SYNTHESIS OF 2-BROMO-2,3-DIHYDRO-1H-PYRAZOLO[1,2-a]INDAZOLIUM BROMIDES AND THEIR REACTIONS WITH ALKALINE SOLUTIONS

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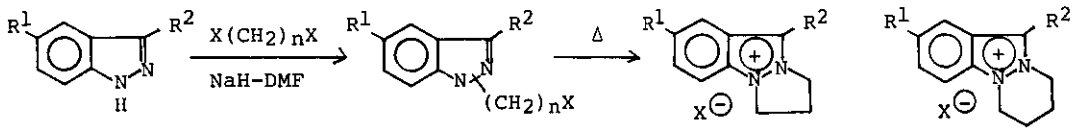
With an aim to obtain indazole derivatives having some therapeutic properties, we synthesized the series of 2,3-dihydro-1H-pyrazolo[1,2-a]- and 6,7,8,9-tetrahydropyridazino[1,2-a]-indazolium halides by the following reaction sequence and found that some of the former compounds show a desirable bronchodilating action.



During the course of this study, 3,5-disubstituted indazoles were similarly transformed into the corresponding 2-bromopyrazoloindazolium bromides (1) through 1-allylindazoles and their dibromides as shown below. Warming 1 at 60°C for 4 h with a $NaHCO_3$ solution resulted in the formation of the 9H-pyrazoloindazolium bromides (2) by dehydrobromination and a proton shift. On the other hand, treatment of 1 with an ice-cooled NaOH solution in a stream of nitrogen afforded a benzene soluble product (3). The reaction of 3 with acetic anhydride in benzene gave no acetyl derivatives but instead 2. The same conversion also occurred when treated with acetic acid or hydrobromic acid. These observations indicate that 3 is not the expected benzodiazapentalene (3') itself. Other chemical behavior and the probable structure of 3 will be discussed.