UNEXPECTED ROUTE TO 3-SUBSTITUTED 4,6-DINITROANTHRANILS BY OXIDATION OF ANIONIC σ-COMPLEXES OF 1,3,5-TRINITROBENZENE

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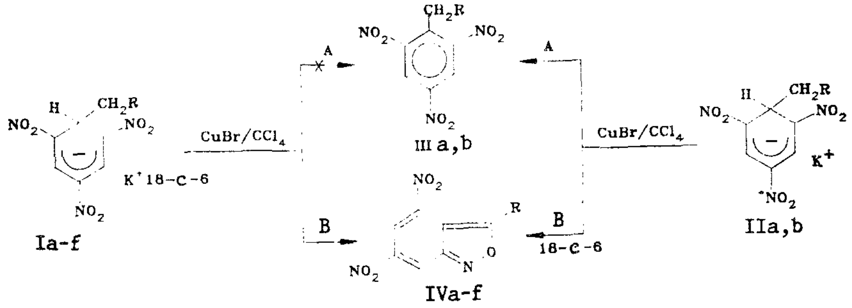
Oxidation of anionic σ-complexes of trinitrobenzene with C—C bonds by the CuBr/CCl_4 system forms 3-R-4,6-dinitroanthranils. When this reaction is carried out a CH_2R group must be at the geminal node of the σ-complex and 18-crown-6-ether.

We have previously proposed a new oxidation system, CuBr/CCl_4, which is efficient for converting anionic σ-complexes of 1-X-2,4-dinitrobenzene with C—C bonds to the respective alkylation products [1]. In the present work we show that σ-complexes of 1,3,5-trinitrobenzene are also oxidized by this system, with retention of the C—C bond. However, when the oxidation takes place in the presence of 18-crown-6-ether, instead of the expected products (III), derivatives of 4,6-dinitroanthranil (IVa-f) are formed. This result is independent of whether the reaction is with σ-complexes (Ia-f) that already contain 18-crown-6, or whether the crown ether is added to the reaction mixture at the same time as CuBr/CCl_4 (IIa, b). The necessary condition for this conversion is the presence of a CH_2R group at the geminal node of the σ-complex.



I, II, IVa R=COMe,b R=COPh; I, IV c R=COEt,d $R=CO\underline{CHCH_2CH_2}$,e R=COOEt,
f R=Ph

The conversion of the anionic σ-complexes to anthranils is very slow; when 5-15 moles of CuBr are used the process is finished after 4-6 days. Raising the temperature or increasing the amount of CuBr accelerates the reaction. For example, upon boiling the reaction is finished in 6-8 h; but in that case a mixture of products is formed consisting of trinitrobenzene (TNB), a substitution product, and an anthranil. When the σ-complexes are oxidized without preliminary separation, the yield of anthranils is somewhat lower. Thus, after 4 days the yield of compound (IVa) is 62% [when Cu(0)/CCl_4 is used, 40%], that of (IVb) is 65%, that of (IVc) is 70%; for oxidation without separation of σ-complex, the yield of IVc is 50%, of IVd is 54%; after 6 days the yield of IVe is 63%, of IVf is 30%. Oxidation in the absence of 18-crown-6 (route A) is slower; the conversion of σ-complexes (IIa, b) to substitution products (IIIa, b) is finished after 2 days, and the yields are 55 and 62%, respectively. In oxidation by the CuBr/CCl_4 system the σ-complex obtained from TNB and $PhCOCH_3$ in the presence of Et_3N gives a complex mixture of products from which the corresponding anthranil could not be separated.

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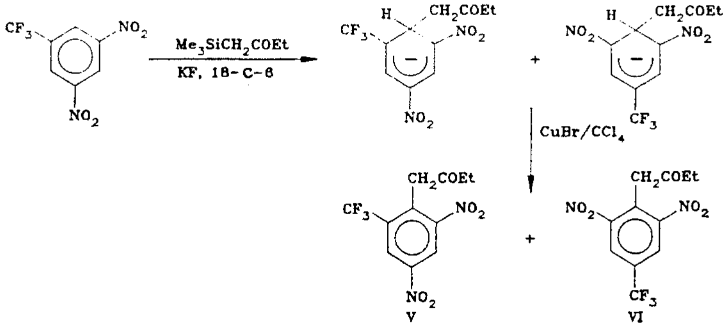
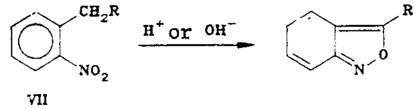
One last condition for anthranil formation is the presence of three nitro groups in the aromatic nucleus. Thus in the oxidation of the σ-complex of 3,5-dinitrobenzyl trifluoride, only substitution products (V) and (VI), in 1:1 mixture, were separated.



It is known that nitroaromatic compounds of type (VII) can be converted to anthranils in both acid and basic medium [3].



It can be assumed that the σ-complexes are first oxidized to substitution products, which then cyclize to anthranils. But attempts to obtain anthranils from substituted TNB in the presence of KF and 18-crown-6 or acid (H_2SO_4, CF_3COOH, HCl) were unsuccessful. Apparently anthranils form directly from the anionic σ-complex.

Thus the oxidation of TNB σ-complexes by $CuBr/CCl_4/MeCN$ makes it possible to obtain 3-substituted 4,6-dinitroanthranils. It should be noted that in spite of the large number of compounds known of this class, there is only one report of the synthesis of 4,6-dinitroanthranil as a byproduct of the irradiation of the respective stilbene [4].

The mass spectrometric behavior of compounds (IVa-f) is unique. Thus with electron-impact ionization the molecular ions can be reliably recorded only in the spectra of (IVb, e, f). On the other hand with compounds (IVa, c, d) only the protonated $(M + H)^+$ or cluster $(M + NH_4)^+$ ions, obtained by chemical ionization, were stable. The primary decomposition processes of the molecular (or protonated molecular) ions of (IVa-f) are related to the elimination of hydroxyl, with participation of the alkyl (or phenyl) hydrogen of the acyl (or phenyl) residue at position 3 and the oxygen of the 4-nitro group of (IVa, c-e); this is typical of the fragmentation of arylnitrenes with radicals containing hydrogen in ortho (or peri) position to nitro]5]. The second decomposition route of M^+ of these compounds is characterized by scission of the RCO—Het bond, with transfer of a hydrogen to the hetaryl fragment (ion 209) of (route A) with formation of RCO^+. Thereafter ion 209 loses NO and NO_2 groups [5]. Finally the third route for dissociative ionization of the molecular ions of (IVa-f) proceeds with loss of a radical, and the resulting 236 ion then loses not CO, but again NO or NO_2 radicals.

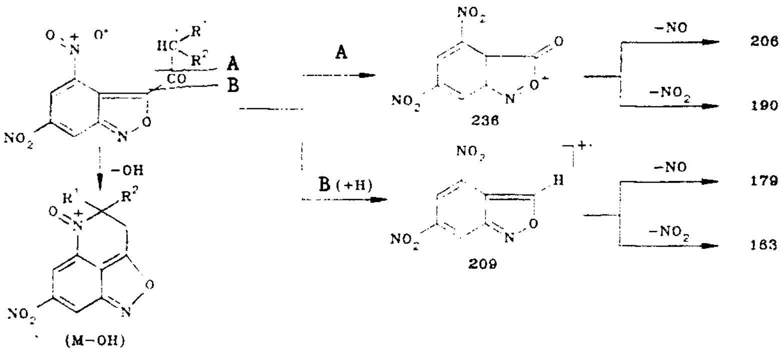


TABLE 1. Spectral Properties of 3-Substituted 4,6-Dinitroanthranils (IVa-f)

Compound	Empirical formula	PMR spectrum, δ, ppm (J, Hz)	IR spectrum (in KBr), ν, cm^{-1}			Mass spectrum, m/z (I_{rel}, %)*
			s, NO_2	as, NO_2	C=O (Ph)	
IV a	$C_9H_5N_3O_6$	2,80 s (3H); 8,92 d (1H, J=2); 9,15 d (1H, J=2)**	1345	1550	1720	269 $[M+NH_4]^+$ (100), 252 $[M+H]^+$ (27), 235 (5), 235 (12), 225 (5), 224 (8), 222 (24), 210 (5), 180 (3), 130 (3), 88 (25)
IV b	$C_{14}H_7N_3O_6$	7,30...8,00 (Ph); 8,91 d (1H, J=2); 9,25 d (1H, J=2)***	1350	1550	(1595)	313 [M] (2), 213 (6), 209 (2), 179 (2), 167 (2), 149 (3), 122 (12), 120 (4), 105 (100), 77 (91), 51 (33)
IVc	$C_{10}H_7N_3O_6$	1,35 t (3H, J=7,3); 3,25 t (2H, J=7,3); 8,85 d (1H, J=2); 9,05 d (1H, J=2)**	1350	1550	1720	283 $[M+NH_4]^+$ (10), 266 $[M+H]^+$ (100), 249 (15), 236 (23), 210 (12), 169 (6), 111 (18), 97 (7), 95 (9), 88 (61), 57 (88)
IVd	$C_{11}H_7N_3O_6$	0,8...1,4 (4H); 2,50...2,70 (1H); 8,91 d (1H, J=2)**	1350	1550	1680	278 $[M+H]^+$ (100), 277 [M] (12), 261 (11), 250 (38), 236 (44), 220 (16), 190 (10), 144 (6), 129 (4), 116 (5), 88 (62)
IVe	$C_{10}H_7N_3O_7$	1,52 t (3H, J=7); 4,58 q (2H, J=7); 8,98 d (1H, J=2); 9,08 d (1H, J=2)**	1345	1545	1735	281 [M] (43), 236 (70), 209 (100), 179 (5), 163 (2), 137 (7), 116 (15), 105 (9), 89 (50), 88 (97), 61 (30)
IVf	$C_{17}H_7N_3O_5$	7,40...7,60 (Ph); 8,85 d (1H, J=2); 9,05 d (1H, J=2)**	1345	1540	(1605)	285 [M] (55), 268 (30), 239 (25), 181 (40), 165 (33), 105 (24), 103 (58), 93 (42), 91 (97), 77 (100), 51 (90)

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*M^+ (or cluster) ions and the 10 most intense peaks are shown. For compounds (IVa, c, d) by chemical ionization; for (IVb, e, f), by electron impact.

**Solvent CD_3CN.

***Solvent $(CD_3)_2CO$.

EXPERIMENTAL

PMR spectra were recorded with a Tesla BS-467 spectrometer (60 MHz), TMS internal standard. IR spectra were obtained with KBr tablets and a UR-20 instrument. Mass spectra were obtained with a Varian MAT-111 apparatus by electron-impact ionization (EI) at 80 eV energy, and with a Finnigan 4615 instrument by chemical ionization (Reagent gas, NH_3).

MeCN and CCl_4 were purified by standard procedures. KF was dried for 2 h at 200°C at 1 mm Hg. 18-Crown-6 ether was distilled from the commercial complex with MeCN at 165°C (1 mm Hg). σ-Complexes of TNB were obtained according to [2].

Spectral properties of compounds (IVa-f) are shown in Table 1. For the first time satisfactory data for C, H, and N content were obtained for compounds (IIIb), (IVa-f), and (V) (VI).

TNB–Acetone Complex (Ia). A mixture of 0.5 g (2.5 mmole) of TNB, 0.66 g (2.5 mmole) of 18-crown-6, and 0.3 g (5.2 mmole) of KF in 5 ml of acetone was stirred for 10 min. The mixture was filtered, acetone was distilled off, and ether was added to the residue. The precipitated solid was filtered off and dried in vacuum. Yield 1.3 g (95%). Mp 154-156°C.

Trinitrobenzene–Acetophenone Complex (Ib) was obtained similarly in 80% yield. PMR spectrum [in $(CD_3)_2CO$], ppm (J, Hz): 8.5 s (2H); 8.1-7.7 m (5H); 5.21 t (1H, J = 3); 3.15 d (2H, J = 3).

2,4,6-Trinitrophenylacetone (IIIa). A mixture of 0.31 g (1 mmole) of σ-complex (IIa), obtained according to [6], 0.015 g (0.1 mmole) of CuBr, and 0.03 g (0.2 mmole) of α,α'-bipyridyl in 10 ml of 1:1 MeCN–CCl_4 was stirred for 4 days. The reaction mixture was treated with 10 ml of 10% HCl and extracted with benzene. The extracts were washed with water and dried with $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a SiO_2 column (40/100) and eluted with benzene. Yield, 0.15 g (55%), bp 87-89°C. According to [7], bp 89°C.

2,4,6-Trinitrophenylacetophenone (IIIb, $C_{14}H_9N_3O_7$) was obtained similarly from 0.37 g (7 mmole) of complex (IIb). Yield 0.2 g (62%), bp 161-162°C. PMR spectrum [in $(CD_3)_2CO$], ppm: 9.14 s (2H); 8.2-7.5 m (5H); 5.24 s (2H).

3-Propionyl-4,6-dinitroanthranil (IVc). (A). A mixture of 1.2 g (2 mmole) of σ-complex (Ic), 0.03 g (0.2 mmole) of CuBr, and 0.03 g (0.2 mmole) of α,α'-bipyridyl in 10 ml of 1:1 MeCN–CCl_4 was stirred for 4 h. The mixture was treated with 10 ml of 10% HCl and extracted with benzene. The extracts were washed with water and dried with $MgSO_4$. The benzene was evaporated and the residue was chromatographed on a SiO_2 column (40/100) and eluted with benzene. After evaporation of benzene the residue was recrystallized from ethanol. Yield 0.37 g (70%), mp 120-121°C.

(B). A mixture of 0.21 g (1 mmole) of TNB, 0.11 g (1 mmole) of Me_3SiCH_2COEt, 0.26 g (1 mmole) of 18-crown-6, and 0.08 g (1.4 mmole) of KF in 5 ml of MeCN was stirred for 3 h in an argon atmosphere. The mixture was filtered and the filtrate was treated with 5 ml of CCl_4, 0.02 g (0.15 mmole) of CuBr, and 0.02 g (0.15 mmole) of α,α'-bipyridyl, and stirred for 4 days. Separation was carried out as in the preceding experiment. Yield 0.13 g (50%).

3-Acetyl-4,6-dinitroanthranil (IVa) was obtained by method (A) from 1.11 g (2 mmole) of σ-complex (Ia). Yield 0.31 g (62%), mp 143-144°C. When the Cu(0)/CCl_4 system was used, anthranil (IVa) was separated in 40% yield.

(C). A mixture of 0.31 g (1 mmole) of σ-complex (IIa), 0.26 g (1 mmole) of 18-crown-6, 0.015 g (0.01 mole) of CuBr, and 0.015 g (1 mmole) of α,α'-bipyridyl in 5 ml of MeCN was stirred for 4 days. (IVa) was separated as in the preceding experiment. Yield 0.12 g (48%).

3-Benzoyl-4,6-dinitroanthranil (IVb) was obtained by method (A) from 0.63 g (1 mmole) of σ-complex (Ib). Yield 0.2 g (65%), mp 163-164°C.

Compound (IVb) was obtained, like (IVa), by method C from 0.37 g (1 mmole) of complex (IIb) and 0.26 g (1 mmole) of 18-crown-6 in 0.19 g (62%) yield.

3-Carbethoxy-4,6-dinitroanthranil (IVe) was obtained by method A from 1.2 g (2 mmole) of σ-complex (Ie) by mixing for 6 days. Yield 0.35 g (63%), mp 72-73°C.

3-Phenyl-4,6-dinitroanthranil (IVf) was obtained by method A from 1.3 g (2 mmole) of σ-complex If with stirring for 6 days. Yield 0.17 g (30%), mp 158-159°C.

3-Cyclopropylcarbonyl-4,6-dinitroanthranil (IVd) was obtained by method (B) from 0.16 g (1 mmole) of $CH_2{=}C(OSiMe_3){-}\underbrace{CHCH_2CH_2}$. After addition of CuBr, CCl_4, and α,α'-bipyridyl the mixture was stirred for 5 days. Yield 0.15 g (54%), mp 110-112°C.

Oxidation of a Mixture of σ-Complexes of 3,5-Dinitrobenzyl Trifluoride with Methyl Ethyl Ketone (B). A mixture of 0.48 g (2 mmole) of 3,5-dinitrobenzyl trifluoride, 0.28 g (2 mmole) of Me_3SiCH_2COEt, 0.53 g (2 mmole) of 18-crown-6, and 0.12 g (2.1 mmole) of KF in 10 ml of MeCN was stirred for 3 h. The mixture was filtered, and the filtrate was treated with 5 ml of CCl_4, 0.03 g (0.2 mmole) of CuBr, and 0.03 g (0.2 mmole) of α,α'-bipyridyl and stirred for 1 day. Then 10 ml of 10% HCl was added and the mixture was extracted with benzene. The extracts were washed with water and dried with $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a column of SiO_2 (40/100). The yield of the mixture of (V) and (VI) ($C_{11}H_9F_3N_2O_5$) was 0.38 g (63%). The PMR spectrum indicates formation of two isomeric alkylation products. PMR spectrum (in CD_3CN), ppm (J, Hz): 9.05 d (J = 2); 8.61 d (J = 2) and 8.55 s (2H); 4.48 s and 4.45 s (2H); 2.75 q (2H, J = 7.3), 1.15 t (3H, J = 7.3).

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SYNTHESIS AND STRUCTURE OF DERIVATIVES OF AZADITHIAPENTALENEANTHRONE AND ISOTHIAZOLEANTHRONE

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The reaction of N,N'-dialkyl- or N,N'-diaryl-1,5-diaminoanthrones with sulfur in a polar aprotic solvent in the presence of a base leads to the formation of 4-alkyl(aryl)amino-9-alky(aryl)-5H-anthra[1,9,8-bcde]-9-aza-1,10λ^4-dithiapentalen-5-ones. The reaction of the 1,5-diaminoanthrone, followed by methylation, leads to 7-amino-10-methylthio- and 7-amino-8,10-dimethylthio-6H-anthra[9,1-cd]isothiazol-6-ones. The structures of the last two compounds and of 4-methylamino-9-methylazadithiapentaleneanthrone were studied by x-ray crystallography. Elimination of the amino group occurs in each series. The structural features and the spectral characteristics of the new heterocyclic systems are discussed.

Compounds of 1,6,7λ^4-trithiapentalene and its heteroanalogs have been investigated intensively in connection primarily with the problem of aromaticity and "no bond—single bond" resonance of the I ↔ I' ↔ I" type [1-5]. Together the known data show that trithiapentalene is an aromatic 10π-electron system similar to naphthalene. Condensed compounds containing the bicycle (I) have been investigated to a significantly lesser degree.

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