

## $\sigma$ -ANIONIC COMPLEXES OF 1,3,5-TRINITROBENZENE WITH $R_3E$ GROUPS (E = Si, Ge, Sn; R = Me, Et, Ph) AND THE ROUTES OF THEIR TRANSFORMATIONS

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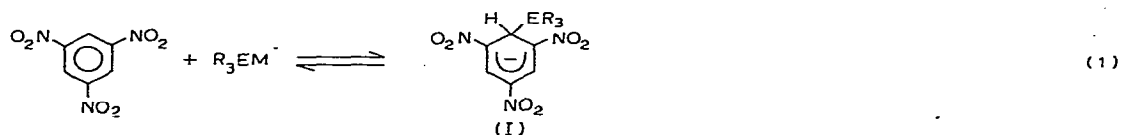
### Summary

Anionic  $\sigma$ -complexes,  $[\text{TNB} \cdot \text{ER}_3]^- \text{M}^+$ , were obtained by the reaction of 1,3,5-trinitrobenzene (TNB) with  $R_3\text{EM}$  (E = Si, Ge, Sn; R = Me, Et, Ph; M = Li, K). Their reactions with CH, NH and OH acids,  $\text{CBr}_4$  and *N*-bromosuccinimide were studied. The mechanism of these transformations was proposed. It was found that in the reaction of  $\text{Me}_3\text{SnM}$  with 2,4,6-trinitroanisole the latter acts as an alkylating agent, it also exhibits this property towards the other nucleophiles.  $\sigma$ -Complexes  $[\text{TNB} \cdot \text{ER}_3]^- \text{M}^+$ , where M = K, Cs, in solution undergo irreversible rearrangement into the metal 3,5-dinitrophenolates. The mechanism for such processes and reactions of  $R_3\text{SnM}$  with nitroaromatic compounds in general, are discussed.

### I. Introduction

Many anionic  $\sigma$ -complexes with different C–E bonds, where E = C, O, S and N [1], and recently obtained complexes, where E = P [2] and F [3], are described in the literature nowadays. We now wish to report the preparation and properties of new anionic  $\sigma$ -complexes of 1,3,5-trinitrobenzene (TNB) with  $R_3E^-$ , where E = Si, Ge and Sn, which are yielded by the reaction of TNB with  $R_3\text{EM}$  [4,5].

The complexes were prepared in THF at 0–5°C under nitrogen or in vacuum and isolated as dark brown, amorphous powders containing THF, which



(E = Si, Ge, Sn; M = Li, K; R = Me, Et, Ph)

decompose explosively on heating \* and shows poor solubility in organic

\* Spontaneous explosion of the  $\sigma$ -complex  $[\text{TNB} \cdot \text{SnMe}_3]^- \text{K}^+$  was observed at room temperature.

solvents. All complexes have characteristic electronic and PMR spectra [5]. They are stable for one to two weeks under vacuum, but their stability decreases in the presence of air and especially in solution.

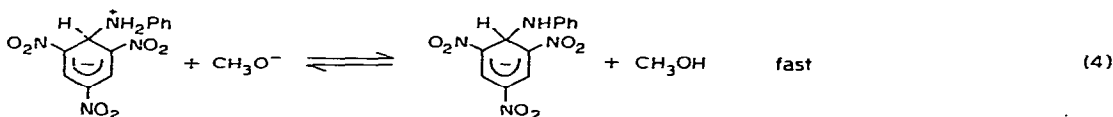
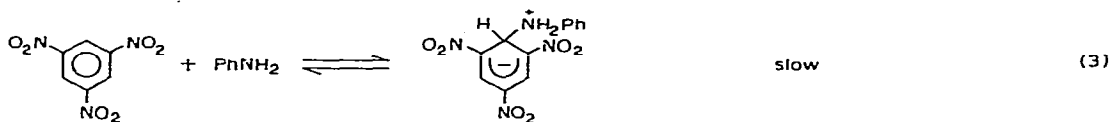
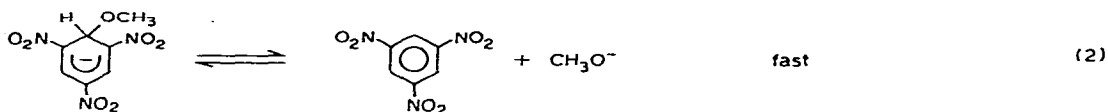
In the case of  $M = K$ , reaction 1 is complicated by the formation of potassium 3,5-dinitrophenolate (whose mechanism of formation is shown in Scheme 1). In all reactions a paramagnetic mixture ( $10^{-2}$ – $10^{-1}$  mol %) and an unidentified insoluble substance (10–15%) were found. The presence of a paramagnetic mixture in  $\sigma$ -complexes makes the PMR study difficult because of the width of signals, whose intensity is often high enough to mask the PMR spectrum. ESR spectra of the  $\sigma$ -complexes in solution indicate the presence of a mixture rather than an individual compound. Only in several cases could we obtain the spectra of individual compounds and their hyperfine structures agree with the formation of an anion-radical of a  $\sigma$ -complex, i.e. a dianion-radical.

The prepared  $\sigma$ -complexes may be made to undergo some interesting transformations, which may be specific for all  $\sigma$ -complexes and which are the reason for their instability in solution.

## II. Results and discussions

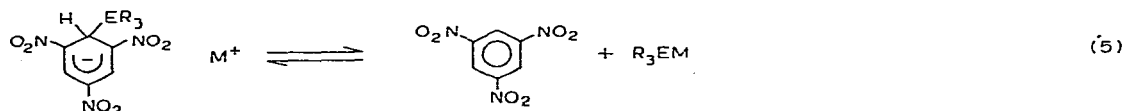
### 1. The transcomplexing reaction

It is known that anionic  $\sigma$ -complexes of TNB with hydroxy and methoxy groups are transformed into acetic  $\sigma$ -complexes when dissolved in acetone [6,7]. We may call such a reaction "transsolvation" or "transcomplexing". Further examples of such reactions are the formation of hydroxy complexes from the complexes of TNB with DMF or DMSO in water [7], or trichloromethyl or anilide complexes from methoxy complexes of TNB in their reaction with  $\text{CHCl}_3$  [8] or aniline [9] respectively. The mechanism of these interesting transformations apart from the last case has not been studied so far. Earlier it was supposed that the mechanism of these reactions was similar to the  $S_N2$  mechanism of substitution at the saturated carbon atom [10]. However, in 1977, Buncel studying the reaction of  $[\text{TNB} \cdot \text{OCH}_3]^-$  with  $\text{PhNH}_2$ , proposed the dissociative mechanism, in which the slow step is the formation of anilide zwitter-ion [9,11].



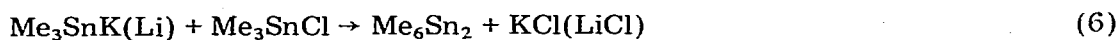
This mechanism is, probably, operative only for the reaction with non-charged bases having lone pair electrons which are necessary for nucleophilic attack.

Studying the complexes of TNB with organoelement anions of Group IVB  $[\text{TNB} \cdot \text{ER}_3]^- \text{M}^+$  ( $\text{E} = \text{Si, Ge, Sn}$ ;  $\text{M} = \text{Li, K}$ ) we tried to oxidise them with the following organic and inorganic oxidants, whilst preserving the C—E bond: quinone, chloranil, tetracyanoquinodimethane, *N*-bromosuccinimide (NBS),  $\text{Ph}_3\text{CBF}_4$ ,  $\text{I}_2$ ,  $\text{CuBr}_2$ ,  $\text{Tl}(\text{OAc})_3$  and  $\text{Me}_3\text{SiCl}$ . Only TNB, however, was obtained in all cases even under the action of such strong hydride-ion acceptors as NBS,  $\text{Ph}_3\text{CBF}_4$  or  $\text{Me}_3\text{SiCl}$ . It is obvious that these complexes dissociate strongly in solution and the oxidants react with anions  $\text{R}_3\text{E}^-$ , which are in equilibrium with the complexes [12].



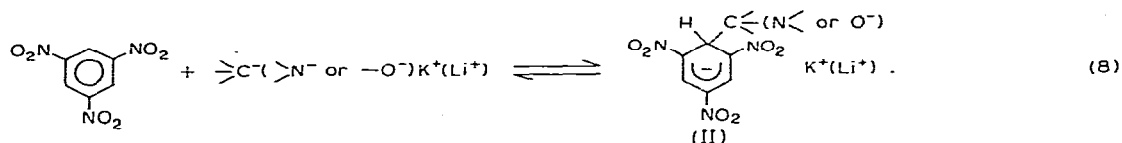
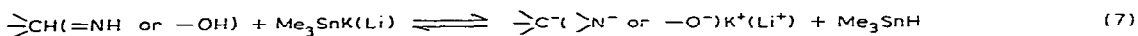
It is impossible to determine the equilibrium constants of  $\sigma$ -complexes  $[\text{TNB} \cdot \text{ER}_3]^- \text{M}^+$  (I) since the values of extinction coefficients of these complexes are unknown. Some data show that the dissociation is rather strong; for example, the broadening of the signals in PMR spectra of  $\sigma$ -complexes; and absence of  $J(^{117,119}\text{Sn}-\text{CH}_3)$  for the TNB complex with  $\text{R}_3\text{E} = \text{Me}_3\text{Sn}$  and  $\text{M} = \text{Li}$  (Ia), which appears, however, on addition of  $\text{LiClO}_4$ , i.e. the salt with the same cation.

The conclusive evidence of equilibrium 5 in solution of  $\sigma$ -complex Ia ( $\text{M} = \text{Li, K}$ ) is supplied by its reaction with  $\text{Me}_3\text{SnCl}$ . Addition of a stoichiometric quantity of  $\text{Me}_3\text{SnCl}$  to the solution of complex Ia in  $\text{DMSO}-d_6$  leads to a fast reaction (2–5 min) that results in the disappearance of the signals of initial  $\sigma$ -complexes Ia ( $\delta$ ) (ppm) 8.20s, 6.13s, 0.22s, (2/1/9) for  $\text{M} = \text{Li}$ , 8.30s, 6.20s, 0.33s (2/1/9) for  $\text{M} = \text{K}$  in the PMR spectrum and the appearance of signals of TNB and  $\text{Me}_6\text{Sn}_2$  with 1/6 ratio in integral intensity.



The same reaction in THF proceeds more slowly (3–4 days) which is probably due to the low solubility or dissociation of complex Ia in this solvent.  $\sigma$ -Complexes Ia ( $\text{M} = \text{Li, K}$ ) react with  $\text{Me}_3\text{SiCl}$  in the same way.

Anionic  $\sigma$ -complexes of TNB with  $\text{R}_3\text{E}$  groups, like the  $\text{OH}^-$  and  $\text{MeO}^-$   $\sigma$ -complexes of TNB mentioned above [6,7], when dissolved in acetone give the acetonic  $\sigma$ -complex [5]. The mechanism of such reactions of “transcomplexing” may be described in the following way, equilibrium 5 being taken into account.



The  $\text{Me}_3\text{Sn}^-$  anion formed during dissociation reacts with CH acids (or NH, OH acids) giving the anion, which reacts with TNB to form the new anionic  $\sigma$ -complex II.

It is obvious that the possibility of a "transcomplexing" reaction in the general case depends on the positions of equilibria 5, 7, 8, and for a given  $\sigma$ -complex I is determined by the stages 7 and 8. The likelihood of reaction in the first stage depends on the difference of  $pK_a$  values of acid and  $\text{Me}_3\text{SnH}$ . Since the  $pK_a$  of  $\text{Me}_3\text{SnH}$  is 23.5–23.8 in DMF or in DMSO [13], it is clear, that reaction 7 will proceed only with acids with  $pK_a \leq 23$ . CH acids with  $pK_a$  about or more than 23, for example  $(\text{C}_6\text{F}_5)_2\text{CH}_2$  ( $pK_a = 21.2$  in cyclo- $\text{C}_6\text{H}_{11}\text{NH}_2$  [14]) and  $\text{C}_6\text{F}_5\text{H}$  ( $pK_a$  23 in DMF [15]) do not react with complex Ia in DMSO. In the case of  $\text{C}_6\text{F}_5\text{H}$ , the reaction does not proceed in even a mixture of  $\text{C}_6\text{F}_5\text{H}/\text{DMSO}$  3/1. Also complex Ia does not react with DMSO ( $pK_a$  33.3). The  $pK_a$  value of acetone (20 in water [16]), probably characterises the upper limit of  $pK_a$  values for which the reaction is possible. But the reaction proceeds easily with  $\text{CH}(\text{NH}, \text{OH})$  acids with  $pK_a$  less than 20. For example, complex Ia reacts with  $\text{CHCl}_3$ ,  $\text{C}_6\text{F}_5\text{CH}_2\text{COC}_6\text{F}_5$ ,  $\text{CHBr}_3$ , succinimide ( $pK_a$  15 in DMF [15], 11.7 in DME [17], 9 in DMF [15], 10.5 in the gas phase [18], respectively). New complexes are formed with the following spectral characteristics:  $\delta$  (ppm) 8.61d; 6.35t,  $J$  1.5 Hz, (2/1),  $\lambda_{\text{max}_1}$  432 nm,  $\lambda_{\text{max}_2}$  492 nm for  $\text{CHCl}_3$  [8];  $\delta$  (ppm) 8.00s, 6.43s, (2/1),  $\lambda_{\text{max}_1}$  460 nm,  $\lambda_{\text{max}_2}$  560 nm for  $\text{C}_6\text{F}_5\text{CH}_2\text{COC}_6\text{F}_5$ ;  $\delta$  (ppm) 8.50d, 6.33t,  $J$  1.5 Hz, (2/1), for  $\text{CHBr}_3$  [8];  $\delta$  (ppm) 8.40s, 6.83s, (2/1);  $\lambda_{\text{max}_1}$  440 nm,  $\lambda_{\text{max}_2}$  530 nm for succinimide. The spectral characteristics of the last complex coincide with those for the complex obtained in the reaction of TNB with potassium succinimide. The rate of the reaction with  $\text{CHBr}_3$  or succinimide is much faster than that for the reaction with  $\text{CHCl}_3$ .

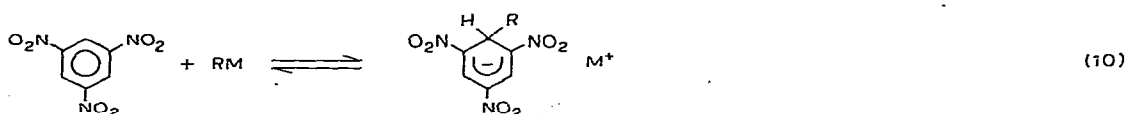
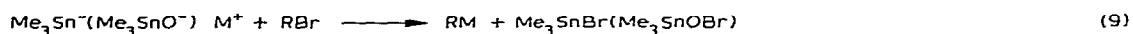
The rate of reaction 7 increases with decrease of the  $pK_a$  values of CH (or NH, OH) acids but, on the other hand, the stability of the conjugated anion increases and hence its reactivity decreases. It follows that the rate of its interaction with TNB (stage 8) will decrease. Thus, there should be a lower limit of  $pK_a$  for "transcomplexing". This limit is, probably in the range of 5–7 units. It is known that acetic acid ( $pK_a$  4.76) does not form the new complex but leads to decomposition of complex Ia ( $M = \text{Li}$ ), yet TNB is not formed. In this case we are dealing with the products of its reduction by  $\text{Me}_3\text{SnH}$ , with 3,5-dinitrophenol among them, as may be seen from the PMR spectrum. The blank experiment showed that such a reaction ( $\text{TNB} + \text{Bu}_3\text{SnH}$  in THF) is very rapid. The rate of reduction of TNB by  $\text{Me}_3\text{SnH}$  is probably much faster in this case than in those of interaction of TNB with acetate anion or  $\text{Me}_3\text{SnH}$  with AcOH. To confirm this, we carried out the reaction of TNB with AcONa in DMSO and showed that the reaction proceeded very slowly and that a  $\sigma$ -complex with an AcO group was formed with a small yield (10% from PMR-spectral data); its spectral characteristics are: PMR spectrum:  $\delta$  (ppm) 8.03d, 5.97t,  $J$  0.5 Hz, 1.70s, (2/1/3); electronic spectrum:  $\lambda_{\text{max}_1}$  436 nm,  $\lambda_{\text{max}_2}$  516 nm,  $\epsilon_1/\epsilon_2$  1.46. It should be noted that when there is rapid formation of new complexes, the values of complexing constants are high and we do not observe the reduction of TNB.

Only CH acids with  $pK_a < 5$  decompose  $\sigma$ -complexes. Thus, TNB is only formed in the reaction of  $\sigma$ -complex Ia with trinitromethane ( $pK_a$  0 in  $\text{H}_2\text{O}$  [16]) which is completely ionized in DMSO, judging the  $\lambda_{\text{max}}$  value (350 nm). The products of reduction of TNB by  $\text{Me}_3\text{SnH}$  are absent in this case since  $\text{Me}_3\text{SnH}$  reacts rapidly with  $\text{CH}(\text{NO}_2)_3$ , whose acidity is 5 orders stronger than

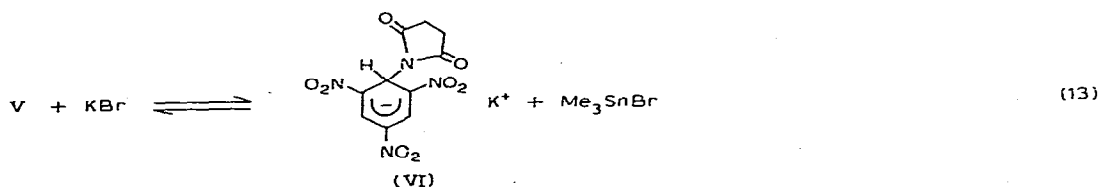
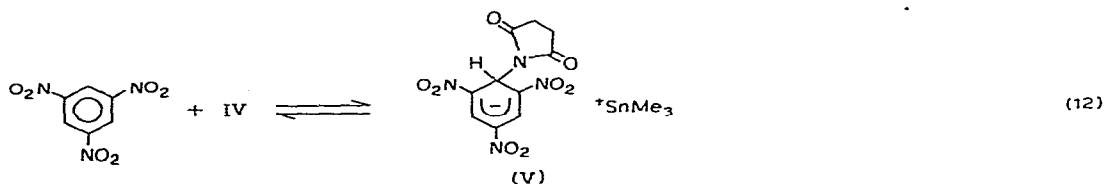
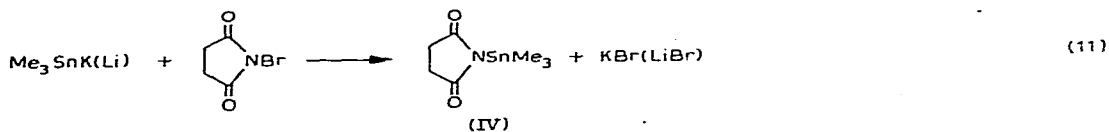
AcOH. The anions of such CH acids do not form anionic  $\sigma$ -complexes with TNB because of their high stability and low reactivity. Indeed, there are no changes in the PMR or UV spectra upon the addition of  $\text{KC}(\text{NO}_2)_3$  or  $\text{NaC}(\text{CN})_3$  ( $\text{p}K_a = -5.0$  in  $\text{H}_2\text{O}$  [16]) to a solution of TNB in DMSO.

We consider that this mechanism proposed for the interaction of anionic  $\sigma$ -complexes containing a C-E bond with "acid" compounds is valid for  $\sigma$ -complexes with other bonds. We showed, for example, that the  $\sigma$ -complex with an  $\text{OSnMe}_3$  group (III) reacted not only with  $\text{Me}_3\text{SiCl}$  to form TNB in quantitative yield but was also transformed to acetic, hydroxylic and succinimide  $\sigma$ -complexes.

It seems promising to use the compounds which may provide a source of positive halogen, for example,  $\text{CBr}_4$  or NBS, as the trap for  $\text{Me}_3\text{Sn}^-$  and  $\text{Me}_3\text{SnO}^-$  anions in the solutions of complexes Ia and III.



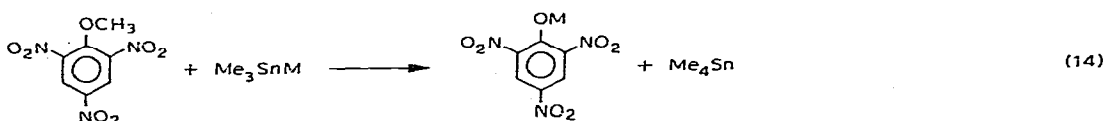
In fact, the signals of complexes Ia and III in PMR and UV spectra rapidly become the signals of tribromomethyl and succinimide  $\sigma$ -complexes when  $\text{CBr}_4$  and NBS are added to the solutions of Ia and III in DMSO. In an excess of NBS the last complex is converted to TNB. The mechanism of these reactions may be more complex than is represented by reaction 9. In fact, the interaction between  $\text{Me}_3\text{SnK}$  and NBS in THF in vacuum, results in *N*-trimethyltin succinimide (IV), which may then react with TNB yielding  $\sigma$ -complex V. We have shown that complex IV reacts slowly with TNB with the formation of  $\sigma$ -complex V (10%) the yield of which may be increased by addition of  $\text{KBr}$ . This transformation may be depicted by eq. 11–13.



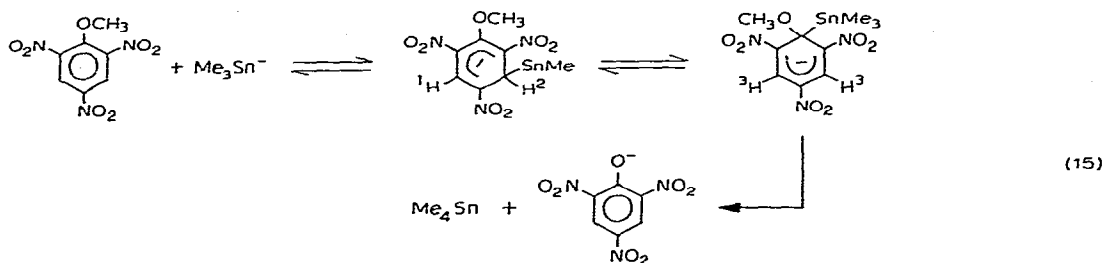
Reaction 11 has a probable free radical nature since  $\text{Me}_6\text{Sn}_2$  is one of the products of the reaction leading to the quantitative formation of  $\text{KBr}$  (98%). The true mechanism, naturally, depends on the ratio of rate constants for 9 and 11. It is quite possible that in the presence of TNB some part of complex VI is formed directly by reaction 9 and 10 in DMSO.

## 2. The reaction of $\text{Me}_3\text{SnM}$ ( $M = \text{Li}, \text{K}$ ) with 2,4,6-trinitroanisole

We have found another route of decomposition of anionic  $\sigma$ -complexes in the reaction of  $\text{Me}_3\text{SnM}$  with 2,4,6-trinitroanisole (TNA). It is known that 1,1  $\sigma$ -complexes of TNA are more stable than those of TNB [1,19]. On the other hand, their dissociation, in theory, can lead not only to the original compounds but also nucleophilic aromatic substitution of the  $\text{CH}_3\text{O}$  group may occur. We have studied the reaction of  $\text{Me}_3\text{SnM}$  ( $M = \text{Li}, \text{K}$ ) with TNA in THF and found that the corresponding picrate ( $\text{PiOM}$ ,  $M = \text{Li}$  or  $\text{K}$ ) and  $\text{Me}_4\text{Sn}$  are its products. Both of them were isolated and characterized by their PMR spectra.  $\text{PiOM}$ :  $\delta$  8.50 ppm in  $\text{DMSO}-d_6$ ,  $\text{Me}_4\text{Sn}$   $\delta$  0.06 ppm,  $J(^{117,119}\text{Sn}-\text{CH}_3)$  52 Hz in  $\text{CCl}_4$ , b.p.  $72^\circ\text{C}$ . An acyclic derivative from  $\text{PiOM}$  was obtained and characterized by its PMR spectrum ( $\delta$  8.88 and 4.18 ppm on  $\text{CDCl}_3$  with ratio of integral intensities 2/3) and m.p.  $120^\circ\text{C}$  (lit.  $120^\circ\text{C}$  [20]). Thus TNA reacts with  $\text{Me}_3\text{SnM}$  as the alkylating agent.



The reaction proceeds probably, via a  $\sigma$ -complex. It was registered as a 1,3  $\sigma$ -complex in the reaction of  $\text{Me}_3\text{SnLi}$  with TNA in the dipolar aprotic solvent HMPTA (where  $\sigma$ -complexes are known [19] to be much more stable). In the PMR spectrum there are signals  $\delta$  (ppm) 8.44, H(1), 6.10, H(2) (1/1); in the electronic spectrum  $\lambda_{\text{max}_1}$  424 nm,  $\lambda_{\text{max}_2}$  484 nm,  $\epsilon_1/\epsilon_2$  1.37. It then converts to the 1,1  $\sigma$ -complex (in the PMR spectrum signals 8.60 ppm, H(3); in the electron spectrum  $\lambda_{\text{max}_1}$  424 nm,  $\lambda_{\text{max}_2}$  480 nm,  $\epsilon_1/\epsilon_2$  1.75); the latter decomposes into picrate and  $\text{Me}_4\text{Sn}$ .



TNA also alkylates other nucleophiles such as  $\text{KI}$ ,  $\text{AcONa}$  and lithium succinimide giving  $\text{MeI}$ ,  $\text{AcOCH}_3$  and *N*-methylsuccinimide respectively, which were isolated and identified by their PMR spectra.

In the reaction with lithium succinimide in DMSO the formation of a very unstable  $\sigma$ -complex was found (electronic spectrum  $\lambda_{\text{max}_1}$  426 nm,  $\lambda_{\text{max}_2}$  504 nm,  $\epsilon_1/\epsilon_2$  1.67). The signals disappeared after 1 h and the band of picrate appeared ( $\lambda_{\text{max}}$  350 nm). However, only signals of picrate and *N*-methylsuccin-

nimide were found in the PMR-spectrum after the mixed solutions of reagents were prepared in DMSO- $d_6$ . In THF, a  $\sigma$ -complex could not be identified even in an electronic spectrum. A very unstable 1,3  $\sigma$ -complex is formed in the reaction of TNA with KCN (or Hg(CN) $_2$  + KI) \* in DMSO (PMR-spectrum signals  $\delta$  (ppm) 8.30 and 5.60, with ratio integral intensities 1/1). The complex decomposes rapidly to potassium picrate. It is possible that a  $\sigma$ -complex is formed in the reaction of TNA with KI and AcONa but cannot be identified due to its extreme lability.

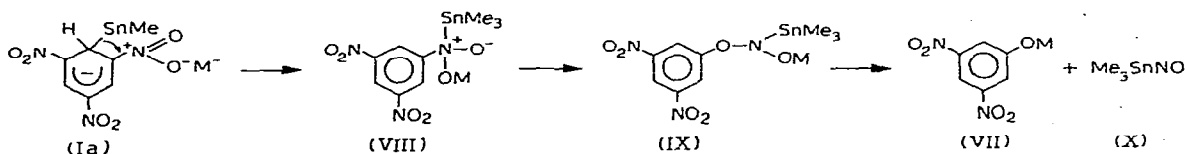
### 3. New transformations of anionic $\sigma$ -complexes of TNB with formation of 1,3-dinitrophenolate

It is known that anionic  $\sigma$ -complexes of TNB are rather unstable. Now we would like to discuss one of the possible reasons of such instability. We have shown that in the reaction of TNB with R $_3$ EK (but not with R $_3$ ELi) in THF, potassium 3,5-dinitrophenolate (VII) was formed together with the main product,  $\sigma$ -complex I [21]. The amount of VII depends on the reaction time; the shorter the time, the smaller the concentration of VII. The same situation was observed on dissolution of  $\sigma$ -complex I in DMSO; its concentration was decreasing gradually while the content of VII was increasing. In the PMR spectra of complex Ia (M = K) in DMSO- $d_6$ , intensities of signals at 7.40t and 7.20d ppm, and  $J$  2 Hz (the ratio of intensities 1/2), corresponding to VII, were increasing, and those of the  $\sigma$ -complex at 8.30 and 6.20 ppm were decreasing, while the sum of integral intensities remained unchanged.

The same occurred for the  $\sigma$ -complex Ia with a caesium cation as counter-ion. The solution of this complex was prepared directly in vacuum in a PMR tube, in order to exclude atmospheric oxygen. Only the signals of complex Ia (M = Cs), which broadened strongly because of the presence of paramagnetic impurities, were registered in the PMR-spectrum immediately after mixing of the reactants; but after 24 h they became narrow and the signals of VII (M = Cs) appeared (yield ~30%). After a week the content of complex Ia decreased by four times with the corresponding increase of VII and without the formation of any other products. On heating the solution, complex Ia decomposed completely to TNB and signals of VII shifted downfield, probably, owing to hydrolysis of VII by traces of water.

Since the reaction of one of the nitro groups occurs when complex Ia transforms to VII, one may suppose that two intramolecular rearrangements (Ia  $\rightarrow$  VIII and VIII  $\rightarrow$  IX) have taken place, with the ensuring fragmentation of IX into the products of the reaction (Scheme 1). There is some analogy for the rearrangement of VIII  $\rightarrow$  IX [22].

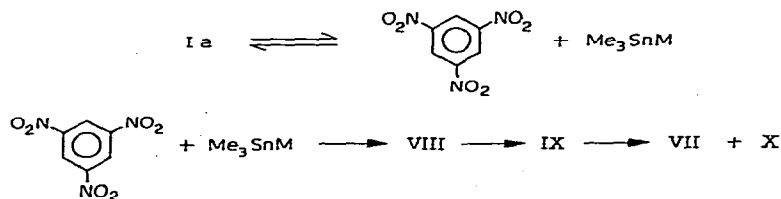
SCHEME 1



\* Including MeI.

We cannot, however, exclude the possibility of an intermolecular reaction for the formation of VIII, since we know that complex Ia dissociates strongly in solution and the behaviour of complexes is often determined by this fact.

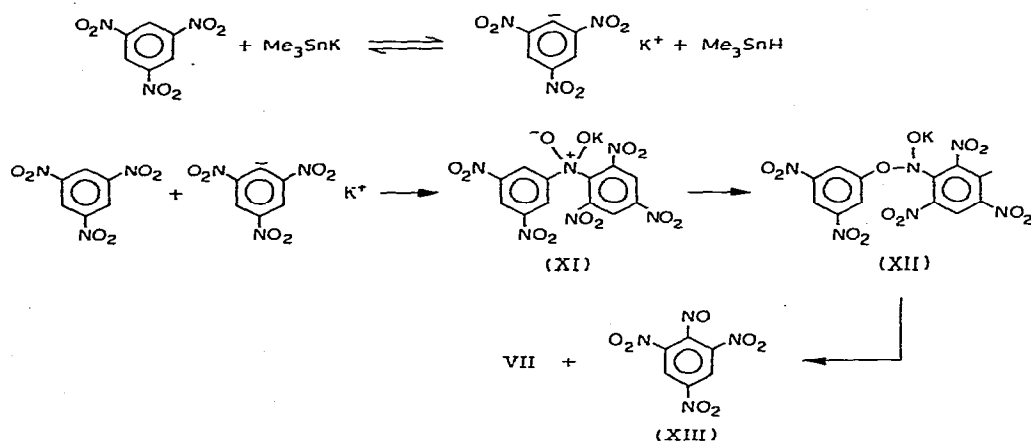
SCHEME 2



Both the schemes involve the formation of IX and its consecutive transformation.

The possibility of formation of VII as the result of reduction of a nitro group by the anion  $(\text{NO}_2)_3\text{C}_6\text{H}_2^-$ , which could be formed by deprotonation of TNB by the action of  $\text{Me}_3\text{Sn}^-$ , seems less probable.

SCHEME 3



The deprotonation of TNB is known to proceed very slowly even under the action of strong bases [23]. Besides, as we have mentioned above, the sum of integral intensities in the reaction  $\text{Ia} \rightarrow \text{VII}$  remained constant, which excluded the formation of other products, for example, XIII.

The data described testify to the fact that complex I is formed much faster than phenolate VII, but is irreversibly transformed to VII in solution. Thus, we have found a new type of transformation of anionic  $\sigma$ -complexes, probably connected with the existence of equilibria in solution and with the properties of the  $\text{R}_3\text{E}^-$  anion.

The most interesting thing in this reaction is the unusual dependence of the reaction on a counter-ion. The transformation of  $\sigma$ -complexes I to phenolate VII is observed only for K and Cs but not for Li salts. It is quite reasonable to explain this dependence by the states of the salts  $\text{Me}_3\text{SnM}$  (if Scheme 2 is



realised) or  $\sigma$ -complexes (if Scheme 1 is realised) in solution, since in the both cases Li derivatives must be the more dissociated.

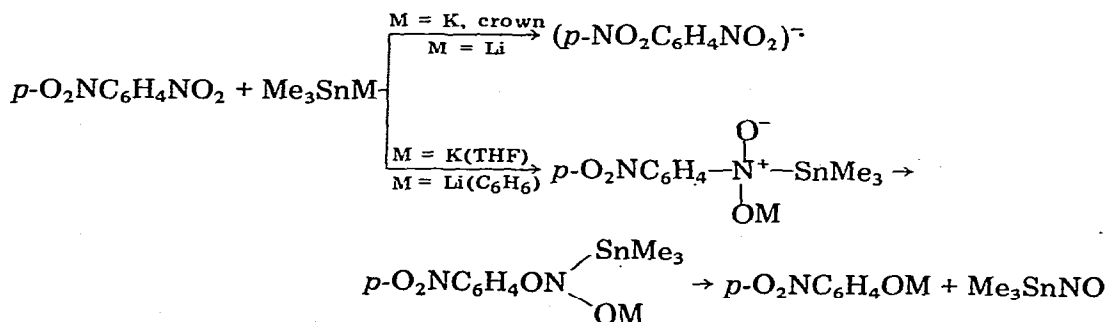
It is known that  $\text{Me}_3\text{SnM}$  exists in solution as a mixture of contact and solvent-separated ion pairs (or free ions) and that equilibrium shifts towards solvent-separated ion pairs or free ions in strongly solvating solvents such as DMSO, HMPTA and tetraglyme [24,25]. This shift may be considerable for Li compounds [25]. The absence of transformation of I to VII for Li  $\sigma$ -complexes, allows us to suppose that coordination of the alkali cation at the oxygen of a  $\text{NO}_2$  group of TNB is the important factor for such a reaction. It is known that coordination of the lithium cation at a carbonyl group is the necessary condition of addition of  $\text{RLi}$  to cyclohexanone [26].

We carried out the reaction of TNB with  $\text{Me}_3\text{SnK}$  in THF in the presence of an equimolecular concentration of dicyclohexyl-18-crown-6. It turned out that phenolate VII ( $\text{M} = \text{K}$ ) was not formed under these conditions, only the signals of  $\sigma$ -complex Ia being present in the PMR spectrum. Thus, the rearrangement does not proceed if coordination of the alkali metal with an oxygen atom of the  $\text{NO}_2$  group is hindered or impossible. One may expect that the rearrangement would be promoted by the addition of an inorganic lithium salt. In fact the addition of  $\text{LiClO}_4$  to a solution of complex Ia ( $\text{M} = \text{Li}$ ) in DMSO causes the appearance of signals of phenolate VII in the PMR spectrum, the intensity of which increases with time. The same result was obtained for the  $\sigma$ -complex I ( $\text{R}_3\text{E} = \text{Me}_3\text{Si}$ ,  $\text{M} = \text{Li}$ ) in the presence of  $\text{KBr}$ .

Considering the results obtained, one may expect that the transformation of complex I to VII would proceed more rapidly in nonpolar solvents. This process, however, cannot be studied in THF because of the poor solubility of  $\sigma$ -complexes in this solvent. Nevertheless, the decomposition of  $\sigma$ -complexes I in THF, judging by the PMR spectra, is more rapid in THF (several hours) than in DMSO (several day). This explains the presence of VII in  $\sigma$ -complexes I ( $\text{M} = \text{K}$ ,  $\text{Cs}$ ), obtained in THF solution. The absence of VII in  $\sigma$ -complex I ( $\text{M} = \text{Li}$ ) in THF, is, probably, due to its very low solubility leading to precipitation in the course of its formation.

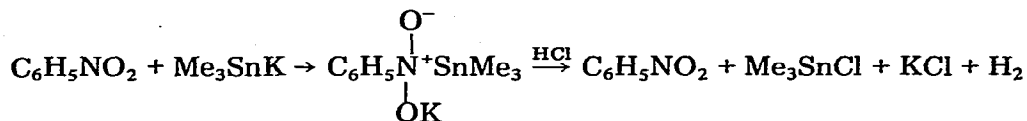
#### 4. Interaction of $\text{Me}_3\text{SnM}$ with *p*-dinitrobenzene and nitrobenzene. The influence of counter-ion and association

We found that the rules for the reaction of  $\text{R}_3\text{EM}$  with a nitro group present in TNB, hold also for the reactions with other nitroaromatic compounds. Thus  $\text{Me}_3\text{SnK}$  reacts with *p*-dinitrobenzene (DNB), yielding potassium *p*-nitrophenolate (70%), while  $\text{Me}_3\text{SnLi}$  reduces DNB into an anion-radical.



In the presence of 18-crown-6, the reaction of DNB with  $\text{Me}_3\text{SnK}$ , which forms the free anion  $\text{Me}_3\text{Sn}^-$ , gives also an anion-radical of DNB (30–40%) and products of its decomposition. On the other hand, the use of benzene as solvent in the reaction of DNB with  $\text{Me}_3\text{SnLi}$ , where dissociation of the latter is suppressed, led to the formation of lithium *p*-nitrophenolate (20%).

$\text{Me}_3\text{SnK}$  can add even to the nitro group of nitrobenzene in THF, forming a solid compound which immediately decomposes in air. It is probable that the presence of an electron withdrawing group in the aromatic nucleus is necessary for further rearrangement. Nitrobenzene is regenerated quantitatively under the action of HCl.



## Experimental

NMR spectra were recorded on Varian T-60, XL-100-15 and JEOL C-60HL instruments with HMDS as internal standard. The electronic spectra were recorded on an Hitachi-124 spectrophotometer. ESR spectra were recorded on a Varian E-3 instrument. The calculation of the number of paramagnetic particles was made according to ref. 27.

Anionic  $\sigma$ -complexes  $[\text{TNB} \cdot \text{ER}_3]^- \text{M}^+$  and  $[\text{TNB} \cdot \text{OSnMe}_3]^- \text{Li}^+$  were described previously [5]. The TNB complex with  $\text{Me}_3\text{SnCs}$  was obtained in vacuum according to the procedure for the potassium derivative. The syntheses of  $\text{Me}_3\text{SnK}$  and its reactions were carried out in evacuated sealed glass apparatus.

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