

Synthesis of 2,3'-Biindolyl from Indole in One-step Reactions

Jan Bergman

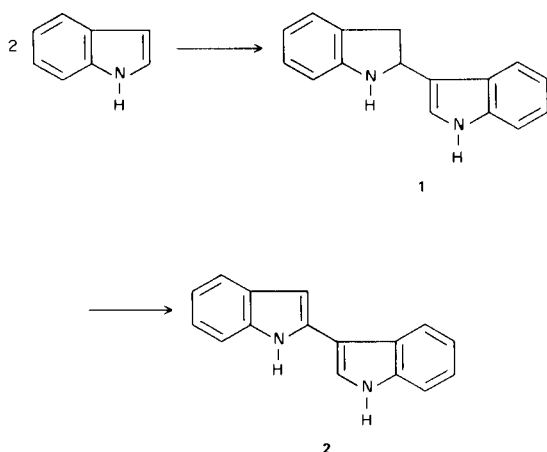
Department of Organic Chemistry, Royal Institute of Technology,
S-100 44 Stockholm, Sweden

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Several years ago Fujise and Tiba (1) studied the action of selenium on indole at 305-315°. A product (A, m.p. 192-195°) was isolated, but its structure was not elucidated. In connection with a study of some selenium-containing indoles (2), the experiment of the Japanese workers has now been repeated and the product A identified as 2,3'-biindolyl (2). Neither 3,3'-biindolyl, 2,2'-biindolyl nor 3,3-diindolyl selenides (2) could be detected (tlc) in the reaction mixture.

For comparison, the action of sulfur on indole was also studied in the temperature range 100-315°. Heating (115-125°) of indole with sulfur has been claimed (3) to give 3,3'-biindolyl. An attempt was made to repeat this preparation, but neither 3,3'-biindolyl nor 2,3'-biindolyl could be detected (*cf.* ref. 4). Similar experiments at 200-210° and 305-315° also failed to give any biindolyl.

A possible mechanism for the coupling reaction is shown in the Scheme. A supplemental experiment showed that selenium readily dehydrogenated 2-(3-indolyl)indoline (1) to give 2,3'-biindolyl (2).



The results obtained suggested a study of the effect of other dehydrogenative reagents on indole. Thus, heating indole with palladium on carbon gave a fair

yield of 2,3'-biindolyl. Again, no isomers were detected. When similarly treated pyrrole gave 2,2'-bipyrrolyl (5).

The action of both liquid sulfur dioxide and aqueous sulfur dioxide on indole gave 2,3'-biindolyl in poor yield together with indole oligomers.

EXPERIMENTAL

Action of Selenium on Indole.

Indole (23.4 g., 0.2 mole) and selenium (25 g.) were heated for 48 hours at reflux temperature (310°). Hydrogen selenide was formed. The cooled reaction mixture was powdered and extracted with hot toluene. The extract was evaporated and the residue fractionated. The fraction 230-245°/1 mm was taken. The solid obtained, after recrystallization twice from toluene, gave 2,3'-biindolyl (2.7 g., 12%), m.p. 203-205° (*lit.* (6) 203.5-205°); *tlc.* 2,3'-biindolyl ($R_f = 0.43$). 2,2'-Biindolyl ($R_f = 0.55$) and 3,3'-biindolyl ($R_f = 0.51$) could not be detected in the reaction mixture. The chromatograms were run with dichloromethane-methanol (98:2) on silica gel GF (Merck).

Action of 5% Palladium-Charcoal on Indole.

Indole (23.4 g.) and 5% palladium on carbon (20 g.) were heated (310°) for 24 hours. The cooled reaction mixture was extracted with hot toluene. The extract was filtered hot and finally cooled to -50°. The crystals, recrystallized from toluene, gave 2,3'-biindolyl (4.7 g., 20%), m.p. 203-205° (*lit.* (6) 203.5-205°).

Action of Selenium on 2-(3-Indolyl)indoline (1).

A mixture of 2-(3-indolyl)indoline (7) (2.4 g., 0.01 mole) and selenium (3 g.) was heated for 8 hours at 300°. The cooled reaction mixture was powdered and extracted with hot toluene, and the extract obtained was evaporated to a small volume (20 ml.). The crystals formed, when recrystallized from toluene, gave 2,3'-biindolyl (1.6 g., 69%), m.p. 203-205° (*lit.* (6) 203.5-205°).

Action of Sulfur Dioxide on Indole.

Method A.

A solution of indole (11.7 g., 0.1 mole) in methanol (70 ml.) and water (30 ml.) was saturated with sulfur dioxide every 12h for 4 days. The reaction mixture was poured into water (400 ml.), and made alkaline with 4 *N* sodium hydroxide. The

solid formed was collected, washed with water, and dried. Two recrystallizations from toluene gave 2,3'-biindolyl (0.7 g., 6%).

Method B.

Indole (11.7 g.) was dissolved in liquid sulfur dioxide (50 ml.) and the solution kept at -10° for 24 hours. The solvent was then allowed to evaporate slowly during 12 hours. The oil obtained dissolved in methanol (100 ml.) and then worked up as described in method A, gave 2,3'-biindolyl (0.9 g., 8%).

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