Disilverdiazomethane

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Summary Disilverdiazomethane has been prepared by the reaction of certain silver(I) salts with diazomethane in aprotic solvents; it is unstable in air or in light, and its reactions and spectral properties suggest the structure I(a).

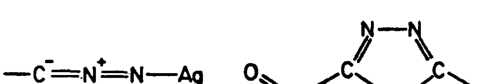
METAL derivatives of diazomethane of constitution M_2CN_2 have not hitherto been described, although disubstituted derivatives of the type $(Me_3M)_2CN_2$ (M = Ge, Sn, and Pb)[1] and monosubstituted compounds $MCHN_2$ (M = Li,[2] Na[3]) and $M(CHN_2)_2$ (M = Cd,[4] Hg[5]) have been prepared.

We now report the preparation of disilverdiazomethane, Ag_2CN_2 (I), by reaction of certain silver(I) salts with diazomethane in an aprotic solvent. Typically, addition of a solution of AgOAc in pyridine to an excess of CH_2N_2 in diethyl ether at −5° gives a yellow-orange precipitate of disilverdiazomethane-pyridin, $Ag_2CN_2{\cdot}(py)$ (II), within several seconds. Reaction occurs quantitatively according to equation (1). At 25° *in vacuo*, (II) readily loses pyridine to give the crimson parent compound (I).†

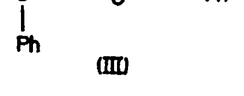
$$2AgOAc + 3CH_2N_2 \xrightarrow{py} Ag_2CN_2{\cdot}(py) + 2AcOMe + 2N_2 \quad (1)$$

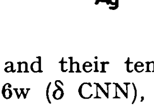
In the above preparation, AgOAc may be replaced by other pyridine-soluble silver(I) salts, although salts of strong acids, *e.g.* $AgNO_3$ or AgO_2CCF_3, react slowly to give a low yield of impure (II) unless more than 1 equiv. of a strong tertiary base such as triethylamine is also present. Complexes analogous to (II), from which removal of the ligand gives (I), are obtained if pyridine is replaced by another heterocyclic tertiary base such as quinoline or 3-methylpyridine. Reaction in the absence of a heterocyclic base gives (I) directly, but in low yield and heavily contaminated with polymethylene, AgCN, and Ag metal.

The i.r. spectrum of disilverdiazomethane broadly resembles that of its relatively stable isomer silver cyanamide, Ag_2NCN,[6] and of other isoelectronic silver compounds containing linear triatomic groups, *e.g.* silver ketenide, Ag_2C_2O.[7] Observed absorption bands in the 250—4000 cm^{-1} region and their tentative assignments are: 426w (ν Ag–C), 626w (δ CNN), 1128m (ν_s CNN), and 2000vs (ν_{as}CNN) cm^{-1}: in the spectrum of the pyridinate (II) these bands occur at 420, 637, 1184, and 1978 cm^{-1} respectively.

I(a)


I(b)



(III)

I(c)


Compound (I) and its complexes with tertiary heterocyclic bases may be stored in the dark in sealed tubes under dry argon at 25° for several months without decomposition, but all are light-sensitive and decompose in daylight under air within a few days giving silver cyanide as a major product. The complexes (I) and (II) are insoluble in all common solvents, including 0·880 ammonia, although slow decomposition occurs in protic solvents.

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† *Caution.* Both (I) and (II) are highly explosive and extremely shock sensitive in the dry state.

All the complexes are decomposed by aqueous KCN giving CH_2N_2. Reaction with glacial AcOH gives only AgOAc and MeOAc, indicating the liberation of diazomethane H_2CN_2 rather than isodiazomethane $\overset{-}{C}\equiv\overset{+}{N}\cdot NH_2$ which would yield *N*-acetyl-*N'*-formylhydrazine.[9] With monosubstituted alkynes, *e.g.* phenylacetylene, the corresponding alkynylsilver is obtained. Reaction of (I) with an excess of CS_2 at 25° gives silver thiocyanate and an as yet unidentified, ammonia-insoluble black residue of the same empirical formula, AgCNS, the i.r. spectrum of which shows only a single absorption in the 625—4000 cm^{-1} region at 1074 cm^{-1}. Treatment of (I) suspended in n-pentane with benzoyl chloride (2 mol.) gives AgCl and a compound of molecular formula $C_{15}H_{10}N_2O_2$ the i.r., n.m.r., and mass spectra of which indicate it to be 5-benzoyl-2-phenyl-1,3,4-oxadiazole (III).[8]

(I)a, (I)b, and (I)c represent three possible structures of (I): its synthesis directly from diazomethane, its reactions, and the presence of only a single absorption band in the 300—600 cm^{-1} region of its i.r. spectrum suggest a constitution as in I(a). Such a species could associate to form a polymeric structure in which the silver atoms are adjacent to both nitrogen and carbon (*cf.* Ag_2NCN[6] and Ag_2C_2O[7]) and react in the manner found. An analogy is provided by AgCN which also shows only a single i.r. absorption band in the 300—600 cm^{-1} region, assigned as νAg–C,[10] but which reacts with alkyl iodides to give mainly RNC and a smaller amount of RCN. The highly explosive nature and insolubility of (I) and (II) have hindered the determination of their structure by *X*-ray diffraction.

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