PREPARATION OF DICHLOROSILOXADIHYDROPHENANTHRENE FROM DIBENZOFURAN AND TRICHLOROSILANE BY A VAPOR-PHASE RADIOCHEMICAL METHOD

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We have found that the reaction of dibenzofuran with trichlorosilane in sealed Pyrex ampuls at 250-450°C with initiation by a beam of accelerated electrons (with an ÉG-2.5 accelerator, an electron-beam energy of 2 MeV, and a beam current of 60 μA) leads to 10,10-dichloro-10-sila-9-oxa-10,10-dihydrophenanthrene (I).

The yield of I increases linearly as the temperature is raised, and the highest yield is reached, other things being equal, at a dibenzofuran to trichlorosilane molar ratio of 1:3 and doses of $(10\text{-}15)\cdot 10^4$ J/kg. A stepwise reaction commences at 300°C, at which point the yield is 1-25%; the yield at 420°C reaches 70%.

As compared with the method of high-temperature condensation, impurities and still residues are virtually absent in this synthesis.

The kinetic dependency of the yields of I on the temperature, molar ratios of the starting reagents, and the absorbed dose were recorded by means of gas—liquid chromatography (GLC) with an LKhM-72 chromatograph and a catharometer as the detector; the carrier gas was helium, the stationary phase was SKTFT-100 rubber on Celite C-22 (0.25-0.40 mm), and the column was 3 m long and had a diameter of 4 mm.

The compound obtained was identified by means of PMR, IR, and mass spectrometry.

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PERHYDRO-1,4-BENZOXAZECINE DERIVATIVES

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We have found that alkylation of 2-methyldihydroresorcinol Ia with ethyl bromoacetate in the presence of potassium methoxide gives the corresponding 2-carbethoxymethylene derivative Ib [bp 115°C (0.1 mm) and mp 77-78°C (from ether)] in up to 75% yields, which, by partial ketalization, was converted to ethylene ketal Ic, with mp 70-71°C (from petroleum ether), in 100% yield. The reduction of ketal Ic with sodium borohydride in ethanol at −70°C leads to hydroxy ester IIa, with mp 99-100°C (from ether), in 100% yield. In conformity with the configuration indicated for hydroxy ester IIa, keto lactone III (70%) in the form of an oil, which was characterized in the form of the 2,4-dinitrophenylhydrazone with mp 101-102°C (from methanol), is formed from it by alkaline saponification and subsequent acidification. Amido ester IIb (60%), with mp 30-32°C (from ether), was obtained by the action on hydroxy ester IIa of sodium hydride and chloroacetic acid N-methylamide in tetrahydrofuran. Heating amido ester IIb with potassium bisulfate in xylene leads to imide IVa, which we were able to convert to oxazecine derivative IVb (60%) in the form of an oil by reaction with lithium alum

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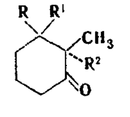
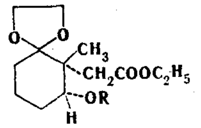
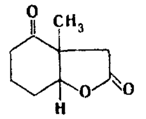
num hydride in dioxane. Hydrolysis of IVb with hydrochloric acid in dioxane gave the corresponding keto amine IVc, with mp 30-32°C, in 52% yield. Keto amine IVc gives a hydrochloride with mp 125-130°C (dec., from alcohol – ether) and a methiodide with mp 132-135°C (from ethanol). Reduction of keto amine IVc with lithium aluminum hydride in dioxane easily leads to hydroxy amine IVd (83%) in the form of an oil, which was characterized in the form of the 3,5-dinitrobenzoate with mp 111-113°C (from ethanol).



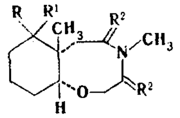
I a-d



IIa, b



III



IVa-d

I a $R+R^1=O$, $R^2=H$; b $R+R^1=O$, $R^2=CH_2COOEt$; c $R+R^1=OCH_2CH_2O$, $R^2=CH_2COOEt$; II a $R=H$; b $R=CH_2CONHCH_3$; IV a $R+R^1=OCH_2CH_2O$, $R^2=O$; b $R+R^1=OCH_2CH_2O$, $R^2=H$; c $R+R^1=O$, $R^2=H_2$; d $R=OH$, $R^1=H$, $R^2=H_2$

The structures of the compounds obtained were confirmed by data from the IR, PMR, and mass spectra. The results of elementary analysis were in agreement with the calculated values.

SYNTHESIS OF TETRAHYDROPYRROLOISOQUINOLONES

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We have shown that amides Ib and IIb are formed in the acylation of aminomethylindoles Ia and IIa with ethyl mandelate. Amides Ib and IIb readily undergo cyclization to give substituted tetrahydropyrroloisoquinolones III-V in high yields when they are heated with polyphosphoric acid (PPA). Thus 0.245 g (84%) of 2,3-dimethyl-8-phenyl-5,6,7,8-tetrahydropyrrolo[2,3-g]isoquinol-7-one (III), with mp 243-244°C, which was purified by chromatography on silica gel 5/40 in a benzene – ethyl acetate system (1:1), was obtained from 0.308 g of 2,3-dimethyl-5-[N-(α-hydroxyphenacetyl)aminomethyl]indole (Ic, mp 129-130°C, in 67% yield from amine Ia) after heating for 50 min with 5 g of PPA. The PMR spectrum (in CF_3COOH) of III contains singlets at 6.93 and 7.20 ppm, which correspond to the hydrogen atoms in the para positions of the benzene ring, and a C_6H_5 multiplet centered at 6.83 ppm. Amide IIc, with mp 160-161°C (from benzene), was similarly obtained from amine IIa. Cyclization of 0.3 g of amide IIc gave 0.26 g (90%) of a mixture of the linear and angular (IV and V) isomers in a ratio of 3:1. Chromatography on silica gel 5/40 in a benzene – ethyl acetate system (1:1) yielded 2,3-dimethyl-5-phenyl-5,6,7,8-tetrahydropyrrolo[3,2-g]isoquinol-6-one (IV), with mp 273-274°C, and 2,3-dimethyl-9-phenyl-6,7,8,9-tetrahydropyrrolo[2,3-f]isoquinol-8-one (V), with mp 297-298°C (after vacuum sublimation). In contrast to the PMR spectra of III and IV, the PMR spectrum (in d_6-DMSO) of V contains two doublets of signals of aromatic protons at 6.90 and 7.30 ppm (J = 8 Hz), which correspond to the AB system of ortho-coupling protons. (See scheme on following page.)

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