3. V. M. Zhulin and I. Kh. Milyavskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1487 (1974).
4. V. M. Zhulin, B. I. Rubinshtein, and M. Ya. Botnikov, Izv. Akad. Nauk SSSR, Ser. Khim., 293 (1975).
5. V. M. Zhulin, M. Ya. Botnikov, and I. Kh. Milyavskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1131 (1975).
6. V. M. Zhulin and B. I. Rubinshtein, Izv. Akad. Nauk SSSR, Ser. Khim., 353 (1976).
7. V. M. Zhulin and B. I. Rubinshtein, Izv. Akad. Nauk SSSR, Ser. Khim., 2201 (1976).
8. G. A. Russell, J. Am. Chem. Soc., 80, 4987 (1958).
9. G. A. Russell, Free Radicals, J. K. Kochi (editor), Vol. 1, Chapt. 7, Wiley-Interscience, New York (1973).
10. K. B. Wiberg and L. H. Slaugh, J. Am. Chem. Soc., 80, 3033 (1958).
11. C. Walling and J. A. McGuiness, J. Am. Chem. Soc., 91, 2053 (1969).
12. I. Kh. Milyavskaya, Dissertation, Moscow (1976).

BROMINATION OF TEREPHTHALALDEHYDE

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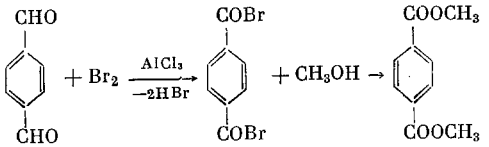
UDC 542.944: 546.14: 547.571

Based on the data given in [1], the direct halogenation of benzaldehyde in the presence of excess $AlCl_3$ leads to 3-bromo (or 3-chloro)-benzaldehyde in 50-60% yields.

However, when terephthalaldehyde is brominated in dry CCl_4, in the presence of a 5-fold excess of $AlCl_3$, at 55-60°C we obtained a complex mixture of products. Treatment of the mixture with boiling methanol gave a 25% yield of dimethyl terephthalate, which was identified by the melting point, and the IR and NMR spectra. As a result, the direct bromination of terephthalaldehyde in the presence of excess anhydrous $AlCl_3$ leads to the formation of terephthaloyl bromide, and not to nuclear substitution, as was described for benzaldehyde [1], which is apparently associated with the presence of a second electron-acceptor CHO group.



EXPERIMENTAL

Bromination of Terephthalaldehyde. With stirring, to a mixture of 17 g (0.125 mole) of anhydrous $AlCl_3$ in dry CCl_4 (80 ml) was added 3.3 g (0.025 mole) of terephthalaldehyde in dry CCl_4 (30 ml); heat evolution was not observed. The mixture was brought up to CCl_4 boil, cooled to 55-60° and, with stirring, 1.5 ml (0.03 mole) of bromine was added dropwise. After adding all of the bromine the mixture was stirred for 4 h at 60° and let stand overnight. Then it was poured into a mixture of dilute HCl solution and ice (100 g of ice and 150 ml of 2 N HCl solution), the organic layer was separated, washed in succession with 2 N HCl solution, Na_2CO_3 solution, and water, dried over $MgSO_4$, and the solvent was distilled off. The residue was boiled in methanol, filtered, cooled, and the obtained crystals were filtered. We obtained 1.3 g (25%) of dimethyl terephthalate, mp 141°.

CONCLUSIONS

The direct bromination of terephthalaldehyde in the presence of excess anhydrous $AlCl_3$ leads to the formation of terephthaloyl bromide.

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LITERATURE CITED

1. D. E. Pearson, H. W. Pope, W. W. Hargrove, and W. E. Stamper, J. Org. Chem., 23, 1412 (1958).

SYNTHESIS OF OPSOPYRROLEDICARBOXYLIC ACID

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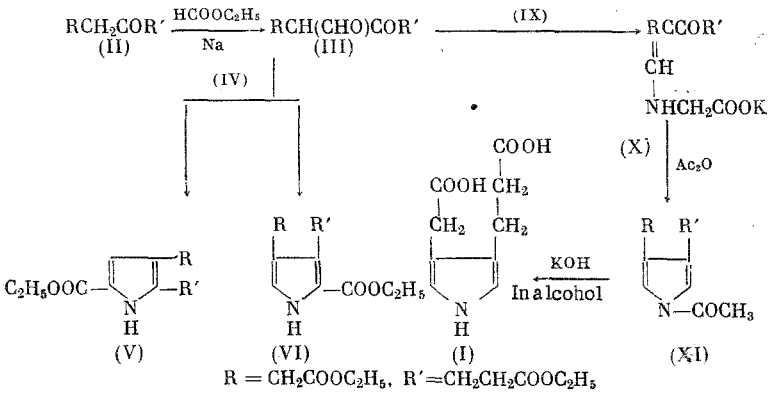
UDC 542.91.547.746

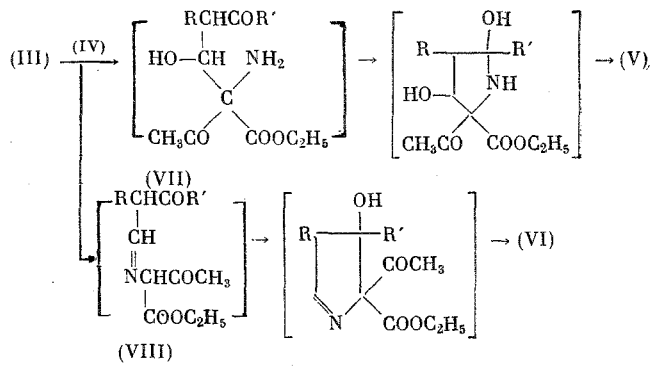
3-Carboxymethyl-4-(β-carboxyethyl)pyrrole (opsopyrroledicarboxylic acid) (I) enters into the composition of uroporphyrinogen [1] and displays the ability to form porphyrins when treated with CH_2O in HCl medium [2].

In order to make a further study of the conditions for converting (I) to porphyrins we investigated in the present paper some new simple routes for the synthesis of (I), starting with the diethyl ester of 4-ketopimelic acid (II). In selecting the scheme for the synthesis of (I) we employed the rational principle of building an unsymmetrical molecule from a symmetrical molecule [(I) from (II)], which lies at the base of the biogenesis of certain natural compounds, for example, lanosterol and γ-carotene [3].



The reaction of (II) with HCOOEt in the presence of Na gave the diethyl ester of 3-formyl-4-ketopimelic acid (III), which with α-aminoacetoacetic ester (IV) by the Knorr method gave 2-carbethoxy-4-carbethoxymethyl-5-(β-carbethoxyethyl)pyrrole (V). The structure of (V) was adopted in harmony with the data given in [4-6] regarding the structural directivity of the Knorr synthesis with an α-formyl ketone, and was confirmed by the IR, UV, and NMR spectra. The structural isomer of (V), viz., 2-carbethoxy-3-(β-carbethoxyethyl)-4-carbethoxymethylpyrrole (VI), was isolated from the mother liquor, and was identified by comparison with an authentic specimen.

The formation of (V) and (VI) from (III) can be considered to be the result of the Knorr reaction proceeding in two directions, with involvement of the intermediate amino diketone (VII) or amine (VIII), by the following schemes:



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