Asian Journal of Chemistry Vol. 10, No. 4 (1998), 986–989

NOTE

Reaction Mechanism for the Formation of Newly Synthesised 3-Aryl-5-tetra-O-acetyl-β-D-Glucopyranosylimidino-1,2,4-Dithiazolidines and 1-Aryl-2-Benzylimino-5-tetra-O-Acetyl-β-D-Glucopyranosyl amidinothiocarbamides, Part II

D.T. TAYADE
Department of Chemistry
S.R.R.L. Science College, Morshi, Amaravati 444 906, India

In the present work the synthesis of 3-aryl-5-tetra-O-acetyl-β-D-glucopyranosylimidino-1,2,4-dithiazolidines and 1-aryl-2-benzylimino-5-tetra-O-acetyl-β-D-glucopyranosyl amidinothiocarbamides are described.

Elemental sulphur has been known to be an oxidising, dehydrogenating and aromatizing reagent.[1] It is also used as a sulphurizing and dealkylating agent.[2, 3] Debenzylation of certain S-benzyl-2,4-isodithiobiurets was carried out by elemental sulphur.[4] Debenzylation of S-benzyl-1-aryl-isothiocarbamide and 1,5-diaryl-2-S-benzyl-2,4-isodithiobiurets was carried out with the help of thiocarbamides.[4, 5]

Recently, certain 3-aryl-5-tetra-O-acetyl-β-D-glucopyranosylimidino-1,2,4-dithiazolidines and 1-aryl-2-benzylimino-5-tetra-O-acetyl-β-D-glucopyranosyl-amidinothiocarbamides have been successfully synthesised by the interaction of certain 1-aryl-2-S-benzyl-5-tetra-O-acetyl-β-D-glucopyranosyl-2,4-isodithiobiurets with elemental sulphur and thiocarbamide in presence of pyridine and benzylamine respectively.[6] The mechanism of reactions is based on the views of Jadhav, Verma and Paranjape's work[5, 7] and is given below.

All chemicals used were of pure analytical grade as required -1-aryl thiocarbamide, 5-benzyl-1-aryl isothiocarbamide, tetra-O-acetyl-β-D-glucopyranosyl isothiocyanate and 1-aryl-2-S-benzyl-5-tetra-O-acetyl-β-D-glucopyranosyl-2,4-isodithiobiurets were prepared as described[4] where aryl group are phenyl, -*p*-Cl-phenyl or -*o*-Cl-phenyl.

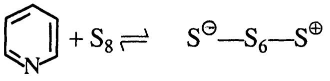
Reaction mechanism for the formation of 3-phenyl-imino-5-tetra-O-acetyl-β-D-glucopyranosylimino-1, 2, 4-dithiozolidine

Sulphur exhibits a valency of two in the ground state and also valency of four and six by dp^3 and d^2sp^3 hybridisation respectively. Atomic sulphur is an extremely energy-rich form of sulphur, as it forms relatively strong bonds within itself. This species of sulphur is generally never encountered as its generation demands drastic conditions.

The lowest energy excited state of sulphur lies about 26 kcal above the ground state. It is a carbene like singlet. In the elemental state, however, sulphur exists mainly as a cyclic system of eight sulphur atoms; as cycloctasulphur or electron decet. The S_8 ring is stable and less strained than S_6 ring, as the S_8 ring has more favourable values of bond angle and dihedral angle and is thus geometrically possible. One more reason for the stability of the S_8 ring is the involvement of one lone pair of electrons of each sulphur atom in the formation of an electron decet. This explains the colour of sulphur.

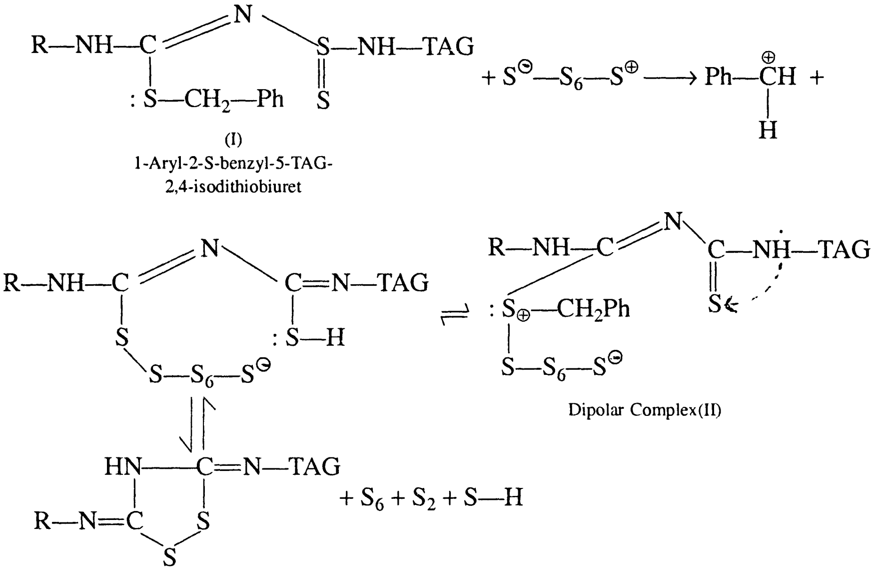
An interesting property of elemental sulphur is that although a sulphur molecule (S_8) has 16 electron pairs, it is a Lewis acid rather than a Lewis base. To explain this abnormal behaviour, it is argued that sulphur has a strong tendency to expand its electron shell by means of its d-orbital. This possibility arises because of the existence of vacant 3d orbitals, which may either be occupied by its own 3s and 3p electrons, or by external electrons. The attack of a Lewis base thus opens up the S_8 ring and generates a dipolar open chain.

During the reaction the amine opens up the 8 membered elemental sulphur ring resulting in the formation of a dipolar open chain structure (a polysulphide) having eight sulphur atoms. The lone pair of electrons of sulphur having benzyl group in 1-aryl-2-S-benzyl-5-tetra-O-acetyl β-D-glucopyranosyl-2,4-isodithiobiuret (I) will attack the positively charged sulphur atom in the sulphur chain, resulting in the formation of yet another dipolar complex, with a positive charge on the sulphur carrying the benzyl group. This complex will then eliminate a benzyl carbonium ion, which will involve an intramolecular proton transfer, followed by cyclisation resulting in the formation of 1,2,4-dithiazolidines (IV). Formation of benzaldehyde and hydrogen sulphide will be a multistep process, involving benzyl carbonium ion and mercaptanic (SH) ion respectively. All are represented as follows:



Pyridine (Lewis base)

Polysulphide (Dipolar structure)



(I) 1-Aryl-2-S-benzyl-5-TAG-2,4-isodithiobiuret

Dipolar Complex(II)

3-Aryl-5-TAG imidino-1,2,4-dithiazolidine(IV)

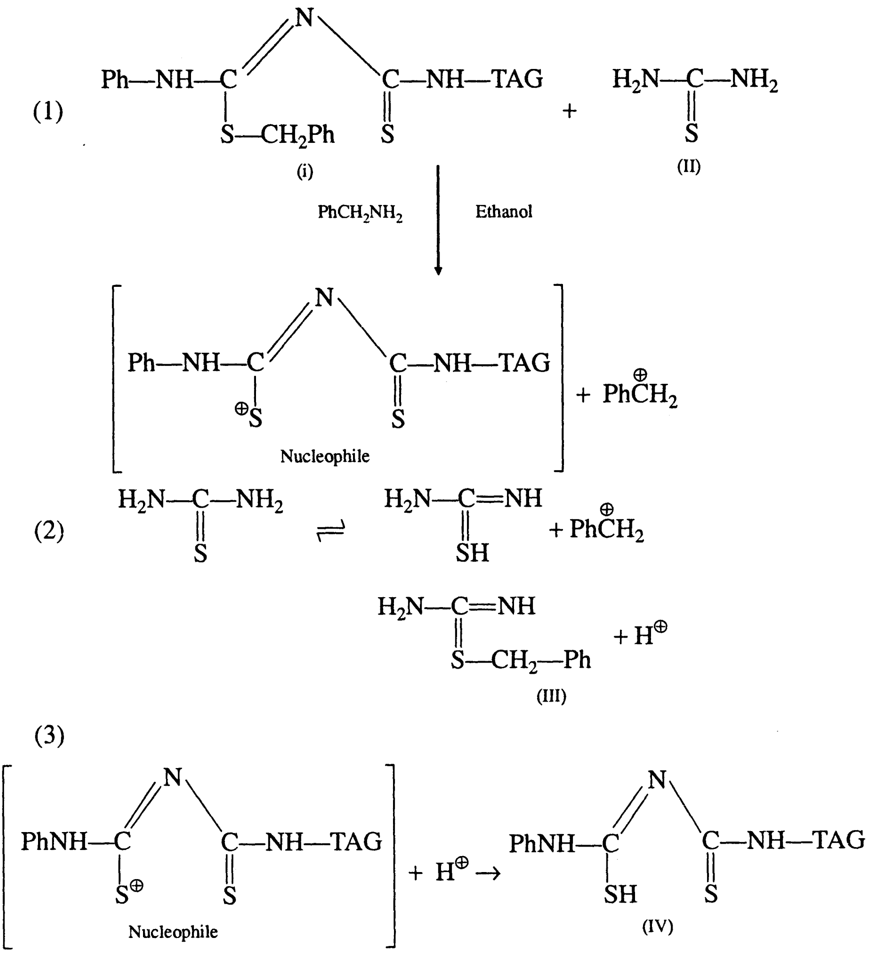
where R = -phenyl, -*o*-Cl-phenyl or -*p*-Cl-phenyl

TAG = Tetra-O-acetyl, β-D-glucopyranosyl

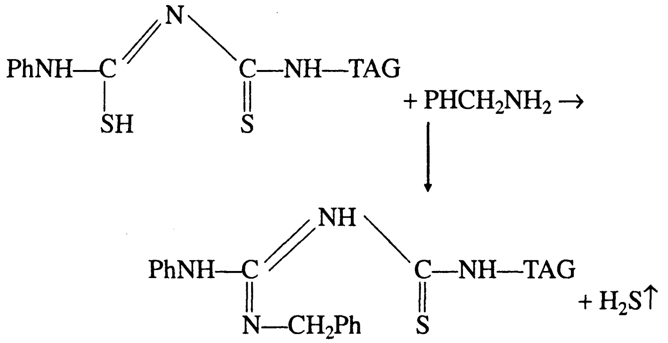
Final product gives Molish test confirm the presence acetylated glucosyl group. On boiling with alkali it did not give a smell of mercaptans indicating the absence of mercaptobenzyl group. It is soluble in ethanol, methanol, acetone and benzene while insoluble in petroleum ether.

Reaction mechanism for the formation of 1-aryl-2-benzylimino-5-tetra-O-acetyl-β-D-glucopyranosylamidino thiocarbamide

When the interaction of 1-aryl-2-S-benzyl-5-TAG-2,4-isodithiobiruet (I) was carried out with thiocarbamide in presence of benzylamine in boiling ethanolic medium, evolution of hydrogen sulphide gas was noticed. During this reaction an exchange of benzyl group takes place between 1-aryl-2-S-benzyl-5-TAG-2,4-isodithiobiuret (I) and thiocarbamide (II) with the initial formation of 1,5-disubstituted-2,4-dithiobiuret(III) and S-benzylisothiocarbamide(IV). The former will then react with benzylamine resulting into 1-aryl-2-benzylimino-5-TAG-amidinothiocarbamide (V) with the elimination of hydrogen sulphide. Thus



(4)



(v)

where (1) R = Phenyl, *o*-Cl-phenyl or *p*-Cl-phenyl
(2) TAG = Tetra-O-acetyl-β-D-glucopyranosyl
(3) Ph = Phenyl

ACKNOWLEDGEMENT

The author is thankful to Dr. Atul Tayade and Dr. Surekha Tayade for cooperation during this work.

REFERENCES

1. S.N. Dixit, *J. Indian Chem. Soc.*, **37**, 151 (1960).
2. N.P. Buu-Hoi and G. Saint-Ruf, *J. Chem. Soc.* (*Org.*), 924 (1966).
3. N.G. Caufuil, Acasadevall and R. Greze, *Bull. Soc. Chim .France* ,1276 (1961).
4. R.T. Jadhao, Ph.D. Thesis, Nagupr University, Nagpur (1981).
5. V.K. Verma, *Indian J. Chem.*, **1**, 50 (1963).
6. D.T. Tayade, *Asian J. Chem.*, **7**, 672 (1995).

(*Received*: 1 March 1998; *Accepted*: 15 June 1998) AJC-1526