4,6,12,14-Tetrakis (2-phenethyl)-1,9-dithia-4,6,12,14-tetraazacyclohexadecane (V, $C_{42}H_{56}N_4S_2$) was prepared analogously from 3.28 g (0.01 mole) diamine II and 4 ml 40% formaldehyde solution with 2.3 g (68% yield. Oil.

7,9,18,20-Tetrakis(2-phenethyl)-1,4,12,15-tetrathia-7,9,18,20-tetraazacyclodocosane (VI, $C_{46}H_{64}N_4S_4$) was prepared analogously from 3.88 g (0.01 mole) 1,8-bis(2-phenethylamino)-3,6-dithiaoctane and 4 ml 40% formaldehyde solution. Yield 2.52 g (63%). Oil. PMR spectrum: 7.21 (m, $C_6H_5$), 4.20 (m, $C_6H_5CH_2$), 3.37-3.14 (q, $NCH_2N$), 2.76 (m, $NCH_2$), 2.68 ppm (m, $SCH_2$).

Complex 7,9,18,20-Tetrakis(2-phenethyl)-1,4,12,15-tetrathia-7,9,18,20-tetrazacyclodocosane with Chloroform (VII, $C_{46}H_{64}N_4S_4 \cdot CHCl_3$). A solution of 1.0 g macroheterocycle VI in 20 m. chloroform was heated to boiling. After cooling, VII was precipitated by petroleum ether or by removal of chloroform and the residue was recrystallized from methanol. Yield 0.9 g (82%). mp 209-210°C. PMR spectrum: 8.61 (s, $CHCl_3$), 7.29 (m, $C_6H_5$), 5.36 (m, $C_6H_5CH_2$), 3.42 (s, $NCH_2N$), 2.93 ppm (m, $NCH_2$, $SCH_2$).

## LITERATURE CITED

1. M. G. Voronkov, V. I. Knutov, and M. K. Butin, Khim. Geterotsikl. Soedin., No. 11, 1563 (1988).
2. M. Hiraoka, Crown-Compounds [Russian translation], Mir, Moscow (1986).
3. K. B. Yatsimirskii and Ya. D. Lampeka, Physicochemistry of Metal Complexes with Macrocyclic Ligands [in Russian], Nauk. Dumka, Kiev (1985).
4. M. G. Voronkov and V. I. Knutov, Sulfur Rep., 6, 137 (1986).
5. Yu. A. Zolotov, V. P. Ionov, E. V. Rybakova, V. I. Knutov, and M. G. Voronkov, Zh. Neorg. Khim., 32, 2228 (1987).
6. M. G. Voronkov, V. I. Knutov, V. A. Usov, M. K. Butin, and O. B. Bannikova, Khim. Geterotsikl. Soedin., No. 11, 1474 (1979).
7. M. G. Voronkov, V. I. Knutov, M. K. Butin, and O. B. Bannikova, Khim. Geterotsikl. Soedin., No. 9, 1228 (1981).
8. H. Bestian, Annalen, 556, 210 (1950).
9. F. Vogtle, H. Puff, E. Friedrichs, and W. M. Müller, J. Chem. Soc. Chem. Commun., No. 24, 1398 (1984).

# REACTIONS OF 10-TELLURONIAANTHRACENE PERCHLORATES WITH NUCLEOPHILES

A. A. Ladatko, I. D. Sadekov,
L. N. Étmetchenko, and V. I. Minkin

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10-Telluroniaanthracene perchlorates react with nucleophiles ($X^-$ = halide, hydroxide, methoxide) via intermediate free telluroxanthyl radicals. With 9-aryl-10-telluroniaanthracene perchlorates, high yields of 9-aryl-9-X-telluroxanthenes are obtained, but with 10-telluroniaanthracene the principal product is 9,9'-bis(telluroxathenyl) as a result of rapid competitive dimerization.

The first 10-telluroniaanthracene perchlorates (I) were reported in 1980 [1]. Other than reduction with aluminohydride to give 9-aryltelluroxanthenes, however, no reactions of these compounds have been described. We have now examined the reactions of (I), exemplified by 9-(p-tolyl)-10-telluroniaanthracene perchlorate (Ia, R = p-$CH_3C_6H_4$) and 10-telluroniaanthracene perchlorate (Ib, R = H), with some nucleophiles. The nucleophiles used water, sodium hydroxide, sodium methoxide, and ammonium halides. The latter were chosen in view of their adequate solubility in the solvent used for the reactions. All the reactions were carried out in dry THF under argon, at ambient temperature.

The perchlorate (Ia) reacted with ammonium halides to give, ultimately, 9-(p-tolyl)-9-halotelluroxanthenes (IIa-c) in satisfactory yields. The formation of the latter compounds,

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M. A. Suslov Research Institute for Physical and Organic Chemistry, Rostov State University, Rostov-on-Don 344071. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 691-695, May, 1989. Original article submitted August 20, 1987.

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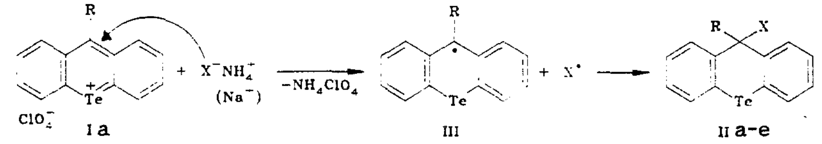
apparently involves the formation of free 9-aryltelluroxanthyl radicals (III). This mechanism is analogous to that described previously [3] for the reaction of pyrilium cations with nucleophiles.

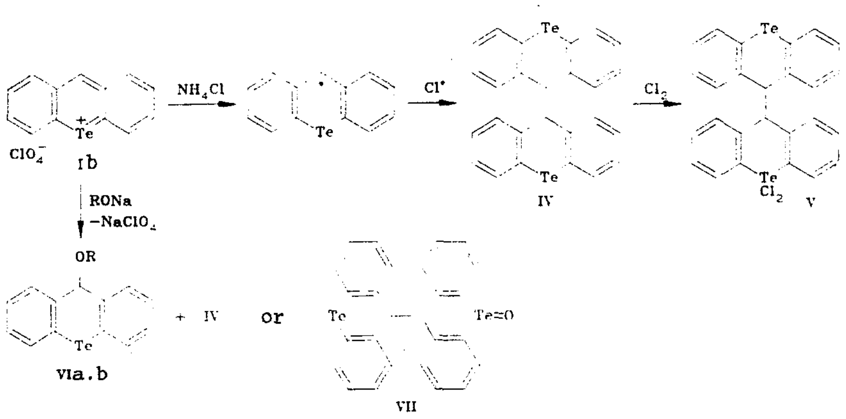


R=$p$-CH$_3$C$_6$H$_4$; a X=Cl; b X=Br; c X=F; d X=OH; e X=OCH$_3$

When the reaction of (Ia) with ammonium chloride was carried out in the cell of an ESR spectrometer, the free radical (III) was detected, its ESR spectrum being identical with that of the radical generated by reduction of (Ia) with zinc dust in tetrahydrofuran [4, 5].

The reaction of (Ia) with sodium hydroxide gave 9-(p-tolyl)-9-hydroxytelluroxanthene (IId). The structures of (IIa-c) were proved by direct synthesis, in addition to their elemental analyses and PMR spectra. Treatment of solutions of (IId) in ether or tetrahydrofuran with gaseous HX (X = Br or Cl) afforded compounds which were identical with (IIa, b) obtained by exchange reactions in their physical constants and spectral characteristics.

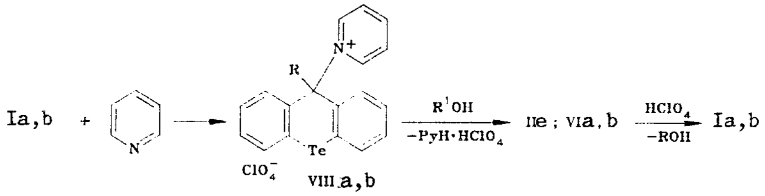
Different behavior was seen in the reactions of the unsubstituted perchlorate (Ib) with nucleophiles. Although no free radicals were detected when the reaction was carried out in the cell of an ESR spectrometer, the formation in most of the reactions of 9,9'-bis(telluroxanthenyl) (IV) as a by-product (obtained previously by reduction of telluroxanthone with zinc dust in a mixture of hydrochloric and acetic acids [6]), indirectly suggests the radical nature of the reaction. The mechanism proposed for the reaction of 9-(p-tolyl)-10-telluronia-anthracene with nucleophiles is also operative in these cases, but the resulting unsubstituted telluroxanthyl radical is so reactive that it undergoes rapid dimerization. The classical method for the preparation of free xanthyl radicals, by reduction of xanthylium salts with zinc dust in an inert atmosphere [7, 8], results in the case of 10-telluroniaanthracene, as expected, in the formation of the dimer (IV). Neither could the telluroxanthyl radical (III) (R = H) be detected on heating (IV) in an inert atmosphere to temperatures over 200°C, although this method has been used successfully to generate free xanthyl radicals [9]. Treatment of (Ib) with ammonium chloride under the same conditions as used for (Ia) gave a mixture of two compounds, which could be separated by virtue of their different solubilities. The other compound contained chlorine, and from its elemental analysis and conversion into (IV) on treatment with Na$_2$S$_2$O$_5$ was 9,9'-bis(telluroxanthenyl)-10,10-dichloride (V). Compound (IV) and (V) are probably formed as follows:



II a R=OCH$_3$; b R=CH(CH$_3$)$_2$

The compound (IV), obtained by recombination of the telluroxanthyl radicals, is further chlorinated by chlorine, formed by recombination of Cl.

Compound (IV) or its reaction products are also formed when 10-telluronaanthracene perchlorate reacts with sodium methoxide and isopropoxide. In the first case, in addition to 9-methoxytelluroxanthene (VIa), the telluroxanthenyl (IV) was obtained, and in the second, in addition to 9-isopropoxytelluroxanthene (VIb), the compound (VII), which was converted into the dimer (IV) on treatment with aqueous $Na_2S_2O_5$. This compound appears to be 9,9'-bis(telluroxanthenyl)-10-telluroxide. In order to identify the ethers (VI) unambiguously, they were obtained by an independent method which enabled side reactions to be avoided. This method, proposed previously for the oxygen and sulfur analogs of (I) [10, 11], involves the reaction of N-(9-R-telluroxanthenyl)pyridinium perchlorates (VIII) with the appropriate alcohols. Compound (VIII) was obtained in high yields by reacting the 10-telluroniaanthracene perchlorates (I) with pyridine. The $C_{(9)}$—N bonds in these compounds, as in their oxygen and sulfur analogs [10, 11], are extremely labile, and are readily cleaved on treatment with alcohols to give pyridinium perchlorate and the telluroxanthenes (VI). The constants of the (VI) obtained in this way, and those of the compounds obtained by treating 10-telluroiniaanthracene perchlorates with sodium alkoxides, were fully identical. It is noteworthy that (VI) are readily converted into the perchlorates (I) by treating their ethereal solutions with 70% $HClO_4$.



## EXPERIMENTAL

IR spectra were obtained on a UR-20 instrument as suspensions in Vaseline grease, and PMR spectra on a Tesla BS-487C (80 MHz), internal standard HMDS.

The 10-telluronaianthracene picrates (Ia) and (Ib) were synthesized as described in [2]. The elemental analyses of (II-VIII) for C and H were in agreement with the calculated values.

General Method of Preparation of 9-Halo-9-(p-tolyl)telluroxanthenes (IIa-c), by reaction of the perchlorates (I) with ammonium salts. Into a flask fitted with a magnetic stirrer, containing a mixture of 1 g (2.5 mmole) of (Ia) and 1 g of the appropriate ammonium salt, was distilled over sodio-diphenylketyl under argon 50 ml of tetrahydrofuran. The suspension was stirred until its color had changed from dark blue to yellow. The solvent was removed under reduced pressure, and (IIa-c) extracted with boiling benzene (3 × 15 ml). The solution was filtered and the solvent removed. The product (IIa-c) was recrystallized from benzene—octane.

9-Chloro-9-(p-tolyl)telluroxanthene (IIa, $C_{20}H_{15}ClTe$). Yellow crystals, mp 267-269°C (decomp.), yield 1 g (96%).

9-Bromo-9-(p-tolyl)telluroxanthene (IIb, $C_{20}H_{15}BrTe$). Yellow crystals, mp 237-238°C (decomp.), yield 1 g (86%).

9-Fluoro-9-(p-tolyl)telluroxanthene (IIc, $C_{20}H_{15}FTe$). Yellow crystals, mp 269-271°C (decomp.), yield 0.81 g (81%).

General Method of Preparation of 9-Halo-9(p-tolyl)telluroxanthenes (IIa-c) by Reaction of Telluroxanthenol (IId) with Hydrohalic Acids (HX). To a solution of 1 g (2.5 mmole) of (IId) in 50 ml of ether was added 15 ml of an aqueous solution of the appropriate HX with vigorous stirring. After stirring for 30 min, the ether was allowed to evaporate. The solid was filtered off and dried, to give (IIa-c), the constants of which corresponded to those of the compounds described above. The yields were: (IIa) 96; (IIb) 86, and (IIc) 87%.

9-Hydroxy-9-(p-tolyl)telluroxanthene (IId). To a solution of 0.5 g of KOH in 50 ml of water was added 1 g (2.1 mmole) of the perchlorate (Ia), and the mixture stirred at 80-90°C for 30 min. The mixture was then cooled, and the solid filtered off, washed with water, and dried to give 0.8 g (90%) of pale yellow crystals, mp 194°C (from benzene—octane) (literature mp 195°C [2]).

9-Methoxy-9-(p-tolyl)telluroxanthene (IIe, $C_{21}H_{18}OTe$). To a solution of sodium methoxide, obtained from 0.115 g (5 mmole) of sodium and 10 ml of methanol, was added 1 g (2.1 mmole) of (Ia), and the mixture boiled for 30 min. The solution was cooled and poured into 50 ml of ice water. The solid which separated was filtered off, washed with water, and dried to give 0.7 g (91%) of yellow crystals, mp 125°C (from octane).

Reaction of 10-Telluroniaanthracene Perchlorate (Ib) with Ammonium Chloride. In a flask fitted with a magnetic stirrer, containing a mixture of 1.96 g (5 mmole) of perchlorate (Ib) and 1 g (20 mmole) of ammonium chloride, was distilled over sodio-diphenylketyl under argon 50 ml of tetrahydrofuran. The suspension was stirred at room temperature for 2 h, and the solvent removed under reduced pressure. The residue was extracted with boiling toluene (3 × 20 ml), filtered, and the solvent removed to give 0.7 g (48%) of 9,9'-bis(telluroxanthenyl) (IV, $C_{26}H_{18}Te_2$) as yellow crystals, mp 300°C (from benzene–octane). The residue of (V) after extraction (0.4 g) was washed with hot water and dried. Reduction of this material with aqueous $Na_2S_2O_5$ in the usual way gave 0.3 g of (IV), mp > 300°C.

Reaction of (Ib) with Sodium Methoxide. To a solution of sodium methoxide, obtained by dissolving 0.07 g (3 mmole) of sodium in 10 ml of methanol, was added with stirring 1.308 g (3 mmole) of (Ib). After stirring for 1 h at room temperature, the solution had become colorless. The solution was poured into 70 ml of cold water, and the solid which separated was filtered off and dried. Extraction with boiling hexane followed by removal of the solvent gave 0.55 g (51%) of 9-methoxytelluroxanthene (VIa, $C_{14}H_{12}OTe$), yellow crystals, mp 71°C (from hexane–benzene). The residue after extraction with hexane weighed 0.35 g. Yellow crystals of (IV), mp > 300°C.

Reaction of (Ib) with sodium isopropoxide was carried out by the method described above Yield of 9-isopropoxytelluroxanthene (VIb, $C_{16}H_{16}OTe$) 0.60 g (51%), yellow crystals, mp 85°C. The residue after extraction (0.45 g) was insoluble in the usual organic solvents, and on reduction with $Na_2S_2O_5$ gave 0.2 g of (IV).

N-(9-(p-Tolyl)telluroxanth-9-yl]pyridinium Perchlorate (VIIIa, $C_{25}H_{20}ClNO_4Te$). The perchlorate (Ia) (2.4 g, 5 mmole) was added in small portions with vigorous stirring to 5 ml of freshly-distilled pyridine. After stirring for 30 min at room temperature, 15 ml of dry ether was added, and the solid filtered off, washed with dry ether, and dried in vacuo until the odor of pyridine had disappeared. Yellow crystals, mp 173°C (decomp.), yield 2.6 g (90%).

N-(9-Telluroxanthyl)pyridinium Perchlorate (VIIIb, $C_{18}H_{13}ClNO_4Te$). The perchlorate (Ib) (3.925 g, 10 mmole) was added with vigorous stirring to 3.5 ml of freshly-distilled pyridine at a temperature not exceeding 10°C. After stirring for 30 min, the mixture had become viscous. Excess pyridine was distilled off under reduced pressure, and the residue washed with dry ether and dried. Yellow crystals, mp 192°C, yield (VIIIb) quantitative.

9-Methoxytelluroxanthene (VIa, $C_{14}H_{12}OTe$). The perchlorate (VIIIb) was boiled with vigorous stirring in 10 ml of dry methanol for 30 min. The solvent was removed under reduced pressure, the residue extracted with benzene, and the solvent removed to give (VIa) as yellow crystals, mp 71°C (from octane–benzene). Yield 1.23 g (90%). PMR spectrum ($CCl_4$): 3.65 (3H, s, $OCH_3$), 4.45 (1H, s, 9-H), 6.75-8.75 ppm (8H, m, $H_{arom}$).

Similarly, from (VIIIa) there was obtained the telluroxanthene (IIe), as yellow crystals, mp 125°C (from octane–benzene), yield 70%.

9-Isopropoxytelluroxanthene (VIb, $C_{16}H_{16}OTe$) was obtained similarly to (VIa). Yellow crystals, mp 85°C (from hexane), yield 84%. PMR spectrum ($CCl_4$); 1.26 (6H, d, ($CH_3$) , 3.77 1H, m, CH), 4.50 (1H, s, 9-H), 6.80-7.80 ppm (8H, m, $H_{arom}$).

## LITERATURE CITED

1. I. D. Sadekov, A. A. Ladatko, E. I. Sadekova, and V. I. Minkin, Khim. Geterotsikl. Soedin, No. 2, 274 (1980).
2. I. D. Sadekov, A. A. Ladatko, E. I. Sadekova, G. N. Dorofeenko, and V. I. Minkin, Khim. Geterotsikl. Soedin., No. 3, 343 (1981).
3. M. V. Nekhoroshev, V. B. Panov, A. A. Bumbar, and O. Yu. Okhlobystin, Zh. Obshch. Khim., 50, 958 (1980).
4. V. B. Panov, I. D. Sadekov, A. A. Ladatko, O. Yu. Okhlobystin, and V. I. Minkin, Khim. Geterotsikl. Soedin., No. 10, 1421 (1980).
5. A. A. Bumber, E. P. Ivakhnenko, A. A. Ladatko, A. A. Arutyunyants, I. D. Sadekov, and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., No. 9, 1196 (1988).
6. K. Sh. Karaev, N. G. Furmanova, N. V. Belov, I. D. Sadekov, A. A. Ladatko, and V. I. Minkin, Zh. Skh. Khim., 22, 106 (1981).
7. L. Lunazzi, A. Mangini, G. Placucci, C. Vincenzi, and J. Degani, Mol. Phys., 19, 543 (1970).
8. M. Hori, T. Kataoka, H. Shimizu, C. F. Hsu, Y. Asaki, and E. Mizuta, Chem. Pharm. Bull., 22, 32 (1974).
9. M. D. Sevilla and G. Wincow, J. Phys. Chem., 72, 3635 (1968).
10. G. E. Ivanov, G. V. Pavlyuk, and B. T. Kaminskii, Zh. Org. Khim., 18, 1996 (1982).
11. G. E. Ivanov, G. V. Pavlyuk, A. V. Turov, and M. K. Ryzhakov, Zh. Org. Khim., 22, 842 (1986).