Insertion Reaction of Tetra Organobismuth with Various Unsaturated Compound

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ABSTRACT

Organ-metallic compounds can be defined as any member of a class of substance containing at least one metal to carbon bond in which carbon is a part of organic group. In these compounds, Metal acts as main group compound or transitional metal compound. The main group metals of organometallic compounds are typically considered to be those of S-block (gp 1 and 2) and heavier of p block (gp 13, 14, 15) respectively of the periodic table.

The properties of organometallic compounds depend upon the type of carbon-metals bonds involved. Some are ordinary covalent bond (in which pair of bonded electron is shared between atoms). Some are ionic bond (in which pair of bonded electron is denoted by only one atom) making the bond polarized where one bond is more negative than the other. Thus in organometallic compounds the metal atom is less electro negative than the carbon atom. The polarity of M-C bond makes the organometallic compound a good substrate for studying electrophillic substitution at the metal atom. Due to this polarity organometallic compounds are susptible to be attached by a wide variety of reagents, which opens a vast area for the synthesis of various type of new organometallic compounds.

Introduction

As the name suggest, an insertion reaction, involves the formal insertion of one ligand (usually unsaturated) into another metal-ligand bond on the same complex the generic reaction is shown below, where u= an unsaturated ligand.

U= RCN, CR_2, NO, CO_2, CS_2, RMCO, X= N_2O_7, CH_3 and Br [1-11] are extensively studied. Such reaction has been reviewed by lappert and Prokai [2]

Exploratory works reveals that addition reaction of multiple bounded reagents across M-X bonds (M= Si, Ge, Sn, P, As & Sb etc; X=N, O, C, H & Br) [1-11] have extensively been studied. Such reaction has been reviewed by Lappert & Prokai [2]. Reaction involving M-M in particular has been confined to arganometal amines [2-12], cyanamides carbodiimide [13-15] with various unsatured substrates (CO_2, CS_2, RCN, RNCO and RNCS) yielding carbamates, thiocarbamates and isocyanates or to inorganic metal azides, $M(N_3)_n$, (M=Na, Al) (n=1,3) [15,16,17] with considerable polar nature (of M- N_3 bond) and provided novel 5- substituted tetrazoles by the 1,2-dipolar addition to isothiocynates and nitriles encouraged by these results various group of workers in the recent past studied the reactions of organometallic azides with the number of multiple bonded reagents. Thus nitriles and isocynates have been found to undergo 1,2 cycloaddition reaction with triorganosilicon azides yielding 5-substituted tetrazoles [18-20].

The formation of tetrazole derivative has been confirmed by Sisido et.al in the parallel reaction of trialkytin azides with nitriles [21]. Dunn and Oldfield independently in the same year examined the insertion reactions of triorganotin azides with CS_2, PhNCO and PhNCS and tended support to the formation of tetrazoles derivates [22].

A systematic and comprehensive study on the insertion reaction of non transition metal azides have been undertaken in the past. Thus Prem and Co-workers studied the reaction of organometal azides $R_3M(N_3)$ (M=Ge &Sn) and $R_4M(N_3)$ (M=P, As & Sb) and successfully isolated a number of organometal substituted tetrazoles [4,23]. The activity pattern of unsaturated substrates together with the mechanism of the reactions involved has also been eatablished. Srivastava et. al reported the reaction of group 13 organometal azides $R_2M(N_3)$ (M=Ga, In &Ti) with CS_2RNCO and RNCS [24].

Considering the past pattern of reactions occurred between slibonium salt and 1.2

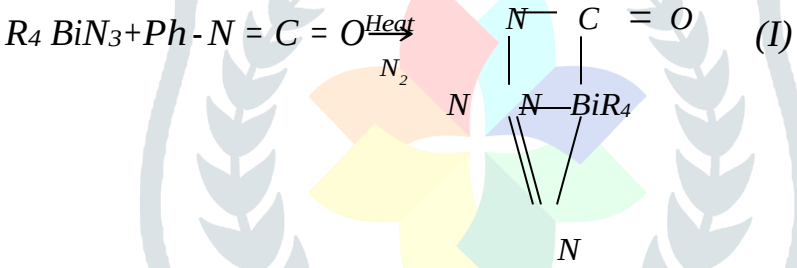
dipole, the author will prepare different bismuthonium azide Ph_4BiN_3 which have in vast biological importance. These compounds have synthetically utility and among them the tetrezode derivatives are water soluable.

RESULT AND DISCUSSION

1. Reaction with Ph-N=C=S

Cyclization reaction of tetraogano bismuthonium azides with organic isothiocynates proceeded essentially in the same manner as those of symmetrical organometal azides. Thus, under as oxygen free atmosphere and in the absence of any solvent, 1:1 molar reaction of bismuthonium azides with phenyl isothiocynates

afforded tetrazole-5-thiones(I)



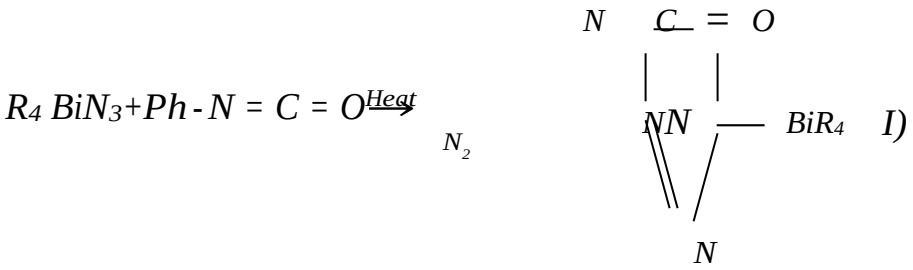
(I)

Where [R=C_6H_5, p-$CH_3C_6H_4$, C_6F_5]

2. Reaction with Ph-N=C=O

The similar couse of reaction was found to occur between tertaorganobismuthonium azides and phenylisocynate were allowed to react producting 1- phenyl-4-(tetraorganobismuthonium)

-5- tetrazolthione(II)



3. Reaction with S=C=S

The reaction of tetraoganbismuthonium azide with an excess of CS_2 *under refluxing condition afforded tetrasorganobismuthonium thiocynates ,* $(C_6H_5)_4$ *BiNCS together with some sulphur. The formation of sulphur suggests that the ring compound formed in the course reaction are unstable and split to give organobismuth isothiocynates and sulphur with the evolution of nitrogen. It is not surprising since such course of reactions has earlier been observed in case of Sn, Pb, As, P, Ga, In,and Ti, [21-24].*

IR SPECTRA

The IR spectra of the cyclic product are in the conformity with there structure. The IR spectra of organobismuth isothiocynates are similar to those reported for symmetrical organbismuth compound [26].

The formation of the tetrazole derivate obtained by the reaction of PhNCS and PhNCO could be well ascertained by the IR spectra. It is well known that $\sqrt{asym}$ N_3 *strong and suffers negligible shift due to structural changes. The absence of this band, therefore is the gurantee's [20,26], the products are free of this structural entity. The cyclic derivative (I and II) exhibit a band in the region 1300 to 1250 cm^{-1} of variable intensity assignable to the cyclic -N=N=N- linkage [25]. The symmetrical azide strectching usually of a week intensity also appear in the same region [2,26] but Lieber et. al from a study of several tetrazole derivatives have assigned the absorption in the range of 1300-1270 cm^{-1} to cyclic -N=N=N- stretching [27]. The absence of* $\sqrt{(N=C=S)}$, $\sqrt{(N=C=O)}$ *absorption band around 2080, 2275, 2100 cm^{-1} respectively and the appearance of a new band due to* [28] $\sqrt{(C=O)}$ *around 1700 cm^{-1} strongly support to the proposed cyclic structures. A new band of week to medium intensity between 1100-1000 cm^{-1} may be assisgend to skeletal mode of vibration of the tetrazole ring as reported by Grzonka et. al [29].*

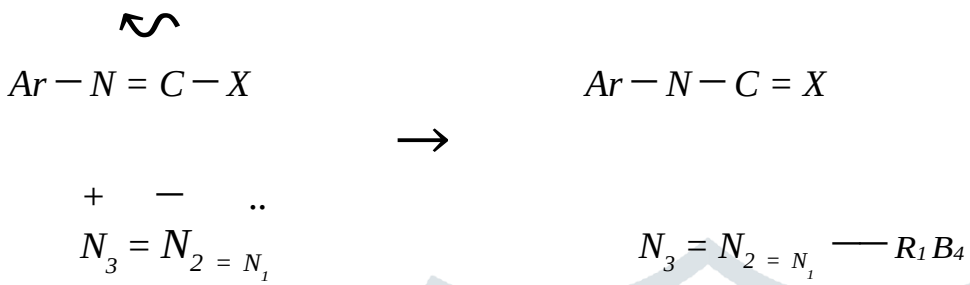
ULTRAVIOLET SPECTRA

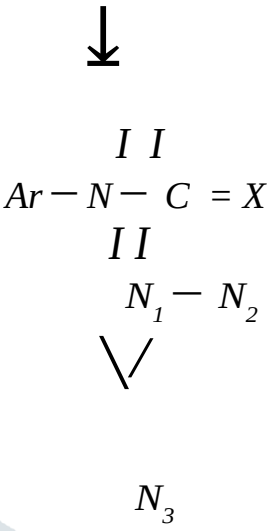
The UV spectra of the compound in the methanol and n-hexane exhibit characteristic maximum absorption to the region 260-290 nm similar to that of exhibited by 1-phenyl-tetrazole-5-thiol and thus support the formation of tetrazole derivatives (I_{max} 276nm)[4].

MECHANISM

The most probable mechanism for such reaction can be considered as 1:2

dipolar addition to the unsaturated substrate Ar- $N^1 = C^2 + S$ or Ph- $N^1 = C = O$ or in the view of conjugation to the tetrabismuthonium azide and the reaction proceed through the cyclic intermediate III and IV. This similar course of mechanism has been suggested carbon et al [4, 23-24].





Where (Ar=ph, p=Cl C_6H_4, p CH_3 C_6H_4 O-CH_3 C_6H_4, p-Br C_6H_4, X=S or O)

Thus, the formation of cyclic products appear to proceed through the nucleophlic attack of the azide ion on the electron deficient carbon atom of the unsaturated substrate followed by the ring closer to form tetrazole ring by donation of electron to an electron deficient and its atom of the azide moiety.

It has been established by Jones and Lappert [3] that has essential characteristic of an unsaturated substrate is that it should be susceptible to attack by nucleophiles, therefore, the ideal reaction should be the one in which the unsaturated substrate contain an electron withdrawing group and organometal azide possessed, an electron releasing group.

EXPERIMENTAL

Preparation of unsymmetrical tetraoganbismuthonium azide was done by the reported method. Phenyl isocyanate and phenlisothiocynates were used as (CS_2), was dried over molecular sieve and distilled before use. All the reaction were carried out in the absence of solvent in dry nitrogen atmosphere, some representative experiments are described below, further details are given in the table from (1-5).

1. ***Reaction of $(C_6H_5)_4$ Bi N_3 with S=C=S***

In a typical experiment data pheny bismuthonium azide (2mol) was refluxes with carbon disulphide (1.52g, 2mol) for 10 hr in dry nitrogen atmosphere. Off white suspension of sulphur appeared which was filtered off and the filtrate on concentration yielded white crystal which were washed with cold petroleum ether (60-80℃) and dried in vacuum. It was characterized as ***$(C_6H_5)_4$ Bi NCS.***

2. ***Reaction of $(C_6H_5)_4$ Bi N_3 with PhNCS***

A mixture containing equimolar amounts of dicylohexyl (phenly) bismuth azide (0.40g; 1 mmole) and phenyl isocyanate (012g; 1mmole) were gently heated at 130℃ for 4 hours in nitrogen atmosphere. The resulting brown viscous liquid was treated with dried n-hexane to afford the compound, 1 phenly1-4(tetradiphenyl)Bi tetrazole-5-thione.

Yield : 62%, M.P. : 187℃

3. ***Reaction of Dicylohexylphenlybismuth azide with phenyl isothiocyanate***

A mixture containing equimolar amounts of dicylohexylphenlybismuth azide (0.40g; 1 mmole) and phenyl isothiocyanate (1.13g; 1mmole) were gently heated at 130℃ for 4 hours in nitrogen atmosphere. The obtained compound is 1 phenyl-4- [tetrapentafluro ethyl] tetrazole-5-thione.

Yield : 60%, M.P. : 147℃

4. ***Reaction Dicylohexylphenlybismuth azide with p-toly phenyl isothiocyanate***

Dicylohexyl(phenyl)bismuth azide (0.40g; 1 mmole) and p-toly phenyl isothiocyanate (0.14g; 1mmole) were stirred together at 1300 ℃ for 3 hours.

The resulting brown viscous liquid was extracted with dried hexane, the extract gave the desire compound, 1-p-tolyphenyl-4-[tetra tolyl diecyclohexy(phenyl) bismuth] tetrazole-5-thioene.

Yield : 58%, M.P. : 136℃

Insertion Reaction of tetraorgano Bismuthonium Azide

TABLE-1

S.No.	***Reactants***	***M.P. ℃***	***Products***	***Yields***
1.	***$(C_6H_5)_4$ Bi N_3 + PhNCS***	*187*	*1-Phyenyl-4 (tetra phenyl bismuthonium Phenyl)tetrazole-5-thiones*	*62*
2.	***$(C_6H_5)_4$ Bi N_3 + PhNCS***	*147*	*1-Phyenyl-4 tetra (penta fluro bismuthonium Phenyl) tetrazole -5-thione*	*60*
3.	***$(p\text{-}CH_3C_6H_5)_4$ Bi N_3 + PhNCS***	*136*	*1-Phyenyl-4 tetra (tolyl bismuthonium Phenyl)tetrazole-5-thiones*	*58*
4.	***$(C_6H_5)_4$ Bi N_3 + PhNCO***	*208*	*1-Phyenyl-4 (tetra phenyl bismuthonium) tetrazole-5-tetrazothiones*	*59*
5.	***$(C_6H_5)_4$ Bi N_3 + CS_2***	*195*	*tetraphenyl bismuthonium isocynate*	*57*

6.	***$(C_6H_5)_4$ Bi N_3 + CS_2***	*188*	*tetra penta fluro phenyl bismuthonium isothiocyanates*	*68*
7.	***$(p\text{-}CH_3C_6H_5)_4$ Bi N_3 + CS_2***	*160*	*tetra (p-tolyl) bismuthonium Isothiocyanate*	*70*

TABLE-2

S.No	***Products***	***Cyclic $u_{(-N=N=N)}$ cm^{-1}***	***$u_{(C-H)}$ aromatic bond***	***$u_{(Br-C)}$ band***	***$u_{C=S/C=O}$ Exocyclic (1395-1310/17500)****	***Skeletal Ring 1100-1000****
1.	*1-Phyenyl-4 (tetra phenyl bismuthonium Phenyl)tetrazole-5-thiones*	*1250m*	*3044w*	*455 m*	*1375m*	*1010*
2.	*1-Phyenyl-4 tetra (penta fluro bismuthonium Phenyl) tetrazole -5-thione*	*1255m s*	*3048w*	*452 m*	*1325*	*1030*
3.	*1-Phyenyl-4 tetra (tolyl bismuthonium Phenyl)tetrazole-5-thiones*	*1262m*	*3040w*	*463 m*	*1390w*	*1050*

4.	*1-Phyenyl-4 (tetra phenyl bismuthonium)*	*1307ms*	*3048w*	*458 m*	*1710ms*	*1080*
	tetrazole-5-tetrazothiones					

Characteristics Infrared data of cyclic derivative of tetraarylorganobismuthioum Azide

****Literature value m=medium, ms=medium strong, w=week***

TABLE-3

S.No.	***Products***	***UV (m) n-Hexane***	***Methanol***
1.	*1-Phyenyl-4 (tetra phenyl bismuthonium Phenyl)tetrazole-5-thiones*	*260*	*285*
2.	*1-Phyenyl-4 tetra (penta fluro bismuthonium Phenyl) tetrazole -5-thione*	*262*	*288*
3.	*1-Phyenyl-4 tetra (tolyl bismuthonium Phenyl)tetrazole-5-thiones*	*268*	*278*
4.	*1-Phyenyl-4 (tetra phenyl bismuthonium) tetrazole-5-tetrazothiones*	*266*	*270*

TABLE-3

S.No.	***Compound***	$_{asy}N_{cs}$	***Sym*** $^{(C-S)}$	***NCS***
1.	$(C_6H_5)_4$ *Bi* N_3 + *PhNCS*	*2050mbr*	*760m 840vw*	*470m*
2.	$(C_6H_5)_4$ *Bi* N_3 + *PhNCS*	*2045 mbr*	*753m 840m*	*472m*
3.	$(p\text{-}CH_3C_6H_5)_4$ *Bi* N_3 + *PhNCS*	*2060m*	*765m 850vw*	*476m*
4.	$(C_6H_5)_4$ *Bi* N_3 + *PhNCO*	*2058*	*770m 842vw*	*468m*

Where mbr=medium broad spectra

m=medium spectra

vw=very week spectra

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