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

B. I. Vainshtein, I. P. Tokareva,
T. L. Krasnova, V. V. Stepanov,
and E. A. Chernyshev

UDC 541.15:547.916:543.422.25.4'51

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.

L. Ya. Karpov Scientific-Research Physicochemical Institute, Moscow 107120.
Original article submitted March 1, 1978.

PERHYDRO-1,4-BENZOXAZECINE DERIVATIVES

N. K. Levchenko, G. M. Segal',
and I. V. Torgov

UDC 547.895

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-

---

M. M. Shemyakin Institute of Bioorganic Chemistry, Academy of Sciences of the USSR, Moscow 117312. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1277-1279, September, 1978. Original article submitted March 14, 1978.