ATRANES

X. 1-Aroxytitatranes*

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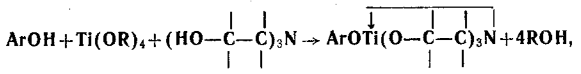
A method is developed for synthesizing hitherto unknown 1-aroxytitatranes $ArOTi(O{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}})_3N$, where Ar is aryl, and the carbon atoms in the O—C—C—N groups are linked to hydrogen atoms or hydrocarbon substituents. It is based on transesterification of tetra-alkyltitanates with an equimolecular mixture of tri(β-hydroxyalkyl)amine and appropriate phenol (naphthol). 17 compounds of the given type were prepared and characterized by this means, the yields basically exceeding 90%.

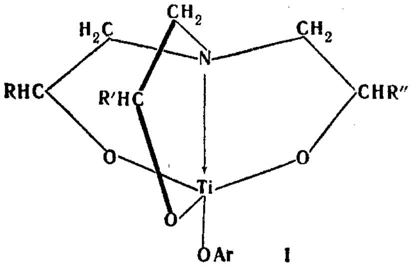
Trialkanolamine derivatives of titanium are described only very briefly in the literature [2–9], which is mainly patent. In most cases the structures of the compounds were not determined.

We have developed a method of synthesizing hitherto unknown 1-aroxytitatranes (I), the equation being



$$ArOH+Ti(OR)_4+(HO{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}})_3N \rightarrow ArO\overset{\downarrow}{Ti}(O{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}})_3N+4ROH,$$

Ar = aryl, R = alkyl (C_2H_5,C_4H_9,etc)



I

The synthesis is carried out by heating together equimolecular amounts of tetraalkyltitanate, tri (β-hydroxyalkyl) amine, and appropriate phenol (or naphtol) in the presence of an appropriate inert solvent (or without it), until the alcohol formed in the reaction completely distils over. Frequently, the 1-aroxytitatranes separate out directly in a crystalline state from the reaction products, and in the presence of the alcohol formed, or even when using the latter as solvent. This shows, that the equilibrium of the reaction is displaced to the right.

In most cases the yield of I is over 90% theory. When some phenols (phenol, o- and p-cresols, p-tert-butylphenol, p-chlorophenol, m- and p-nitrophenol) are mixed with the triethanolamine and tetralkyltitanate, preferably in a solvent medium, the corresponding 1-aroxytitatranes separate out quantitatively, and this can be used analytically to determine esters of orthotitanic acid and triethanolamine. We are unable to prepare 1-(2', 4', 6'-trinitrophenoxy) titatrane, obviously because of steric hindrance due to the two nitro groups ortho to the phenolic hydroxyl.

The Is which we synthesized were pale yellow or colorless crystalline substances. 1-α- and 1-β-naphthoxytitatranes are exceptions, being bright yellow, and also some amorphous titatranes which it was not possible to crystallize. Most of the Is dissolve when heated with dimethylformamide, nitrobenzene, and alcohols, but they are insoluble in water and ether.

The molecular weights of 1-phenoxy and 1-α-naphthoxytitatranes as found cryoscopically in nitrobenzene, and of 1-(2',4',6'-trichlorophenoxy) titatrane found ebullioscopically in nitrobenzene, show those compounds to be monomeric.

That I contains the intramolecular coordination link T ← N is confirmed by the high dipole moments (about 8D) of the compounds, and by IR and NMR spectroscopy data which will be published in subsequent communications.

The table gives the yields, melting points, and analytical data of the compounds.

EXPERIMENTAL

Starting materials. The triethanolamine sold as "pure" was twice vacuum-distilled. Methyl-substituted triethanolamines were prepared by reacting propene oxide with ammonia, mono- and diethanolamine, and purified by vacuum-distillation. The starting phenols (labelled "pure") were purified by vacuum-distillation, or by crystallizing.

Analysis. C and H in the Is were determined by a single sample in oxygen, and N was determined by the micro-Dumas method. Titanium was determined as TiO_2 remaining after ashing at 1000°.

Methods of Synthesis. All the syntheses were carried out in apparatus with ground glass joints, consisting of a 2-necked flask with an 18 cm rod-and-disk fractionating column fitted with a thermometer and condenser set for downward distillation, or in a 2-necked flask with reflux condenser and mercury-sealed stirrer. According to the first method A, the alcohol formed was distilled off from the reactants by heating on a water-bath, (under vacuum), and the solid I which remained was purified by recrystallization. According to the second method B, the crystals precipitated (as an amorphous mass) from the reaction products were filtered off with suction, washed with ether (to remove phenol), and then vacuum-dried. They were subsequently purified by recrystallization.

Three syntheses are described below by way of examples.

1-Phenoxytitatrane. (Method A). A mixture of 17.0 g (0.05 mole) tetra-n-butyltitanate, 7.5 g (0.05 mole) triethanolamine, and 4.7 g (0.05 mole) phenol, was slowly distilled under a slight vacuum; the theoretical quantity of n-butanol distilled over in a day, bp 44–45° (30 mm) (18.4 ml). The amorphous yellow precipitate which was left was suspended in dry ether, filtered off with suction, washed a

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*For Part XI see [1].

1-Aroxytitatranes (I)

Ar	Mp, °C (decomp temp °C)	Recrystallization solvent	Formula	Found					Calculated %					Yield of crude product, %(method),
				C	H	Cl	N	Ti	C	H	Cl	N	Ti	
C_6H_5*	(80.5—84.5)		$C_{12}H_{17}NO_4Ti$	50.56	6.07		5.11	16.51	50.18	5.98		4.88	16.67	100 (A)
2-$CH_3C_6H_4$*	91 —92 (84—85)	Benzene ether	$C_{13}H_{19}NO_4Ti$	51.33	6.35		4.54	15.81	51.83	6.35		4.65	15.90	100 (A)
3-$CH_3C_6H_4$*	91 —91.5 (77—79)	Benzene ether	$C_{13}H_{19}NO_4Ti$	52.01	6.23		4.61	15.75	51.83	6.35		4.65	15.90	100 (A)
2-$CH_3OC_6H_4$*	123 —123.5	Xylene	$C_{13}H_{19}NO_5Ti$	48.95	6.01		3.99	14.95	49.22	6.03		4.41	15.10	74 (A)
4-$(CH_3)_2CHC_6H_4$*	105.5—108	Xylene ether	$C_{15}H_{23}NO_4Ti$	54.28	6.89		4.20	14.37	54.71	7.04		4.25	14.57	81 (A)
4-$(CH_3)_3CC_6H_4$*	108 —109	Dichlorobenzene ether	$C_{16}H_{25}NO_4Ti$	55.45	7.24		4.18	14.16	55.98	7.34		4.08	13.95	100 (A)
5-CH_3-2-(i-C_3H_7)C_6H_3*	(104 —107)	Benzene ether	$C_{16}H_{25}NO_4Ti$	55.64	6.91		4.26	13.63	55.98	7.34		4.08	13.95	97 (A)
4-ClC_6H_4*	124 —126	Xylene	$C_{12}H_{16}ClNO_4Ti$	44.72	5.23	10.84	4.05	14.58	44.80	5.01	11.02	4.35	14.88	100 (A)
2,4,6-$Cl_3C_6H_2$*	209 —210	Dichlorobenzene	$C_{12}H_{14}Cl_3NO_4Ti$	37.15	3.69	27.54	3.74	12.00	36.97	3.61	27.23	3.58	12.26	97 (B)
2,4,6-$Br_3C_6H_2$*	210 —212	Dichlorobenzene	$C_{12}H_{14}Br_3NO_4Ti$	27.16	2.84	45.83 (Br)	2.67	8.79	27.49	2.69	45.76 (Br)	2.66	9.10	79 (B)
3-$O_2NC_6H_4$*	94 —95	—	$C_{12}H_{16}N_2O_6Ti$	43.36	5.13		8.20	14.20	43.52	4.87		8.46	14.46	100 (A)
4-$O_2NC_6H_4$*	118 —120	—	$C_{12}H_{16}N_2O_6Ti$	43.32	5.07		8.07	14.26	43.52	4.87		8.46	14.46	100 (A)
1-$C_{10}H_7$*	147 —148	Dichloroethane	$C_{16}H_{19}NO_4Ti$	57.17	5.30		4.08	13.73	57.45	5.72		4.14	14.23	95 (A)
2-$C_{10}H_7$*	84 —85	Benzene ether	$C_{16}H_{19}NO_4Ti$	57.41	5.63		3.95	14.51	57.45	5.72		4.14	14.23	93 (A)
2,4,6-$Cl_3C_6H_2$**	206 —208	Xylene	$C_{13}H_{16}Cl_3NO_4Ti$	38.69	3.92	26.25	3.79	11.00	38.59	3.98	26.29	3.46	11.09	75 (B)
2,4,6-$Cl_3C_6H_2$***	272 —273	Dichlorobenzene	$C_{14}H_{18}Cl_3NO_4Ti$	39.99	4.18	25.77	3.13	11.25	40.17	4.32	25.41	3.34	11.44	71 (B)
2,4,6-$Cl_3C_6H_2$****	204.5—205.5	Xylene	$C_{15}H_{20}Cl_3NO_4Ti$	41.98	4.99	23.81	3.41	10.95	41.65	4.66	24.59	3.23	11.07	83 (B)

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* $R^3=R^7=R^{10}=H$.

** $R^3=CH_3$; $R^7=R^{10}=H$.

*** $R^3=R^7=CH_3$; $R^{10}=H$.

**** $R^3=R^7=R^{10}=CH_3$.

few times with the same solvent, and vacuum-dried. Yield of 1-phenoxytitatrane, mp 80–84.5°, 14.3 g (100%).

1-(2', 4', 6'-Trichlorophenoxy)titatrane (Method B). 17.0 g (0.05 mole) tetra-n-butyltitanate, 7.5 g (0.05 mole) triethanolamine, 9.9 g (0.05 mole) 2, 4, 6-trichlorophenol, and 25 ml n-butanol were mixed and heated to 70–80° till solution was complete, and then held at that temperature for a further 20 min. The precipitate was filtered off, washed with ether, and vacuum-dried. Yield of unpurified 1-(2', 4', 6'-trichlorophenoxy)titatrane, mp 204–205°, was 19.1 g (97%), recrystallization from o-dichlorobenzene gave 17.8 g (91%). White crystalline compound mp 209–210°.

1-(1'-Naphthoxy)titatrane (Method A). A mixture of 17.0 g (0.05 mole) tetra-n-butyltitanate, 7.5 g (0.05 mole) triethanolamine, and 7.2 g (0.05 mole) α-naphthol, was vacuum-distilled with heating on a water-bath. In 30 min the theoretical amount (18.4 ml) of n-butanol distilled over, bp 46–47° (30 mm). The solid residue was recrystallized from dichloroethane or boiling benzene. The crystals which separated were filtered off with suction, washed with cold ether, and vacuum-dried. Yield of 1-(1'-naphthoxy)titatrane 16.1 g (95%). Repeated recrystallization from dichloroethane gave 14.8 g (88%) mp 147–148°.

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