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PHOTOLYTIC REARRANGEMENT OF GERMANIUM AZIDES. EVIDENCE FOR TRANSIENT GERMA-IMINES

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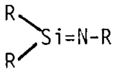
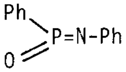
Photolysis of germanium azides gives rise to transient germa-imines which have been quantitatively trapped by pinacol. Evidence for the formation of diphenylgermylene in the photolysis of hexaphenylcyclodigermazane is also reported.

In the last few years, synthesis and reactivity of unusually hybridized organometallic compounds has been the subject of a lot of publications ([1]).

Although many methods of generating these species are known, few of them may be used in different series. The rearrangement of carbon azides is a well known method for obtaining imines ([2]). Sommer et al. have demonstrated that photolysis ([3]) or thermolysis ([4]) of silicon azides leads to sila-imines (A). In the same way, we generated the metaphosphonimidate (B) from the oxide of diphenylphosphine azide ([5]). Here we wish to report photolysis of germanium isologues, which leads to germa-imine intermediate (C) ([6]).


(A)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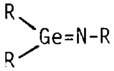
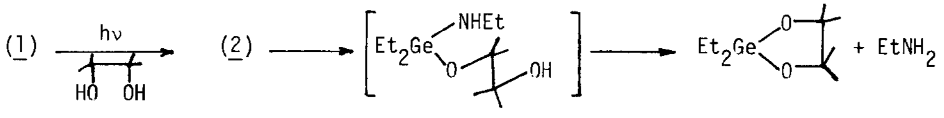

(C)

Triethylgermanium azide (1) irradiated overnight at 2537 Å in benzene, in the absence of trapping agent, gives rise to polymers (3) with loss of two thirds of the original quantity of nitrogen. The product (3) contains a germanium nitrogen bond (ν_{Ge-N} = 841 cm^{-1}) and an etnyl group bound to nitrogen (δ = 2.9 ppm, quartet like).

$$\underset{(1)}{Et_3GeN_3} \xrightarrow[PhH]{h\nu} N_2\uparrow + \underset{(2)}{\left[Et_2Ge{=}NEt\right]} \longrightarrow \underset{(3)}{(Et_2Ge{-}NEt)_n}$$

The transient germa-imine (2) was characterized by its adduct (5) with pinacol. Note that, as in the phosphorus series ([5]), the preliminary addition product (4) was not observed, because of the lability of the germanium nitrogen σ bond. Germadioxolanne (5) ([7]) was obtained in quantitative yield along with ethylamine.



(4) (5)

In the case of triphenylgermanium azide (6) ([8]), photolysis is more complex and leads to four products.

$$Ph_3GeN_3 \xrightarrow[PhH]{h\nu} (Ph_2Ge\text{-}NPh)_{2,n} + (Ph_2Ge)_{4,n} + PhNH_2 + Ph\text{-}Ph$$

(6) (7) (n=2 ; 10%) (8) (9) (12%) (10) (7%)

Formation of dimers and polymers (7) is consistent with a triphenylgerma-imine intermediate (11) while 8, 9 and 10 involve diphenylgermylene (12) and phenylnitrene (13).

$$\left[Ph_2Ge{=}NPh\right] \longrightarrow (7)$$

(11)

$$\left[Ph_2Ge{:}\right] \longrightarrow (8)$$

(12)

$$\left[PhN|\right] \xrightarrow{PhH} (9) + (10)$$

(13)

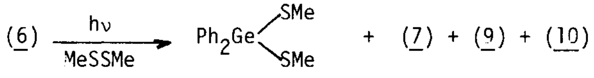
Indeed, hydrogen abstraction from benzene by phenylnitrene giving aniline (9) and biphenyle (10) is a well known reaction ([2]).

In order to prove that the phenylnitrene (13) comes from preliminary migration of phenyl group from the azide, compound (6) was irradiated in deuterated benzene :

$$(C_6H_5)_3GeN_3 \xrightarrow[C_6D_6]{h\nu} C_6H_5N(H(D))_2 + \underline{10} \quad \text{(partially deuterated)}$$

(6)

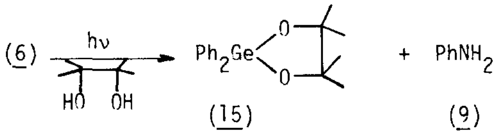
Evidence for transient formation of diphenylgermylene (12) was given by trapping with an excess of dimethyldisulphur ([9]). Product (14) was obtained in 10 % yield, as well as polymer (7) and a small amount of (9) and (10).



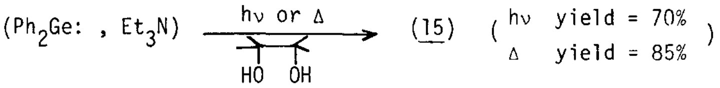
$$(6) \xrightarrow[MeSSMe]{h\nu} Ph_2Ge(SMe)_2 + (7) + (9) + (10)$$

(14)

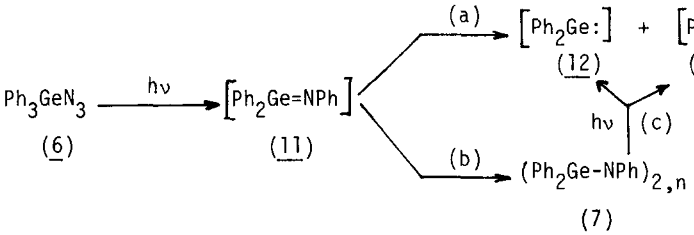
Germa-imine (11) was characterized by its adduct (15) with pinacol. Diphenyldioxagermolanne (15) was obtained in quantitative yield. No trace of (8) and (10) was detected by TLC.



Although, in the course of this study, we noted that diphenylgermylene (12) prepared using another method (9) reacts with pinacol giving (15), it seems reasonable to postulate that the dioxagermolanne obtained during photolysis of azide (6) in the presence of pinacol comes (at least in part) from a transient germa-imine (11).

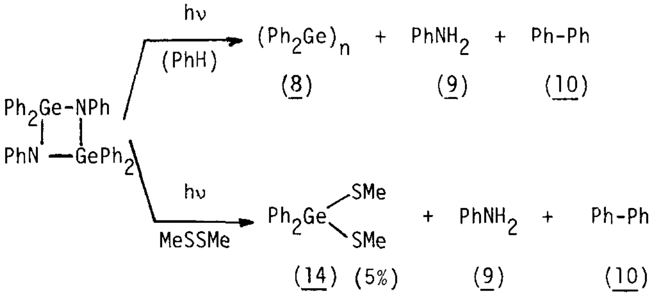


Thus, two possible mechanisms might explain our experimental results :



The first one would involve two competitive reactions : disproportionation (a) and dimerization (b) of the germa-imine (11). The second possibility would be the formation of (12) and (13) indirectly through (7) (c).

In fact, photolysis of (7) (n=2) leads to (8), (9) and (10) in the absence of trapping agent and to (14), (9) and (10) in the presence of dimethyldisulphur.



Moreover, pathway (a) would be the reverse of the reaction demonstrated by Satgé et al. (6a) :

$$[Ph_2Ge:] \quad + \quad PhN_3 \longrightarrow [Ph_2Ge{=}NPh]$$

So, it can be concluded that photolysis of trialkyl or triaryl germanium azides leads to a germa-imine intermediate. It was also noted that photolysis of hexaphenylcyclodigermazane gives rise to germylene and nitrene.

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