REACTIONS OF METHYL ESTERS OF N-(2,4-DINITROPHENYL)-GLYCINE AND N-METHYL-N-(2,4-DINITROPHENYL)GLYCINE WITH SODIUM METHOXIDE

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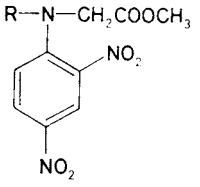
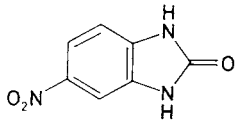
The reaction of methyl ester of N-(2,4-dinitrophenyl)glycine (*I*) with sodium methoxide produces 5-nitro-2(3*H*)benzimidazolone (*III*). The product identity has been proved by its isolation from the reaction mixture under conditions similar to those of kinetic experiments and by independent synthesis. The reaction of methyl ester of N-methyl-N-(2,4-dinitrophenyl)glycine with methoxide proceeds in two steps, the second one being substantially slower. The first step produces N-methyl-2-nitroso-4-nitroaniline (*IV*), which can be prepared by this reaction in good yield and purity. N-Methyl-2-nitroso-4-nitroaniline undergoes subsequent reactions in the methoxide solutions. Products of the subsequent reactions have not been identified at the starting ester *II* concentrations of about 10^{-4} mol l^{-1}, whereas at higher concentrations of the starting substance the reaction produces 2-amino-2′-methylamino-5,5′-dinitro-ONN-azoxybenzene (*V*) and 2,2′-bis(methylamino)-5,5′-dinitroazoxybenzene (*VI*).

In our previous papers[1-3] we studied the formation of 2-nitroso-4,6-dinitroaniline and N-methyl-2-nitroso-4,6-dinitroaniline in the reactions of esters and amides of N-(2,4,6-trinitrophenyl)glycine and esters of N-methyl-N-(2,4,6-trinitrophenyl)-glycine with sodium methoxide in methanol. The key intermediate in the formation of the nitroso compounds is the aziridinone derivative formed by the intramolecular attack of carboxyl carbon atom by the electron pair at the nitrogen atom of either the conjugated base of the starting substance or its adduct with methoxide ion. In the present paper analogous reactions of esters of N-(2,4-dinitrophenyl)glycine



I, R = H
II, R = CH_3



III

and N-methyl-N-(2,4-dinitrophenyl)glycine and subsequent reactions of the nitroso compounds primarily formed are studied.

EXPERIMENTAL

The ^{1}H *and* ^{13}C NMR *spectra* of compounds *I*, *II*, *III*, *IV*, and *V* were measured at 99·603 and 25·047 MHz, resp., with a JNM FX-100 (JEOL) spectrometer. The ^{15}N NMR spectrum of compound *IV* was measured at 10·095 MHz with the same spectrometer. The ^{15}N NMR spectrum of compound *V* was measured at 30·405 MHz with a VXR-300 (Varian) apparatus, the ^{1}H and ^{13}C NMR spectra of compound *VI* were measured at 400·13 and 100·62 MHz, resp., with an AM-400 spectrometer (Bruker). For the measurements, about 10% solutions (compounds *I* and *II*) or saturated solutions in hexadeuteriodimethyl sulphoxide were used. The chemical $\delta(^1H)$ shifts are related to hexamethyldisiloxane (δ 0·05), the $\delta(^{13}C)$ shifts to the solvent signal (δ 39·6), the $\delta(^{15}N)$ shifts to neat external $CH_3{}^{15}NO_2$ (δ 0·0). Chromium(III) tris-acetylacetonate (about 10 mg/ml) was added to the samples for the ^{15}N NMR spectra measurement.

The mass spectra were measured with a JMS 01 SG-2 (JEOL) apparatus at the resolution $R_{10\%} = 1\,000$, at the ionization energy of 75 eV and ionization current of 200 μA. The elemental composition of selected ions was specified on the basis of a high-resolution measurement ($R_{10\%} = 5\,000 - 10\,000$).

Methyl ester of N-(2,4-*dinitrophenyl)glycine* (I). 40 ml 1 mol l^{-1} (40 mmol) sodium methoxide was added to 6 g (48 mmol) hydrochloride of glycine methyl ester and, after 10 min shaking, the precipitated NaCl was filtered off. The solution of ester base was added dropwise to a stirred solution of 1-chloro-2,4-dinitrobenzene (4·05 g; 20 mmol) in 10 ml methanol. The product precipitated on standing overnight (3·3 g, 65%) was collected and recrystallized from methanol, m.p. 123–125°C. For $C_9H_9N_3O_6$ (255·2) calculated: 42·36% C, 3·55% H, 16·47% N; found: 42·20% C, 3·73% H, 16·57% N. ^{1}H NMR: 9·07 bt, 1 H (NH); 8·91 d, 1 H (H-3, $J(3, 5) = 2·6$Hz); 8·31 dd, 1 H (H-5, $J(5, 6) = 9·5$ Hz); 7·17 d, 1 H (H-6); 4·48 d, 2 H (CH_2, $J = 5·9$ Hz); 3·77 s, 3 H (CH_3). ^{13}C NMR: 169·59 (CO), 148·00, 135·66, 130·16, 129·99 (CH), 123·43 (CH), 116·00 (CH), 52·41 (CH_3), 44·51 (CH_2).

Methyl ester of N-*methyl*-N-(2,4-*dinitrophenyl)glycine* (II). A mixture of 9·8 g (48·4 mmol) 1-chloro-2,4-dinitrobenzene, 15·12 g (180 mmol) $NaHCO_3$, and 9·0 g (65 mmol) hydrochloride of sarcosine methyl ester in 50 ml methanol was stirred 15 min at 50°C and then without heating 3 h. The precipitated solid was collected by suction, mixed with 300 ml 0·2 mol l^{-1} hydrochloric acid, again collected by suction, and washed with water. After recrystallization from benzene yield 7·65 g (59%), m.p. 106–108°C. For $C_{10}H_{11}N_3O_6$ (269·2) calculated: 44·62% C, 4·12% H, 15·61% N; found: 44·66% C, 4·31% H, 15·53% N. ^{1}H NMR: 8·61 d, 1 H (H-3, $J(3, 5) = 2·8$ Hz); 8·25 dd, 1 H (H-5, $J(5, 6) = 9·3$ Hz); 7·35 d, 1 H (H-6); 4·41 s, 2 H (CH_2); 3·77 s, 3 H (OCH_3); 2·99 s, 3 H (NCH_3). ^{13}C NMR: 169·12 (CO), 148·41, 136·42, 135·54, 127·59 (CH), 123·49 (CH), 118·52 (CH), 54·63 (CH_2), 52·24 (OCH_3), 41·53 (NCH_3).

The same procedure was applied in the preparation of *ethyl ester* of N-*methyl*-N-(2,4-*dinitrophenyl)glycine* from hydrochloride of sarcosine ethyl ester. The yield after recrystallization from benzene 51%, m.p. 97–99°C. ^{1}H NMR: 8·63 d, 1 H (H-3, $J(3, 5) = 2·9$ Hz); 8·27 dd, 1 H (H-5, $J(5, 6) = 9·3$ Hz); 7·25 d, 1 H (H-6); 4·40 s, 2 H (NCH_2); 4·23 q, 2 H (OCH_2, $J = 7·2$ Hz); 2·99 s, 3 H (NCH_3); 1·27 t, 3 H (CH_3). ^{13}C NMR: 168·66 (CO), 148·47, 136·48, 135·60, 127·65 (CH), 123·55 (CH), 118·58 (CH), 61·19 (OCH_2), 54·81 (NCH_2), 41·65 (NCH_3), 14·15 (CH_3).

Preparation of 6-*nitro*-2(3*H*)*benzimidazolone* (III) from ester *I*. A solution of 30 ml 1 mol l^{-1} (30 mmol) sodium methoxide in 20 ml methanol was stirred and treated with 1·2 g (4·7 mmol)

methyl ester of N-(2,4-dinitrophenyl)glycine *I* added portionwise within 20 min. Three minutes after the last addition of the ester *I*, the mixture was partially neutralized with 8 ml 2 mol l^{-1} (16 mmol) hydrochloric acid, and the neutral substances were extracted with benzene. The aqueous methanolic layer was acidified by addition of another 12 ml 2 mol l^{-1} (24 mmol) hydrochloric acid, and the reaction mixture was filtered. The filtrate was saturated with NaCl and twice extracted with 80 ml ethyl acetate. The combined organic portions were extracted with 40 ml water, and the water layer was reextracted with 50 ml ethyl acetate. The organic phases were dried, and the solvent was removed by distillation under reduced pressure. The evaporation residue (0·8 g) was ground with 20 ml 0·1 mol l^{-1} (2 mmol) cold sodium methoxide, washed with water and dried. Yield 0·6 g (71%), m.p. 300—305°C after reprecipitation with hydrochloric acid from a hot NaOH solution. ^{1}H NMR (55°C): 11·1 b, 2 H (2× NH); 7·91 dd, 1 H (H-6, $J(6, 7) = 8·8$ Hz, $J(4, 6) = 1·95$ Hz); 7·71 d, 1 H (H-4); 7·09 d, 1 H (H-7). ^{13}C NMR: 155·55 (CO), 141·34, 135·78, 129·81, 117·88 (CH), 108·17 (CH), 103·72 (CH). Mass spectrum: *m/z* 179 (M^+). 5-Nitro-2(3*H*)benzimidazolone was prepared independently by the reaction of 4-nitro-1,2-diaminobenzene with urea[4], m.p. 305—308°C, ref.[4] gives m.p. 308°C. Both ^{1}H and ^{13}C NMR spectra of this 5-nitro-2(3*H*)benzimidazolone were identical with those of the substance prepared from ester *I*.

2-*Nitroso*-4-*nitro*-N-*methylaniline* (IV). A solution of 1·26 g (4·46 mmol) ethyl ester of N-methyl-N-(2,4-dinitrophenyl)glycine in 8 ml dimethyl sulphoxide was diluted with 40 ml methanol. With continuous stirring, 4·5 ml 0·1 mol l^{-1} (0·45 mmol) sodium methoxide was added, and the formation of nitroso compound was followed spectrophotometrically. After the reaction was finished (after about 25 min), the product suspension was acidified by addition of 8 ml 0·1 mol l^{-1} (0·8 mmol) aqueous hydrochloric acid and, after cooling, the crystals formed were collected by suction, washed with 5 ml cold methanol and dried. Yield 0·62 g (77%), m.p. 165—168°C. For $C_7H_7N_3O_3$ (181·1) calculated: 46·41% C, 3·89% H, 23·20% N; found: 46·25% C, 4·23% H, 22·99% N. ^{1}H NMR: 10·60 b, 1 H (NH); 8·97 b, 1 H (H-3); 8·23 dd, 1 H (H-5, $J(3, 5) = 2·4$ Hz, $J(5, 6) = 9·8$ Hz); 7·17 d, 1 H (H-6); 3·02 d, 3 H (CH_3, $J = 5·4$ Hz). ^{13}C NMR: 153·25 (C-2), 142·53 (C-1), 135·66 (C-4), 130·79 (C-5), 129·91 (C-3), 116·46 (C-6), 29·27 (CH_3). The absorptions of C-3 and C-5 carbon atoms were assigned on the basis of selective decoupling from the protons. ^{15}N NMR: −297·0 (NH), −12·0 (NO_2). The signal of nitroso group was not found in the spectrum due to low solubility of the substance. Mass spectrum: *m/z* 181 (M^+).

2-*Amino*-2′-*methylamino*-5,5′-*dinitro*-ONN-*azoxybenzene* (V) *and* 2,2′-*bis*(*methylamino*)-5,5′-*dinitroazoxybenzene* (VI). A solution of 3 g (10·6 mmol) ethyl ester of N-methyl-N-(2,4-dinitrophenyl)glycine in 5 ml dimethyl sulphoxide was treated with 10 ml methanol and 20 ml 0·1 mol l^{-1} (2 mmol) sodium methoxide. After 15 min, the suspension of the nitroso compound *IV* formed was treated with 3 ml 5 mol l^{-1} (15 mmol) aqueous sodium hydroxide. A red-brown substance precipitated immediately. After further 10 min stirring, 9 ml 2 mol l^{-1} (18 mmol) aqueous hydrochloric acid was added. The precipitated solid was collected by suction on a sintered glass filter and washed with several ml methanol, water, and again with methanol. Yield 0·9 g, m.p. 230—240°C. Recrystallization from dimethyl sulphoxide gave the product with m.p. 248—253°C (decomp.). For $C_{13}H_{12}N_6O_5$ (332·3) calculated: 46·99% C, 3·64% H, 25·29% N; found: 47·05% C, 3·90% H, 25·02% N. ^{1}H NMR: 9·46 d, 1 H (H-6, $J(4, 6) = 2·9$ Hz); 8·09 dd, 1 H (H-4, $J(3, 4) = 9·1$ Hz); 6·93 d, 1 H (H-3); 8·79 d, 1 H (H-6′, $J(4′, 6′) = 2·5$ Hz); 8·26 dd, 1 H (H-4′, $J(3′, 4′) = 9·1$ Hz); 7·02 d, 1 H (H-3′); 8·2 b, 1 H ($NHCH_3$;) 7·23 b, 2 H (NH_2); 3·02 d, 3 H (CH_3NH, $J = 4·9$ Hz). From the spectrum it is impossible to find which aromatic ring of compound *V* contains the given triad of protons. ^{13}C NMR: 152·23, 147·74, 134·64, 134·49, 130·98, 127·57 (CH), 126·98 (CH), 125·77, 122·16 (CH), 119·38 (CH), 114·51 (CH), 112·46 (CH), 30·05 (CH_3). ^{15}N NMR: −9·8 and −11·4 (2× NO_2), −56·5 and −60·1 (—N=N(O)—), −296·4 and −301·5 ($NHCH_3$ and/or NH_2). Mass spectrum: *m/z* 332 (M^+).

The undissolved residue of the substance from the first crystallization from dimethyl sulphoxide was submitted to another crystallization from excess hot dimethyl sulphoxide to give about 100 mg product, m.p. 275–278°C (decomp.). For $C_{14}H_{14}N_6O_5$ (346·3) calculated: 48·56% C, 4·08% H, 24·27% N; found: 48·53% C, 4·12% H, 24·15% N. ^{1}H NMR (60°C): 9·39 d, 1 H (H-6, $J(4, 6) = 2·7$ Hz); 8·19 dd, 1 H (H-4, $J(3, 4) = 9·4$ Hz); 6·88 d, 1 H (H-3); 8·78 d, 1 H (H-6′, $J(4', 6') = 2·7$ Hz); 8·27 dd, 1 H (H-4′, $J(3', 4') = 9·4$ Hz), 7·05 d, 1 H (H-3′); 8·05 b, 1 H (NH); 7·15 b, 1 H (NH); 3·04 s, 3 H (CH_3); 2·98 s, 3 H (CH_3). A reliable assignment of the proton triads to the individual nuclei is impossible. ^{13}C NMR (60°C): 150·83, 147·73, 134·69, 134·26, 131·32, 127·51 (CH), 127·26 (CH), 126·59, 122·04 (CH), 118·42 (CH), 112·41 (CH), 109·62 (CH), 29·91 (CH_3), 29·68 (CH_3). Mass spectrum: m/z 346 (M^+).

The kinetics of the reactions of esters I *and* II *with methoxide.* The kinetic measurements were carried out at 25°C with a Specord UV-VIS spectrophotometer (Zeiss, Jena). A 1 cm cell was charged with 2 ml sodium methoxide solution and 20 or 50 μl methanolic solution of ester *I* or *II*, resp., (concentration $6 . 10^{-3}$ mol l^{-1}) was injected thereinto, whereupon the absorbance–time dependence was followed (the absorbance decrease at 350 nm for ester *I*, and the abosrbance increase at 460 nm for ester *II*). The reactions were followed in methoxide solutions of $3 . 10^{-2}$ to 0·5 mol l^{-1} concentration (for ester *I*) and $2 . 10^{-2}$ to 0·1 mol l^{-1} concentration (for ester *II*). The rate constants were obtained by the standard procedure according to the equations $kt = -2·3 \log (A_\infty - A_t) +$ const. or $kt = -2·3 \log (A_t - A_\infty) +$ const.

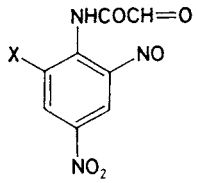
RESULTS AND DISCUSSION

Reactions of Methyl Ester of N-(2,4-*Dinitrophenyl*)*glycine* (I) *with Methoxide*

After addition of methoxide solution to methanolic solution of ester *I* ($6 . 10^{-5}$ mol . l^{-1}) the absorbance decrease at 340 nm (λ_{max} of the starting ester *I*) and increase at 395 nm are observed. The spectral records do not cross in a single isosbestic point, but the isosbestic point slightly shifts with time from about 375 nm to about 380 nm. The isosbestic point at 380 nm was maintained in the experiments carried out at the lowest methoxide concentrations ($[CH_3O^-] < 5 . 10^{-2}$ mol l^{-1}). The attempts at isolation of the reaction product from ester *I* and methoxide (carried out by addition of the ester *I* solution to the methoxide solution or vice versa) always ended in formation of a mixture of substances whose electronic spectra did not resemble that of the products formed at $[I] < 10^{-4}$ mol l^{-1}. Only the procedure involving addition of small portions of solid ester *I* to methoxide solution with stirring gave the substance with the electronic spectrum identical with that obtained from the reaction of ester *I* at the concentrations $[I] < 3 . 10^{-4}$ mol l^{-1}. In the procedure mentioned the concentration of the intermediates formed during the reaction is very low, as it is in the kinetic experiments, too. From the mass and ^{1}H NMR spectra it was found that the product is 5-nitro-2(3*H*)benzimidazolone (*III*). Structure of the product isolated from the reaction of ester *I* with methoxide was confirmed by the independent synthesis[4] of imidazolone *III*. The two products had identical ^{1}H NMR spectra, identical λ_{max} in methoxide solutions, and the same acid-base properties (the substances are half dissociated in about $5 . 10^{-4}$ mol l^{-1}

sodium methoxide, the isosbestic point of the neutral compound *III* and its conjugated base being at 375 nm in both the cases).

In the cases studied earlier[1-3] we observed a two-electron intramolecular reduction of nitro to nitroso group. The reaction of ester *I* with methoxide giving imidazolone *III* involves a six-electron reduction of nitro to amino group. The carbonyl group remains bonded in the imidazolone *III* molecule, whereas the formation of nitroso compounds[1-3] involved a solvolytic splitting off of glyoxylic acid ester (or its hemiacetal). This means that the presumed analogous intermediate *VII* of both the reactions undergoes – in the case of the dinitro derivative – rather further reduction than methanolysis.



VII, X = H or NO_2

The formation of 2-nitroso-4-nitroaniline was not observed during the reaction of ester *I* with methoxide. 2-Nitroso-4-nitroaniline is formed[5] in 70% yield after a three days irradiation of a solution of N-(2,4-dinitrophenyl)leucine in aqueous $NaHCO_3$ with a mercury discharge lamp, 3-methylbutanal and CO_2 being side products.

The dependence of experimental rate constants of the reaction of ester *I* with methoxide (k_{obs}) on the methoxide concentration is not linear (Fig. 1). The increase is much too large to be assigned merely to the fact that the methoxide activity increases faster than its concentration in more concentrated solutions[6]. The dependence of k_{obs} on $[CH_3O^-]$ can be explained by the reaction being 1st order and predominantly 2nd order in methoxide anion (Eq. (*1*)) at low and at the highest sodium methoxide concentrations, resp.

$$k_{obs} = k_2[CH_3O^-] + k_3[CH_3O^-]^2 . \qquad (1)$$

The solid line in Fig. 1 was calculated from Eq. (*1*) with application of the values $k_2 = 0{\cdot}105\ l\ mol^{-1}\ s^{-1}$ and $k_3 = 0{\cdot}333\ l^2\ mol^{-2}\ s^{-1}$. At higher methoxide concentrations ($[CH_3O^-] \geqq 0{\cdot}2\ mol\ l^{-1}$) correction was introduced with respect to the methoxide activity: the H_M acidity function was used which was determined[7] from the methanolysis kinetics of N-methylformanilides.

The non-linearity of the dependence of $\log k_{obs}$ on $[CH_3O^-]$ was also found[1] for the reaction of methyl ester of N-(2,4,6-trinitrophenyl)glycine with methoxide giving 2-nitroso-4,6-dinitroaniline. The character of the dependence was interpreted

as a consequence of the fact that beside the reaction pathway giving the nitroso compound via an intermediate with a single negative charge there exists – at higher methoxide concentrations – another pathway involving an intermediate with two negative charges (diadduct or anionadduct). The same interpretation can also be applied to the dependence in Fig. 1 with the only difference that – in the case of the dinitro derivative *I* – the formation of the anionadduct cannot make itself felt until at higher methoxide concentration ($>0{\cdot}1$ mol l^{-1}); at the same time, this anionadduct of ester *I* is substantially more reactive than that corresponding to the trinitro derivative (the negative charge is delocalized from the nucleus to a smaller number of nitro groups).

Reactions of Methyl Ester of N-*Methyl*-N-(2,4-*dinitrophenyl*)*glycine* (II) *with Sodium Methoxide*

The title reaction was followed spectrophotometrically and was found to proceed in two steps (Fig. 2). The second step is much slower, hence at the moment the first reaction is practically finished the second one is only little advanced. The two reactions show well-developed isosbestic points in the spectral records. After the second step is finished and the reaction mixture is acidified the absorbance at 395 nm (λ_{max} of the final product) considerably decreases, whereas, on the other hand, the electronic spectra of the product of the first step are the same in acidic and basic solutions. This means that this intermediate exists in its neutral form in the reaction medium and does not consume any methoxide during its formation (its formation is only catalyzed by methoxide). This finding was made use in preparation of this intermediate: solution of the starting ester *II* (or the corresponding ethyl ester) was treated with only such low amount of methoxide that the formation of the intermediate was sufficiently fast but the second step was insignificant. The isolated intermediate was identified by its ^1H, ^{13}C, ^{15}N NMR and mass spectra as

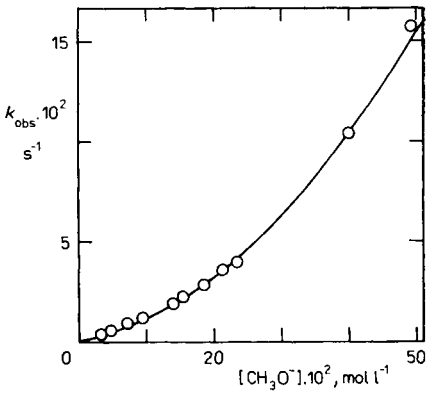
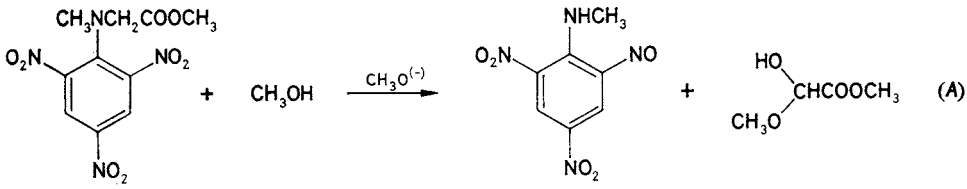


FIG. 1

Dependence of experimental rate constants k_{obs} of reaction of ester *I* with methoxide on methoxide concentration. The solid line was calculated from the equation $k_{obs} = 0{\cdot}105\,[CH_3O^-] + 0{\cdot}333\,[CH_3O^-]^2$

2-nitroso-4-nitro-N-methylaniline (*IV*). The nitroso compound *IV* was prepared by the method described (Eq. (*A*)) in good yields and sufficient purity for a satisfactory elemental analysis.



(*A*)

It is presumed that the mechanism of formation of the nitroso compound *IV* is analogous to that suggested earlier for the formation of 2-nitroso-4,6-dinitroaniline[1,3] and 2-nitroso-4,6-dinitro-N-methylaniline[2] via the key aziridinone intermediate.

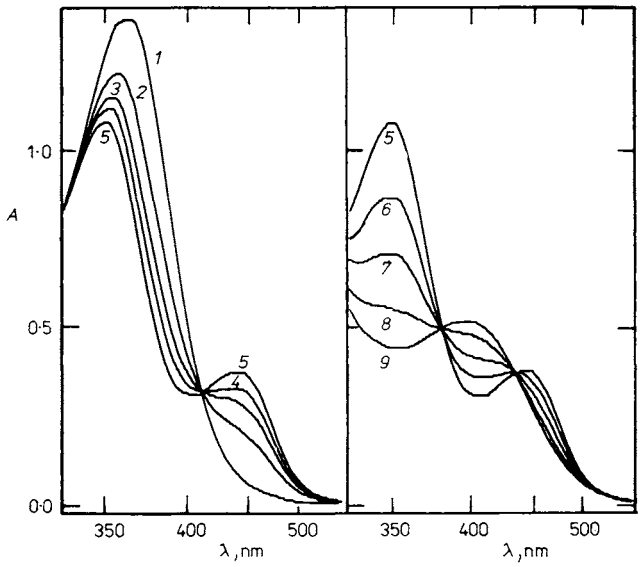
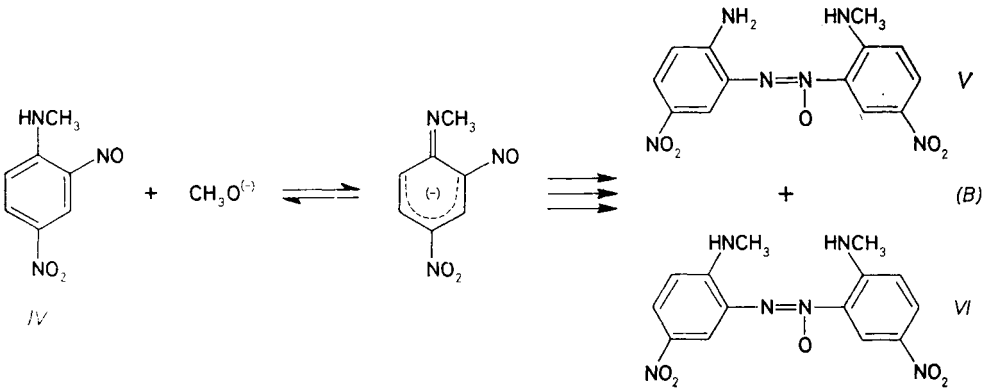


FIG. 2

Spectral records of the reaction course of ester *II* with methoxide. Spectrum of ester *II* ($1{\cdot}7 \cdot 10^{-4}$ mol l^{-1} (record *1*)), spectra after addition of 20 µl sodium methoxide (1 mol l^{-1}) to 2 ml solution of ester *II* after time intervals Δt = 150, 330, 510, and 1 050 s (spectra 2—5). At the time Δt = 1 200 s 40 µl 5 mol l^{-1} sodium methoxide was added and spectra were measured after Δt = 1 530, 1 890, 2 550, and 4 800 s (from the beginning of the experiment) (records 6—9)

The dependence of the rate constant k_{obs} of formation of the nitroso compound *IV* on methoxide concentration is linear. The bimolecular rate constant is $k_2 = 0{\cdot}25 \pm 0{\cdot}02\ l\ mol^{-1}\ s^{-1}$ ($r = 0{\cdot}999$, $n = 9$), being 2·5 times greater than that of the reaction of ester *I* with methoxide. In the case of the analogous trinitro derivatives[2], too, methyl ester of N-methyl-N-(2,4,6-trinitrophenyl)glycine reacted (three times) faster than methyl ester of N-(2,4,6-trinitrophenyl)glycine.

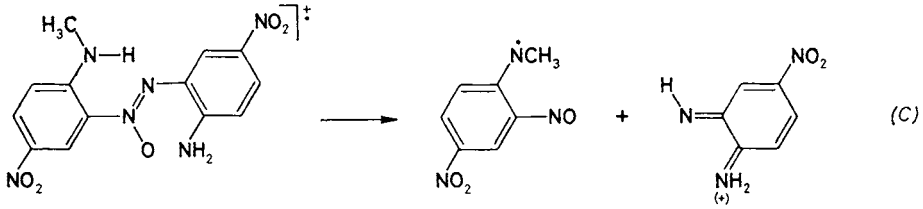
All attempts at preparation of the product of the second reaction step of the reaction of ester *II* with methoxide gave products with electronic spectra different from those of the product formed at the starting ester concentration of about 10^{-4} mol l^{-1} (i.e. the concentration used in the kinetic experiments). In the end we applied the following procedure: The solution of ester *II* was treated with only such small amount of sodium methoxide that only the nitroso compound *IV* was formed, and then the reaction was finished by further addition of concentrated sodium methoxide or aqueous sodium hydroxide. In this way we obtained a mixture containing about 90% 2-amino-2'-methylamino-5,5'-dinitro-ONN-azoxybenzene (*V*) and about 10% 2,2'-bis(methylamino)-5,5'-dinitroazoxybenzene (*VI*) (Eq. (*B*)).



Both the compounds were identified by their ^1H, ^{13}C NMR and mass spectra (compound *V* by its ^{15}N NMR spectrum, too). The ^{15}N NMR spectrum provides the strongest evidence about structure of compound *V*, since the signals with δ −56·5 and −60·1 can be unambiguously assigned only to the azoxy group[8]. The ^{15}N NMR spectrum of compound *VI* could not be measured because of its slight solubility in dimethyl sulphoxide.

Mutual positions of oxygen atom of azoxy group and methylamino group in compound *V* were determined from the mass spectrum. The dominant fragmentation of azoxy compounds giving the most intensive peak (the base peak) proceeds according to Eq. (*C*). In the spectrum of compound *V* we found the base peak m/z 152. On the other hand, the fragment with m/z 166, which would be formed from

the isomeric 2-amino-2'-methylamino-5,5'-dinitro-NNO-azoxybenzene, was not observed in the spectrum. A very intensive peak with m/z 166 was found in the mass spectrum of 2,2'-bis(methylamino)-5,5'-dinitroazoxybenzene (*VI*).



(C)

The azoxy compounds isolated are not identical with the reaction product of ester *II* with methoxide at the concentrations used in the spectral measurements. The azoxy compounds *V* and *VI* are formed by bimolecular reactions whose rates must be negligibly low at the concentrations of the starting nitroso compound *IV* below 10^{-4} mol l^{-1}. This fact explains the observed absence of the azoxy compounds *V* and *VI* under the conditions of the kinetic experiments. The respective azoxy compound is also formed from 2-nitroso-4,6-dinitro-N-methylaniline[2], whereas no formation of azoxy compound was observed in the case of 2-nitroso-4,6-dinitroaniline[1]. This fact indicates that an N-methyl group is necessary for the above-described formation of azoxy compounds.

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