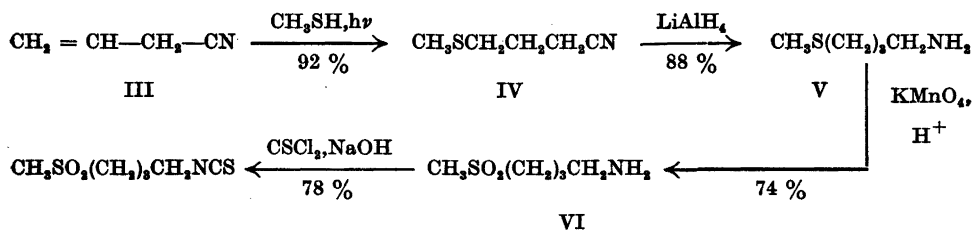


tions. However, the addition of mercaptans to carbon-carbon double bonds in unconjugated systems has been shown by various authors (see *e. g.* Ref.³⁻⁶) to be catalysed by light and peroxides, a fact which strongly suggests a free radical mechanism of the reaction. Consequently, it was not surprising to find that the addition of methanethiol to allyl cyanide under such conditions proceeded smoothly in almost quantitative yields. That the addition takes the desired course (contrary to Markownikoff's rule) appears from the identity of the further reaction products with those from the unambiguous synthetic route of Schneider and Kaufmann¹.

From γ -methylthiobutyronitrile (IV) the synthesis proceeds analogous to that of cheiriline² as shown in the following scheme.



The over-all yield in the above four-step reaction series is *ca.* 50 %, a considerable improvement over the *ca.* 20 % of the original synthesis. Furthermore, the present reactions can be conducted in a reasonably short time. Thus, ten grams of erysoline are readily produced in the course of three ordinary working days.

Erysoline has been characterised by its reactions with ammonia, aniline, *p*-toluidine and α -naphthylamine to the corresponding thioureas (VII, a-d).



VII

- a. R = H
- b. R = C₆H₅
- c. R = *p*-CH₃C₆H₄
- d. R = α -C₁₀H₇

The physical and analytical data of these derivatives are summarized in Table 1.

Table 1.

Amine	Formula	Composition	M. p., °C	Analyses			
				Nitrogen		Sulphur	
				Calcd.	Found	Calcd.	Found
Ammonia	VII a	C ₆ H ₁₄ O ₂ N ₂ S ₂	147 ^a	13.32	13.32	30.50	30.36
Aniline	VII b	C ₁₅ H ₁₈ O ₂ N ₂ S ₂	105	9.78	10.04	22.39	22.55
<i>p</i> -Toluidine	VII c	C ₁₃ H ₂₀ O ₂ N ₂ S ₂	108	9.33	9.41	21.34	21.32
1-Naphthylamine	VII d	C ₁₆ H ₂₀ O ₂ N ₂ S ₂	163	8.33	8.54	19.06	19.27

^a Ref.¹ reports 143-144°.

The ultra-violet absorption spectra of erysoline (I) and its thiourea-derivative (VII, a) were determined in ethanol solutions and found similar to those previously reported in the cheiroline series². Both exhibited a broad maximum, which in the case of erysoline was located at 243 $m\mu$ (ϵ 910), while the thiourea curve had its peak at 242 $m\mu$ (ϵ 13 420) and a minimum at 223 $m\mu$ (ϵ 3 600).

Bacteriological tests have indicated a very pronounced effect of both cheiroline and erysoline on a rather large selection of pathogenic bacteria. Gilliver⁸ formerly reported on the strong inhibitory action of cheiroline on plant pathogenic bacteria and fungi. The plant pathogenic fungus *Alternaria circinans* was included in the present studies and it was observed that both cheiroline and erysoline exhibited a 50 % growth inhibition of this organism in dilutions of 1 : 200 000 in a 2 % malt extract substrate.

EXPERIMENTAL *

γ -Methylthiobutyronitrile (IV). A mixture of 33.5 g (0.5 mole) of freshly distilled allyl cyanide⁷, 24.0 g of methanethiol (0.5 mole) and 200 mg of benzoyl peroxide was placed in a quartz flask and irradiated at room temperature for 24 hours with an effective mercury-quartz lamp. The mixture was then distilled *in vacuo*, 53.0 g (92 %) of pure (IV) being collected at 101–103° and 13 mm.

Schneider and Kaufmann¹ obtained the same compound in 63 % yield from the metathetical reaction between γ -chlorobutyronitrile and sodium methylmercaptide. They report the b.p. 218° at ordinary pressure.

δ -Methylthio-n-butylamine (V). The above nitrile was reduced with lithium aluminium hydride as previously described for the lower homologue nitrile². From 34.5 g of (IV) and 16.0 g of the hydride in 350 ml of anhydrous ether, a total amount of 31.6 g (88 %) of the colourless amine (V) was obtained after distillation. B. p. 77.5–78.5° at 12 mm.

The same compound, b. p. 188–190° at ordinary pressure, was formerly prepared¹ in unstated yield by reduction of the nitrile with sodium and ethanol.

δ -Methylsulphonyl-n-butylamine (VI). The oxidation of the above amine to the sulphone (VI) was conducted in acid solution, essentially as described¹. A 74 % yield of the hydrochloride of (VI) was obtained. M. p. 162–163°. (Ref.¹ reports the m. p. 160°.)

Erysoline (I). Upon treatment of the above hydrochloride in aqueous solution with thiocarbonyl chloride and sodium hydroxide, closely following the directions from the cheiroline synthesis², a 78 % yield of crude erysoline with almost correct m. p., (58.5–59.5°), was obtained. An analytically pure specimen was prepared as beautiful colourless needles upon an additional recrystallization from ether, m. p. 60.0–60.5°; (Ref.¹ gives the m. p. 59–60°).

$C_6H_{11}O_2NS_2$ (193.3)	Calc.	N 7.25	S 33.16
	Found	» 7.24	» 33.16

Thiourea-derivatives (VII, a–d). Erysoline was transformed into the corresponding thiourea-derivative (VII, a) upon treatment with concentrated aqueous ammonia in ethanol solution at room temperature for 18 hours. The derivatives with the aromatic amines were prepared by heating the isothiocyanate with a slight excess of the amine in ethanol to boiling for half an hour. All derivatives were recrystallized to constant melting points from 95 % ethanol. The melting points and analytical data are summarized in Table 1.

Ultra-violet absorption spectra. The spectra of (I) and (Va) were determined in ethanol solutions on a Beckman model DU quartz spectrophotometer in 1 cm cells.

* All melting points are uncorrected and determined in capillary tubes in an electrically heated block.

SUMMARY

A convenient synthesis of the isothiocyanate, erysoline (I), occurring in the seeds of *Erysimum Perofskianum* Fisch. et M., is described. It proceeds from allyl cyanide in four steps with an over-all yield of ca. 50 %.

Erysoline has been characterized by its transformation into four thiourea-derivatives.

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