Thermal Isomerisation of Mesoionic Tetrazoles. A New Type of Heterocyclic Rearrangement

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Summary The thermal isomerisation of two mesoionic tetrazoles is described; the structure of 2,4-diphenyl tetrazolium-5-thiolate has been elucidated by *X*-ray crystallography.

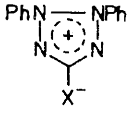
IN principle, if a 1,2-shift of a group (R) occurs in mesoionic compounds[1] [*cf.*[2] (**1**) and (**2**)] a different heterocycle is produced. For most systems the primary product would be a conventional heterocycle but in a minority of cases an isomeric mesoionic compound would be formed.

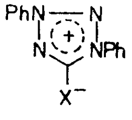
We report a rearrangement of the latter type induced by thermolysis of the mesoionic tetrazoles (**3a** and **b**). Pyrolysis[3] of (**3a**)[4,5] gave the isomeric (**4a**)[5,6] in 45% yield† and (**3b**) was converted into 2,4-diphenyl tetrazolium-5-thiolate (**4b**), m.p. 153 °C, λ_{max} (Et_2O) 252sh and 280 nm; λ_{max} (Me_2CO) 400 nm, in low yield (16%).† The structure of (**4b**) was elucidated *X*-ray crystallographically. *Crystal data:* monoclinic, space group $P2_1/c$ (from systematic absences), $a = 12{\cdot}596(2)$, $b = 11{\cdot}220(2)$, $c = 8{\cdot}818(1)$ Å, $\beta = 99{\cdot}49(2)°$, $Z = 4$, $D_c = 1{\cdot}373$, $D_m = 1{\cdot}38$ g cm^{-3}.


(1)


(2)

X = O, S, or NR, Y = O, S, or NR
V = CR or N, W = CR or N
Z = O, S, or CR^{1}R^2


(3)


(4)

a; X = O
b; X = S

Reflections were measured on a Hilger–Watt four-circle diffractometer with monochromated Mo-K_α radiation to $\theta = 25°$. 2164 reflections had net counts $>3\sigma$ and all these were used in the subsequent calculations. The structure was solved using the centro-symmetric direct methods routine in SHEL X[7] and refined using CRYSTALS (the Oxford University set of crystallographic programs). Hydrogen atoms were located from a difference map and the final stages of refinement were by full-matrix least-squares with hydrogen treated isotropically and the other atoms anisotropically. The maximum least-squares shift for the heavier atom parameters at convergence was $0{\cdot}03\sigma$ and for the hydrogen parameters $0{\cdot}12\,\sigma$. The final conventional R was 4·07%.

The three rings in the structure were each essentially planar. The angle of twist between the heterocyclic ring and the phenyl rings were 52° for the ring nearer sulphur and 13·5° for the other ring. The bond lengths and angles showed no unusual values and the calculated estimated standard deviation for these quantities involving the heavier atoms only lay between 0·003 and 0·005 Å and 0·2 and 0·3°, respectively.

We thank the S.R.C. and Allen and Hanburys Research Ltd. for support. One of us (K.K.T.) was the recipient of a British Government Technical Assistance Training Award under the Colombo Plan, and thanks Central Fuel Research, Dhanbad, Bihar, India, for leave of absence.

(*Received, 23rd February* 1976; *Com.* 182.)

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† Yields are based on consumed starting material; the conversions were 80% and 60% for (**3a**) and (**3b**) respectively.

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[3] Pyrolyses of (**3a**) and (**3b**) were carried out at 150 °C for 6 h as 2% w/w dispersions in acid washed sand (BDH) under N_2. Compound (**3a**) is also converted (10%) into (**4a**) in *o*-xylene under reflux after 6 h. Under these conditions, thermolysis of (**3b**) gives a complex product containing (**4b**) (7%).

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