# 論 文 内 容 の 要 旨

The thesis deals with studies on molecular design and synthesis of quinolonesactivated by steric effect between the 1-methyl and 8-substituent groups.

While the 1-methyl-2-quinolone (**MeQone**) framework is not reactive because ofaromatic property in the pyridone ring, 1-methyl-3,6,8-trinitro-2-quinolone (**TNQ**) exhibits extremely high reactivity. Indeed, **TNQ** undergoes *cine*-substitution to afford 4-substituted 6,8-dinitro-1-methyl-2-quinolones upon treatment with versatile nucleophiles. Moreover, **TNQ** also undergoes cycloaddition reactions at the 3- and the 4-positions under mild conditions leading to polycyclic compounds, which reveals that the pyridone moiety of **TNQ** shows nitroalkene property rather than aromatic property.

It is considered that the high reactivity of **TNQ** is caused by steric repulsion between the 1-methyl and the 8-nitro groups. In other words, the **MeQone** framework can be sterically activated even in the absence of electronic activation. In the present work, the molecular design and synthesis of the sterically activated **MeQone**s was studied on the basis of this hypothesis.

Firstly, reactivity of several kinds of **MeQone**s having both 1-methyl and the 8-substituent was predicted by DFT calculation, by which the dihedral angles between N1-Me and C8-R8 bonds are estimated. The calculated results suggested 1,6-dimethyl-3,8-dinitro-2-quinolone and 1,8-dimethyl-3,6-dinitro-2-quinolone are considered to surely reveal high reactivity as well as **TNQ**.

As a result of study on the preparation, the latter quinolone was successfully synthesized in addition to 3,5,7-trinitrated and 3,5-dinitrated 1,8-dimethyl-2-quinolones.

When nitrated 1,8-methyl-2quinolones were subjected to the reactions with 2,4-pentanedione in the presence of triethylamine, the *peri*-substituent (R5) was found to prevent the *cine*-substitution. Thus, a small nucleophile, potassium cyanide, was employed for estimation of the reactivity of the **MeQone** framework. The high reactivity was maintained, even when the 6-nitro or 8-nitro groups of **TNQ** was replaced with a methyl group, to afford corresponding *cine*-substituted products upon treatment with potassium cyanide. These results strongly support our consideration that the steric repulsion between 1-methyl and 8-methyl groups activated the **MeQone** by disturbing the coplanarity, which decreases aromaticity of the pyridone moiety.

This work affords researchers valuable information for the functionalization of the **MeQone** framework, which is helpful for finding new biologically active compounds.