It was established by chemical degradation that RhCl₃·3H₂O catalyzed tritiation with HTO occurred with virtually 100% regioselectivity at the ortho-positions of benzamide as well as various anilides and benzoic acid. While tritiation has not been found in the alkyl C-H bond in anilide molecules, in the present experiments tritium was incorporated into the active methylene group of α-phenylacetamide. This finding suggests that the present tritiation occurs more readily at polar C⁶⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅┅・・・・・
with the catalyst\textsuperscript{1,2}. On the other hand, from the synthetic viewpoint, it was reported that \( \text{RhCl}_3\cdot3\text{H}_2\text{O} \) catalyzed deuterium-hydrogen isotope exchange occurred with high regioselectivity at the o-positions of various aromatic acids, anilides, amides, and amines\textsuperscript{3-5}. The location of deuterium was determined by NMR. Recently, some studies with HTO were carried out to shed light on the mechanism of the present regioselective hydrogen isotope exchange reaction\textsuperscript{6-9}. Experimental results with various anilides as substrates showed electronic and steric effects by acyl groups\textsuperscript{8} and an electronic effect by the substituent at the para-position\textsuperscript{9} on the extent of T-for-H exchange. The former effects supported the previous suggestion that the observed regioselectivity arose via initial coordination of the nitrogen atom of anilides to the rhodium(III) chloride catalyst\textsuperscript{6,7}. The latter one agreed with the mechanism that the electron-withdrawing substituent promoted the exchange reaction. A plausible mechanism for the effect is that tritiation proceeds by T-for-H exchange between C-H\textsuperscript{δ+} at the o-position of anilides and O-T\textsuperscript{δ+} of HTO as a ligand of rhodium(III).

The rhodium(III) chloride catalyzed T-for-H exchange has not been reported in nonpolar alkyl C-H bonds of the N-acyl and methyl groups attached to the benzene ring of anilides. However, if the mechanism described above is correct, tritiation will be observed at the polar C\textsuperscript{δ-}-H\textsuperscript{δ+} bond of a so-called active methylene group with substituents delocalizing a negative charge on the carbon atom at both sides through the present catalyzed reaction. This encouraged the authors to confirm the mechanism with \( \alpha \)-phenylacetamide.