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京都大学
25. Syntheses of Organic Fluorescent Compounds

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In order to study the emissivity of fluorescence of naphth [1, 2] imidazoles and perimidines, the following naphth [1, 2] imidazoles were synthesized naphth [1, 2] imidazole, 2-methylnaphth [1, 2] imidazole, 2-phenylnaphth [1, 2] imidazole, 1, 4 bis (2-naphth [1, 2] imidazolyl) benzene and 1, 5 bis (2-naphth [1, 2] imidazolyl) naphthalene.

The first, second and third compounds were synthesized according to Fiscers’ report (Ber. 25, 2714 (1892); 32, 1317 (1899); 34, 934 (1901)). Others were synthesized in the following method: 1, 2-diaminonaphthalene in alcohol was partially acylated with the corresponding acid chloride (a position was attacked), subsequently refluxed in 4N hydrochloric acid (or chlorobenzene) for 3–5 hours. The hydrochloride obtained was hydrolysed with NaOH in aq. alcohol, added into water, filtered, washed with water and dried. The yields were as follows:

Naphth [1, 2] imidazole, 53.6%; 2-methylnaphth [1, 2] imidazole, 66%; 2-phenylnaphth [1, 2] imidazole, 53.4%; 1, 4-bis (2-naphth [1, 2] imidazolyl) benzene, 40.2%; 1, 5-bis (2-naphth [1, 2] imidazolyl) naphthalene, 61.4%.

The following perimidines were synthesized according to Sachs (Ann. 365, 53–166 (1909); Ber. 39, 3027 (1906); 42, 3577 (1909)); perimidine, 2-methylperimidine and 2-phenylperimidine. However, 1, 4-bis (2-perimidinyl) benzene and 1, 5-bis (2-perimidinyl) naphthalene were synthesized in the following manner: To 1, 8-diamino-naphthalene in benzene a little excess of the acid chloride was added under stirring at room temperature. After the addition of acid chloride, the stirring was continued for 15 min. and subsequently for 15 min. at 60°C. The hydrochloride was, then, dissolved in a large quantity of hot water, treated with active carbon, neutralized with 10% NH₃ solution, filtered, washed with water, and dried. The yields were as follows

Perimidine, 47%; 2-phenylperimidine, 50%; 1, 4-bis (2-perimidinyl) benzene, 23.5%; 1, 5-bis (2-perimidinyl) naphthalene, 48%.

It was recognized that the formation of perimidines is easier than that of naphth [1, 2] imidazoles, that is, amino groups in 1, 8-positions in naphthalene ring are more reactive than those in 1, 2-positions.