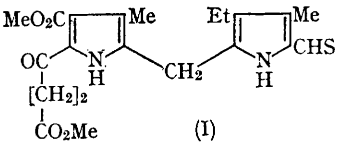
Stable Heterocyclic Thioaldehydes

By S. McKENZIE and D. H. REID

(*Department of Chemistry, The University, St. Andrews, Scotland*)

THE dipyrrylmethane (I), a key compound in Woodward's synthesis of chlorophyll *a*,[1] is the only authentic thioaldehyde to have been isolated, in spite of numerous investigations since about 1850. Various synthetic endeavours have led to cyclic or linear polymers of thioaldehydes by opening of the transient C=S bond, whose instability depends on the reluctance of elements of the second and succeeding Periods in the Periodic Table to form multiple bonds. We now report the synthesis of stable thioaldehydes in the indolizine, pyrrolo[2,1-*b*]thiazole, and indole series.



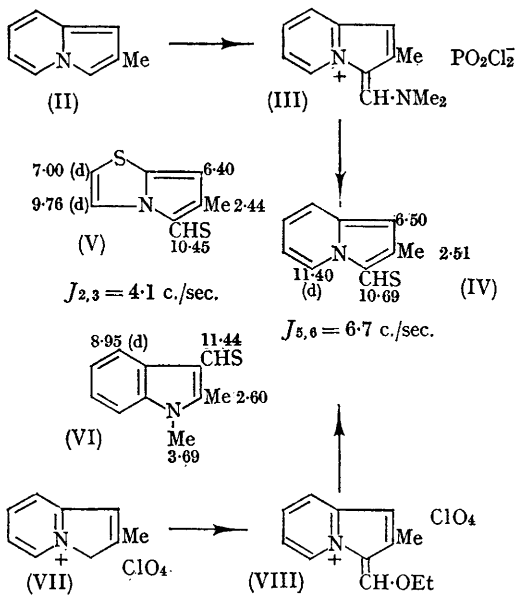
(I)

Addition of phosphoryl chloride to a solution of 2-methylindolizine (II) in dimethylformamide at −60° gave the Vilsmeier salt (III) which, when treated with 2M-aqueous sodium hydrogen sulphide afforded 2-methyl-3-thioformylindolizine (IV) (86%) as orange-red needles (from cyclohexane), m.p. 88—89°, $\lambda_{\max}$ 442, 432,420 sh mμ (log ϵ, 4·60, 4·44, and 4·28),[2] molecular weight 176 (osmometric)[3] 175 (mass spectrometry).[4] In a similar manner 6-methyl-5-thioformylpyrrolo[2,1-*b*]thiazole (V) (89%), orange-red needles, m.p. 101—103°, $\lambda_{\max}$ 427, 418,407 sh mμ (log ϵ, 4·55, 4·53, and 4·43), molecular weight 181 (osmometric) 181 (mass spectrometry), and 1,2-dimethyl-3-thioformylindole (VI) (86%), orange needles which decompose > 160°, $\lambda_{\max}$ 373 mμ, molecular weight 189 (mass spectrometry) were obtained from 6-methylpyrrolo[2,1-*b*]thiazole[5] and 1,2-dimethylindole, respectively. Significantly, the mass spectra of all three thioaldehydes showed large $(M - 45)^+$ peaks, corresponding to the loss of the thioformyl group.

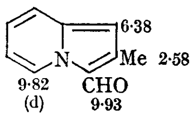
Treatment of 2-methyl-3*H*-indolizinium perchlorate (VII)[6] in ethanol with an excess of triethyl orthoformate gave 3-ethoxymethylene-2-methylindolizinium perchlorate (VIII) (85%), green needles, m.p. 172—174° (decomp.) which, when warmed with aqueous sodium hydrogen sulphide, also gave the thioaldehyde (IV) in good yield.

Proton magnetic resonance spectral data[7] were in full agreement with the thioaldehyde structures. Comparison of the spectra of the thioaldehydes (IV) and (V) with those of the corresponding aldehydes (IX) and (X), respectively, shows that the thioformyl proton is more strongly deshielded (0·76 p.p.m.) than the formyl proton, and that the diamagnetic anistropy of the C=S group is larger than that of the C=O group. The latter conclusion follows from a comparison of the chemical shifts of H-5 in compounds (IV) and (IX) and of the chemical shifts of H-3 in compounds (V) and (X).

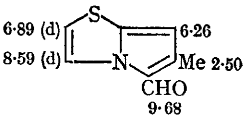
The infrared spectra of the thioaldehydes (IV)—(VI) show a strong absorption band in the range 985—950 cm.$^{-1}$, which we attribute to the C=S stretching vibration on the basis of solvent shift studies. Thus this band in the spectrum of the thioaldehyde (IV) shifts from 978 cm.$^{-1}$ in cyclohexane to 956 cm.$^{-1}$ in 1,1,2,2-tetrabromoethane solution.



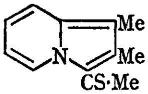
Thioketones may also be obtained by the foregoing procedure. Treatment of 1,2-dimethylindolizine with phosphoryl chloride in *NN*-dimethylacetamide at 60°, followed by aqueous sodium hydrogen sulphide, gave 1,2-dimethyl-3-thioacetyl-



(IX)



$J_{2,3} = 4{\cdot}1$ c./sec. (X)



(XI)

indolizine (XI) as ochre needles (66%), m.p. 156—158°, λ_{max} 452 mμ (log ϵ, 4·46), molecular weight 204 (osmometric).

We believe that the stability of the thioaldehydes is a function of the polarisation of the thioformyl group and, in general, will be greater the higher the electron availability at the site in the heterocyclic nucleus to which the thioformyl group is attached.

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[1] R. B. Woodward, W. A. Ayer, J. M. Beaton, F. Bickelhaupt, R. Bonnett, P. Buchschacher, G. L. Closs, H. Dutler, J. Hannah, F. P. Hauck, S. Itô, A. Langemann, E. Le Goff, W. Leimgruber, W. Lwowski, J. Sauer, Z. Valenta, and H. Volz, *J. Amer. Chem. Soc.*, 1960, **82**, 3800.

[2] Ultraviolet-spectral data refer to the long-wave transitions measured with cyclohexane solutions.

[3] Osmometric molecular-weight determinations were made with benzene solutions.

[4] Mass spectra were kindly determined by Dr. W. Bonthrone, using an AEI MS-9 spectrometer.

[5] B. B. Molloy, D. H. Reid, and F. S. Skelton, *J. Chem. Soc.*, 1965, 65.

[6] M. Fraser, A. Melera, B. B. Molloy, and D. H. Reid, *J. Chem. Soc.*, 1962, 3288; M. Fraser, S. McKenzie, and D. H. Reid, *J. Chem. Soc.* (*B*), 1966, 44.

[7] Numbers attached peripherally to formulae refer to chemical shifts (δ) of the corresponding protons in p.p.m. downfield from the Me_4Si signal. Solutions were 0·4 M in deuterochloroform, except that of the thioaldehyde (V), which was saturated ($<$ 0·4 M).