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BIALKYLS FROM DIALKYLMETALS
I. PHOTOCHEMISTRY AND MASS SPECTRA OF SOME (2-CYANOETHYL)- AND [2-(METHOXYCARBONYL)ETHYL]METALS*

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SUMMARY

We have studied the photolysis and the fragmentation in the mass spectrometer of bis(2-cyanoethyl)mercury, bis(2-cyanoethyl) selenide, bis(2-cyanoethyl) sulphide, dibutylbis(2-cyanoethyl)stannane, and bis[2-(methoxycarbonyl)ethyl] selenide. The mercury compound gave a high yield of adiponitrile on photolysis and in the mass spectrometer it gave the fragmentation pattern of adiponitrile, including the molecular ion, as part of the total fragmentation pattern. A low yield of bialkyl was also formed on photolysis of the bis[2-(methoxycarbonyl)ethyl] selenide but no peaks corresponding to bialkyl were observed in the mass spectrum. None of the other compounds yielded alkyl dimer.

A preliminary discussion of the results in terms of orbital symmetry is presented.

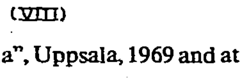
INTRODUCTION

We are presently investigating the dimerisation of acrylonitrile to adiponitrile via organometallic intermediates. As a preliminary step, we have investigated the photolysis and the mass spectrometry of some stable bis(2-cyanoethyl)metals, namely, bis(2-cyanoethyl)mercury (I), bis(2-cyanoethyl) selenide (II) and dibutylbis(2-cyanoethyl)stannane (IV). Bis[2-(methoxycarbonyl)ethyl] selenide (V) and a non-metal derivative, bis(2-cyanoethyl) sulfide (III) were also included in the investigation.

$X(CH_2CH_2CN)_2$
(I) $X=Hg$; (II) $X=Se$;
(III) $X=S$; (IV) $X=Sn(C_4H_9)_2$

$X(CH_2CH_2CO_2CH_3)_2$
(V) $X=Se$; (VI) $X=Hg$

$(SeCH_2CH_2CN)_2$
(VII)



(VIII)

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* Some of these findings were reported at "Organikerdagarna", Uppsala, 1969 and at the IVth International Conference on Organometallic Chemistry, Bristol 1969.

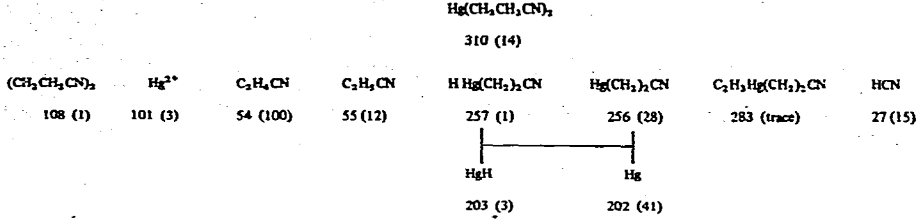
SCHEMES 1–5

PRINCIPAL PEAKS (m/e) IN THE MASS SPECTRA OF SOME DIALKYLMETALS AND RELATED COMPOUNDS

Relative abundances (in brackets) are calculated for monoisotopic spectra.

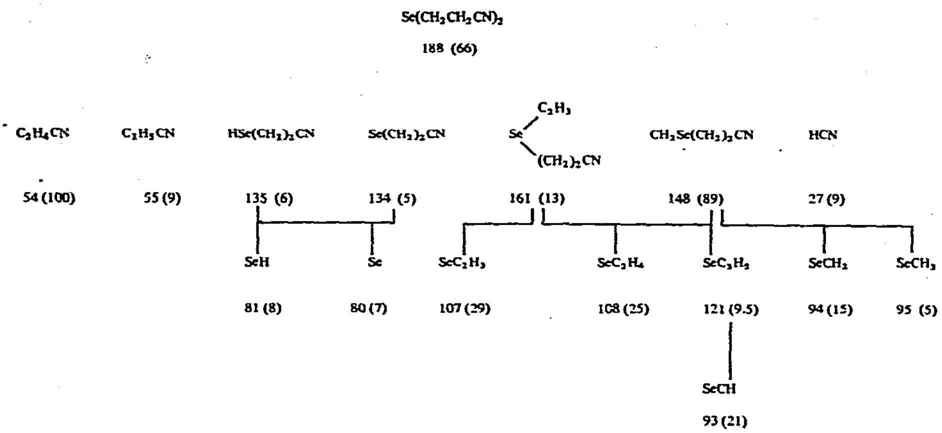
SCHEME 1

BIS(2-CYANOETHYL)MERCURY



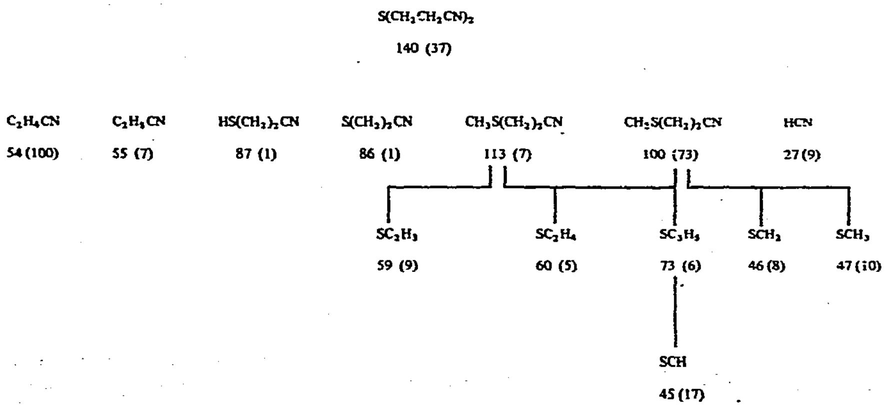
SCHEME 2

BIS(2-CYANOETHYL) SELENIDE



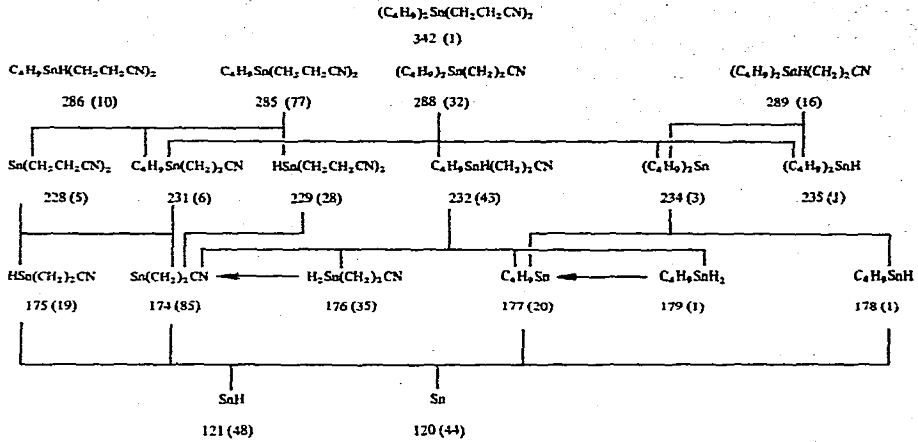
SCHEME 3

BIS(2-CYANOETHYL) SULFIDE



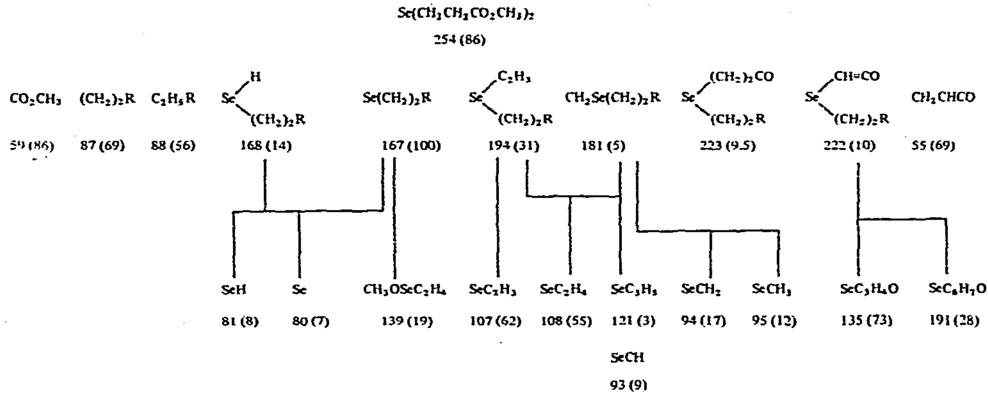
SCHEME 4

DIBUTYLBIS(2-CYANOETHYL)STANNANE



SCHEME 5

BIS[2-(METHOXYCARBONYL)ETHYL] SELENIDE ($R=CO_2CH_3$)



RESULTS

Photolysis

Photolysis of dialkyl- and diarylmercurials generally generates "free" alkyl and aryl radicals, the combination of which is only a minor reaction in solution (for a review, see ref. 1). High yields of alkyl dimers have been obtained only from dibenzylmercury[2] and bis[2-(methoxycarbonyl)ethyl]mercury (VI)[3]. Bis(2-cyanoethyl)mercury (I), which might be expected to behave similarly to the ester (VI), was indeed found to give a high yield of adiponitrile on photolysis. The photoinduced decomposition of dibenzylmercury may partly be concerted and partly give benzyl radicals which are sufficiently stable to couple to give dibenzyl rather than to abstract hydrogen from the solvent[4]. Since there is no evidence for such stability for the $\cdot CH_2CH_2CN$ radical, it is probable that the adiponitrile is formed from the compound (I) in a concerted reaction (*cf.* ref. 5). The decomposition of bis[2-(methoxycarbonyl)ethyl]-mercury (VI) may also be concerted.

The photolysis of bis(2-cyanoethyl) selenide (II) and bis[2-(methoxycarbonyl)-ethyl]selenide (V) gave a complex mixture of products. Bialkyl was formed only from the ester (V). In addition, the photolyses were strongly solvent dependent. It is interesting that the photolysis of diindolyl selenide gives biindolyl in a fairly clean reaction[6].

In methanol solution, bis(2-cyanoethyl) selenide (II) gave elemental selenium (64%) and traces of hydrogen selenide and acrylonitrile. In tetrahydrofuran solution, less selenium (23%) was obtained. The major product was bis(2-cyanoethyl) diselenide [(VII), 66%). A small amount of the tetrahydrofuran adduct (VIII) was also isolated and traces of hydrogen selenide and acrylonitrile were detected.

Photolysis of bis[2-(methoxycarbonyl)ethyl] selenide (V) in methanol solution gave a result similar to those for the nitrile (II) except that a trace of dimethyl adipate (1%) was formed. In tetrahydrofuran solution, substantial amounts of dimethyl adipate (10%) were obtained together with an essentially quantitative yield of selenium. Traces of hydrogen selenide and methyl acrylate were detected.

A possible reason for the low yield of bialkyl on photolysis of the selenides (II) and (V) would be that free radicals are formed. This is clearly shown by the formation of the diselenide (VII) and the tetrahydrofuran adduct (VIII) from bis(2-cyanoethyl)-selenide (II). The ease of such fission is demonstrated by the fact that photolysis of dimethyltellurium yields CH_3 and CH_3Te radicals in addition to triplet tellurium atoms[7].

In the photolysis of bis[2-(methoxycarbonyl)ethyl] selenide, no products corresponding to (VII) and (VIII) are formed. This could imply that dimethyl adipate is formed by concerted decomposition of (V). Another possibility, which cannot at present be rejected, is that the $^{\cdot}CH_2CH_2CO_2CH_3$ radicals are sufficiently stable to couple rather than to abstract hydrogen atoms from the solvent. However, the absence of bis[2-(methoxycarbonyl)ethyl] diselenide seems to be inconsistent with the cleavage of (V) into radicals.

Although the evidence is not conclusive, the major photo reaction of bis-[2-(methoxycarbonyl)ethyl] selenide (V) may be a retro-Michael addition to give hydrogen selenide and methyl acrylate, which are subsequently consumed in secondary reactions (*cf.* ref.[8]). In fact, the retro-Michael type of photoreaction is symmetry-allowed and should also compete with other reactions in the case of the selenonitrile (II) (see Fig. 8).

Bis(2-cyanoethyl) sulfide and dibutylbis(2-cyanoethyl)stannane were largely unaffected by irradiation.

Mass spectrometry

The fragmentation patterns suggested in Schemes 1 to 5 are all tentative. No metastable peaks were observed in the mass spectra. Concerted elimination in the mass spectrometer of neutral fragments like adiponitrile could therefore not be detected. The molecular ion of adiponitrile was observed, however, but with certainty only from bis(2-cyanoethyl)mercury (I).

Fragmentation in the mass spectrometer of compound (I) gave essentially the pattern characteristic of dialkylmercurials[9] (Fig. 1, Scheme 1). The major fragments

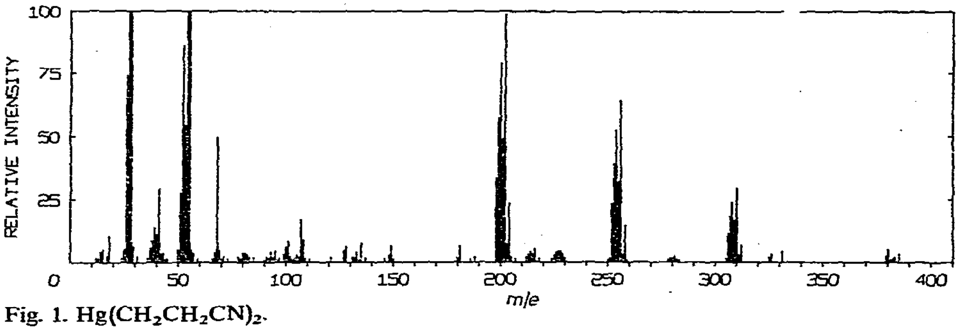


Fig. 1. $Hg(CH_2CH_2CN)_2$.

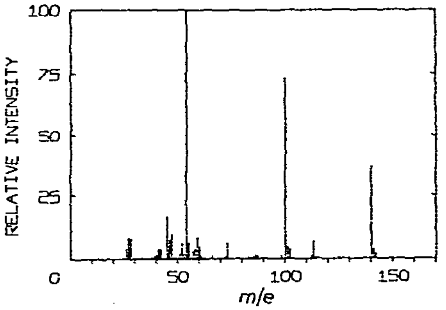


Fig. 2. $Se(CH_2CH_2CN)_2$.

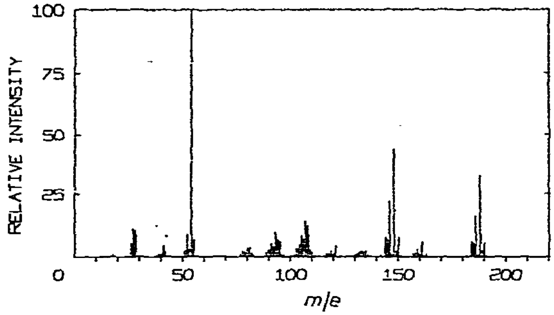


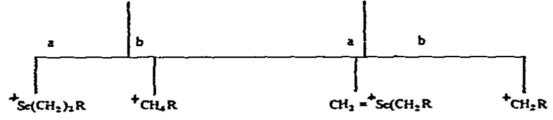
Fig. 3. $S(CH_2CH_2CN)_2$.

result from consecutive cleavage of the carbon–mercury bonds. The charge is preferentially retained by the alkyl fragments. As for the selenium (II) and sulfur (III) analogues, the abundance of the molecular ion is exceptionally high for a nitrile. The $(CH_2CH_2CN)_2^+$ ion is more abundant than the corresponding ions from dimethyl- and dibutylmercury[9].

Bis(2-cyanoethyl) selenide (II) and the corresponding sulfide (III) are fragmented essentially as simple dialkyl sulfides[10] (Figs. 2, 3, Schemes 2, 3). The $CH_2CH_2CN^+$ and $CH_2{=}XCH_2CH_2CN^+$ ions (X = Se, S) are formed as major fragments owing to approximately equal efficiency in the cleavage of the C–X (X = Se, S) and the C–C (α-cleavage) bonds (Schemes 2, 6). An unexpected feature is the low abundance

SCHEME 6

FRAGMENTATION OF $Se(CH_2CH_2R)_2$ (R = CN or CO_2CH_3. The intensities are expressed as % of Σ 40^{29}).



	$^+Se(CH_2)_2R$	$^+CH_4R$	$CH_2={}^+Se(CH_2R$	$^+CH_2R$
R = CN	1.1	23.0	20.5	< 0.6
R = CO_2CH_3	11.6	8.0	0.55	0.1

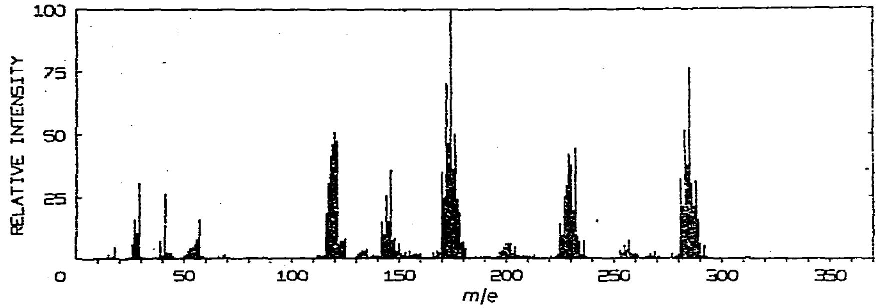


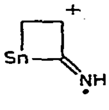
Fig. 4. $(C_4H_9)_2Sn(CH_2CH_2CN)_2$.

of the $XCH_2CH_2CN^+$ ions. A reasonable explanation would be that the $CH_2CH_2CN^+$ ion is far more stable than an ordinary alkyl carbonium ion.

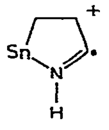
Bis[2-(methoxycarbonyl)ethyl] selenide (V) is fragmented essentially as the corresponding acid[11] (Fig. 5, Scheme 5). An interesting difference between the spectra of the ester (V) and the nitrile (II) is the virtual absence of α-cleavage in the ester. We tentatively suggest that cleavage of the ester (V) according to path 1, Scheme 6, becomes very efficient relative to path 2 (α-cleavage) due to unusual stability of *both* the $CH_2CH_2CO_2CH_3^+$ ion and the $^{\cdot}CH_2CH_2CO_2CH_3$ radical, which is expelled as neutral fragment in path 1. The only way in which the $^{\cdot}CH_2CH_2CO_2CH_3$ radical can achieve high stability appears to be through interaction between the radical centre and the ester group. Calculations indicate that a double bond should stabilize a radical in homoallylic position[12a].According to experimental evidence, such interaction must be small when carbon–carbon double bonds are involved[12b]. However, the carbon–oxygen double bond should be a better electron acceptor, possibly sufficiently good to stabilize from the homoallylic position.

The mass spectral fragmentation of dibutylbis(2-cyanoethyl)stannane (IV) did possibly yield a trace of $(CH_2CH_2CN)_2^+$ but the assignment is highly uncertain (Fig. 4, Scheme 4). In the mass spectrum of diethyldiphenylstannane, which is qualitatively very similar to that of dibutylbis(2-cyanoethyl)stannane (IV), a metastable peak indicated the elimination of biphenyl as a neutral fragment[13]. Unfortunately, no corresponding elimination of adiponitrile was observed in the spectrum of (IV).

Practically all charged fragments from the stannane (IV), as from other tin compounds[13], contained tin. As might be expected, the tin atom in these fragments preferentially attains the formal oxidation states IV and II. The molecular ion, formally tin(V), and the tin(III) fragments have low relative abundance. The unexpectedly high stability of the tin(V) fragments $C_4H_9Sn(H)(CH_2CH_2CN)_2^+$ and $(C_4H_9)_2Sn(H)CH_2CH_2CN^+$ may be due to the cyano group acting as an electron donating ligand, an effect precluded in the parent ion for steric reasons. The high intensity of the peak corresponding to the tin(II) fragment $SnCH_2CN^+$ again could



(IX)



(X)

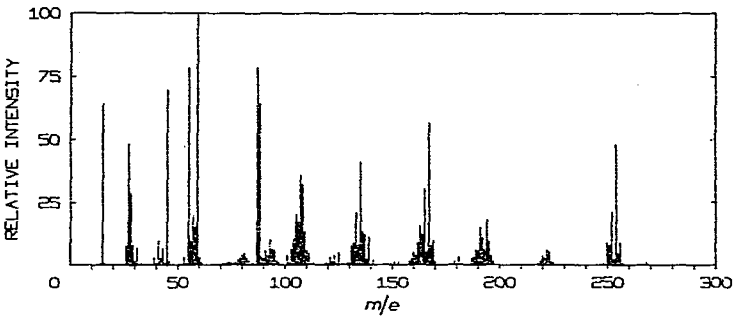


Fig. 5. $Se(CH_2CH_2CO_2CH_3)_2$.

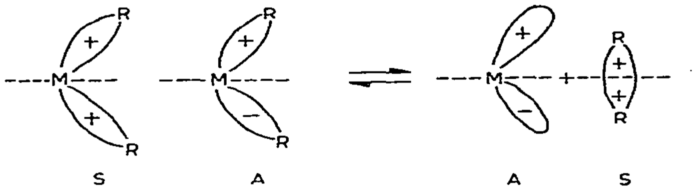


Fig. 6. Orbital symmetries for allowed formation of bialkyl and the reverse reaction. The dotted line denotes

indicate a stabilizing effect of the cyano group. It is even possible that the stability of tin(IV) and tin(II) fragments is partly due to the formation of cyclic ions, *e.g.* (IX) or (X).

Finally, it is interesting to note that the butyl radical is expelled in slight preference over the $^{\cdot}CH_2CH_2CN$ radical, indicating that homoallylic stabilization is indeed negligible in this radical.

DISCUSSION

Photolysis of bis(2-cyanoethyl)mercury (I) appears to yield adiponitrile in a concerted reaction. This may be rationalised reasonably well by using simple symmetry considerations according to Woodward and Hoffmann[14]. However, the application of orbital symmetry is complicated and gives inconclusive results (*cf.* ref. 15). According to the simplest theoretical model, concerted decomposition of a dialkyl metal into metal atom and alkyl dimer requires that the highest occupied orbital of the metal is antisymmetric after the reaction (Fig. 6). Evidently, both thermal and photochemical decompositions can be concerted.

For dialkylmercurials thermal reaction should be disallowed, since ground state mercury with the symmetric ^1S $(6s^2)$ configuration should be formed. Photo-induced decomposition, which would yield mercury in the antisymmetric ^1P $(6s^1, 6p^1)$ state, should be allowed. In spite of this the photoreactions are generally non-concerted also in the case of dialkylmercurials[1].

For dialkyl selenides (and sulfides) the situation is somewhat more complex. The $s \rightarrow p$ excited state (^1P) is probably not available energetically* but there are

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* *Cf.* oxygen, the ^1P $(s \rightarrow p)$ state of which is 542.2 kcal above the ground state[16].

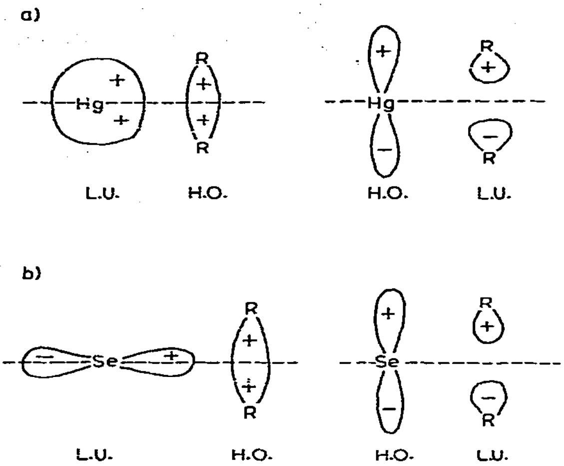

Fig. 7. Orbital interactions according to the perturbation model. The metal atoms are in their first excited states. a) Hg: ^1P b) Se: ^1D. R=alkyl, L.U.=lowest unoccupied, H.O.=highest occupied.

three states corresponding to the $4s^2 4p^4$ configuration. The ground state is a triplet (^3P), the first excited singlet state (^1D) is 27.4 kcal above the ground state and the second excited state (^1S) is 64.1 kcal above the ground state[17]. Only if the selenium atom ends up in the antisymmetric ^1D state should concerted reactions be possible according to Fig. 6. In principle this could be achieved thermally or photochemically but in our limited experience radical reactions are involved in both methods of decomposition. An exception is the photochemical decomposition of bis[2-(methoxycarbonyl)ethyl] selenide (V), which appears to give bialkyl in a concerted reaction.

For reactions involving carbon–carbon and carbon–nitrogen bonds[18–20] "allowedness" has been estimated to be 10–20 kcal/mole. Although it is uncertain what "allowedness" means in terms of energy for organometallic compound, the large singlet–triplet splitting for selenium (27.4 kcal) and excited mercury (^1P–^3P, 41.9 kcal)[21] may generally preclude concerted reaction for energetic reasons. It is even possible that concerted decomposition only occurs in the presence of ligands which decrease the energy difference between the singlet and triplet states (*cf.* ref. 22).

A simple perturbation model[23,24] gives the same results as the simple "symmetry" model. For simplicity, the insertion of a metal atom in the central carbon–carbon bond of the alkyl dimer is considered instead of the reverse reaction. It is assumed, that "allowedness" depends on the symmetry in the interaction between the respective highest occupied (H.O.) and lowest unoccupied (L.U.) orbitals of the reactants (Fig. 7). The mutual interactions refer to mercury in the ^1P state or selenium in the ^1D state. Thus the insertion (and the reverse reaction) could be concerted in agreement with the results from the simpler model (Fig. 6). These models seem to be applicable to bis(2-cyanoethyl)mercury and bis[2-(methoxycarbonyl)ethyl]mercury but not to the corresponding selenium compounds. This problem is further discussed in a separate paper[5].

From symmetry point of view, the decomposition of an alkylmetal into excited metal hydride and ground state alkene (or *vice versa*) should be concerted (Fig. 8). In fact, a major photo reaction of bis[2-(methoxycarbonyl)ethyl] selenide (V) and the

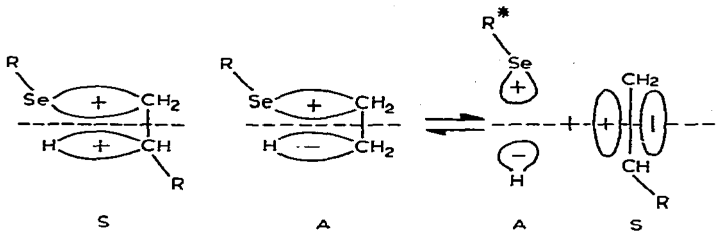

Fig. 8. Orbital symmetries for allowed elimination of monohydrogen selenide from a dialkyl selenide.

corresponding nitrile (II) appears to be the elimination of hydrogen selenide. This type of decomposition is also the major photoreaction of ethyllithium[25].

The photochemical decomposition of *e.g.* bis[2-(methoxycarbonyl)ethyl] selenide shows that solvent can strongly influence the course of a photoreaction. Mass spectrometry seemed to offer a rapid, solvent independent way to determine if a desired concerted photochemical reaction was possible.

However, electron impact in the mass spectrometer presumably excites each compound to several different excited states. Different symmetry and, presumably, different fragmentation patterns will apply to each of these states (for a discussion, see ref. 30). Furthermore, the simple Woodward–Hoffmann rules are difficult to apply to odd-electron systems (*cf.* ref. 31). Theoretical correlation between mass spectrometry and photochemistry should therefore be done with caution but as more experimental data are gathered such correlations should become useful. It is reassuring that bis(2-cyanoethyl)mercury which appears to decompose to adiponitrile in a concerted manner on photolysis, is also decomposed to adiponitrile in the mass spectrometer.

EXPERIMENTAL

The photochemical experiments were done in quartz tubes in a Rayonet Photochemical Reactor at 2537 Å. Mass spectra were run on a LKB mass spectrometer at 70 eV. NMR spectra were recorded with a Varian A60A spectrometer. Chemical shifts were determined in $CDCl_3$ and are expressed as δ-values relative to TMS as internal standard. The analyses were done at Alab, Uppsala, Sweden.

Bis(2-cyanoethyl) selenide (II)

An excess of hydrogen selenide, generated from aluminium selenide and water was added at room temperature during 6 h to acrylonitrile (24 g) containing a small amount of sodium methoxide (0.050 g). Unreacted acrylonitrile was removed and the residue distilled through a Vigreux column. The fraction boiling at 140–170°/0.5 mm (7.3 g) was essentially pure selenonitrile (II). Recrystallisation from benzene/ether gave the pure bis(2-cyanoethyl) selenide (II), m.p. 50–52° (lit 53°)[26]. (Found: C, 38.5; H, 4.4. $C_6H_8N_2Se$ calcd.: C, 38.5; H, 4.3.) IR (cm^{-1}) 2220 (CN)· NMR 2.85 (s).

Bis[2-(methoxycarbonyl)ethyl] selenide (V)

This compound was synthesized in an analogous manner to the nitrile (II). Fractional distillation gave bis[2-(methoxycarbonyl)ethyl] selenide (V), b.p. 96–102°/0.2 mm. (Found: C, 37.2; H, 5.5. $C_8H_{14}O_4Se$ calcd.: C, 37.9; H, 5.6.) IR 1730

(CO). NMR 2.73 [s, slightly broadened, 8 H, Se–$(CH_2)_2CO_2$–], 3.64 (s, 6 H, –CO_2-CH_3).

Dibutylbis(2-cyanoethyl)stannane (IV)

IV was prepared in the same way as the corresponding diethyl compound[27]. Dibutylbis(2-cyanoethyl)stannane, b.p. 175–183°/0.03 mm was obtained in 74% yield. (Found: C, 49.1; H, 7.8. $C_{14}H_{26}N_2Sn$ calcd.: C, 49.3; H, 7.7.) IR 2220 (CN). NMR 2.56 (t, 4 H, J 8 Hz, –CH_2CN), 1.20 (r, 4 H, J 8 Hz, Sn–CH_2–), superimposed on multiplet at 0.8–1.6 (18 H, C_4H_9).

Photolyses

Bis(2-cyanoethyl)mercury (I)

Bis(2-cyanoethyl)mercury[28] (0.5 g) in methanol (4 ml) was irradiated for 20 h. Adiponitrile (90% by GLC) and mercury (0.33 g, 100%) was formed. No other products were detected (GLC).

Bis(2-cyanoethyl) selenide (II)

(*a*). Bis(2-cyanoethyl) selenide (1.0 g) in methanol (60 ml) was irradiated for 40 h. Selenium (0.273 g, 63%) was precipitated. No adiponitrile was formed (GLC) and no organic compounds could be isolated.

(*b*). The selenonitrile (II) (1.50 g) in tetrahydrofuran (10 ml) was irradiated for 96 h. Selenium (0.080 g, 23%) was isolated. The solvent was removed from the reaction mixture and the residue was chromatographed on silica (eluant 20% in ether in light petroleum). Considerable amounts of starting material were recovered (0.70 g, 47%). The major product was bis(2-cyanoethyl) diselenide (VII) (0.26 g, 66% based on reacted starting material). Mass spectrum molecular ion at $m/e = 268$, IR 2250 (CN), NMR 2.95 (m; $SeCH_2CH_2CN$).

A small amount of another product, probably 2-[2-(cyanoethyl)seleno]-tetrahydrofuran (VIII) was also isolated (0.05 g, 6%). IR 2250 (CN), 1245 (–C–O–), NMR 2.08 (m, 4 H, H_3 and H_4), 2.83 (s, 4 H, $SeCH_2CH_2CN$), 3.92 (t, 2 H, H_5), 5.86 (m, 1 H, H_2). No adiponitrile was formed.

Bis[2-(methoxycarbonyl)ethyl] selenide (V)

(*a*). Bis[2-(methoxycarbonyl)ethyl] selenide (1.4 g) in methanol (10 ml) was irradiated for 90 h. Selenium (0.24 g, 54%) was precipitated. Small amounts of dimethyl adipate and methyl acrylate were formed (1% by GLC).

(*b*). Dimethyl 3,3′-selenodipropionate (1.4 g) in tetrahydrofuran (10 ml) was photolysed for 90 h. Selenium (0.43 g, 96%) was precipitated. Dimethyl adipate (10% by GLC) and a small amount of methyl acrylate were formed.

Bis(2-cyanomethyl) sulfide (III)

Bis(2-cyanomethyl) sulfide (1 g) in methanol (10 ml) was irradiated for 20 h. No sulfur was precipitated and no adiponitrile was formed.

Dibutylbis(2-cyanomethyl)stannane (IV)

Dibutylbis(2-cyanoethyl)stannane was essentially unchanged after irradiation for 20 h in either methanol or tetrahydrofuran.

ACKNOWLEDGEMENTS

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