Experimental

The 1-organyl- and 1-organoxysilatranes were synthesized and purified as described previously [1-4]. The melting points and analytical data were the same as previously recorded.

The spectra were determined with an INM-3 spectrophotometer working at 40 Mc. Saturated solutions of silatranes in chloroform were used for measuring the PMR spectra. Cyclohexane was used as the internal standard. The chemical shifts τ were measured as ppm (millionths) relative to the reference signal from C_6H_{12} protons, whose chemical shift was taken as 8.56 ppm on the τ scale. The side band method was used to determine the positions of the resonance signals in the spectra to an accuracy of ±0.01-0.03 ppm, using the arithmetic mean of not less than four measurements.

REFERENCES

1. M. G. Voronokov, and G. I. Zelchan, KhGS, 210, 1965.
2. M. G. Voronokov, I. B. Mazheika, and G. I. Zelchan, KhGS, 58, 1965.
3. Ya. Ya. Baltkais, M. G. Voronkov, and G. I. Zelchan, Izv. AN LatvSSR, no. 2, 102, 1964.
4. M. G. Voronkov, and G. I. Zelchan, KhGS, 51, 1965.
5. NMR Spectra Catalog. Varian Associates, N. Y., 1962.

29 October 1964

Scientific Research Institute of Chemistry,
Lobachevskii Gor'kii State University,
Institute of Organic Synthesis
AS Latvian SSR, Riga.

UDC 547.78+542.95

ALKYLATION OF AMINOTHIAZOLES; IV*. ALKYLATION OF 2-AMINO-4, 5-DIMETHYLTHIAZOLE

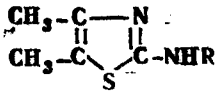
V. A. Krasovskii, and S. I. Burmistrov

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 1, No. 2, pp. 303-305, 1965

Alkylation of 2-amino-4, 5-dimethylthiazole with isopropanol and cyclohexanol in 85% sulfuric acid gives good yields of isopropylamino- and 2-cyclohexylamino-4, 5-dimethylthiazole. The structures of the products are demonstrated by reverse synthesis from 3-chlorobutanone and substituted thioureas.

Previous papers described the alkylation of 2-amino-4-methylthiazole and 2-aminothiazole with secondary and tertiary alcohols and 80-85% sulfuric acid, which in all of the cases examined gave up to 98% yields of 2-alkylaminothiazoles, i.e. alkylation took place at the nitrogen atom outside the ring. The present communication describes experiments on alkylating 2-amino-4-, 4-dimethylthiazole with cyclohexanol and isopropanol.

Related compounds (I) were obtained in up to 85% yields at an alcohol : aminothiazole ratio of 1.5 : 1.



I

The structures of the alkylation products (I) were demonstrated by synthesis from 3-chlorobutan-2-one and the appropriate thiourea [3].

Experimental

2-Amino-4, 5-dimethylthiazole was prepared from 3-chlorobutan-2-one and thiourea. B.p 120°/ 3-4 mm, m.p. 80-82° (the literature [4] gives m.p. 82-83°).

Alkylation was effected by the following standard method: 0.075 mole of the anhydrous secondary alcohol was added dropwise, with stirring, to 0.05 mole (6.4 g) 2-amino-4, 5-dimethylthiazole which had been dissolved with cooling in 100 ml 85% sulfuric acid and then heated to 60-90°. When addition was complete, the mixture was stirred at this temperature for 5-7 hr, cooled, and poured onto 200 g ice, then neutralized, while cooling, with concentrated aqueous ammonia. The solid was separated and washed with water. If the amine came out as an oil, it was extracted with benzene, the benzene layer dried with anhydrous sodium sulfate, and then vacuum-distilled.

*For Part III see [1].

2-Isopropylamino-4, 5-dimethylthiazole was prepared in 85% yield. Colorless needles, mp 100.5-102°(from aqueous alcohol). Found N 16.40; S 18.75%. Calculated for $C_8H_{14}N_2S$: N 16.45; S 18.83%.

The product of reaction of 3-chlorobutan-2-one with 1-isopropylthiourea melts at 101-102°. Mixed mp undepressed.

The picrate forms yellow transparent prisms, mp 215° (decomp.) (from alcohol-acetic acid). Found: N 17.12%. Calculated for $C_8H_{14}N_2S \cdot C_6H_3N_3O_7$: N 17.05%.

2-Cyclohexylamino-4, 5-dimethylthiazole. Viscous yellow oil, bp 124° (3-4 mm), n_D^{20} 1.5578; d_4^{20} 0.8688. Yield 41%. Found: N 13.29; S 15.10%. Calculated for $C_{11}H_{18}N_2S$: N 13.3; S 15.24%.

The picrate forms long yellow fibrous needles, mp 238-239° (decomp.) (from acetic acid). Found: N 15.95%. Calculated for $C_{11}H_{18}N_2S \cdot C_6H_3N_3O_7$: N 16.15%.

The reaction product from 3-chlorobutan-2-one and 1-cyclohexylthiourea give a picrate, mixed mp with the picrate above 238°.

REFERENCES

1. S. I. Burmistrov, and V. A. Krasovskii, ZhOKh, 34, 627, 1964.
2. S. I. Burmistrov, and V. A. Krasovskii, ZhOKh, 34, 3822, 1964.
3. Organic Syntheses [Russian translation], IL, 2, 40, 1949.
4. Iensen, Thorsteinsson, Dansk Tids. Farm., 15, 41, 1941; C. A., 35, 5109, 1941.

30 November 1963

Dnepropetrovsk Chemical Engineering Institute

UDC 547.835+542.941

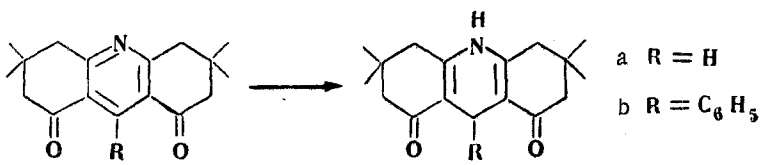
POLYNUCLEAR HETEROCYCLIC COMPOUNDS. XIX*. REDUCTION OF 3, 3, 6, 6-TETRAMETHYLOCTAHYDROACRIDINE-1, 8-DIONES

E. I. Stankevich, and G. Ya. Vanag

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 1, No. 2, pp. 305-306, 1965

Reduction in alcohol solution, using hydrogen at atmospheric pressure and platinum oxide catalyst, of 3, 3, -6, 6-tetramethyl-1, 2, 3, 4, 5, 6, 7, 8-octahydroacridine-1, 8-dione and its 9-phenyl derivative gives the corresponding 3, 3, 6, 6-tetramethyl-1, 2, 3, 4, 5, 6, 7, 8, 9, 10-decahydroacridine-1, 8-dione and its 9-phenyl derivative.

The present authors [2] have previously described borohydride and sodium hydrosulfite reduction of 3, 3, 6, 6-tetramethyl-1, 2, 3, 4, 5, 6, 7, 8-octahydroacridine-1, 8-dione (Ia), to 3, 3, 6, 6-tetramethyl-1, 2, 3, 4, 5, 6, 7, 8, 9, 10-decahydroacridine-1, 8-dione (IIa).



I a, b II a, b

In the reactions described the yields of the corresponding dihydropyridines were not very high, so further attempts were made to improve the yields and quality of the dihydro-derivatives. The best results were obtained by catalytically hydrogenating Ia, b over platinum oxide. In ethanol solution the necessary amount (1 mole) of hydrogen is taken up in two hours, and under the particular conditions the yields of decahydroacridinediones IIa, b amount to 80-90%. Under the reaction conditions used, there is no further reduction of the decahydroacridinediones, and no hydrogen is taken the next 24 hr. The IIa, b, thus prepared, are identical with the compounds previously synthesized [2].

*For part XVIII see [1].