796. *The Addition of* N-*Alkyl-substituted Dithiocarbamic and Alkoxydithioformic Acids to Propiolic Acid.*

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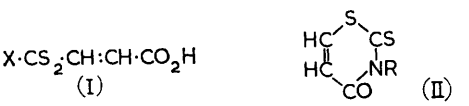
N-Alkyldithiocarbamic and alkoxydithioformic acids add to propiolic acid, forming *cis*-β-substituted acrylic acids (I). β-(*N*-Alkylthiocarbamoylthio)acrylic acids (I; X = R·NH) cyclise to 3-alkyl-3,4-dihydro-4-oxo-2-thiothiazines (II). The ultraviolet absorption spectra and stability of these compounds are discussed.

ADDITION of dithiocarbamic acid and its *N*-substituted derivatives to ethylenic compounds is well known.[1] Their addition to acetylenic bonds, however, has not been reported. No information exists about the addition reactions of alkoxydithioformic acids to αβ-unsaturated compounds.

In a study of the antifungal activity of some organosulphur compounds a number of β-substituted acrylic acids were prepared by nucleophilic addition of dithiocarbamic acid, its *N*-substituted derivatives, and alkoxydithioformic acid to propiolic acid in



(I) (II)

methanol. The stereochemistry of the addition was of interest as an exception to the rule of *trans*-nucleophilic addition of thiols to sodium propiolate has been discovered by Truce and Heine.[2] The formation of *trans*-β-substituted acrylic acids was attributed to the presence of the ionised carboxyl group. As experimental conditions of our preparative methods were sufficient to maintain complete ionisation of the carboxyl group, it was necessary to ascertain if these adducts also had *trans*-configuration.

The products from *NN*-dimethyl- and *NN*-diethyl-dithiocarbamic acid and propiolic acid had $\nu_{max.}$ 1600, 1345, and 700—800 cm.$^{-1}$, characteristic of a *cis*-ethylenic compound and when refluxed with hot water containing a trace of hydrobromic acid gave acids having $\nu_{max.}$ 1600, 1305, and 840 cm.$^{-1}$, indicating a *trans*-configuration. This investigation could not be pursued with β-substituted acrylic acids derived from *N*-alkyldithiocarbamic or alkoxydithioformic acid as the adducts are unstable in hot aqueous solution. β-(*N*-Alkylthiocarbamoylthio)acrylic acids, however, cyclised in phosphorus trichloride to 3,4-dihydro-4-oxo-2-thiothiazines, indicating a *cis*-configuration in the parent compound. It is concluded, therefore, that *N*-alkyldithiocarbamic and alkoxydithioformic acids undergo *trans*-nucleophilic addition with propiolic acid to form *cis*-β-substituted acrylic acids.

NN-Di-isopropyldithiocarbamic acid failed to yield an adduct with propiolic acid, possibly owing to its relative instability.[3] Similarly no product was obtained with *N*-aryldithiocarbamic acids, although these give adducts with acrylic acid.[4] *NN*-Diphenyldithiocarbamic acid, which is more stable than *N*-aryldithiocarbamic acids, also failed to form an adduct.

β-Substituted acrylic acids obtained from *N*-methyldithiocarbamic and dithiocarbamic acid underwent unimolecular or pseudo-unimolecular fragmentation in absolute alcohol; those derived from *NN*-dimethyldithiocarbamic and methoxydithioformic acid were

[1] D'Amico and Harman, Monsanto Chemical Co., B.P. 769,222/1957; Buess, *J. Amer. Chem. Soc.*, 1955, **77**, 6613; Hook, Beegle, and Wystrach, American Cyanamide Co., U.S.P. 2,786,866/1957; Janssen and Mathes, *J. Amer. Chem. Soc.*, 1955, **77**, 2866; Seyden-Penne, *Ann. Chim.* (*France*), 1958, **3**, 599.

[2] Truce and Heine, *J. Amer. Chem. Soc.*, 1957, **79**, 5311.

[3] Zuman and Zahradník, *Z. phys. Chem.*, 1957, **208**, 135.

[4] Garraway, *J.*, 1961, 3733.

TABLE 1.

β-(*N*-Alkylthiocarbamoylthio)acrylic acids (I; X = RR'N).

R	R'	Method of prep.	M. p.	Yield (%)	Formula	Equiv. Found	Equiv. Reqd.	$\lambda_{max.}$ (mμ) and log ε					
H	H	A	164° *	18	$C_4H_5NO_2S_2$	—†	—	263	4·04	298	4·11	316 ‡	3·63
Me	H	A	139 *	28	$C_5H_7NO_2S_2$	177·9	177·1	264	4·20	290	4·16	317 ‡	3·32
Et	H	A	133 *	18	$C_6H_9NO_2S_2$	191·1	191·1	266	4·19	290	4·13	326 ‡	3·24
Pr^n	H	A	137 *	17	$C_7H_{11}NO_2S_2$	205·1	205·1	267	4·23	290	4·15	328 ‡	3·25
Pr^i	H	A	134 *	9	$C_7H_{11}NO_2S_2$	204·1	205·1	268	4·19	291	4·10	327 ‡	3·46
Bu^n	H	A	139 *	23	$C_8H_{13}NO_2S_2$	219·8	219·1	268	4·19	290	4·12	325 ‡	3·54
Bu^i	H	A	133 *	28	$C_8H_{13}NO_2S_2$	218·2	219·1	268	4·20	290	4·13	330 ‡	3·38
Me	Me	*cis* B	165 *	21	$C_6H_9NO_2S_2$	190·6	191·1	270 §	4·32	298 §‡	4·02	—	—
		trans C	155 *	25		192·3		269 §	4·39	298 §‡	3·68	—	—
Et	Et	*cis* B	158 *	41	$C_8H_{13}NO_2S_2$	219·5	219·1	276 §	4·34	305 §‡	3·83	—	—
		trans C	116—118	20		217·8		271	4·39	?	?	—	—
Pr^n	Pr^n	B	155 *	40	$C_{10}H_{17}NO_2S_2$	247·1	247·2	275 §	4·30	298 §‡	3·97	—	—
Pr^i	Pr^i	B	—	—	$C_{10}H_{17}NO_2S_2$	—	247·2	—	—	—	—	—	—
Bu^n	Bu^n	B	128—129	60	$C_{12}H_{21}NO_2S_2$	275·2	275·2	275 §	4·39	299 §‡	4·04	—	—
Bu^i	Bu^i	B	125—127	43	$C_{12}H_{21}NO_2S_2$	275·0	275·2	280 §	4·39	301 §‡	3·94	—	—
·$[CH_2]_4$·		B	199 *	30	$C_8H_{11}NO_2S_2$	217·0	217·1	271 §	4·36	296 §‡	4·00	—	—
·$[CH_2]_5$·		B	152—154	26	$C_9H_{13}NO_2S_2$	232·1	231·1	277 §	4·36	298 §‡	3·84	—	—

* With decomp. † Found: N, 8·6. Reqd.: N, 8·6%. ‡ Shoulder. § Considerable interaction of both bands; λ and log ε are approximate.

TABLE 2.

β-(Alkoxythiocarbonylthio)acrylic acids (I; X = RO).

R	Method of prep.	M. p.	Yield (%)	Formula	Equiv. Found	Equiv. Reqd.	$\lambda_{max.}$ (mμ) and log ε			
Me	A	169° *	17	$C_5H_6O_3S_2$	180·3	178·0	235	4·06	305	4·30
Et	A	150 *	21	$C_6H_8O_3S_2$	193·3	192·1	236	4·10	306	4·31
Pr^n	A	113—114	9	$C_7H_{10}O_3S_2$	207·8	206·1	238	4·11	306	4·30
Pr^i	A	152 *	15	$C_7H_{10}O_3S_2$	206·0	206·1	239	4·06	307	4·31
Bu^n	A	90—92	10	$C_8H_{12}O_3S_2$	220·8	220·1	237	4·10	307	4·34
Bu^i	A	106—107	5	$C_8H_{12}O_3S_2$	219·8	220·1	238	4·16	306	4·40

* With decomp.

TABLE 3.

3-Alkyl-3,4-dihydro-4-oxo-2-thiothiazines (II).

R in (II)	Method of prep.	M. p.	Yield (%)	Formula	Nitrogen (%) Found	Nitrogen (%) Reqd.	$\lambda_{max.}$ (mμ) and log ε			
Me	D	75—76°	42	$C_5H_5NOS_2$	9·0	8·8	250	4·24	308	4·09
Et	D	48—49	14	$C_6H_7NOS_2$	7·9	8·1	250	4·25	311	4·09
Pr^n	D	39—40	42	$C_7H_9NOS_2$	7·6	7·5	251	4·01	312	4·07
Bu^n	D	38—39	41	$C_8H_{11}NOS_2$	6·8	7·0	252	4·23	312	4·07
Bu^i	D	*	19	$C_8H_{11}NOS_2$	6·6	7·0	252	4·20	312	4·06

* Liquid, b. p. 136—138°/2 mm.

relatively stable. In contrast to their tetrahydro-analogues,[5] 3-alkyl-3,4-dihydro-4-oxo-2-thiothiazines were stable.

The high-intensity ($\log \varepsilon > 3$) ultraviolet absorption bands of the compounds in absolute alcohol were investigated. Janssen [6] has discussed this property of related compounds. All the bands of β-substituted acrylic acids, when compared with those of substituted β-propionic acids,[5] showed a bathochromic displacement of 15—20 mμ. The presence of the double bond in 3-alkyl-3,4-dihydro-4-oxo-2-thiothiazines, however, resulted in a hypsochromic shift of the lower-wavelength band which could be due either to acute ring strain or competitive resonance interactions. Alkyl-substitution produced effects similar to those observed with other thion compounds,[6,7] although it is doubtful with this particular type of compound whether they can be satisfactorily accounted for by a direct hyperconjugative effect as examination of hypothetical structures associated with ground and excited states fails to demonstrate effective conjugation.

β-(*N*-Alkylthiocarbamoylthio)- and β-(alkoxythiocarbonylthio)-acrylic acids (I; X = RO) were the most fungitoxic of all these compounds. β-(*NN*-Dialkylthiocarbamoylthio)acrylic acids and 3-alkyl-tetrahydro-4-oxo-2-thiothiazines had little such activity. Detailed results will be published elsewhere.

Experimental

The *products* and the methods used in their preparation are listed in Table 1—3. The following are examples of the methods.

β-(*Thiocarbamoylthio*)*acrylic Acid* (I; X = NH_2) (*Method* A).—91% Propiolic acid (0·8 ml.) was added to ammonium dithiocarbamate (1·1 g.) in methyl alcohol (25 ml.) with cooling. The alcohol was removed by dry air at room temperature, the residue dissolved in water (10 ml.), and the solution acidified. The precipitate was twice recrystallised from water, forming colourless plates.

Table 4.

Velocity constants (10^{-5} min.$^{-1}$) for the fragmentation of β-substituted acrylic acids (I) in absolute alcohol at 26°.

X	NH_2	NHMe	NMe_2	MeO
k	2·86	250	2·86	2·86

cis-β-(NN-*Dimethylthiocarbamoylthio*)*acrylic Acid* (I; X = NMe_2) (*Method* B).—91% Propiolic acid (0·8 ml.) was added to a cooled solution of sodium *NN*-dimethyldithiocarbamate (1·8 g.) in methyl alcohol (25 ml.). After 2 days, the solvent was removed by a stream of dry air at 40°, the residue dissolved in water (20 ml.), and the solution acidified. The precipitate was twice recrystallised from 50% aqueous methanol, forming colourless needles.

trans-β-(NN-*Dimethylthiocarbamoylthio*)*acrylic Acid* (I; X = NMe_2) (*Method* C).—*cis*-β-(*NN*-Dimethylthiocarbamoylthio)acrylic acid (0·4 g.) was refluxed with water (50 ml.) and concentrated hydrobromic acid (2 drops) for 1 hr. The solution was filtered and cooled to 60°, at which point the crystals were filtered off. This was repeated four times, after which the combined products (1·4 g.) were recrystallised from ethyl acetate, forming a mixture of plates and needles. The plates were sifted from the needles and recrystallised from ethyl acetate.

3,4-*Dihydro*-3-*methyl*-4-*oxo*-2-*thiothiazine* (II; R = Me) (*Method* D).—β-(*N*-Methylthiocarbamoylthio)acrylic acid (0·4 g.) was refluxed for 1 hr. with phosphorus trichloride (2·5 ml.). The excess of phosphorus trichloride was removed by a stream of air, and the residue extracted with ether and water. After being shaken with sodium hydrogen carbonate solution and dried, the ether extract was distilled and the residue recrystallised from water, forming pale yellow needles.

[5] Garraway, preceding paper.
[6] Janssen, *Rec. Trav. chim.*, 1960, **79**, 454, 464.
[7] Svaték, Zahradník, and Kjaer, *Acta Chem. Scand.*, 1959, **13**, 442; Zahradník, *Coll. Czech. Chem. Comm.*, 1959, **24**, 3678.

The ultraviolet absorption spectra of all compounds, in absolute alcohol, were plotted in a S.P. 500 Unicam ultraviolet spectrophotometer.

The stabilities of the compounds was determined for solutions (3—5 $\times$ 10^{-6}M) in absolute alcohol at 26·0° $\pm$ 0·2% as described elsewhere,[5] and are given in Table 4.

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