held at 5–7°, and 1.29 g (0.0053 mole) acid chloride in 40 ml benzene added. The whole was then stirred for 50 min more, and the reaction products poured onto ice plus HCl. The precipitate was filtered off, and washed with water, when compound I was obtained. The organic layer of the filtrate was washed with water, the solvent distilled off, the residue treated with 2% NaOH, the mixture filtered, and the filtrate acidified to give N-carbazolylacetic acid, yield 0.3 g (25%). The NaOH-insoluble reaction product was dried, and along with compound I, exhaustively extracted with benzene. The extract was chromatographed on Al_2O_3, using benzene, when carbazole was isolated, yield 0.18 g (20%), mp 236–238° (ex xylene). Undepressed mixed mp with authentic carbazole. The residue remaining after extraction was CF condensate, an infusible amorphous powder (when heated above 360° it gradually charred) of very low solubility in organic solvents (pyridine, nitrobenzene, aniline, etc). There was N-H valence vibrations absorption band [5]. Yield of CF condensate 0.42 g (60% on the acid chloride decomposed, as calculated on the fragment $C_{12}H_8NCH_2$). The gas mixture collected during the reaction was analyzed with a VTI-2 gas analyzer, yield of CO 84.2 ml (NTP), 71%.

IR spectra were recorded with a IKS-14 spectrophotometer: a) for the 3600–3100 cm^{-1} and 2000–700 cm^{-1} regions a vaseline mull was used (LiF and NaCl prisms), in the 3100–2800 cm^{-1} region, tablets with KBr (LiF prism).

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ATRANES

XI. 1-Hydrosilatranes*

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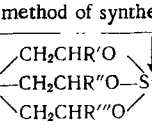
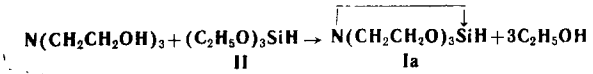
UDC 542.95 + 546.287+547.89

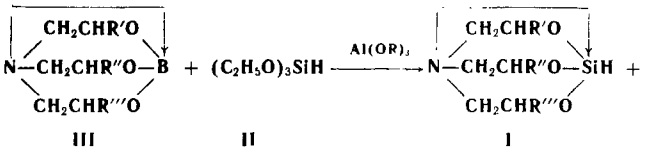
A new and original method of synthesizing difficultly accessible 1-hydrosilatranes  , is developed. It is based on transesterification of the appropriate boratranes in the presence of aluminum alkoxide catalyst. The method is used to prepare four compounds of the type stated, only one of which ($R'=R''=R'''=H$) was previously known.

Up to the present the only known representative of 1-hydrosilatranes with a Si—H bond, is silatrane itself (Ia), which was prepared by reacting triethanolamine with triethoxysilane (II) [2]:



However this reaction, for which the reaction conditions are not given in the literature, is complicated by side reaction of the triethanolamine with the Si—H bond, resulting in quite a low yield of Ia (22%) [3].

We have developed a quite new and original method of preparing silatrane and its C-derivatives containing the Si—H bond [4, 5]. It is based on the aluminum alkoxide-catalyzed transesterification of the readily accessible corresponding boratranes (III) [6] by triethoxysilane (II), the equation being

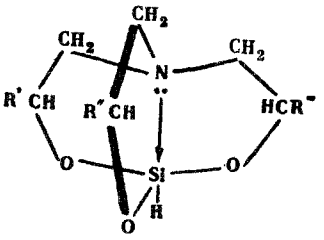


+ $B(OC_2H_5)_3$,

*For Part X see [1].

where R', R'', R''' = H or an organic group, and R = = alkyl. Unlike trialkanolamines III does not give rise to scission of the S—H bond either in the starting II, or in the I formed.

Synthesis is effected by 3-hours boiling in xylene solution of a mixture of the appropriate boratrane and 50% excess triethoxysilane in the presence of a catalytic amount of an aluminum alkoxide, e.g. $Al(OEt)_3$. The resultant I crystallizes straight out of the solution, or is isolated from it after distilling off the solvent. Yields are 64–94% theory.



I

a) R'=R''=R'''=H; b) R'=CH_3, R''=R'''=H; c) R'=R''=CH_3, R'''=H; d) R'=R''=R'''=CH_3.

In the absence of the reaction catalyst, formation of I proceeds rather more slowly, the reaction time is increased to 50 hours, and the yield of I is somewhat lowered (in the case of Ia to 80%).

The table below gives melting points, yields, and analytical data for the I compounds prepared in the above way. 1-Hydrosilatranes are white fibrous crystalline substances, reminding one of glass wool. They are readily soluble in polar organic solvents and water, which hydrolyzes them considerably faster than Si-substituted organyl and organosilatranes.

Due to the presence of the Si—H bond, they react readily with bromine and iodine, while in the presence of catalysts they react readily with organic compounds containing active hydrogen (alcohols, phenols, carboxylic acids). Unsuccessful attempts were made to react compounds I with olefins, in the presence of chloroplatinic acid catalyst or ultraviolet light.

EXPERIMENTAL

Triethoxysilane starting material was an industrial product, which was purified by distilling through a column, bp 131–133°, n_D^{20} 1.3772.

Boratranes (III) were prepared by the method which we previously developed [6], using azeotropic distilling-off of water from a mixture of equimolecular amounts of the appropriate trialkanolamine and boric acid in isoamyl alcohol solution. A description of the boratrane synthesis is given below.

A flask was fitted with a water-separating trap and reflux condenser, and charged with 14.9 g (0.1 mole) triethanolamine, 6.2 g (0.1 mole) boric acid, and 75 ml iso-AmOH. The mixture was refluxed until all the water had separated in the trap. The theoretical amount (5.4 ml) of water separated after 1 hr 30 min. On cooling white crystals of borotrane came down, and were filtered off with suction, washed and vacuum-dried, yield 14.3 g (91%), mp 237–238°.

In the same way isopropanoldiethanolamine and boric acid gave a 90% yield of **3-methylboratrane.** It was isolated from the reaction products after distilling off the iso-AmOH, and was purified by recrystallizing from benzene, mp 196.5–197.5°.

3, 7-Dimethylboratrane was obtained in 59% yield from diisopropanolethanolamine and boric acid. After recrystallizing from benzene-petrol ether it had mp 168–169°.

3, 7, 10-Trimethylboratrane was obtained in 88% yield from trisiopropanolamine and boric acid, mp 150–151° (ex n-heptane).

Silatrane (Ia). A flask fitted with a reflux condenser, was charged with 7.83 g (0.050 mole) boratrane, 12.30 g (0.075 mole) triethoxysilane, 0.06 g $Al(OEt)_3$, and 400 ml xylene. The mixture was heated to boiling, when the boratrane did not dissolve in the xylene. However, after heating for 1 hr–1 hr 30 min, all the boratrane dissolved. The mixture was heated for 1 hr 30 min longer, then filtered hot, and cooled to room temperature. Minute fibrous crystals of Ia came out, were filtered off, washed with petrol ether, and vacuum-dried, mp 250.5–252.5°, yield 8.26 g (94%). After recrystallizing from xylene it had mp 256–258° (the literature gives [2] 253–256°). When the reaction was run similarly, but without adding $Al(OEt)_3$, all the boratrane dissolved only after 50 hrs heating, and the yield of Ia, mp 256–258°, was 81%.

3, 7, 10-Trimethylsilatrane (Id). A mixture of 1.99 g (0.01 mole) 3, 7, 10-trimethylboratrane, 2.46 g (0.015 mole) triethoxysilane, 0.06 g $Al(OEt)_3$, and

1-Hydrosilatranes (I)

Compound number	R'	R''	R'''	Mp °C (recrystallizing solvent)	Formula	Found, %				Calculated, %				Yield, %
						C	H	N	Si	C	H	N	Si	
Ia	H	H	H	256—258 (xylene)	$C_6H_{13}NO_3Si$	41.50	7.39	7.94	15.80 15.73	41.12	7.48	7.99	16.03	94
Ib	CH_3	H	H	207—208 (xylene)	$C_7H_{15}NO_3Si$	44.41	8.21	7.50	14.56 14.68	44.42	7.99	7.40	14.82	87
Ic	CH_3	CH_3	H	158—160 (xylene)	$C_8H_{17}NO_3Si$	47.21	8.35	6.95	13.85 13.67	47.26	8.43	6.89	13.81	78
Id	CH_3	CH_3	CH_3	115—116 (n-heptane)	$C_9H_{19}NO_3Si$	49.81	8.77	6.52	12.80 12.85	49.74	8.81	6.44	12.92	64

80 ml xylene was distilled off, and petrol ether added to the solution after cooling. A white precipitate of Id formed, and was worked up as described for Ia. Yield of Id 1.39 g (64%). After recrystallizing from n-heptane it had mp 115–116°.

3-Methylsilatrane (Ib) and 3, 7-dimethylsilatrane (Ic). These were prepared similarly to Ia, from 3-methyl- and 3, 7-dimethylboratrane respectively.

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SYNTHESIS OF DERIVATIVES OF 1, 2, 3, 4-TETRAHYDRO-4-AZAFLUOREN-3, 9-DIONES

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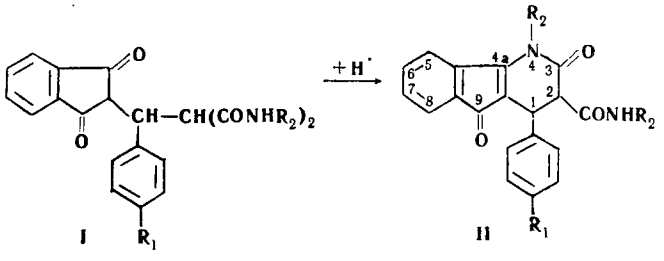
Cyclization of amides of α-carbamido-β-(indan-1, 3-dione-2-yl) hydrocinnamic acid gives 1-aryl-2-carbamido-1, 2, 3, 4-tetrahydro-4-azafloren-3, 9-dione. Alkaline and acid hydrolysis of these compounds are investigated.

Condensation of an amide amino group with a carbonyl group has been but little studied [1–3]. Cyclization of this kind can give new types of heterocyclic compounds. We have shown [4] that condensation of 2-arylindenindan-1, 3-diones with malonic diamide gives amides of α-carbamido-β-(indan-1, 3-dione-2-yl)hydrocinnamic acids (Ia–e). The resultant amides I readily undergo cyclization in acid solution, giving 1-aryl-2-carbamido-1, 2, 3, 4-tetrahydro-4-azafluoren-3, 9-diones (IIa–e)

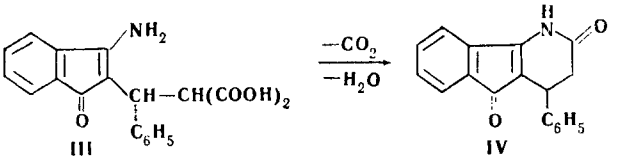


I II

a) $R_1=R_2=H$; b) $R_1=NO_2$, $R_2=H$; c) $R_1=OCH_3$, $R_2=H$; d) $R_1=Cl$, $R_2=H$; e) $R_1=H$, $R_2=CH_3$

In the case in question, condensations between amide and carbonyl groups are facilitated by the steric proximity of the indandione carbonyl group to the amido group, as well as by the possibility of formation of an unstrained 6-membered ring in II. As was shown for the examples of N, N'-disubstituted I compounds, an important role in their cyclization is played by the nucleophilicity of the nitrogen atom of the attacking amido group. Thus, in general I ($R_1=H_1$, $R_2=C_6H_5$) where the basicity of the nitrogen atom is much decreased due to the presence of N-phenyl groups, is not cyclized. At the same time the N, N'-dimethyl derivative Ie cyclizes more readily than the N-substituted I (inductive effect of N-methyl groups). IR and UV spectra data confirm the structure of compound II.

The compounds II prepared were submitted to alkaline and acid hydrolysis. Unlike 4-azafluorenones [5, 6], substituted tetrahydro-4-azafluoren-3, 9-diones are readily cleaved by alkali at the 3—4 bond. The end product of alkaline hydrolysis is α-(3-aminoind-2-en-1-one-2-yl)-benzylmalonic acid (III), which is decarboxylated when heated in diethylene glycol. Decarboxylation is accompanied by intramolecular acylation of the free amino group, with ring closure and formation of 1-phenyl-1, 2, 3, 4-tetrahydro-4-azafluoren-3, 9-dione (IV).



III IV