. absorption. However, Bergson<sup>1</sup> claimed that the best interpretation was that it was due to a perturbed  $n \to \pi^*$  carbonyl transition.



The presence of the 285 nm band in the  $\alpha$ -(alkylthio)thioester (VIII), in which two hydrogen atoms are substituted by methyl groups, is evidence against structure (A).

The possibility of electron transfer from sulphur to the carbonyl group (B) cannot be ruled out owing to the fact that the  $\alpha$ -(alkylsulphonyl)thioester (XIII) does not exhibit the 285 nm band (Table 3). However, in the spectra of ethyl a-(ethylthio)thioacetate in different solvents, the 235 nm band was practically unchanged and the 285 nm band was only very slightly shifted to longer wavelength as the solvent polarity increased (Table 4). This shift does not seem to be sufficiently significant to be evidence for structure (B).

## TABLE 4

U.v. absorption maxima  $(\lambda_{max}/nm)$  for EtS•CH<sub>2</sub>•C(:O)•SEt in various solvents

n-Hexane 236·0 286·5	Dioxan * 287.5	Abs. ethanol 237·0 288·0	96% Ethanol 237·0 288·0	Chloro- form * 288.5	80% Ethanol 237·0 289·0
		* Not m	neasured.		

It seems reasonable that the 285 nm band is a perturbed  $n \to \pi^*$  carbonyl transition and that the lack of shift to shorter wavelength as solvent polarity increases may be due to the reduced basicity of the carbonyl group. In fact, the basicity of the carbonyl group of even the unsubstituted thioesters decreases in comparison with ketones.<sup>5</sup> A study of the hydrogen-bond strength between the carbonyl group of the alkylthiocarbonyl compounds and various proton donors, such as phenylacetylene and phenol, by i.r. and n.m.r. methods † showed that the basicity of the carbonyl group also

<sup>†</sup> Presented at the Fourth Symposium on Organic Sulphur sponsored by the Sulphur Institute—C.N.R. (Italy), June 1970.

<sup>4</sup> C. C. Price and S. Oae, 'Sulfur Bonding,' The Ronald Press, New York, 1962, pp. 36 and 55. <sup>5</sup> A. W. Baker and G. H. Harris, J. Amer. Chem. Soc., 1960,

82, 1923.
<sup>6</sup> A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. Toops, jun., in 'Technique of Organic Chemistry,' ed. A. Weissberger, Interscience, New York, 1955, vol. 8.

decreases in comparison with that of the corresponding unsubstituted compounds. The decrease of both the basicity and force constant of the carbonyl group, shown by the shift of the carbonyl stretching band toward lower frequencies, indicates that some transfer of charge density from the carbonyl group to a vacant orbital on the a-sulphur atom occurs in the ground state.

## EXPERIMENTAL

Solvents .--- Commercial chloroform, dioxan, and absolute ethanol were purified as described elsewhere.6 n-Hexane and carbon tetrachloride were commercial spectrograde reagents and were used without further purification.

Thioesters.--S-Ethyl thioacetate (I),7 b.p. 112°, S-ethyl thiopropionate (II),<sup>8</sup> b.p. 127°, S-benzyl thioacetate (III),<sup>9</sup> b.p. 109° at 5 mmHg, S-ethyl (ethylthio)thioacetate (IV),<sup>10</sup> b.p. 76-77° at 1 mmHg were prepared by literature procedures. S-Ethyl(benzylthio)thioacetate (V), b.p. 154-156° at 1 mmHg (Found: S, 28.7. C<sub>11</sub>H<sub>14</sub>OS<sub>2</sub> requires S, 28.3%); S-ethyl 2-(ethylthio)thiopropionate (VI), b.p. 100-101° at 9 mmHg (Found: S, 36.0. C<sub>7</sub>H<sub>14</sub>OS<sub>2</sub> requires S, 36.0%); S-ethyl 2-(benzylthio)thiopropionate (VII), b.p. 131-132° at 0.4 mmHg (Found: S, 26.5. C12H16OS2 requires S, 26.7%); S-ethyl 2-(ethylthio)-2-methylpropionate (VIII), b.p. 64-66° at 0.7 mmHg (Found: S. 33.4.  $C_8H_{16}OS_2$  requires S,  $33\cdot3\%$ ; S-benzyl (ethylthio)thioacetate (IX), b.p. 145-146° at 0.7 mmHg (Found: S, 28.4.  $C_{11}H_{14}OS_2$  requires S, 28.3%), S-benzyl(benzylthio)thioacetate (X), b.p. 194° at 0.55 mmHg (Found: S, 22.4. C16H16OS2 requires S, 22.2%); S-benzyl 3-(benzylthio)thiopropionate (XI), b.p. 204-206° at 0.5 mmHg (Found: S, 21.0. C17H18OS2 requires S, 21.2%); and S-benzyl (ethoxy)thioacetate (XII), b.p. 120.5° at 0.7 mmHg (Found: S, 15.3. C<sub>11</sub>H<sub>14</sub>OS<sub>2</sub> requires S, 15.2%) were prepared from the corresponding acyl chlorides, obtained by the reaction of the acids with thionyl chloride, by essentially the method described 7 for the S-ethyl thioacetate. S-Ethyl (ethylsulphonyl)thioacetate (XIII), m.p. 43-45° (Found: S, 32.6.  $C_6H_{12}O_3S_2$  requires S, 32.6%), was prepared by the same method. The corresponding acid 11 was obtained from (ethylthio)acetic acid by oxidation with hydrogen peroxideglacial acetic acid.

Light Absorption Measurements .--- I.r. spectra were recorded on Perkin-Elmer 221 and 337 i.r. spectrophotometers. U.v. spectra were determined with a Zeiss PMQ II spectrophotometer. All measurements were made at room temperature (26  $\pm$  1 °C).

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<sup>11</sup> E. Rothstein, J. Chem. Soc., 1937, 309.