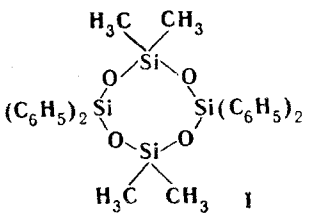
UDC 546.287 + 543.422.8

1,1,5,5-TETRAMETHYL-3,3,7,7-TETRAPHENYLCYCLOTETRASILOXANE AND 1,1,3,3-TETRAMETHYL-5,5,7,7-TETRAPHENYLCYCLOTETRASILO XANE

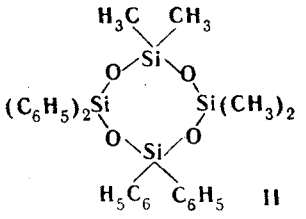
K. A. Andrianov, S. E. Akuskina, and L. N. Guniava

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 6, p. 944, 1966

1,1,5,5-Tetramethyl-3m3,7,7-tetraphenylcyclotetrasiloxane (I) and 1,1,3,3-tetramethyl-5,5,7,7-tetraphenylcyclotetrasiloxane (II) are not described in the literature. Vacuum-distillation of the products of



I



II

joint hydrolysis of dimethyldichlorosilane and diphenyldichlorosilane gave a cut bp 230–245° C (1.5 mm), from which were crystallized out successively two isomers of tetramethyltetraphenylcyclotetrasiloxane, which were crystalline compounds with mps 72 and 126° C after recrystallization from MeOH. Their elementary compositions were identical. Isomer mp 72° C: Found: C 61.45; H 5.81; Si 20.57%. Cl 61.85; H 5.90; Si 20.69%. $C_{28}H_{32}O_4Si_4$: C 61.86; H 5.92; Si 20.61%. The two isomers had identical IR spectra at 1429, 1130, 725 cm^{-1} (C_6H_5), 1410, 1259, 800–814 cm^{-1} (CH_3), and 1080–1020 cm^{-1} (Si–O–Si).

X-ray analysis* reveals that the isomers have different crystal structures. The crystals of tetramethyltetraphenylcyclotetrasiloxane mp 72° C were colorless prisms. The elementary cell parameters were a-12.62± 0.06 Å, b-26.19 ± ± 0.01 Å, c-9.13± 0.01 Å, β = 96.48°. The crystals belonged to the monoclinic system, and the space group was P2/n. Number of molecules per cell z = 4, d_{found} 1.15, d_{calc} 1.17 v = 3582 A [3].

The crystals of tetramethyltetraphenylcyclotetrasiloxane, mp 126°C, had the following elementary cell parameters: a–11.05 Å, b–8.33 Å, c–17.47 Å. They belonged to the triclinic system and had angles: α = 146°48′, β = 118°58′, γ = 59°0.8′. The space group was P1. Number of molecules per cell 1. d_{found} 1.18°, d_{calc} 1.20, v = 750 Å [3]. The crystals have a center of symmetry which coincides with the center of symmetry of the ring molecule.

This gives grounds for assigning the symmetric structure I to the isomer mp 126°C.

The crystals mp 72° C lack a center of symmetry, and probably the ring molecule has the unsymmetric structure II.

22 June 1965

Institute of Heteroorganic Compounds, AS USSR

UDC 547.895 + 542.953

SYNTHESIS AND ACIDOCHROME CONDENSATION OF N-BENZYLOYL-1,2,3,4-TETRAHYDROQUINOLINE

P. A. Petyunin

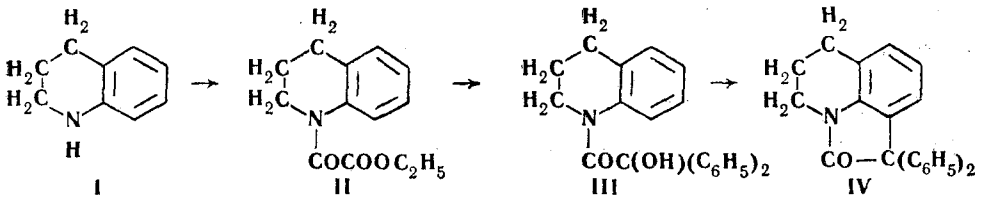
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 6, pp. 944–945, 1966

Acidchrome condensation of N-substituted amides of hydroxycarboxylic acids has been studied mainly with aromatic compounds [1].

It is now shown that the reaction can also be extended to heterocyclic compounds. Thus reaction of 1,2,3,4-tetrahydroquinoline (1) with the acid chloride of monoethyloxalate gave N-ethoxalyl-1,2,3,4-tetrahydroquinoline (II), and

* The X-ray analysis was carried out by Yu. T. Struchkov's team in the X-ray analysis laboratory of this Institute.

this on reaction with phenyl magnesium bromide gave N-benzyloyl-1,2,3,4-tetrahydroquinoline (III). The latter exhibits halochromism, and when treated with conc. H_2SO_4 undergoes acidochromic condensation. From the synthetic route, and analytical results for the product, the latter is assigned a structure 1,7-trimethylene-3,3-diphenyloxyindole [α'-oxo-β,β'- diphenyllilolidine (IV)].



II was obtained by adding 0.127 mole of the acid chloride of monoethyloxalate to a solution of 0.125 mole I and 0.125 Et_3N in 50 ml dry ether. After 30 min refluxing on a water-bath, 20 ml H_2O was added, the ether layer separated off, and after evaporating off the ether, the residue was distilled, to give 22.1 g (79.5%), bp 187–189° (8 mm), d_4^{21} 1.1099, n_D^{21} 1.5471. Found: N 6.15, 6.23%. Calculated for $C_{13}H_{15}NO_3$: N 6.0%.

To synthesize III, a solution of 0.02 mole II in 10 ml dry ether was added to 0.08 mole phenyl magnesium bromide in 50 ml ether, the mixture heated for 30 min, and the organomagnesium complex decomposed with NH_4Cl solution. Solvent and volatile reactions products were steam-distilled off. The residue was recrystallized first from aqueous EtOH and then from benzene-petrol ether. Plates mp 119–120° C, yield 5.9 g (86%). Found: C 80.35, 80.21; H 6.32, 6.29; N 4.15, 4.33%. Calculated for $C_{23}H_{21}NO_2$: C 80.43; H 6.17; N 4.08%.

IV was prepared by adding 5 ml concentrated H_2SO_4 to a solution of 1 g III in glacial AcOH, and after disappearance of the reddish-brown color, pouring into 30 ml H_2O. The precipitate was filtered off and recrystallized from AcOH. Hexahedral plates, mp 220–221° C, yield 0.9 g (94.7%). Readily soluble in benzene, less soluble in EtOH and AcOH, insoluble in petrol ether. Found: C 84.59, 84.67; H 5.93, 5.98; N 4.51, 4.43%. Calculated for $C_{23}H_{19}NO$: C 84.88; H 5.87; N 4.33%.

Our further task is a further study of the acidochrome condensation of heterocyclic amides of hydroxycarboxylic acids.

REFERENCE

1. P. A. Petyunin, Arylamides of hydroxycarboxylic acids, and their conversion to heterocyclic compounds [in Russian], Doctoral Thesis, 1949.

9 December 1965

Khar'kov Pharmaceutical Institute

UDC 547.785.5'789.6

SYNTHESIS OF THIAZOLO [3, 2-a] BENZIMIDAZOLE

P. M. Kochergin and A. N. Krasovskii

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 6, pp. 945-946, 1966

Thiazolo [3,2-a] benzimidazole (I) is not described in the literature, and only derivatives of it are known [1–6]. We have investigated the reaction between 2-mercaptobenzimidazole (II) and chloro (bromo) acetaldehyde (III, IV), and their diethylacetals (V, VI), when I is obtained. Heating II with III or IV in water, ethanol, or dimethylformamide leads to isolation of the intermediate 3-hydroxythiazolino [3,2-a] benzimidazole, converted by H_2SO_4 or $POCl_3$ to I.