ACTA CHEMICA SCANDINAVICA 7 (1953) 518–527

Unsaturated Five-Carbon *Iso*thiocyanates

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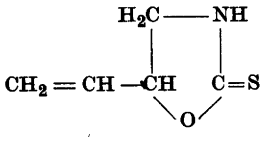
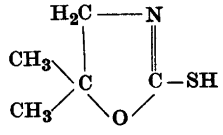
Recently Astwood *et al.*[1] isolated from turnip root and the seeds of various *Brassicae* an antithyroid compound which was demonstrated to possess the thioöxazolidone structure (I), later corroborated by the synthesis of Ettlinger [2]. In 1938 Hopkins [3] obtained a structurally similar compound (II) from the seeds of the crucifer *Conringia orientalis*.

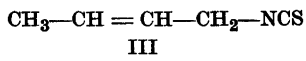


I

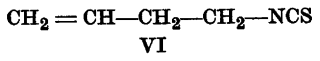


II

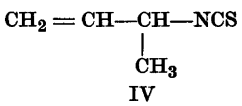
The widely recognised occurrence of mustard oils in seeds of numerous *Cruciferae* led us to consider the unsaturated 5-carbon *iso*thiocyanates as possible biogenetic or chemical precursors of (I) and (II) as has been suggested previously by Hopkins [3] and Astwood *et al.*[1]. Consequently, it was deemed desirable to synthesise the isomeric, unsaturated mustard oils (III)–(VI) and also to test their antithyroid activity. The present paper gives an account of the chemical results. The biological findings will be reported elsewhere.



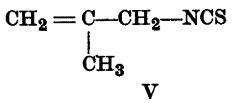
III



VI



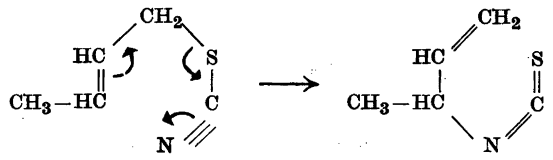
IV



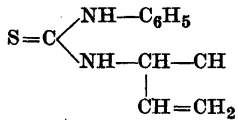
V

Disregarding stereochemical isomerides and structures containing a double bond adjacent to the NCS-grouping the compounds (III)–(VI) represent the theoretically possible unsaturated 5-carbon *iso*thiocyanates.

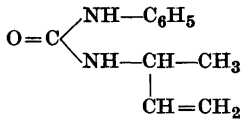
A search of the literature discloses that crotyl *iso*thiocyanate (III) has never been unequivocally prepared and identified. In 1899 Charon [4] obtained a mustard oil from the reaction between crotyl bromide and ammonium thiocyanate, which was characterised as a thiourea derivative with m.p. 105°. The alleged crotyl *iso*thiocyanate was shown by Mumm and Richter [5] in 1940 to be in fact α-methallyl *iso*thiocyanate (IV) formed through intramolecular rearrangement of crotyl thiocyanate according to the following scheme.



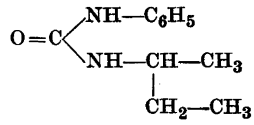
This method of synthesis was employed in the present investigation, and the α-methallyl *iso*thiocyanate (IV) was characterised as thioureas, formed upon reaction with ammonia, aniline, *p*-toluidine and α-naphthylamine. Desulphurisation of N-phenyl-N′-(α-methallyl)-thiourea (VII) with silver nitrate yielded the corresponding urea-derivative (VIII) which, upon catalytic hydrogenation, was transformed into N-phenyl-N′-*sec*-butyl-urea (IX), melting in accord with the literature value [6]. No attempts were made to prepare the optically active isomerides of (IV).



VII



VIII

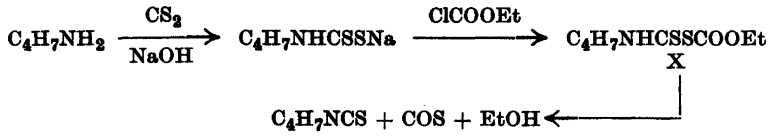


IX

In 1910 a communication from Schimmel & Co.[7] appeared in which a synthesis of crotyl *iso*thiocyanate (III) was described. Crotonaldehyde was transformed into its oxime which, in turn, was reduced with sodium amalgam to crotylamine. The classical Hofmann synthesis finally afforded the desired *iso*thiocyanate which gave a thiourea melting at 65—66°. Numerous attempts in this laboratory to repeat the above sequence of reactions under varying conditions either failed completely or led to minute amounts of reaction products of questionable purity. Therefore, alternative routes of synthesis were explored.

Experiments employing silver thiocyanate instead of the ammonium salt met with no better success, the rearranged α-methallyl *iso*thiocyanate again being the sole reaction product. Attention was next turned to the preparation

of *trans*-crotylamine by a modified Gabriel-synthesis. In dimethylformamide solution, a valuable improvement introduced recently by Sheehan and Bolhofer [8], the reaction between potassium phthalimide and crotyl bromide proceeded exothermically and gave an 83 per cent yield of N-crotylphthalimide. Hydrazinolysis, according to Ing and Manske [9], afforded crotylamine hydrochloride in 92 per cent yield. This was further processed to *trans*-crotyl *iso*thiocyanate by the Andreasch-Kaluza procedure [10,11], utilising the spontaneous decomposition of the ester (X) according to the following scheme.



In one instance, when a crude preparation of crotylamine hydrochloride was employed, a considerable amount of a crystalline by-product of unidentified structure resulted. The analytical data did not suggest any definite composition and no further attempts were made to reveal its chemical nature. The isomeric *cis*-crotyl *iso*thiocyanate will be described in a forthcoming paper.

Crotyl *iso*thiocyanate gave, on reaction with aqueous ammonia, a thiourea melting at 58—60°, somewhat lower but hardly incompatible with the value reported previously by Schimmel & Co.[7]. The mustard oil was further characterized as thioureas formed upon reaction with aniline, *p*-toluidine and *α*-naphthylamine. The presence of an unbranched side-chain was proved by desulphurisation of the phenylthiourea, followed by catalytic hydrogenation to give N-phenyl-N′-*n*-butylurea, whose m.p. was in accord with the literature values and was not depressed when mixed with an authentic sample.

To prove rigorously that no isomerisation of the double bond had taken place, N-crotyl-N′-phenylthiourea was submitted to various degradative treatments. Attempts to oxidise the thiourea with alkaline permanganate at 0° proved abortive, while oxidations at higher temperature yielded an unidentified volatile acid, isolated as its S-benzyl thiuronium salt and apparently different from formic and acetic acid. Performic acid at 0° oxidised the thiourea, largely to free sulphur. The method of Criegee [12] for oxidative cleavage of unsaturated compounds to aldehydes by means of ethereal hydrogen peroxide and osmium tetroxide gave interesting results in our hands. As expected from the structure of the thiourea studied, acetaldehyde was consistently obtained in these experiments. It was demonstrated in blank experiments, however, that the ether used as a solvent was partly oxidised to acetaldehyde under the usual reaction conditions. Consequently, informations gained by

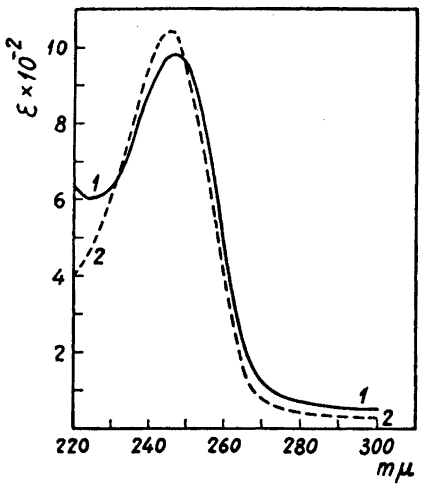


Fig. 1. Ultra-violet spectra of 1: α-methallyl isothiocyanate and 2: β-methallyl isothiocyanate, both in methanolic solution.

application of the Criegee-method to unsaturated compounds must be interpreted with caution. Reaction of the thiourea with hydrogen peroxide and osmium tetroxide in tertiary butanol, followed by treatment with periodic acid, yielded a carbonyl-fraction, again originating mainly from oxidative attack of periodic acid on the solvent.

Eventually, confirmation of the structure (III) was provided by synthesis of the sole alternative isomeride, *viz.* 3-butenyl *iso*thiocyanate (VI). The readily accessible allyl cyanide was reduced with lithium aluminium hydride to 3-butenylamine which was transformed into 3-butenyl *iso*thiocyanate by the procedure described above. Again, reaction with ammonia gave the corresponding thiourea, m.p. 65—66°, and aniline, *p*-toluidine and α-naphthylamine yielded the analogous substituted derivatives.

The only remaining isomeride, β-methallyl *iso*thiocyanate (V) was obtained upon reaction between β-methallyl chloride and ammonium thiocyanate, following the directions given by Bruson and Eastes [13]. The thiourea, m.p. 93—94°, as well as the usual substituted thioureas were prepared for comparison purposes.

A "crotonylsenföl", yielding a thiourea with m.p. 85°, was reported in 1874 by Hofmann [14]. From its mode of synthesis in conjunction with the melting point reported for the thiourea, it appears safe to conclude that Hofmann's mustard oil represents an impure preparation of β-methallyl *iso*thiocyanate. Less readily interpreted is a recent patent claim by Searle [15] accord-

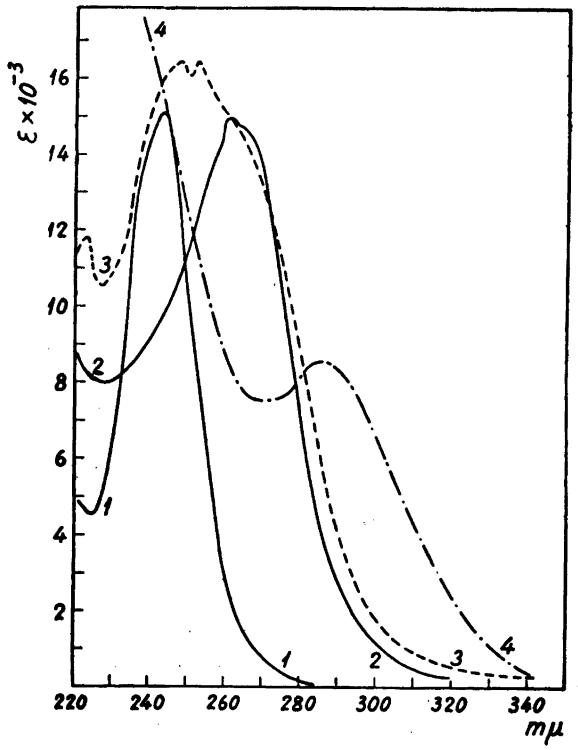


Fig. 2. Ultra-violet spectra of 1: allylthiourea, 2: phenylthiourea, 3: N,N'-crotylphenylthiourea and 4: N,N'-(α-methallyl)-α-naphthylthiourea, all in methanolic solution.

ing to which the reaction between crotyl chloride, sodium cyanide and sulphur gives rise to crotyl *iso*thiocyanate, characterised as its thiourea with m.p. 91.8—92.5°. From the results in the present paper it can be definitely excluded that Searle's compound represents the authentic *trans*-crotyl *iso*thiocyanate (III). The melting point of the corresponding thiourea points to its structure being that of (V) although the formation of α-methallyl *iso*thiocyanate (IV) under the conditions used would have been far less surprising in view of the well-established intramolecular rearrangement mentioned above.

The ultraviolet absorption spectra of the different types of compounds reported above were determined. In Fig. 1 the curves for α- and β-methallyl *iso*thiocyanate are given as representatives of the isomerides (III)—(VI). The curves are in accord with previously reported absorption data for allyl *iso*thiocyanate [16] and *n*-butyl *iso*thiocyanate [17]. These findings serve to confirm the conclusions of Pestemer and Litschauer [18] that the characteristic absorption

is due solely to the NCS-grouping and not interfered with by unconjugated double bonds in the remaining part of the molecules.

In Fig. 2 the absorption curve for allylthiourea is presented, again as typical for all of the isomeric N-alkenylthioureas prepared in the present study. The spectroscopically non-interfering character of the unsaturated substituents appears from the accord in absorption data with the ones reported earlier for unsubstituted thiourea [19]. Somewhat different results are found for the aromatically substituted thioureas. In Fig. 2 the spectrum of N-phenylthiourea is presented. In this case a noticeable and practically constant hypsochromic and hyperchromic effect is the result of introducing the crotyl-, α- or β-methallyl residue in the molecule. A marked difference in absorption is noticed on introducing the 1-naphthyl-residue in the thioureas (Fig. 2). The intensive end-absorption in conjunction with the maximum at 280—290 mμ is reminiscent of the absorption of naphthalene itself and points to less interference with the remaining part of the molecule than in the corresponding phenyl-derivatives. Once again the highly complex nature of the influence of substituents on absorption in the thiourea-series has been recognised.

EXPERIMENTAL *

trans-*Crotyl bromide.* To 93 g of phosphorus tribromide was cautiously added drop by drop a mixture of 72 g of *trans*-crotyl alcohol [20] and 8 g of pyridine. After the initial reaction had ceased the mixture was heated for 15 minutes at 70°. Distillation at 100 mm and a bath temperature of 50—60° gave 125 g (92 %) of colourless bromide, which before being further used, was fractionated in an all-glass column. 116 g, b.p. 100—105°, of the equilibrium mixture described by Young and Winstein [21] was obtained.

This procedure gave better yields and a higher grade of purity than the one hitherto recommended [4,5] employing aqueous hydrobromic acid.

α-Methallyl iso*thiocyanate* (IV). Prepared from ammonium thiocyanate and crotyl bromide as previously described [4,5] with the single deviation, that the reaction mixture was heated under reflux for 3 hours. An 87 % yield of colourless, analytically pure substance was obtained, b.p. 70—72° at 34 mm. The preparation slowly took on a slightly yellow colour, even when kept in the dark at 0° in sealed vessels.

Reaction with concentrated aqueous ammonia at room temperature overnight yielded N-(α-methallyl)-thiourea which, after recrystallisation from water, melted at 109—110°. (Lit. 105° [4] and 107—108° [5]).

General procedure for the preparation of aromatically substituted thioureas. A solution of 0.5 g of the appropriate *iso*thiocyanate and slightly more than one molecular equivalent of aniline, *p*-toluidine or α-naphthylamine in 1 ml of ethanol was heated on the steam-bath for 2 hours. After cooling and scratching, crystalline but somewhat oily products usually formed. These were freed of excess of amine by treatment with a few drops of

* All melting points are uncorrected and determined in capillary tubes, those above 80° in an electrically heated block, the remaining in a water bath.

Table 1. N-Alkenyl-N'-phenylthioureas, R-NH-CS-NH-C_6H_5.

No.	R	M.p., °C	Analyses * C %	H %	N %	S %
1.	$CH_2=CH-CH(CH_3)-$	109–110[a]	64.28	6.89	13.67	15.47
2.	$CH_2=C(CH_3)-CH_2-$	80–81	64.13	6.83	13.59	15.71
3.	$CH_3-CH=CH-CH_2-$	105.5[b]	64.28	7.02	13.75	15.75
4.	$CH_2=CH-CH_2-CH_2-$	123–127[c]	64.17	6.98	13.40	15.42

* Calc. for the isomeric substances: C 64.03 %; H 6.84 %; N 13.58 %; S 15.54%. [a] Ref.[22] 110°. [b]Mixed with No. 1, m.p. *ca.* 80°. Ref.[25] 106°. [c]A non-analysed preparation with this alleged structure is claimed to melt at 91° [25].

Table 2. N-Alkenyl-N'-p-tolylthioureas, R-NH-CS-NH-C_6H_4-CH_3.

No.	R	M.p., °C	Analyses * C %	H %	N %	S %
1.	$CH_2=CH-CH(CH_3)-$	125	65.54	7.35	12.85	14.50
2.	$CH_2=C(CH_3)-CH_2-$	106–107	65.63	7.57	12.93	14.70
3.	$CH_3-CH=CH-CH_2-$	81–82	65.42	7.18	12.94	14.77
4.	$CH_2=CH-CH_2-CH_2-$	66–67	65.39	7.38	12.74	14.60

* Calc. for the isomeric substances: C 65.41 %; H 7.32 %; N 12.72 %; S 14.55 %.

Table 3. N-Alkenyl-N'-(α-naphthyl)-thioureas, R-NH-CS-NH-$C_{10}H_7$.

No.	R	M.p., °C	Analyses * C %	H %	N %	S %
1.	$CH_2=CH-CH(CH_3)-$	129–130	70.30	6.47	11.17	12.60
2.	$CH_2=C(CH_3)-CH_2-$	100–101	70.26	6.29	11.10	12.41
3.	$CH_3-CH=CH-CH_2-$	129–130[a]	70.33	6.10	11.09	12.79
4.	$CH_2=CH-CH_2-CH_2-$	109–110	70.31	6.33	11.04	12.69

* Calc. for the isomeric substances: C 70.26 %; H 6.30 %; N 10.93 %; S 12.50 %. [a]Mixed with No. 1, m.p. *ca.* 110°.

aqueous hydrochloric acid. The colourless products were recrystallised to constant melting points from aqueous ethanol. Melting points and analytical data are presented in the Tables 1, 2 and 3.

N-(α-Methallyl)-N'-phenyl-urea (VIII). To 1 g of α-methallyl-phenylthiourea dissolved in 5 ml of hot ethanol was added a solution of 1.8 g of silver nitrate in 10 ml of 50 % (v/v) ethanol. The mixture was refluxed for 15 minutes and cooled. On addition of water and chilling, crystals separated and were filtered off. They were recrystallised from dilute ethanol with addition of decolourising charcoal. A final crystallisation from aqueous ethanol yielded thin colourless needles, m.p. 154.0–154.5°.

$C_{11}H_{14}ON_2$ (190.2) Calc. C 69.45 H 7.42 N 14.73
Found » 69.65 » 7.69 » 14.77

When a solution of 0.11 g of the unsaturated urea (VIII) in 10 ml of ethanol, containing 5 mg of Adam's platinum-catalyst, was shaken in a hydrogen atmosphere at ordinary

pressure and room temperature, 15.7 ml of hydrogen (theoretical: 15.6 ml) were absorbed within 30 minutes. After filtering off the catalyst and concentrating the filtrate, a colourless crystalline product remained, which separated in clusters of thin needles from aqueous ethanol, m.p. 155.0—155.5°. This value is in accord with the literature value [6] for the m.p. of DL-N-*sec*-butyl-N'-phenylurea (IX) but because no depression was noticed on admixture with the starting material, an analysis served to ascertain its identity. No depression was observed on mixing with an authentic sample of the urea.

$C_{11}H_{16}ON_2$ (192.3)	Calc.	C 68.69	H 8.39	N 14.57
	Found	» 68.89	» 8.46	» 14.60

Reaction of crotyl bromide with silver thiocyanate. When these reagents were brought together in ethanol and left overnight at room temperature, a 90 % reaction took place as estimated from the amount of silver bromide formed. Upon reaction with the usual amines, the ethanolic solution gave thioureas identical with those just described, indicating that allylic rearrangement had occured under these conditions also.

N-Crotylphthalimide. To the well-stirred, thin suspension of 9.8 g of potassium phthalimide in 40 ml of pure dimethylformamide was added 6.7 g of crotyl bromide. The temperature rose spontaneously to 95° and after the first reaction had ceased the mixture was kept for one hour at about 75° by means of a water-bath. 60 ml of chloroform and 200 ml of water were added, the chloroform layer separated and the aqueous phase extracted twice with 20 ml-portions of chloroform. The extracts were washed with 0.2 *N* sodium hydroxide and water, dried over sodium sulphate and the chloroform removed *in vacuo*. The remaining oil solidified in a freezing-mixture and was recrystallised from aqueous ethanol, yielding 8.4 g (84 %) of crotyl phthalimide. An analytical sample was prepared by two additional recrystallisations from ethanol. M. p. 75—76°.

$C_{12}H_{11}O_2N$ (201.2)	Calc.	C 71.63	H 5.51	N 6.96
	Found	» 71.52	» 5.70	» 7.11

Crotyl iso*thiocyanate* (III). A solution of 20 g of crotylphthalimide and 6 ml of hydrazine hydrate in ethanol was boiled under reflux for one hour. After addition of 250 ml of concentrated hydrochloric acid and 250 ml of water, heating was continued for another hour. After cooling, the phthalylhydrazide which crystallised from the mixture was removed. Most of the alcohol was distilled off, additional phthalylhydrazide removed by filtration and the filtrate evaporated *in vacuo* to dryness. By repeated evaporations with fresh portions of water the excess hydrochloric acid was removed. The remaining crotylamine hydrochloride weighed 9.3 g (84 %) after drying. Titration of an aliquote amount of amine, liberated by distillation with strong alkali, indicated a content of *ca.* 95 %. The phthalylhydrazide isolated represented 92 % of the calculated amount.

The hydrochloride was used directly in the preparation of the *iso*thiocyanate which was perfor medby following the procedure given in Organic Syntheses [23] for methyl *iso*thiocyanate. A 61 % yield of colourless crotyl *iso*thiocyanate, b.p. 67—68° at 11 mm, was obtained after distillation. The analytical data were not very satisfactory, in accord with our generally experienced difficulty in obtaining analytically pure samples of *iso*thiocyanates prepared according to the present method. The originators of the procedure [10,11] also noticed these difficulties and they suggested that traces of symmetrically substituted ureas were responsible for the consistently low nitrogen- and sulphur-values found. In spite of the poor analytical data, we consider our product as being essentially pure *trans*-crotyl *iso*thiocyanate, as evidenced from its reaction products with amines described below.

N-Crotyl-thioureas. When the *iso*thiocyanate was shaken with concentrated aqueous ammonia overnight and then taken to dryness *in vacuo* at room temperature, a crystalline product remained. Two recrystallisations from chloroform-petroleum ether yielded a voluminous mass of colourless needles. M.p. 58—60°.

$C_5H_{10}N_2S$ (130.2)	Calc.	C 46.13	H 7.75	N 21.53	S 24.64
	Found	» 46.18	» 7.73	» 21.59	» 24.33

The aromatically substituted thioureas were prepared as described above and are listed in Tables 1, 2 and 3.

N-Crotyl-N'-phenylurea. When desulphurised according to the directions given above, N-crotyl-N'-phenylthiourea yielded the corresponding N-crotyl-N'-phenylurea as thin colourless needles. M.p. 130.5°.

$C_{11}H_{14}ON_2$ (190.2)	Calc.	C 69.45	H 7.42	N 14.73
	Found	» 69.45	» 7.50	» 14.53

Submitted to catalytic hydrogenation as described above, the unsaturated urea was transformed into N-*n*-butyl-N'-phenylurea, m.p. 131—132°, alone or in mixture with an authentic specimen, prepared from *n*-butylamine and phenyl *iso*cyanate. A large depression was observed on mixing with crotyl-phenylurea.

3-Butenyl iso*thiocyanate* (VI). In a three-necked flask, provided with a dropping funnel and a mercury-sealed stirrer was placed a suspension of 13 g of finely pulverised lithium aluminium hydride in 275 ml of Grignard-ether. The flask was kept under a slight nitrogen pressure, and a solution of 20 g of allyl cyanide [24] was slowly added under vigorous stirring at room temperature. The mixture changed from yellow, through green, to pink. After the reaction ended, the excess lithium aluminium hydride was destroyed by cautiously adding wet ether and water. 6 *N* hydrochloric acid was introduced to dissolve the aluminium salts and the red ether phase was separated from the clear and colourless aqueous layer, which was extracted with two additional portions of fresh ether. The aqueous solution was made alkaline with strong sodium hydroxide and distilled. The volatile amine was collected in strong hydrochloric acid and 3-butenylamine hydrochloride isolated by evaporation to dryness *in vacuo*. Yield 9.3 g (30 %). The hydrochloride was further processed to the corresponding *iso*thiocyanate in the usual way. 3-Butenyl *iso*thiocyanate distilled at 60° at 12 mm.

C_5H_7NS (113.2)	Calc.	C 53.04	H 6.23	N 12.38	S 28.32
	Found	» 52.99	» 6.32	» 12.50	» 28.45

N-(3-Butenyl)-thioureas. When a suspension of the *iso*thiocyanate in concentrated aqueous ammonia was left for two days at room temperature, a homogenous solution resulted which, on evaporation *in vacuo* at room temperature, yielded a colourless crystalline product. This was recrystallised from water for analysis. M.p. 65—66°.

$C_5H_{10}N_2S$ (130.2)	Calc.	C 46.13	H 7.75	N 21.53	S 24.64
	Found	» 45.95	» 7.99	» 21.50	» 24.47

Reactions with the usual aromatic amines yielded products which crystallised less readily than in the above cases. The phenylthiourea was induced to crystallise only after sublimation in high-vacuum. The derivatives are listed in Tables 1, 2 and 3.

β-Methallyl iso*thiocyanate* (V). This isomeride was prepared from β-methallyl chloride and ammonium thiocyanate following the directions given by Bruson and Eastes [13]. A possible allylic rearrangement obviously leads to no ambiguity in structure in this case.

N-(β-Methallyl)-thioureas. The reaction product with ammonia was prepared as described by the same authors [13]. M.p. 93—94°. The derivatives with the usual aromatic amines are listed in Tables 1, 2 and 3.

Ultraviolet absorption spectra. All the spectra reported in this paper were determined in methanolic solution with a Beckman model DU quartz spectrophotometer.

SUMMARY

Four unsaturated 5-carbon *iso*thiocyanates (III)—(VI) have been unequivocally synthetised. No stereoisomerides of these have been considered.

The mustard oils have been transformed into characteristic thiourea-derivatives upon reaction with ammonia, aniline, *p*-toluidine and α-naphthylamine.

Structure proofs of the isomeric *iso*thiocyanates have been forwarded by transformation into known derivatives.

The microanalyses have been performed in this laboratory by Mr. A. Grossmann.

We are much indebted to the *Danish Shell Company* for a generous supply of β-methallylic chloride.

Part of this work has been supported by *Laurits Andersen's Fond.*

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Received January 12, 1953.