

A STUDY OF REACTION OF AROMATIC POLYNITRO COMPOUNDS WITH TRIBUTYLSTANNYL HYDRIDE

Vladimír MACHÁČEK^a, Antonín LYČKA^b and Milan NÁDVRNÍK^c

^a Department of Organic Chemistry,

^c Department of General and Inorganic Chemistry,

Institute of Chemical Technology, 532 10 Pardubice and

^b Research Institute of Organic Syntheses, 532 18 Pardubice

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¹H, ¹³C, ¹⁵N, and ¹¹⁹Sn NMR spectra have been used to study composition and structure of reaction products from 1,3,5-trinitrobenzene, methyl 2,4,6-trinitrobenzoate, 1-dimethylamino-2,4,6-trinitrobenzene, 1-methoxy-2,4,6-trinitrobenzene, 1-chloro-2,4,6-trinitrobenzene, 2,4,6-trinitrotoluene, 3,5-dinitrobenzotrile and methyl 3,5-dinitrobenzoate with tributylstannyl hydride in the presence of tetramethylammonium bromide.

Addition of hydride ion to polynitroaromates produces compounds of the type of the Meisenheimer adducts with conjugated cyclohexadienide system. The hydride ions can be obtained from tetramethylammonium tetrahydridoborate¹, higher boranes as *e.g.* tetramethylammonium octahydridotriborate², or tributylstannyl hydride in the presence of tetramethylammonium halogenide³. 1,3,5-Trinitrobenzene reacts with all the above-mentioned reagents to give stable tetramethylammonium 1,1-dihydro-2,4,6-trinitrocyclohexadienide¹⁻³ (*I*). 1-Substituted 2,4,6-trinitrobenzenes ($1 - X = \text{Cl, OCH}_3, \text{CH}_3, \text{N}(\text{CH}_3)_2$) are reduced with tetramethylammonium octahydridotriborate² to give 3-substituted-1,1-dihydro-2,4,6-trinitrocyclohexadienides (*II*). Simultaneously, the X group is, more or less or even completely, split off to give compound *I*. Formation of isomeric 1-substituted trinitrocyclohexadienide *III* was not observed in any of the cases. The reactions mentioned are summarized in ref.⁴. All the compounds cited were identified by their ¹H NMR spectra, other NMR spectra have not been measured yet. The reactions of 1-substituted-3,5-dinitrobenzene with hydride ion have not been investigated so far.

EXPERIMENTAL

Tributylstannyl hydride (IV) was prepared by reduction of tributylstannyl bromide with lithium aluminium hydride in ether under inert atmosphere⁵. The raw product was rectified in vacuum, yield 89%, b.p. 81–84°C/150 Pa (ref.⁶ gives b.p. 65–67°C/80 Pa).

Tetramethylammonium 1,1-dihydro-2,4,6-trinitrocyclohexadienide (*I*): Dry powdered tetramethylammonium bromide (0.77 g, 5 mmol) was added to a solution of 1.07 g (5 mmol) 1,3,5-trinitro-

benzene in 10 ml tetrahydrofuran. The suspension was stirred, and a solution of 1.45 g (5 mmol) hydride *IV* in 10 ml tetrahydrofuran was added thereto in argon atmosphere during 2 h. The product formed was precipitated by addition of about 100 ml ether, collected by suction under argon atmosphere, washed with ether, and dried by passing dry argon therethrough. Yield 1.04 g (72%), m.p. 132–134°C (ref.¹ gives m.p. 131–132°C). The same procedure was applied to the reaction of hydride *IV* with methyl 2,4,6-trinitrobenzoate, 1-dimethylamino-2,4,6-trinitrobenzene, 1-methoxy-2,4,6-trinitrobenzene, 1-chloro-2,4,6-trinitrobenzene, 2,4,6-trinitrotoluene, and methyl 3,5-dinitrobenzoate. In the case of 3,5-dinitrobenzotrile, the hydride *IV* was added during about 30 min. Freshly prepared samples were used in all cases of the NMR spectra measurements.

Tributylstannyl 3,5-dinitrobenzoate: 5 g (8.5 mmol) hexabutyldistannoxane and 3.6 g (17 mmol) 3,5-dinitrobenzoic acid in 40 ml benzene was heated with simultaneous azeotropic distillation (removal) of the water formed. After removing the solvent by vacuum distillation, an oily product was obtained which decomposed during vacuum distillation. Yield 7 g (82%). The NMR spectra: $\delta(^{119}\text{Sn})$ 140.0 (C^2HCl_3); -22.4 (hexadeuteriodimethyl sulphoxide). The $\delta(^{13}\text{C})$ chemical shifts were measured in C^2HCl_3 (hexadeuteriodimethyl sulphoxide): δ_{ipso} 136.21 (139.46); δ_{o} 129.25 (128.93); δ_{m} 147.96 (148.23); δ_{p} 120.72 (120.36); $\delta(\text{COO})$ 165.99 (164.95); $\delta(\text{CH}_2^{\text{a}})$ 16.57 (19.03); $\delta(\text{CH}_2^{\text{b}})$ 27.39 (28.05); $\delta(\text{CH}_2^{\text{c}})$ 26.61 (26.83); $\delta(\text{CH}_3)$ 13.11 (13.72); $^{\text{n}}J(^{119}\text{Sn}-^{13}\text{C})$: $^1J = 351.6$ Hz (481.0 Hz); $^2J = 22.0$ Hz (28.1 Hz); $^3J = 66.0$ Hz (78.0 Hz); $^4J < 5$ Hz (< 5 Hz).

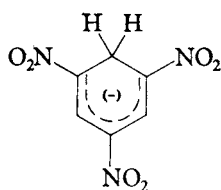
The ^1H , ^{13}C , ^{15}N , and ^{119}Sn NMR spectra were measured at 99.602, 25.047, 10.095, and 37.135 MHz, respectively, using a JEOL JNM-FX 100 apparatus and 10–20% (w/v) solutions of the compounds in hexadeuteriodimethyl sulphoxide. The experimental conditions of the measurement are given in ref.⁷. For the ^{13}C NMR spectra, the hexadeuteriodimethyl sulphoxide signal (δ 39.60) was used as the internal standard. The $\delta(^{15}\text{N})$ values are referred to external neat nitromethane⁸ (24% ^{15}N). Chromium(III) tris(acetylacetonate) (10 mg/ml) was added to the samples for measurements of the ^{15}N NMR spectra. The $\delta(^{119}\text{Sn})$ values are referred to external neat tetramethylstannane. For the ^{119}Sn spectra measurement we used the inverse gated decoupling (decoupler on during the acquisition time)⁹. Positive values of the chemical shifts denote downfield shifts.

RESULTS AND DISCUSSION

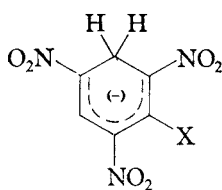
Reduction of 1,3,5-trinitrobenzene with hydride *IV* in the presence of tetramethylammonium bromide gives the compound *I* in good yields. The ^1H NMR spectrum of compound *I* was identical with the published spectra^{1–3}. The signals of the ^{13}C NMR spectrum were assigned on the basis of the intensities and comparison of the proton coupled and proton decoupled spectra. Values of the chemical shifts are given in Table I. The chemical shifts of sp^2 carbon atoms of compound *I* are very close to those of the same carbon atoms of the Meisenheimer adduct of 1,3,5-trinitrobenzene with acetate ion (and other carbanions)⁷. The maximum difference $\Delta\delta = 0.42$ ppm was found for the $\text{C}_{(2,6)}$ carbon atoms. This means that also distribution of electron densities at the sp^2 carbon atoms of compound *I* is very similar to that in the adducts of 1,3,5-trinitrobenzene with acetate ion and other carbanions.

The ^{15}N NMR spectrum of compound *I* exhibits two signals of the intensity ratio 2 : 1 which were assigned to the nitrogen atoms of nitro groups at 2 + 6 and 4

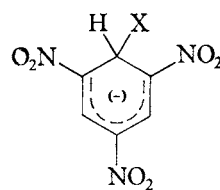
positions: $\delta(N_{2,6}) - 8.5$ and $\delta(N_4) - 17.7$, and the signal of nitrogen atom of the $(CH_3)_4N^{(+)}$ group with $\delta - 336.8$. The chemical shift of nitrogen atoms of the nitro groups at 2 and 6 positions agrees with the values found earlier⁷. Therefrom it is obvious that in the Meisenheimer adducts of 1,3,5-trinitrobenzene with carbanions the interaction of the bound nucleophile with nitro group does not significantly affect the electron density at the nitrogen atoms of the 2- and 6-nitro groups (steric interactions are impossible in compound I). The nitrogen atom of 4-nitro group exhibits the chemical shift $\delta - 17.7$, i.e. lower by 1 ppm than that in the cases studied so far⁷.



I



II



III

I–III: a, X = COOCH₃; b, X = N(CH₃)₂; c, X = OCH₃; d, X = Cl; e, X = CH₃.

TABLE I

Chemical shifts $\delta(^{13}C)$ of carbon atoms of the Meisenheimer adducts in hexadeuteriodimethyl sulphoxide (the solvent signal was used as the internal standard, δ 39.60)^a

Adduct ^c	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	other
I	28.00	133.08	127.42	120.70	127.42	133.08	
IIa	28.59	129.76	134.59	118.90	127.67	132.69	$\delta(CO)$ 165.39 $\delta(CH_3)$ 52.56
IIb	27.85	110.61	151.40	116.94	131.66	132.44	$\delta(CH_3)$ 43.60
IIc	30.19	123.38	158.98	117.00	130.64	128.96	$\delta(CH_3)$ 61.43
IIIc ^b	69.14	132.40	126.35	121.72	126.35	132.40	$\delta(CH_3)$ 56.66
IId	31.46	131.76	130.78	119.53	129.71	128.49	
IIe	30.44	134.00	142.04	124.06	129.86	126.50	$\delta(CH_3)$ 18.89
VI	28.05	130.88	134.98	77.47	134.98	130.88	$\delta(CN)$ 127.18
VII	28.68	95.35	134.34	120.70	128.54	130.88	$\delta(CN)$ 121.74

(+)

^a The signal of carbon atoms of the cation $(CH_3)_4N^{(+)}$ has the chemical shift δ 54.56 (triplet with $^1J(^{14}N-^{13}C) = 4.6$ Hz). For tetramethylammonium picrate: δ_1 161.00, δ_2 141.90, δ_3 125.42, δ_4 124.40. For 2,4,6-trinitrophenol: δ_1 159.4, δ_2 141.9, δ_3 125.8, δ_4 127.9. ^b Ref.⁷.

The X-ray diffraction provides information on distribution of electron density in the Meisenheimer adducts in solid state^{10,11}. In accordance with quantum-chemical calculations^{12,13} it was found that the 4-nitro group carried a greater part of negative charge. The distribution of electron densities can, however, be considerably different in the dissolved molecules of the adducts and those in solid state. Information on π electron densities at the nitro groups of the Meisenheimer adducts in solution can be obtained from the $\delta(^{15}\text{N})$ chemical shifts. The $\delta(^{15}\text{N})$ chemical shifts are more sensitive to changes of π electron densities than $\delta(^{13}\text{C})$ are (about 300 ppm/electron and about 160 ppm/electron, respectively)^{14,15}, and a good linear dependence was found¹⁴ between the calculated π electron densities at the nitrogen atom of nitro group and $\delta(^{15}\text{N})$ in a series of *para*-substituted nitrobenzenes, but changes in the electron densities are relatively small. Increased π electron density at the nitrogen atom of nitro group causes a downfield shift in $\delta(^{15}\text{N})$. Therefrom it follows that at the nitrogen atom of 4-nitro group of compound *I* the π electron density is only slightly higher than that at the nitrogen atoms of 1,3,5-trinitrobenzene (for 1,3,5-trinitrobenzene $\delta(^{15}\text{N}) -18.7$, ref.⁷), the π electron density being mainly increased at 2- and 6-nitro groups. The greater electron density at the 2- and 6-nitro groups* of the Meisenheimer adducts derived from 1,3,5-trinitrobenzene corresponds better to the presumed way of association of these anions with cations in solution**.

Methyl 2,4,6-trinitrobenzoate and 1-dimethylamino-2,4,6-trinitrobenzene are reduced with hydride *IV* giving exclusively the 3-substituted-1,1-dihydro-2,4,6-trinitrocyclohexadienides *Ila* and *Ilb*, respectively (yields about 70%). ¹H NMR spectra for *Ila* δ_1 3.96, δ_5 8.28, $\delta(\text{OCH}_3)$ 3.81; for *Ilb* δ_1 3.96, δ_5 8.34, $\delta(\text{N}(\text{CH}_3)_2)$ 2.84. Table I gives the values of $\delta(^{13}\text{C})$ chemical shifts.

The reaction of 1-methoxy-2,4,6-trinitrobenzene with hydride *IV* in the presence of tetramethylammonium bromide produces tetramethylammonium 3-methoxy-1,1-dihydro-2,4,6-trinitrocyclohexadienide (*Ilc*), tetramethylammonium picrate, and compound *I*. If the reductions with hydride *IV* gave several products, then ratio of the products was not quite constant, due probably to the fact that the reactions took place in heterogeneous systems. The adducts *Ilc* and *I* were formed in the ratio about 8.5 : 1, and the picrate amount was considerably variable. The lowest picrate content was found in a sample containing 83% adduct *Ilc*, 10% adduct *I*, and 7% picrate. All the three compounds were identified by means of ¹H NMR spectra: for compound *I* δ_1 3.90, $\delta_{3,5}$ 8.28; for compound *Ilc* δ_1 3.96, δ_5 8.40, $\delta(\text{OCH}_3)$ 3.80; for the picrate $\delta_{3,5}$ 8.64. The common absorption of tetramethylammonium

* There exists a good linear relation between π electron densities at nitrogen atom and oxygen atoms of nitro groups in ArNO_2 (ref.¹⁴). The nitro groups having a higher π electron density at the nitrogen atom have, at the same time, a higher π electron density at the oxygen atoms.

** The chemical shifts $\delta(\text{N}_{2,6}) -9.7$ and $\delta(\text{N}_4) -14.5$ were measured for 1,1-dimethoxy-2,4,6-trinitrocyclohexadienide for which an energetically favourable association is presumed¹⁶ between cations and oxygen atoms of the methoxy and 2- and 6-nitro groups.

ion shows δ 3.16. Chemical shifts of the protons of compound *IIC* agree well with literature data². Table I gives the $\delta(^{13}\text{C})$ chemical shifts of the three compounds. At least a part of the picrate is formed by direct reaction of the substrate with tetramethylammonium bromide¹⁷, which was proved by an experiment carried out in the absence of hydride *IV*. Tetramethylammonium picrate is also formed by subsequent reactions of the adduct *IIC* dissolved in dimethyl sulphoxide. The original magenta colour of solution of adduct *IIC* turns yellow on standing, and crystalline solid is precipitated with m.p. 321–323°C after recrystallization from methanol (ref.¹⁸ gives m.p. 318–319°C for tetramethylammonium picrate) and with ¹H NMR spectrum identical with the above-described one. When using tetrabutylammonium bromide in the reduction of 1-methoxy-2,4,6-trinitrobenzene with hydride *IV* in tetrahydrofuran we obtain tetrabutylammonium picrate as practically the only product.

The reaction of 1-chloro-2,4,6-trinitrobenzene with hydride *IV* gives the adducts *IId* and *I* and 2,4,6-trinitrophenol. Yields of 2,4,6-trinitrophenol varied within 10 to 20% in various experiments, the adducts *IId* and *I* being formed in the ratio of about 2 : 1. ¹H NMR spectra: for adduct *IId* δ_1 4.08, δ_5 8.38, for 2,4,6-trinitrophenol $\delta_{3,5}$ 8.64.

The main product of reduction of 2,4,6-trinitrotoluene with hydride *IV* is 3-methyl-1,1-dihydro-2,4,6-trinitrocyclohexadienide (*IIE*) (¹H NMR spectrum δ_1 3.93, δ_5 8.41, $\delta(\text{CH}_3)$ 2.61). Besides that about 10% tetramethylammonium 1-methyl-1,1-dihydro-2,4,6-trinitrocyclohexadienide (*IIIE*) is formed which was identified doubtlessly on the basis of identity of the corresponding chemical shifts $\delta(^1\text{H})$ with the tetraphenylarsonium 1-methyl-1,1-dihydro-2,4,6-trinitrocyclohexadienide prepared by reaction of tetraphenylarsonium tetramethylborate with 1,3,5-trinitrobenzene¹⁹. ¹H NMR spectrum of compound *IIIE*: $\delta_{3,5}$ 8.28, δ_1 4.64 (quartet), $\delta(\text{CH}_3)$ 1.18 (doublet, ³*J* = 6.35 Hz). 2,4,6-Trinitrotoluene is attacked by nucleophiles at 3 position and at methyl hydrogen atom^{20–22}, and also its reduction with tetramethylammonium octahydridotriborate only produces the *IIE* adduct². As far as we know, the formation of compound *IIIE* represents the first reliably proved attack of a nucleophile on 1 position of 2,4,6-trinitrotoluene.

In ¹H NMR spectrum of the reduction products of 2,4,6-trinitrotoluene with hydride *IV* we found further signals with the following chemical shifts: δ 9.06, 8.45, 2.24 (singlets) and δ 4.97 (triplet, *J* ~ 3.5 Hz). These signals can most probably be assigned to the protons H₁₀, H₅, CH₃, and CH—CH₂ of compound *V**. The doublet of CH—CH₂ group is obviously overlapped by far more intensive signals of water, (CH₃)₄N⁽⁺⁾, or solvent. The attempts at verification of structure of compound *V* by its independent synthesis failed in the same way as the earlier attempts of other authors^{23,24}.

* The ratios of reduction products from 2,4,6-trinitrotoluene were not quite constant in the experiments carried out. The average ratio was [*IIE*] : [*IIIE*] : [*V*] ≈ 3 : 1 : 1.

The reduction products from 2,4,6-trinitrotoluene in solid state are stable below 0°C in darkness for several days. In dimethyl sulphoxide solution, however, they undergo decomposition within several hours. With respect to the ratio of the reduction products it was only possible to measure and interpret reliably the $\delta(^{13}\text{C})$ chemical shifts of the carbon atoms of compound *Ile* (Table I).

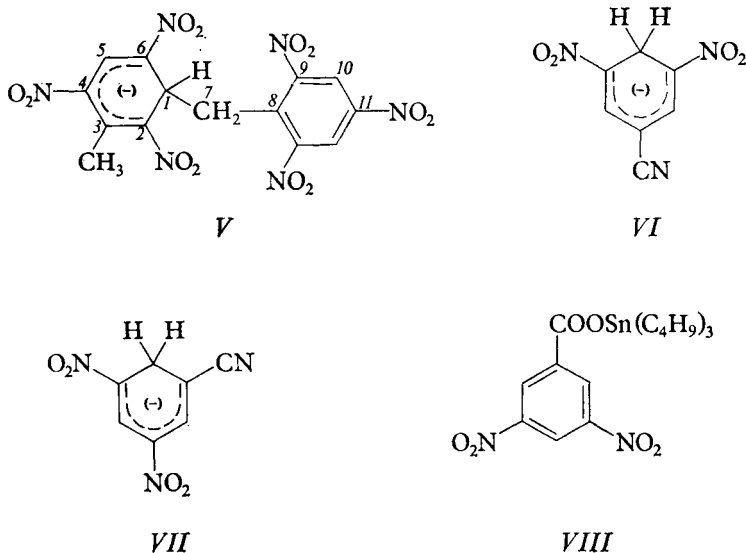
Kaplan and Siedle² suggested 3 mechanisms for the reactions of 1-X-2,4,6-trinitrobenzenes with tetramethylammonium octahydridotriborate leading to adducts *I* and *II*. The found composition of the reaction products² is best interpreted by the mechanism involving participation of the B_3H_7 particle in splitting off of the X group from the substrate with formation of 1,3,5-trinitrobenzene. The content of adduct *II* in its mixture with adduct *I* correlates then with the strength of the B—X bond being formed. For X = CH_3 , Cl, OCH_3 , $\text{N}(\text{CH}_3)_2$ the reduction products contain 100% *Ile*, 75% *IId*, 65% *Iic*, 0% *Iib*. Formation of adduct *III* was not observed in any of the cases.

It is supposed that the studied reduction of 1-X-2,4,6-trinitrobenzenes with hydride *IV* produces the adducts *II* and *III* simultaneously in non-reversible side reactions. The adducts type *II* are relatively stable and remain in the reaction mixture, whereas the adducts type *III* split off $\text{X}^{(-)}$ (for X = Cl or OCH_3) to give 1,3,5-trinitrobenzene which is further reduced to the adducts *I*. In the case of X = CH_3 the $\text{C}_{(1)}$ atom of the adduct *IIIe* carries no group which could be split off as $\text{X}^{(-)}$, and therefore, formation of this adduct could be proved spectrometrically. Methyl 2,4,6-trinitrobenzoate and 1-dimethylamino-2,4,6-trinitrobenzene are not attacked at 1 position. This mechanism also agrees with the quite different proportions of the *II* and *I* adducts in the mixture. For X = COOCH_3 , $\text{N}(\text{CH}_3)_2$, CH_3 , OCH_3 , Cl the reduction products contained 100% *Iia*, 100% *Iib*, 90% *Iie*, 90% *Iic*, 67% *Iid* (the other compounds formed in the reduction besides compounds *I* and *II* are not considered). Hence, nucleophilic attack at 3 position is faster than that at 1 position in all the cases, which is similar *e.g.* to the reactions of 1-methoxy-2,4,6-trinitrobenzene with methoxide ion²⁵. Tin does not take part in splitting off of the X group from the adduct *III*, since tributylstannyl bromide was found (and identified by comparison of ^1H , ^{13}C , and ^{119}Sn NMR spectra with the authentic sample⁹) as the only tin-containing product. Methoxide ion is split off from 1-methoxy-2,4,6-trinitrobenzene in the form of methanol which was identified in the reduction products in the form of methyl 3,5-dinitrobenzoate.

The addition of hydride ion to 1-substituted-3,5-dinitrobenzenes has not been studied yet. The ^1H NMR spectrum of a freshly prepared solution of the reaction products from 3,5-dinitrobenzotrile and hydride *IV* in hexadeuteriodimethyl sulphoxide only contained the proton signals of the adducts *VI* and *VII*. The adducts ratio in the mixture $[\text{VI}] : [\text{VII}] \sim 2 : 1$ was well reproducible. Thus the reaction of 3,5-dinitrobenzotrile with hydride ion resembles reactions of 1-substituted-3,5-dinitrobenzenes with carbanions²⁶⁻²⁹ in which the first kinetically controlled

step usually produces more rapidly the "symmetrical adduct" type *VI*. The adducts *VI* and *VII* are not stable, and even their preparation is accompanied by a deeper reduction giving a mixture of non-identified products. Therefore, the reaction must be interrupted before all the nitrile has reacted, although the yields obtained are low. The prepared mixture of adducts *VI* and *VII* is completely decomposed (within several hours in solid state, and within about 30 min in hexadeuteriodimethyl sulphoxide solutions), the blue colour of the adducts being changed into red colour of the reduction products.

Visible region of electronic spectra of the adducts *VI* and *VII* contains two absorption bands, the one at higher wavelength having greater λ_{\max} in the case of the "symmetrical adduct", as it is the case with the adducts with carbanions²⁶. The adducts *VI* and *VII* have $\lambda_{\max} = 675$ and 580 nm, resp.



The compounds *VI* and *VII* were identified on the basis of ¹H NMR spectra; for compound *VI* δ_1 3.84, $\delta_{3,5}$ 7.61 and for compound *VII* δ_1 3.64, δ_3 7.41, δ_5 8.25, $J_{3,5} = 2.0$ Hz. Table I presents chemical shifts $\delta(^{13}\text{C})$ of carbon atoms of the adducts *VI* and *VII*. The mother liquor after filtration of the adducts *VI* and *VII* contained tributylstannyl bromide as the only tin-containing product.

When solution of hydride *IV* in tetrahydrofuran was added dropwise to a suspension of tetramethylammonium bromide in a solution of methyl 3,5-dinitrobenzoate in tetrahydrofuran, each addition caused formation of a blue precipitate of the Meisenheimer adducts which, however, practically dissolved instantaneously. After addition of the whole amount of hydride *IV*, a brownish suspension was obtained

from which it was possible to recover (by suction and washing with ether) tetramethylammonium bromide in practically quantitative amount. Removal of the solvents from the mother liquor by vacuum distillation gave an oily residue which turned red in air. According to ^1H , ^{13}C , and ^{119}Sn NMR spectra and comparison with the spectra of the authentic substance prepared by independent way, the evaporation residue is tributylstannyl 3,5-dinitrobenzoate (*VIII*), yield 80%. The values of chemical shifts are given in Experimental. Differences in values of chemical shifts and coupling constants between solutions of the compound in C^2HCl_3 and hexadeuteriodimethyl sulphoxide are due to the change of coordination number of tin from 4 to 5 (ref.⁹). Besides the compound *VIII*, the evaporation residue also contained a mixture of unidentified reduction products.

The transient Meisenheimer adducts of methyl 3,5-dinitrobenzoate and hydride ion are so unstable that they cannot be isolated. The main reaction product is then the compound *VIII* which is most likely formed by a subsequent reaction of the unstable Meisenheimer adducts, because methyl 3,5-dinitrobenzoate and tributylstannyl bromide do not react under conditions of preparation of the adducts.

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