NOTES.

132. *The Periodate Oxidation of Pinitol.*

By Alistair M. Stephen.

Formulation of sequoyitol by Riggs (*J.*, 1949, 3199) as the 2- rather than the 5-methyl ether of *meso*inositol (of configuration 1235/46 *) rests upon the observed liberation of less than four equivalents of strong acid per mole of sequoyitol on oxidation with neutral sodium metaperiodate. It is suggested that the course of the oxidation is similar to that of *meso*inositol itself (Fleury, Poirot, and Fievet, *Compt. rend.*, 1945, **220**, 664) in that the initial splitting of the molecule takes place at two points giving two 3-carbon fragments. *cis*-α-Glycol groups are considered to be absent from sequoyitol because such groups would be expected to react first, so rendering the formation of tartrondialdehyde (from which no more than two equivalents of acid could be formed) impossible. According to the mechanism given by Riggs, the amount of acid liberated is in close agreement with that expected from the measured periodate uptake at the 24-hour stage.

The configuration of (+)-inositol (125/346), on the other hand, is such that the behaviour of its monomethyl ether pinitol towards periodate cannot be used to derive a favoured structure for pinitol. On the assumption that *cis*-α-glycol groups react first and Fleury *et al.*'s mechanism operates where possible, a methoxyl group on $C_{(1)}$ or $C_{(4)}$ would cause liberation of more than four equivalents of strong acid, whereas a methoxyl group on $C_{(2)}$ or $C_{(3)}$ would result in less than four equivalents, during the uptake of anything over 6 moles of periodate. With the methoxyl group on $C_{(5)}$ or $C_{(6)}$ two *cis*-α-glycol systems remain and the situation is confused. It is nevertheless of interest that the reaction of pinitol with sodium metaperiodate (at 26°) resembles very closely the oxidation of the isomeric sequoyitol, recorded by Riggs, with respect to periodate consumption and acid production. The initial rapid reaction is followed by a slow increase in the amount of periodate consumed to a value of 6·21 moles per mole of pinitol (at 25 hours) during which time strong acid is produced to the extent of 3·71 equivalents per mole. It would seem, therefore, that $C_{(1)}$ or $C_{(4)}$ is the least likely site for the methoxyl group. Further experiment shows, however, that under different conditions the acid liberated may exceed 4 equivalents per mole: if pinitol is kept for longer than one week or is heated with neutral periodate on a boiling water-bath for 20—40 minutes (cf. Hirst and Jones, *J.*, 1949, 1659) the value averages 3·96 and may rise to as much as 4·16 equivalents per mole. The mechanism of oxidation is no doubt different at the elevated temperature, and sequoyitol might yield considerably more acid under the appropriate conditions. At all events it is certain that conclusions about structure based on measurements of this kind should be treated with the greatest reserve.

Comparison of the oxidation at room temperature of (+)-inositol and *meso*inositol shows

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* This representation, rather than $\frac{1235}{46}$, is used to economise space.—Ed.

that these isomers behave identically, the total periodate uptake (6·74 moles per mole after 25 hours at 26°) being in close agreement with the value (6·7, in 2—3 days) found by Fleury *et al.* (*loc. cit.*). The acid liberated (*ca.* 5·2 equivalents per mole) is, however, considerably in excess of the theoretical as given by these authors (cf. Hirst and Jones, *loc. cit.*); it is not increased by heating.

Experimental.—The pinitol used was isolated from an acetone extract of the timber of *Acacia mollissima* Willd. (cf. Stephen, *J. Sci. Food Agric.*, in the press). It had m. p. 184—186°, undepressed by a sample from *Lotononis laxa* kindly supplied by Professor H. L. de Waal (Found : C, 43·3; H, 7·4; OMe, 15·7. Calc. for $C_7H_{14}O_6$: C, 43·3; H, 7·3; 1OMe, 16·0%), and $[\alpha]_D^{25}$ + 62° (*c*, 2·06 in water). The characteristic penta-acetate, m. p. 96—98° after recrystallisation from ethyl acetate–*iso*hexane, had $[\alpha]_D^{28}$ + 6·6° (*c*, 2·12 in ethanol) (lit., m. p. 98°, $[\alpha]_D^{25}$ + 8·6°). From pinitol was prepared (+)-inositol, m. p. 244°, $[\alpha]_D^{28}$ + 66·2° (*c*, 1·21 in water), by hydriodic acid demethylation. *meso*Inositol (m. p. 220°; hexa-acetate, m. p. 215—216°) was obtained by recrystallisation of a commercial sample.

Samples dried at 100° *in vacuo* were made up to 0·01M-strength with aqueous sodium metaperiodate (0·18M.; 50 c.c.) and water (to 100 c.c.), and the residual periodate was measured by the usual arsenite method at various time intervals; room temperature was 26°. The uptake of periodate in moles/mole was :

Time (min.)	5	12	27	45	62	160	300	1500
Pinitol	3·84	4·37	4·79	5·07	5·17	5·59	5·66	6·21
(+)-Inositol	5·46	5·76	6·14	6·38	6·50	6·55	6·60	6·75
*meso*Inositol	4·80	5·55	6·14	6·38	6·50	6·62	6·70	6·74

The small differences in periodate consumption by pinitol and sequoyitol (5·66 and 5·46 moles after 5·8 hours; 6·20 and 5·81 after 24 hours respectively) may be attributed to dissimilarity of experimental conditions, especially temperature.

The following table shows the quantity of strong acid (in equivalents per mole) liberated from these cyclitols at different times. Concentrations and temperature were the same as for the measurement of periodate uptake, and excess of sodium metaperiodate was destroyed before titration with alkali hydroxide (using methyl-red).

Time (min.)	5	10	25	40	80	120
Pinitol	1·68	2·15	2·50	2·73	3·19	3·40
(+)-Inositol	3·89	4·55	4·98	5·10	5·28	5·28
*meso*Inositol	3·70	4·30	4·95	5·07	5·12	5·16

Separate experiments in which the three cyclitols were warmed on the boiling water-bath for 20—40 minutes showed the acid liberated to be 3·95, 5·18, 5·16 equivalents per mole respectively (Hirst and Jones, *loc. cit.*, record 4·32 to 4·56 for *meso*inositol).

From further experiments with pinitol and *meso*inositol it became clear that oxidation at room temperature (in this case 18°) in the dark for times greatly in excess of 24 hours caused practically no change in the amount of acid liberated. The number of equivalents of acid from one mole of pinitol was 2·92 (1·8 hours); 3·71 (24 hours); 3·74 (48 hours); 3·97 (8 days); and 4·16 (after 20 minutes on boiling water-bath). For *meso*inositol, 5·10 (2 hours); 5·18 (19 hours); 5·13 (25 hours); 5·03 (43 hours); 5·04 (70 hours); 5·01 (144 hours). These titrations were with 0·01N-barium hydroxide (methyl-red).

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133. *The Determination of Vapour Pressures of the Order of* 1 *mm. of Mercury by a Modification of Smith and Menzies's Method. The Vapour Pressure of Dimethylnitramine.*

By R. S. Bradley, S. Cotson, and E. G. Cox.

A modification is described of the method devised by Smith and Menzies (*J. Amer. Chem. Soc.*, 1910, **32**, 907) for measuring vapour pressures of the order of 1 mm.

The substance was contained in a small bulb attached to a capillary tube (diameter about 2 mm.) and placed in a holder in the apparatus as shown in Fig. 1. The U-tube contained previously degassed medicinal paraffin, the surface of which was initially just below the tip of the capillary tube. The system was evacuated with the tap *A* open; *A* was then closed and the height of paraffin oil in the left-hand limb raised by letting in small amounts of air through *B* and *C* so that the rate of evolution of bubbles of vapour from the capillary tip was thus progressively reduced. It was found in practice that because of very slow dissolution of the vapour in the paraffin, no equilibrium position at which bubbles were just about to be released could be obtained. The same phenomenon was observed when the liquid paraffin was replaced by other non-volatile liquids *e.g.*, dibutyl phthalate and phosphoric acid.

Fig. 1.

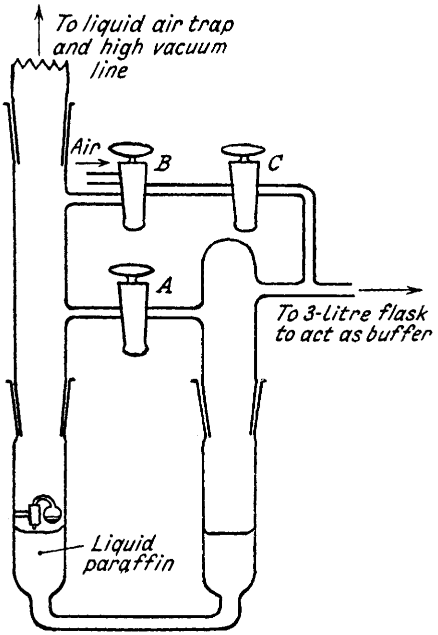
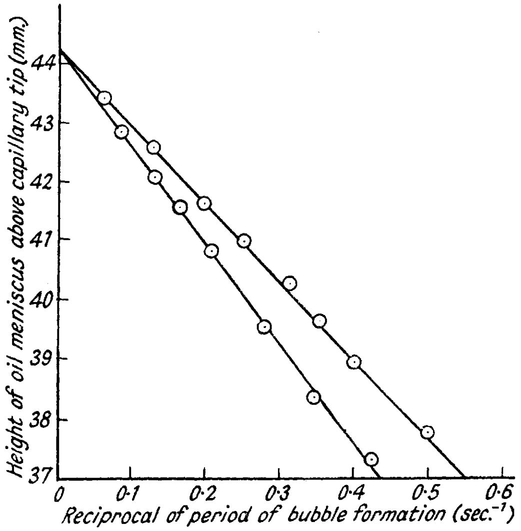


Fig. 2.



(*For* 2 *runs with same bulb at* 49·04°.)

A kinetic method was therefore adopted and the rate of bubble formation at various pressures of oil determined. In most cases the plot of oil pressure against the reciprocal of the period of bubble formation gave a straight line over a range of several mm. of oil just below the theoretical equilibrium pressure (Fig. 2). By extrapolation to the point where the reciprocal of the time was zero, the equilibrium pressure of oil was then obtained. This value was found to be reproducible (to within 1%).

In order to obtain the vapour pressure of the substance, it was then only necessary to correct the equilibrium pressure for the surface tension effect in the capillary. The pressure above the surface of the liquid paraffin on the high-vacuum side was so small as to be negligible.

This correction was determined in a subsidiary experiment. A length of capillary tubing which had been broken off the piece used to make the bulb in the first case was suspended vertically in a boiling-tube. The lower end had exactly the same internal radius as the end of the tube attached to the bulb, since the capillary was broken off at this point to make the bulb. Liquid paraffin was poured into the boiling-tube until the height of the oil surface above the tip was the same as in the kinetic experiment. The upper end of the capillary tube was then attached to a dibutyl phthalate manometer and a mercury dropper which forced air through the system, causing bubbles to appear slowly and regularly at the tip of the tube. The pressure registered on the manometer then gave the combined pressure due to depth of oil and surface tension effect, *i.e.*, the absolute vapour pressure. It was assumed that the difference between the surface tension for the oil–vapour and the oil–air interfaces was negligible. Experiment showed that there was no appreciable reduction in the surface tension of the oil due to dissolution of the vapour.

The method gave values for the vapour pressure of iodine in reasonable agreement (to within ±1·5%) with those previously published (Gillespie and Frazer, *ibid.*, 1936, **58**, 2260).

The vapour pressure of dimethylnitramine was determined over a range of temperatures, with the following results :

T (c.)	41·70°	43·34°	45·24°	47·35°	49·04°	50·72°
P (mm. of Hg)	1·60	1·85	2·15	2·60	2·95	3·37

The plot of $\log_{10} P$ against $1/T$ gave a straight line reproduced by

$$\log_{10} P \text{ (mm. of Hg)} = 11{\cdot}80 - 3650/T$$

The latent heat of sublimation is 16,700 cals./mole.

An attempt was made to confirm the above figures by means of the Knudsen effusion method, but it was found difficult to obtain reproducible results. This was attributed to stray particles of solid partly blocking the hole in the effusion vessel; this hole was necessarily very fine, to fulfil the mean-free-path requirements and to avoid errors due to self-cooling.

We acknowledge gratefully the award of a Monsanto Chemicals research grant to one of us (S. C.).

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University of Leeds.

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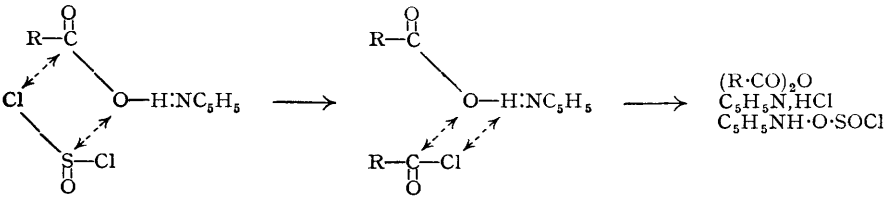
134. *The Function of Pyridine in the Carboxylic Acid–Thionyl Chloride System.*

By W. Gerrard and A. M. Thrush.

During a systematic investigation of the carboxylic acid–thionyl chloride system it was observed that addition of thionyl chloride (0·5 mol.) to an ethereal solution of acetic acid (1 mol.) and pyridine (1 mol.) gave an immediate precipitation of what appeared to be an equimolecular mixture of pyridine hydrochloride and $C_5H_5NH^+\ {}^-O{\cdot}SOCl$, and from the ethereal solution acetic anhydride was obtained in 97% yield. In a similar way high yields of *iso*butyric, *iso*valeric, and *n*-heptanoic anhydrides were obtained.

The method for the preparation of heptanoic anhydride described in *Org. Synth.*, 1946, **26**, 1, entails addition of heptanoyl chloride to pyridine in benzene to effect the formation of a pyridinium complex, to which is added the heptanoic acid. We do not invoke the formation of a complex between pyridine and acyl chloride to explain *our* result, but instead postulate a mechanism entailing the four-centre broadside approach of the reacting molecules :



Discussing the use of pyridine to facilitate formation of acyl chloride, McMaster and Ahmann (*J. Amer. Chem. Soc.*, 1928, **50**, 145) refer to it as an inert solvent in one place, and as a catalyst in another; but there is now no doubt that it plays an essential part in the reaction sequences with regard to the acids of the type referred to above. Nevertheless, in describing these systems it is necessary to pay due attention to the degree of reactivity of the acyl carbon and chlorine atoms. Whereas McMaster and Ahmann were not able to prepare trichloroacetyl chloride by means of thionyl chloride alone, Carré and Libermann (*Compt. rend.*, 1934, **199**, 1422; cf. Mills and Human, *Nature*, 1946, **158**, 887) obtained this in 90% yield when pyridine was used. It is noteworthy that preliminary experiments now indicate that addition of thionyl chloride to an ethereal solution of trichloroacetic acid and pyridine (present largely as the precipitated salt) appears to involve only the first reaction to the acyl chloride, and not the second one to the anhydride. This may conceivably be due to a considerable increase in velocity of the first reaction owing to a decreased electron density on the acyl carbon atom and an increase on the acyl oxygen atom, $CCl_3{\cdot}CO{\cdot}O^-$, and a decrease in velocity of the second reaction due to reduction in the reactivity of the acyl chlorine atom in acyl chloride.

Experimental.—Dry ether and pyridine, and redistilled thionyl chloride and acids were used.

Dropwise addition of thionyl chloride (5·9 g., 0·5 mol.) in ether (5 c.c.) to an ethereal (30 c.c.) solution of acetic acid (6·0 g., 1 mol.) and pyridine (7·9 g., 1 mol.) at −10° afforded immediately a white precipitate, which was separated, washed rapidly with ether, and dissolved in water. The aqueous solution contained C_5H_5N, 0·096 g.-mol. (Calc.: 0·10 g.-mol.); Cl^-, 0·096 g.-ion; and SO_2, 0·042 g.-mol. (Calc: 0·05 g.-mol.). From the ethereal solution acetic anhydride (5·0 g., 97%), b.p. 138° (Found: equiv., 51·7. Calc.: equiv., 51·0), was obtained. As the precipitate tends to lose sulphur dioxide even on the short exposure during filtration, this operation was then performed in a flask fitted with a side arm containing a sintered-glass partition. The aqueous solution of the precipitate then contained C_5H_5N, 0·0975 g.-mol.; Cl^-, 0·0965 g.-ion; SO_2, 0·050 g.-mol. When the reaction was carried out at −80°, the aqueous solution of the precipitate contained: C_5H_5N, 0·099 g.-mol.; Cl^-, 0·097 g.-ion; SO_2, 0·050 g.-mol. These data indicate an equimolecular mixture of pyridine hydrochloride and the salt $C_5H_5NH{\cdot}O{\cdot}SOCl$.

By the same procedure and from the same weights of thionyl chloride and pyridine, *iso*butyric anhydride (7·8 g., 98%), b.p. 180—183°, d_4^{20} 0·9535, n_D^{19} 1·4061, was obtained from the acid(8·8 g.). The aqueous solution of the precipitate (open filtration) contained: C_5H_5N, 0·091 g.-mol.; Cl^-, 0·097 g.-ion; SO_2 0·04 g.-mol.

Similarly from *iso*valeric acid (10·2 g.) the anhydride (9·2 g., 99%), b.p. 100—103°/15 mm., d_4^{27} 0·9260, n_D^{21} 1·4150 (Found: equiv., 93·9. Calc.: equiv., 93·0) was obtained. The aqueous solution of the precipitate contained: C_5H_5N, 0·094 g.-mol.; Cl^-, 0·097 g.-ion; SO_2, 0·04 g.-mol.

n-Heptanoic acid (13·0 g.) afforded the anhydride (11·75 g., 97%), b.p. 102—109°/0·5 mm., 258°/754 mm., d_4^{15} 0·9215, redistilled (7·4 g. from 7·6 g.), b.p. 104—108°/0·4 mm., n_D^{21} 1·4320 (Found: equiv., 121·7. Calc.: equiv., 121·0).

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135. *A Convenient Reagent for the Preparation of Thioamides, and the Thiohydrolysis of S-Alkyl*iso*thiourea Derivatives.*

By A. E. S. FAIRFULL, J. L. LOWE, and D. A. PEAK.

THE preparation of thioamides from cyanides is usually accomplished by heating the cyanide under pressure with an alcoholic solution of either an alkali-metal hydrogen sulphide or an ammonium (or substituted ammonium) hydrogen sulphide (*e.g.*, Gabriel and Heymann, *Ber.*, 1890, **23**, 158; Kindler and Burghard, *Annalen*, 1923, **431**, 201). Olin and Johnson (*Rec. Trav. chim.*, 1931, **50**, 72) converted a number of acylated cyanohydrins into the corresponding thioamides by the addition of hydrogen sulphide at room temperature in alcohol in the presence of triethanolamine but they did not extend the reaction to other cyanides. Renfrew (*J. Amer. Pharm. Assoc.*, 1951, **40**, 467) has recently applied the method to the preparation of 7-methylthiocinchoninamide but the addition took many hours.

We have found that the addition of hydrogen sulphide to aromatic cyanides takes place with remarkable ease in pyridine solution in the presence of a strong base such as triethylamine. Reaction is complete at room temperature in 2—4 hours and the thioamide is obtained, usually in good yield and often in a state of high purity, by pouring the reaction mixture into water. The reaction is equally applicable to other types of cyanides such as cyanamides, aminomethyl cyanides, and azomethyl cyanides. With benzyl cyanide the addition is sluggish and takes about 20 hours. With aliphatic cyanides, such as methyl or octyl cyanides, the addition is so slow that the method offers no advantage over the conventional pressure methods.

Triethylamine was used throughout this work in molar proportion. Presumably other strong bases would be equally effective and catalytic quantities might suffice, but these points have not been investigated. The presence of the strong base is essential since addition occurs at a negligible rate in its absence. Pyridine acts as an excellent solvent for most cyanides but its rôle is not purely passive since it also promotes addition. Thus, the rate of addition of hydrogen sulphide to *p*-methoxyphenyl cyanide is many times greater in pyridine–triethylamine than in chloroform–triethylamine. In the one case tried, benzyl cyanide, the rate of addition was also much greater than with the ethanol–triethanolamine mixture used by Olin and Johnson (*loc. cit.*). These authors mentioned the use of pyridine but were deterred from adopting it because of its desulphurising action on thioamides. This reason is hardly valid since the desulphurising action appears to be appreciable only at high temperatures for long periods (Raffo and Rossi, *Gazzetta*, 1914, **44**, 104; 1915, **45**, 28).

The pyridine need not be specially purified, commercial pyridine proving quite satisfactory. Anhydrous conditions facilitate the addition. Thus, the use of undried hydrogen sulphide reduces the yield of thiobenzamide from phenyl cyanide. This is not due to the simultaneous formation of benzamide since the pyridine–triethylamine mixture does not catalyse the addition of water to phenyl cyanide under comparable conditions.

The reagent is equally effective for the thiohydrolysis of *S*-alkyl*iso*thiourea derivatives to the corresponding thiourea derivatives. This has hitherto been accomplished in boiling alcoholic sodium or potassium hydrogen sulphide (Olin and Dains, *J. Amer. Chem. Soc.*, 1930, **52**, 3326; Underwood and Dains, *Kansas Univ. Sci. Bull.*, 1937, **24**, 5). In pyridine–triethylamine the reaction proceeds rapidly at room temperature. By this means representatives of several types of compounds, including *S*-alkyl-*iso*thioureas, -*iso*dithiobiurets, and -*iso*thiosemicarbazones, have been successfully thiohydrolysed. With *N*-*p*-chlorophenyl-*N'*-cyano-*S*-ethyl*iso*thiourea simultaneous thiohydrolysis and addition of hydrogen sulphide occur with the production of 1-*p*-chlorophenyldithiobiuret.

Thiohydrolysis also proceeds in the absence of triethylamine but at a considerably reduced rate.

Experimental.—*Preparation of thioamides.* The cyanide is dissolved in at least an equal weight of pyridine (more if the cyanide is of low solubility) and triethylamine (1 mol.) is added. Dry hydrogen sulphide is passed through the solution in a steady stream for 2—4 hours. The mixture is then poured into water, and the thioamide collected by filtration and, if necessary, crystallised from a suitable solvent.

The following thioamides were prepared in this manner. The yields recorded are those of pure product, or of unrecrystallised product of stated m. p. where this was close to that of the pure compound, as was frequently the case. No detailed investigation was made in any preparation and the yields are not necessarily optimum, especially as regards the recoveries on recrystallisation of the crude products.

Thiobenzamide (94%), m. p. 116° (Bernthsen, *Ber.*, 1877, **10**, 1241, records m. p. 115—116°); *p*-methoxythiobenzamide (90%), m. p. 149° after recrystallisation from xylene (Rehländer, *Ber.*, 1894, **27**, 2159, records m. p. 148—149°); *p*-chlorothiobenzamide (48·5%), needles or prisms (from benzene), m. p. 129—130° (Kindler, *Annalen*, 1926, **450**, 13, records m. p. 124°);

o-*chlorothiobenzamide* (100% ; m. p. 57°), needles, m. p. 62·5—63°, from benzene–light petroleum (Found : C, 49·35; H, 3·5. C_7H_6NClS requires C, 49·0; H, 3·5%); *p*-aminothiobenzamide 81·5% ; m. p. 168—170°), pale-yellow needles or plates, m. p. 180°, from water (Bogert, *J. Amer. Chem. Soc.*, 1903, **25**, 483, and Engler, *Annalen*, 1869, **149**, 297, record m. p.s 172° and 170° respectively) ; *p*-acetamidothiobenzamide (80%), pale yellow needles, m. p. 216°, from aqueous ethanol (MacCorquodale and Johnson, *Rec. Trav. chim.*, 1932, **51**, 483, record m. p. 215°); p-*ethylsulphonylthiobenzamide* (70%), pale yellow needles, m. p. 181—182°, from ethanol (Found : N, 6·05. $C_9H_{11}O_2NS_2$ requires N, 6·1%); 3 : 4-dimethoxythiobenzamide (70%), pale yellow needles, m. p. 184—185°, from ethanol (Hinegardner and Johnson, *J. Amer. Chem. Soc.*, 1930, **52**, 4141, record m. p. 183°); dithioterephthalamide (60·5% ; m. p. 260°) (Luckenbach, *Ber.*, 1884, **17**, 1430, records m. p. 263°); phenyl(thioacetamide) (95% ; m. p. 95°), m. p. 97° after one recrystallisation from benzene–light petroleum (Bernthsen, *Annalen*, 1876, **184**, 292, records m. p. 97·5—98°); thionicotinamide (86%; m. p. *ca.* 175—183°), m. p. 183° (decomp.) after recrystallisation from water (Karrer and Schukri, *Helv. Chim. Acta*, 1945, **28**, 820, record m. p. 180—181°); thiopicolinamide (65·5%; m. p. 136°) (*idem, loc. cit.*, record m. p. 137°); *p*-methoxyphenylthiourea (90% ; m. p. 204—205°), m. p. 210—211° after two recrystallisations from ethanol (Dyson and George, *J.*, 1924, **125**, 1708, record m. p. 210—211°); anilino(thioacetamide) * (83%), m. p. 165—166° (slight decomp.) after recrystallisation from ethanol [Paradies, *Ber.*, 1903, **36**, 4302, and Johnson and Burnham, *J. Amer. Chem. Soc.*, 1912, **47**, 239, record m. p.s 165° and 166° (decomp.) respectively]; (*N*-benzylanilino)thioacetamide * (83%), m. p. 176° after recrystallisation from ethanol (Turner and Djerassi, *J. Amer. Chem. Soc.*, 1950, **72**, 3081, record m. p. 176—178°); *phenylazo*(*thioacetamide*) (75%), yellow prisms (from methanol), m. p. 185—186° (Found: C, 53·5; H, 4·6. $C_8H_9N_3S$ requires C, 53·6; H, 5·0%).

Thiohydrolyses. The *S*-alkyl*iso*thiourea derivative is dissolved or suspended in pyridine (2—8 parts by weight) and triethylamine (1·1 mols.) added. An additional 1 mol. of triethylamine is added if the *iso*thiourea is in the form of a salt. Dry hydrogen sulphide is passed through the solution at room temperature for 4 hours and the reaction mixture poured into water. The solid is collected and washed with a little dilute acetic acid.

In this way *S*-ethyl-*N*-phenyl*iso*thiourea hydriodide gave *N*-phenylthiourea (60%), m. p. 148—151°, or 149—151° when mixed with authentic *N*-phenylthiourea (m. p. 151—152°); *S*-methyl*iso*thiocarbanilide gave thiocarbanilide (92%), m. p. 150—152°, or 151—152° when mixed with authentic thiocarbanilide (m. p. 153—154°); 2 : 4-dimethyl-1 : 5-diphenyl-2 : 4-di*iso*dithiobiuret (Johnson and Elmer, *Amer. Chem. J.*, 1903, **30**, 167) gave 1 : 5-diphenyldithiobiuret (75%), felted needles (from ethanol), m. p. 148—149° not depressed by a sample (m. p. 147—148°) prepared by the method of Olin and Dains (*loc. cit.*); benzaldehyde *S*-ethyl-*iso*thiosemicarbazone hydrobromide gave benzaldehyde thiosemicarbazone (44%), m. p. and mixed m. p. 158—160° after purification of the initial crude product (m. p. 145—150°) by dissolution in aqueous sodium hydroxide, filtration, and precipitation with acetic acid; and *N*-*p*-chlorophenyl-*N'*-cyano-*S*-methyl*iso*thiourea (Crowther, Curd, Richardson, and Rose, *J.*, 1948, 1639) gave 1-*p*-chlorophenyldithiobiuret (75%), felted needles (from ethanol), m. p. 176—178° not depressed by a sample of 1-*p*-chlorophenyldithiobiuret, m. p. 179—180° (Found : N, 16·9. Calc. for $C_8H_8N_3ClS_2$: N, 17·1%), prepared by a modification of the method of Fernandos and Ganapathi (*Proc. Indian Acad. Sci.*, 1948, **37**, 570) who, however, record m. p. 163—164°.

When triethylamine was omitted, the yield of thiocarbanilide from *S*-methyl*iso*thiocarbanilide was only 61% after 4 hours under comparable conditions to the above.

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* Preparations by Dr. N. W. Bristow.