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授与した学位	博 士
専攻分野の名称	理 学
学位授与番号	博甲第4557号
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学位授与の要件	自然科学研究科 機能分子化学専攻 (学位規則第5条第1項該当)
学位論文の題目	Substituent and temperature effects on the formation of 3 <i>H</i> -azepine derivatives from <i>o</i> -alkylphenylnitrene ( <i>o</i> -アルキルフェニルナイトレンの反応により得られる 3 <i>H</i> -アゼピン誘導体の置換基および温度効果に関する研究)
論文審査委員	教授 佐竹恭介      准教授 花谷正      准教授 岡本秀毅

#### 学位論文内容の要旨

The synthesis of 7-alkyl-3*H*-azepines was selectively obtained from the reaction of bulky ortho substituent on *o*-alkylnitrobenzene by the action of Bu<sub>3</sub>P in the presence of alcohols, although the formation of 3-alkyl-3*H*-azepine isomers can be expected. Moreover, the more bulky the alcohols media used, the more selective the azepines were support the hypothesis for the intermediate structure involved for the final reaction product formation. The addition of alcohols to dehydroazepine smoothly occurred to C=N bond of dehydroazepine intermediate, without the interference of the bulky alkyl group in the C-3 position to gives the selective 7-alkyl-3*H*-azepines. However, an equal opportunity was observed when the small ortho alkyl group and/or the small alcohol media applied in the reaction afford the equal ratio of 7- and 3-alkyl-3*H*-azepine derivatives.

Unprecedented temperature dependent reaction to the formation of 3*H*-azepines was also reported. The reaction of *o*-methylphenylnitrene in the presence of alcohol and amine was expected to give isomeric pair of 3- and 7-methyl-3*H*-azepine derivatives. However, the formation ratio between these isomers found to be obviously influenced by the reaction temperature, that is, reaction at 150°C gave 7-methyl-3*H*-azepine derivative, but it became a minor one under at 70°C in both media. The ratio between 3- and 7-methyl derivative is explained by a scheme of kinetic and thermodynamic controlled products distribution from *o*-methylphenylnitrene to 3- and 7-methyldehydroazepine intermediates which are trapped by nucleophilic media to give 3- and 7-methyl-3*H*-azepine derivatives.

In continuation with the study on effect of reaction temperature in the formation of 3*H*-azepines, the reaction of *o*-isopropylphenylnitrene in the presence of diethylamine was suspected not only gave the 3*H*-azepines but also the generation of isomeric structure of unknown product C<sub>13</sub>H<sub>22</sub>N<sub>2</sub>. This product can be envisaged to rise by the way of the elusive of *o*-alkylphenylnitrene by other plausible modes of formation. Under the intensive structure determination by <sup>1</sup>H, <sup>13</sup>C NMR, IR, UV-vis and ESI Mass spectrometry, the structure of this novel compound is cyclopentencarbonitrile derivatives. The weak stretching of C≡N was clearly detected in the IR spectrum. Moreover, the X-Ray crystal structure leaves no doubt for the structure identification suggests the most stable geometry of the obtained carbonitrile derivatives.

## 論文審査結果の要旨

申請者により、*o*-置換フェニルナイトレンの反応において、生成物分布に影響を与える置換基効果、ならびに温度効果に関する実験結果とそれらに関する考察についての発表（40分）がなされた。フェニルナイトレンの分子内環拡大反応による 3*H*-アゼピン合成反応において、見出された置換基効果および温度効果は新規な知見であり、これらの知見に関する十分な考察もなされていた。発表後、質疑応答（20分）により発表内容や研究成果に関する吟味をおこない、博士論文として相応しいことが確認された。さらに、ここで発表された研究成果は *Unprecedented Temperature Dependent Formation of 3- and 7-Methyl-3H-azepine Derivatives by the Reaction of o-Nitrotoluene with Tributylphosphine in Nucleophilic Media*, Siti Mariyah Ulfa, Hideki Okamoto, Kyosuke Satake, *Chem. Lett.* **2012**, *in press*. および *Steric Effect on the Formation of 3H-azepine Derivatives from o-Alkylphenylnitrene and Alcohol as a Nucleophilic Media*, Siti Mariyah Ulfa, Hideki Okamoto, Kyosuke Satake, *Heterocycles* **2011**, *83*, 1259–1265 に二報の論文として公表されている。以上の点を考慮して審議した結果、申請者 Siti Mariyah Ulfa は出席者全員一致で博士（理学）の学位を与えるに相応しいと判断された。