LETTERS TO THE EDITOR

THE MERCURATION OF INDOLES IN ACETIC ANHYDRIDE

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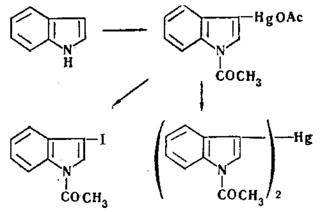
In the mercuration of indole or its homologs containing an unsubstituted NH group in ethanol or water, infusible substances the structure of which has not been established are formed [1, 2]. If the mercuration of such compounds is carried out in acetic anhydride, acetylation of the MH group and the replacement of a hydrogen atom of the pyridine ring by an acetoxymercury group take place simultaneously. Thus, from 0.5 g of indole, 1.3 g of mercuric acetate, and 30 ml of acetic anhydride (at room temperature for 24 hr or boiling for 5–10 min), we obtained, after separation of the precipitate that had deposited and washing it with water and ether, 1.1 g (61%) of 3-acetoxymercuri-1-acetylindole, mp 183–184° C (from benzene). Found, %: C 34.60, H 2.74. Calculated for $C_{12}H_{11}O_3NHg$, %: C 34.49; H 2.64. The mother liquor, after treatment with an aqueous solution of common salt, yielded 0.3 g (18%) of 1-acetyl-3-chloromercuriindole, mp 236–237° C (from ethanol), IR spectrum: ν_{CO} 1710 cm^{-1}. Found, %: C 30.71; H 2.14. Calculated for $C_{10}H_8ONHgCl$, %: C 30.46; H 2.04. Total yield 79%. Similarly, 2-methylindole yielded 1-acetyl-3-chloromercuri-2-methylindole, mp 172–173° C (from aqueous dioxane), IR spectrum: ν_{CO} 1720 cm^{-1}. Found, %: C 32.53; H 2.61. Calculated for $C_{11}H_{10}NOHgCl$, %: C 32.36; H 2.47.



From 3-methylindole we prepared 1-acetyl-2-chloromercuri-3-methylindole, mp 230–232° C (from aqueous dioxane), IR spectrum: ν_{CO} 1670 cm^{-1}. Found, %: C 32.65; H 2.65. Calculated for $C_{11}H_{10}NOHgCl$, %: C 32.36; H 2.47. The reaction takes place similarly in propionic anhydride. The peak of the β-proton in the PMR spectrum of indole (6.25 ppm) and of 2-methylindole (6.17 ppm) is absent from the products of their mercuration. Under the action of sodium iodide in acetone, all the substances undergo symmetrization with the formation of the corresponding diindolylmercury derivatives.

In an aqueous solution of sodium iodide, the mercury group is replaced by iodine with the formation of 1-acetyliodoindoles, which are stable at room temperature. Thus, 1-acetyl-3-chloromercuriindole gave 1-acetyl-3-iodoindole, mp 102–104° C (from petroleum ether).

REFERENCES

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