# **940.** *Heptasulphur* N-*Acylimides.*

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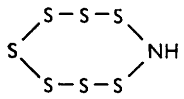
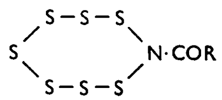
A mild method for preparing heptasulphur *N*-acylimides is the reaction of heptasulphur imide with carboxylic acids in the presence of dicyclohexylcarbodi-imide or ethoxyacetylene.

Heptasulphur imide (I) has been reported[1] to react with acetyl chloride in pyridine at 0°, to give the *N*-acetylimide (II; R = Me) in 70% yield, and with benzoyl chloride in the presence of pyridine at 60° to give the *N*-benzoylimide in low yield. We found that free carboxylic acids and dicyclohexylcarbodi-imide[2] or ethoxyacetylene[3] can be used to prepare compounds of type (II).

(I)





(II)

When molar amounts of the imide, a carboxylic acid, and dicyclohexylcarbodi-imide are allowed to react between 0° and 20° in tetrahydrofuran, dicyclohexylurea is precipitated quantitatively. The *N*-acylimides can be isolated in 50—85% yield (see Table).

The reaction of ethoxyvinyl esters, prepared *in situ* from ethoxyacetylene and carboxylic acids, and the imide at room temperature was sluggish, but proceeded readily in boiling chloroform. The *N*-acylimides prepared in this way were identical with those obtained by the carbodi-imide method.

The structures (II) are based on elemental analysis, infrared spectra, hydrolysis, and reduction. The infrared spectra[4] show bands at 795—838 cm.$^{-1}$, attributed to the $S_7N$ ring. All spectra show a carbonyl band which is shifted by 40—50 cm.$^{-1}$ towards a higher frequency compared with the unsubstituted amide $R{\cdot}CO{\cdot}NH_2$; this indicates that the known ionic contributions to the structure of $R{\cdot}CO{\cdot}NH_2$ are absent in $R{\cdot}CO{\cdot}NS_7$. The carbonyl frequencies of $R{\cdot}CO{\cdot}NS_7$ thus correspond very closely to the frequencies of the analogous methyl ketones $R{\cdot}CO{\cdot}CH_3$. This " abnormal CO-amide bond " could be demonstrated chemically by the extreme ease of hydrolysis. Heptasulphur *N*-acyl imides are quantitatively hydrolysed when shaken with basic aluminium oxide in methylene

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[1] Goehring and Koch, *Z. Naturforsch.*, 1952, **7b**, 634.

[2] Sheehan and Hess, *J. Amer. Chem. Soc.*, 1955, **77**, 1067.

[3] Ahrens, *Rec. Trav. chim.*, 1955, **74**, 769; Wassermann and Wharton, *Tetrahedron*, 1958, **3**, 321.

[4] Steel, unpublished work.

dichloride at room temperature for 5 minutes. Reduction of the *N*-benzoyl- and *N*-cinnamoyl-imide with lithium aluminium hydride gave benzamide (85%) and cinnamamide (80%), respectively.

## EXPERIMENTAL

*Materials.*—Silica plates for thin-layer chromatography (t.l.c.) (Kieselgel G für Dünnschichtchromatographie nach Stahl, E. Merck AG. Darmstadt) were prepared with 1% aqueous phosphoric acid instead of water and activated at 150—160° for 2 hr. Heptasulphur *N*-acylimides develop black or brown spots when sprayed with aqueous silver nitrate. Acidic silica gel (Silica Gel Ltd., 100—200 mesh) for column chromatography was activated at 150—160° for 48 hr.

Heptasulphur imide, m. p. 112—113°, was prepared according to instructions of Becke-Goehring *et al.*[5]

(*A*) *Carbodi-imide Method.*—To a solution of heptasulphur imide (2·4 g., 0·01 mole) and a carboxylic acid (0·011 mole) in anhydrous tetrahydrofuran (20 ml.) at 0°, dicyclohexylcarbodi-imide (2·1 g., 0·01 mole) in cold tetrahydrofuran (15 ml.) was added, and the solution was kept at 0° overnight. The precipitate was filtered off and washed with tetrahydrofuran to give dicyclohexylurea (2·0—2·2 g.), m. p. 231° (lit., 231°). The solution was evaporated and the residue chromatographed on a column (2 × 60 cm.). Carbon tetrachloride was used to elute sulphur and heptasulphur imide, and then gradually increased amounts of methylene dichloride were used to elute the *heptasulphur* N-*acylimide*. T.l.c. was used to check eluates.

(*B*) *Ethoxyacetylene Method.*—Ethoxyacetylene (0·35 g., 5 mmoles) and a carboxylic acid (5 mmoles) were refluxed in dry chloroform (20 ml.) for 30 min. Heptasulphur imide (1·2 g., 5 mmoles) in dry chloroform (70 ml.) was added and the mixture was refluxed for 2 hr. Evaporation to dryness and chromatography gave the heptasulphur *N*-acylimide.

Details are given in the Tables.

Heptasulphur *N*-acylimides (II).

| No. | R | Solvent for crystn. | M. p.* | $R_F$ † | Yield (%) by method A | B |
|---|---|---|---|---|---|---|
| 1 | Me | $C_6H_6$ | 104° | 0·50 | 70 | — |
| 2 | $CH_2Cl$ | $CHCl_3$ | 110 | 0·57 | 79 | 65 |
| 3 | Ph | $C_6H_6$ | 138 | 0·69 | 59 | 43 |
| 4 | $CH_2Ph$ | $CCl_4$ | 110 | 0·56 | 72 | 47 |
| 5 | $[CH_2]_7{\cdot}Me$ | — | Liquid | 0·84 | 60 | — |
| 6 | $[CH_2]_{16}{\cdot}Me$ | $C_6H_{14}$ | 68 | 0·97 | 85 | — |
| 7 | CH=CHPh | $CCl_4$ | 146 | 0·66 | 70 | — |
| 8 | *o*-$Cl{\cdot}C_6H_4$ | $C_6H_6$ | 92 | 0·83 | 48 | — |
| 9 | *p*-$NO_2{\cdot}C_6H_4$ | $C_6H_6$ | 136 | 0·44 | 50 | — |

* Kofler hot-stage microscope. † On silica gel (t.l.c.); $CCl_4$–$CH_2Cl_2$, 4 : 1 v/v.

|  | Found (%) |  |  |  |  |  | Required (%) |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | C | H ‡ | Cl | N | % | Formula | C | H ‡ | Cl | N | % |
| 1 | 8·5 | 1·2 | — | 4·8 | 80·0 | $C_2H_3NOS_7$ | 8·5 | 1·1 | — | 5·0 | 79·7 |
| 2 | 7·9 | 0·8 | 11·5 | 4·4 | 70·2 | $C_2H_2ClNOS_7$ | 7·6 | 0·6 | 11·2 | 4·4 | 71·0 |
| 3 | 25·1 | 1·7 | — | 4·0 | 64·7 | $C_7H_5NOS_7$ | 24·5 | 1·5 | — | 4·1 | 65·4 |
| 4 | 27·1 | — | — | 4·0 | 63·3 | $C_8H_7NOS_7$ | 26·9 | — | — | 3·9 | 62·8 |
| 5 | 28·8 | — | — | 3·8 | 56·6 | $C_9H_{17}NOS_7$ | 28·5 | — | — | 3·7 | 59·1 |
| 6 | 42·5 | — | — | 2·8 | 44·0 | $C_{18}H_{35}NOS_7$ | 42·7 | — | — | 2·8 | 44·4 |
| 7 | 29·2 | — | — | 3·8 | 60·5 | $C_9H_7NOS_7$ | 29·2 | — | — | 3·8 | 60·7 |
| 8 | 22·1 | — | 9·3 | 3·7 | 58·5 | $C_7H_4ClNOS_7$ | 22·2 | — | 9·4 | 3·7 | 59·4 |
| 9 | 21·8 | — | — | 7·0 | 57·7 | $C_7H_4N_2O_3S_7$ | 21·6 | — | — | 7·2 | 57·8 |

‡ In certain cases, carbon was determined with an additional manganese dioxide tube to absorb the excess of sulphur oxides; the hydrogen figures were then not obtained.

*Hydrolysis.*—Heptasulphur *N*-benzoylimide (0·17 g., 0·5 mmole) was dissolved in methylene dichloride (5 ml.), and basic aluminium oxide (∼0·5 g.) containing ∼2% of alkali was added. The slurry was shaken for 5 min. and filtered, and the solution evaporated to yield heptasulphur imide (0·11 g., 92%), m. p. 112—113°.

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[5] Becke-Goehring, Jenne, and Fluck, *Chem. Ber.*, 1958, **91**, 1947.

Similarly, the *N*-chloroacetylimide (0·16 g.) gave 0·12 g. (100%) of heptasulphur imide.

*Reduction.*—To a solution of heptasulphur *N*-benzoylimide (0·86 g., 2·5 mmoles) in anhydrous tetrahydrofuran (20 ml.) at −65°, lithium aluminium hydride (0·05 g., 1·3 mmoles) in tetrahydrofuran was added and the mixture was stirred for 30 min. Ethyl acetate (2 ml.) was added, and the solution was allowed to warm to room temperature, filtered, and evaporated. After extraction with ether and recrystallization from hexane, benzamide (0·25 g., 85%) m. p. 130°, was obtained.

Similarly, 0·13 g. (80%) of cinnamamide, m. p. 147°, was obtained from 0·6 g. of *N*-cinnamoylimide.

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