into the 1-phenyl group, gives $\Delta\mu$ = +1.56D, greater than the value for p-nitroaniline, and close to that for p-nitrodimethyl-aniline [5]. Appreciable too are the $\Delta\mu$ values for the cases where X = Cl and Br when they are introduced into the 3-phenyl group. Thus the above-mentioned difference in the effects of aromatic groups at positions 1 and 3 on the one hand, and at position 5 on the other, is observed for properties of molecules not only in the excited state [4], but also in the ground state, as the dipole moments of the molecules show. A particularly considerable increase in moment with the p-nitro substituent in the 1-phenyl group may indicate that a pair of unextended electrons N_1 participates slightly in the conjugation in the actual heterocyclic ring, and this also determines the possibility of its being shifted appreciably for the nitro group.

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REFERENCES

1. E. A. Andreeshchev, K. A. Kovyrzina, and E. E. Baroni, collection: Scintillators and Scintillation Materials [in Russian], Izd-vo Khar'kovs. gos. univ., 171, 1960.

2. V. G. Tishchenko, E. T. Verkhovtseva, L. M. Kutsina, and B. G. Distanov, collection: Scintillators and Scintillation Materials [in Russian], Izd-vo Khar'kovsk. gos. univ., 126, 1963.

3. G. G. Belous, and V. D. Bezuglyi, ZhAKh, 28, 1250, 1965.

4. A. E. Lutskii, A. V. Shepel, and O. P. Shvaika, KhGS [Chemistry of Heterocyclic Compounds], 1967, (in press).

5. S. A. Hiller, I. B. Mazheika, and I. I. Grandberg, KhGS [Chemistry of Heterocyclic Compounds], 107, 1965.

6. A. E. Lutskii and B. L. Kondratenko, ZhFKh, 33, 2017, 1959.

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RESEARCH ON 2, 1, 3-THIA-AND SELENADIAZOLE

XLVIII.* Synthesis of α-Amino-β-(3, 4-Diaminophenyl) Propionic Acid

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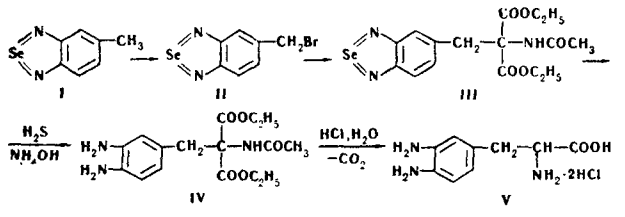
Reductive decomposition followed by hydrolysis of 5-(β, β-dicarethoxy-β-acetylamino)ethylbenz-2, 1, 3-selenadiazole gives β-(3, 4-diaminophenyl)alanine.

The present paper describes the hitherto undescribed synthesis of β-(3, 4-diaminophenyl)alanine (V) from 5-methylbenz-2, 1, 3-selenadiazole.



5-methylbenz-2, 1, 3-selenadiazole (I) is brominated with bromosuccinimide, to give 5-bromomethylbenz-1, 2, 3-selenadiazole (II), which is then reacted with sodioacetylaminomalonic ester, to give the malonate III. The latter is then reductively cleaved with hydrogen sulfide in aqueous alcoholic ammonia, to malonate IV. Acid hydrolysis and decarboxylation of the latter converts it to dihydrochloride V, paper chromatography of which gave one spot with a positive ninhydrin reaction. The reductive cleavage product, malonate IV, is also characterized as an o-diamine by reaction with phenanthraquinone.

An attempt was made to prepared V by reductive cleavage of 5-(β-carboxyoxy-β-amino) ethylbenz-2, 1, 3-selenadiazole (VI), in its turn obtained by acid hydrolysis and decarboxylation of malonate III, but the action of hydrogen sulfide on a solution of VI in ethanol

*For Part XLVII see [1].

and 25% ammonia did not lead to the isolation of any individual compound from among the reaction products.

EXPERIMENTAL

5-Bromomethylbenz-2, 1, 3-selenadiazole (II). A mixture of 5 g (0.025 mole) 5-methylbenz-2, 1, 3-selenadiazole (I) [2], 4.5 g (0.025 mole) bromosuccinimide, 0.05 g Br_2O_2 and 120 ml CCl_4 was refluxed for 7 hr. The succinimide which came out was filtered off, and the solvent distilled off. Yield 4.5 g (64%) yellow powder, mp 125°–126° (ex EtOH). Found: N 10.45; 10.55; Br 28.63; 29.02%, calculated for $C_7H_5BrN_2Se$: N 10.20; Br 29.00%.

5-(β, β-Dicarbethoxy-β-acetylamino)ethylbenz-2, 1, 3-selenadiazole (III). 1.3 g (0.0055 mole) acetylaminomalonic ester was added to a stirred solution of 0.125 g (0.0055 mole) Na in 20 ml absolute EtOH, the whole stirred for 1 hr at 20°, then a solution of 1.52 g (0.0055 mole) mole) II in 20 ml dry benzene was added gradually, and the mixture boiled for 3 hr. The NaBr was filtered off, and the filtrate evaporated to dryness. Yield 1.2 g (54%), mp 152°–153° (ex EtOH) Found: N 10.50; 10.08%, calculated for $C_{16}H_{19}N_3O_5Se$: N 10.20%.

1-(β, β-Dicarbethoxy-β-acetylamino) ethyl-3, 4-diaminobenzene (IV). H_2S was passed into a solution of 2 g III in 45 ml EtOH+10 ml 25% ammonia at 60°, for 1 hr 30 min. After cooling the precipitate was filtered off and the filtrate evaporated. The dry residue, 1.5 g (91%), was recrystalized from EtOH, white transparent plates, mp 182°. Found: N 12.77; 12.58%, calculated for $C_{16}H_{23}N_3O_5$: N 12.45%.

β-(3, 4-Diaminophenyl)-α-aminopropionic acid hydrochloride (V). A mixture of 5 g IV and 120 ml 20% HCl was heated on a steam bath for 4 hr. The solution was then vacuum evaporated to dryness, and a few volumes of water (about 5 ml) added. The oily residue was recrystallized from absolute EtOH and dry ether, yield 2.8 g (78%) while very hygroscopic product, mp 265°–267° (decomp.). Found: N 21.01; 21.07; Cl 25.83%, calculated for $C_9H_{13}N_3O_2 \cdot 2HCl$: N 21.50; Cl 25.50%; R_f 0.165.*

5-(β-Amino-β-carboxy)ethylbenz-2, 1, 3-selenadiazole (VI) hydrochloride. 1.2 g malonate III and 50 ml 20% HCl was refluxed for 10 hr, the products cooled, filtered, and the filtrate vacuum evaporated to dryness. The residue was recrystallized from absolute EtOH-ether. Yield 0.61 g (67%) grayish compound mp 275° (decomp.). Found: N 13.77; 13.75; Cl 12.18; 12.04%, calculated for $C_9H_8N_4O_4Se \cdot HCl$: N 13.71; Cl 11.65%.

REFERENCES

1. V. F. Pesin and V. A. Sergeev, KhGS [Chemistry of Heterocyclic Compounds], 839, 1967.

2. O. Hinsberg, Ber., 22, 862, 1889.

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*The chromatographing was done on Leningrad Factory slow filter paper using n-BuOH:PrOH:0.1 N HCl in the ratios 2:1:1.

EFFECT OF SUBSTITUENT NATURE ON THE EQUILIBRIUM IN THE CATALYTIC REARRANGEMENT OF CYCLOSILOXANES IN SOLUTION

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Determinations are made of the polymer content of mixtures obtained by catalytic rearrangement of cyclosiloxanes with various substituents (CH_3, C_2H_5, n-C_3H_7, i-C_4H_9, C_6H_5, $CF_3CH_2CH_2$, $NCCH_2CH_2CH_2$) at the silicon, in methylethyl ketone and acetone. It is found that the equilibrium cyclosiloxane-polycyclosiloxane is shifted to the left as volumes, and in particular polarities, of substituents increase. The causes of this are considered.

When cyclosiloxanes are rearranged in solution in the presence of bases, the following equilibrium is established:

$$\text{cyclosiloxane} \rightleftharpoons \text{polycyclosiloxane} \quad (1)$$

the position depends on solution concentration [1–3] but not on solvent nature [1, 2] or temperature. We showed [3, 4] that when mixed cyclosiloxanes containing the groups $(CH_3)_2SiO$ and $CF_3CH_2CH_2(CH_3)SiO$ (Φ) rearrange in acetone, the equilibrium concentration of polymer (P) decreases linearly with increase in mole fraction of Φ.

In the present work a method previously described [4] was used to determine P in systems obtained by rearranging cyclosiloxanes at 20° in the presence of potassium polymethylsiloxandiolate. The concentration of siloxane groups in solution was 3.33 mole/l. The rearrangement of the rings $(RR'SiO)_m$ (table, **I–VIII**), was effected in methylethyl ketone, some of the polymers being insoluble in acetone. Mixed cyclosiloxanes (table, **VIII–XIII**) containing in addition to the group D $NCCH_2CH_2(CH_3)SiO$ (N), $NCCH_2CH_2CH_2(CH_3)SiO$(C), and Φ, were rearranged in acetone. Special experiments confirmed (e.g. for I, VI, VII, and VIII) that change of solvent is practically without effect on the equilibrium. Attainment of equilibrium was checked for all rings by repeated keeping with increasing amounts of catalyst, and in the cases of siloxanes I, VI, and VII, it was confirmed that the same P values were obtained both by rearrangement of the rings and by destruction of the corresponding polymers.