9-R-10-TELLURONIAANTHRACENE PERCHLORATES

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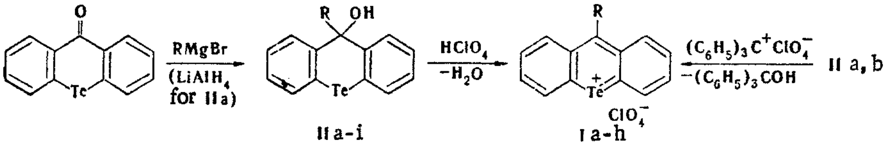
10-Telluroniaanthracene perchlorates with various substituents in the 9 position were obtained by the action of 70% $HClO_4$ on 9-R-10-tellura-9-anthracenols and of trityl perchlorate on 9-R-10-tellura-9-anthracenols and 9-R-9H-10-telluraanthracenes. The IR, UV, and PMR spectral characteristics of the products were investigated.

We obtained the first representatives of 10-telluroniaanthracene salts (I), viz., 10-telluroniaanthracene and 9-(p-tolyl)-10-telluroniaanthracene perchlorates by treatment of the corresponding 10-tellura-9-anthracenols (II) with perchloric acid [1]. The present paper is devoted to a detailed description of methods for the synthesis and some properties of 9-substituted 10-telluroniaanthracene perchlorates.

The starting substances for the preparation of the 9-R-10-telluroniaanthracene perchlorates (I), viz., 9-R-10-tellura-9-anthracenols (II), were synthesized by the reaction of 10-tellura-9-anthrcenone [1, 2] with the corresponding organomagnesium compounds. The use of a 1.5-3-fold excess of the organomagnesium compound for the reaction promotes an increase in the yields. The simplest representative of telluraanthracenols, viz., 10-tellura-9-anthracenol (IIa), was obtained by reduction of 10-tellura-9-anthracenone with lithium aluminum hydride [1, 2].



I, IIa R=H; b R=p-$CH_3C_6H_4$; c R=m-$CH_3C_6H_4$; d R=p-$CH_3OC_6H_4$; e R=p-FC_6H_4; f R=p-BrC_6H_4; g R=α-$C_{10}H_7$; h R=$C_6H_5CH_2$; II i R=CH_3

The 10-Tellura-9-anthracenols (IIa-i) are yellow crystalline compounds that crystallize satisfactorily from nonpolar solvents; the stretching vibrations of the hydroxy group in the IR spectra of these compounds (in mineral oil) show up in the form of broad diffuse bands at 3260-3540 cm^{-1} (Table 1).

The synthesis of 9-R-10-telluroniaanthracene perchlorates I from 9-R-10-tellura-9-anthracenols II was accomplished by two methods. The first method consisted in the reaction of ether solutions of II with a sixfold to sevenfold excess of 70% perchloric acid at 20-25°C, as in the preparation of various 10-thionia- [3] and 10-selenoniaanthracene salts [4, 5]. Compounds Ia,b were also obtained by refluxing the corresponding 10-tellura-9-anthracenols with an equimolar amount of trityl perchlorate in trifluoroacetic acid. An attempt to obtain 10-telluroniaanthracene perchlorate (Ia) by the method commonly used in the chemistry of xanthylium salts, viz., by oxidative dehydrogenation of the corresponding 9H-10-telluraanthracene by refluxing the latter with trityl perchlorate in glacial acetic acid [3, 5, 6], did not lead to the desired product. However, perchlorate Ia was obtained in close-to-quantitative yield in the reaction of 9H-10-telluraanthracene (IIIa) [2, 7] with trityl perchlorate in trifluoroacetic acid. We also used this method to synthesize 9-(p-tolyl)-10-telluroniaanthracene perchlorate (Ib). The 9H-9-(p-tolyl)-10-telluraanthracene (IIIb)

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TABLE 1. 9-R-10-Tellura-9-anthracenols (IIa-i)

Compound	mp, °C*	ν_{OH}, cm^{-1}	Found, %		Empirical formula	Calc., %		Yield, %
			C	H		C	H	
IIa	110—112	3260	50,7	3,4	$C_{13}H_{10}OTe$	50,4	3,2	77
IIb	195	3500	60,4	3,9	$C_{20}H_{16}OTe$	60,1	4,0	78
IIc	158	—	59,9	3,8	$C_{20}H_{16}OTe$	60,1	4,0	98
IId	179	3480	58,0	4,2	$C_{20}H_{16}O_2Te$	57,7	3,9	74
IIe	157—158	3490	56,7	3,4	$C_{19}H_{13}FOTe$	56,5	3,2	57
IIf	174	3440	49,4	2,7	$C_{19}H_{13}BrOTe$	49,1	2,8	53
IIg	175—177	3420	63,8	3,6	$C_{23}H_{16}OTe$	63,4	3,7	57
IIh	115—116	3540	60,6	3,7	$C_{20}H_{16}OTe$	60,1	4,0	77
IIi	158	3320	51,6	3,6	$C_{14}H_{12}OTe$	51,9	3,7	84

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*Compounds IIa,e,f were purified by chromatography on aluminum oxide in benzene, while IIh was purified in ether by the same method. The remaining compounds were purified by recrystallization: IIb from octane—benzene, IIc from octane, IId,g from alcohol—benzene, and IIi from heptane—benzene.

TABLE 2. 9-R-10-Telluroniaanthracene Perchlorates (Ia-h)

Compound	Dec. temp., °C*	IR spectrum, cm^{-1}	Electronic spectrum, λ_{max}, nm (log ε)	Found, %		Empirical formula	Calc., %	
				C	H		C	H
Ia	120	1590, 1525, 1265, 1240, 1070, 760, 710	298 (4,50), 403 (4,25), 595 (3,58), 647 (3,52)	39,4	2,4	$C_{13}H_9ClO_4Te$	39,8	2,3
Ib†	160	1580, 1520, 1270, 1210, 1160, 1070, 720	298 (4,81), 403 (4,56), 590 (3,91), 633 (3,88)	49,6	2,8	$C_{20}H_{15}ClO_4Te$	49,8	3,1
Ic†	165	1620, 1588, 1270, 1105, 790, 740, 720	296 (4,72), 409 (4,11), 595 (3,98), 653 (3,88)	49,5	2,9	$C_{20}H_{15}ClO_4Te$	49,8	3,1
Id†	207	1610, 1580, 1520, 1280, 1100, 800, 720	298 (4,73), 406 (4,38), 596 (4,00), 651 (3,98)	48,3	3,3	$C_{20}H_{15}ClO_5Te$	48,2	3,01
Ie	228	1580, 1530, 1500, 1300, 1220, 1090	299 (4,85), 410 (4,49), 590 (4,08), 639 (4,04)	46,4	2,8	$C_{19}H_{12}ClFO_4Te$	46,9	2,5
If	231	1590, 1540, 1290, 1090, 1000, 800, 720	295 (4,75), 409 (4,37), 595 (3,98), 647 (3,93)	42,1	2,3	$C_{19}H_{12}BrClO_4Te$	41,7	2,2
Ig	233	1590, 1540, 1290, 1100, 800, 720	296 (4,53), 400 (4,00), 597 (3,74), 648 (3,70)	52,9	2,8	$C_{23}H_{15}ClO_4Te$	53,3	2,9
I†	240	1590, 1530, 1260, 1100, 790, 720	294 (4,38), 401 (3,58), 592 (3,31), 639 (3,19)	49,4	3,1	$C_{20}H_{15}ClO_4Te$	49,8	3,1

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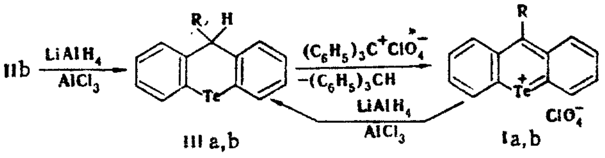
*The substances decomposed explosively when they were melted in a capillary.

†PMR spectra, δ: Ib, 2.17 (s, 3H, CH_3), 6.90-8.70 ppm (m, 12H, aromatic protons); Ic, 2.14 (s, 3H, CH_3), 6.78-8.65 ppm (m, 12H, aromatic protons); Id, 3.81 (s, 3H, OCH_3), 6.88-8.80 ppm (m, 12H, aromatic protons); Ih, 4.93 (s, 2H, CH_2), 6.75-8.60 ppm (m, 13H, aromatic protons).

necessary for its synthesis was obtained by reduction of alcohol IIb with lithium aluminum hydrate, as in the reduction of various diarylmethanols to diarylmethanes [8]. Compound IIIb was also obtained by reduction of perchlorate Ib with lithium aluminum hydride.



The latter two reactions are of independent interest, since they are convenient methods for the preparation of 9-substituted-9H-10-telluraanthracenes, the synthesis of which by presently known methods [2, 7] is extremely difficult.

10-Telluroniaanthracenes perchlorates (Table 2) are black-violet finely crystalline compounds that are soluble (without undergoing any change) in trifluoroacetic acid. They are also soluble in acetic acid, acetone, and nitromethane but react with those solvents. The products of these reactions will be described later. The compositions and structures of I were proved by the results of elementary analysis, IR spectroscopy, and, in some cases (Ib-d, h), by the PMR spectra (see the notes to Table 2).

The electronic spectra of 10-telluroniaanthracene perchlorates Ia-h (CF_3COOH) are characterized by the presence of four absorption maxima at 294-298, 400-410, 590-597, and 633-653 nm that are relatively insensitive to the nature of the substituent in the 9 position. A comparison of the spectra of 10-telluroniaanthracene perchlorate and 10-thioniaanthracene perchlorate (in CH_3COOH, λ_{max}: 241, 276, 377, 480, and 506 nm [3]) attests to a pronounced bathochromic shift of the absorption bands on passing from sulfur to tellurium.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The UV spectra of solutions of the compounds in trifluoroacetic acid were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of solutions in trifluoroacetic acid were obtained with a Tesla BS-487C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard.

10-Tellura-9-anthracenone and 9H-10-telluraanthracene were synthesized by the methods presented in [1, 2, 7].

9-R-10-Tellura-9-anthracenols (IIb-i). These compounds were obtained by the following general method. A 1.2-3-fold excess of an ether solution of the corresponding organomagnesium compound obtained by the usual methods was added with stirring in the course of 20-30 min to a solution of 3.08 g (0.01 mole) of 10-tellura-9-anthracenone in 50 ml of benzene—ether (1:1 by volume), during which a red mixed organomagnesium salt of 10-tellura-9-anthracenol precipitated. Stirring was continued for another 1-2 h, after which hydrolysis was carried out with a saturated solution of ammonium chloride. The organic layer was separated, and the aqueous layer was extracted twice with ether (two 30-ml portions). The organic layers were combined, washed with water, and dried over anhydrous magnesium sulfate. The solvent was then evaporated. The subsequent purification of the 10-tellura-9-anthracenols was carried out either by recrystallization from a suitable solvent or by chromatography on aluminum oxide (see Table 1).

10-Tellura-9-anthracenol (IIa). A 9.24-g (0,03 mole) sample of thoroughly ground 10-tellura-9-anthracenone was added in small portions to a suspension of 1.5 g (0.039 mole) of $LiAlH_4$ in 100 ml of absolute ether, and the mixture was stirred at room temperature for 2 h. Ethyl acetate (100 ml) was then added with cooling and vigorous stirring, and the mixture was decomposed with a saturated solution of ammonium chloride and filtered. The organic layer was separated, and the aqueous layer was extracted twice with ether. The organic layers were combined, washed with water, dried over anhydrous sodium sulfate, and evaporated. The product was chromatographed with a column filled with aluminum oxide (elution with benzene).

9-R-10-Telluroniaanthracene Perchlorates (Ia-h, Table 2). A) A 7-ml (0.07 mole) sample of 70% $HClO_4$ was added dropwise with stirring to a solution of 0.01 mole of the corresponding 9-R-10-tellura-9-anthracenol (IIa-h) in 60 ml of absolute ether, during which the mixture turned dark-blue. The product, which precipitated in quantitative yield, was removed by filtration and washed with absolute ether.

B) A mixture of 5 mmole of 10-tellura-9-anthracenol (IIa,b) or 9H-10-telluraanthracene (IIIa,b) and 5.5 mole of trityl perchlorate in 30 ml of trifluoroacetic acid was refluxed for 30 min, after which it was cooled, and the resulting solution was diluted with 50 ml of absolute ether. The precipitate of the corresponding 10-telluroniaanthracene perchlorate (Ia,b) was removed by filtration, washed on the filter with absolute ether (three 50-ml portions), and air dried. The yields were close to quantitative.

9H-9-(p-Tolyl)-10-telluraanthracene (IIIb). A 0.004-mole sample of telluraanthracenol IIb or perchlorate Ib was added at room temperature to a stirred suspension of 0.5 g (0.013

mole) of $LiAlH_4$ and 3 g (0.023 mole) of aluminum chloride in 50 ml of absolute ether. At the end of the addition the mixture was refluxed with stirring for 1 h, after which it was cooled, and 50 ml of ethyl acetate was added to it gradually. The resulting solution was poured into 100 ml of 20% sulfuric acid, and the mixture was filtered. The organic layer was separated, and the aqueous layer was washed twice with 50-ml portions of ether. The combined ether extracts were dried over sodium sulfate, and the solvent was evaporated to give colorless needles of 9H-9-(p-tolyl)-10-telluraanthracene with ml 163°C (from heptane–benzene) in 75-85% yield. Found: C 62.4; H 4.6%. $C_{20}H_{16}Te$. Calculated: C 62.6; H 4.4%.

LITERATURE CITED

1. I. D. Sadekov, A. A. Ladatko, E. I. Sadekova, and V. I. Minkin, Khim. Geterotsikl. Soedin., No. 2, 274 (1979).
2. I. D. Sadekov, A. A. Ladatko, and V. I. Minkin, Khim. Geterotsikl. Soedin., No. 10, 1342 (1980).
3. C. C. Price, M. Hori, T. Rarasaram, and M. Polk, J. Amer. Chem. Soc., 85, 2278 (1963).
4. M. Renson and L. Christiaens, Bull. Soc. Chim. Belg., 79, 511 (1970).
5. M. Hori, K. Kataoka, and Chen-Fu Hsu, Chem. Pharm. Bull., 22, 15 (1974).
6. W. Bonthrone and D. H. Reid, J. Chem. Soc., No. 9, 2773 (1959).
7. I. D. Sadekov, A. A. Ladatko, and V. I. Minkin, Khim. Geterotsikl. Soedin., No. 11, 1567 (1978).
8. J. Blackwell and W. J. Hickinbottom, J. Chem. Soc., No. 3, 1405 (1961).

SYNTHESIS OF COMPOUNDS OF THE BICYCLO[2.2.1]HEPTANE SERIES THAT ARE FUSED WITH AN OXAZECINE RING

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Derivatives of the bicyclo[2,2,1]heptane series that are condensed with an oxazecine ring were obtained. A number of transformations of the compounds obtained were realized. Data from the IR, NMR, and mass spectra that confirm the structures of the synthesized compounds are presented.

In the course of our research on the preparation of analogs of natural alkaloids we have realized the synthesis of polycyclic nitrogen-containing structures that have the norbornane skeleton. A number of compounds of this type have high spasmolytic [1], antiarrhythmic [2], hypotensive [3], or cardiotonic [4, 5] action. Several highly active natural alkaloids that contain 8-azabicyclo[3.2.1]octane and 9-azabicyclo[4.2.1]nonane systems can be included in this group of compounds [6].

We selected the accessible endo-5-norbornene-2,3-dicarboxylic acid anhydride (I), which is formed by the reaction of cyclopentadiene with maleic anhydride [7], as the starting compound. The corresponding imide (II) is formed smoothly in 65% yield when anhydride I is heated with urea by the method in [8]. The condensation of cyclopentadiene with maleinimide also makes it possible to obtain imide II; however, the yield of the adduct decreases in this case.

The reduction of imide II with lithium aluminum hydride leads to norbornene IIIa, condensed with a pyrrolidine ring. Compound IIIa was characterized in the form of the N-acetyl derivative (IIIb) and the benzenesulfonamide (IIIc).

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