THERMAL AND PHOTOCHEMICAL REARRANGEMENTS
OF S-SUBSTITUTED 2,5-DIPHENYL-1,4-DITHIINS

Keiji Kobayashi and Kiyoshi Mutai

Department of Chemistry, College of Arts and Sciences
University of Tokyo, Komaba, Meguro, Tokyo 153, Japan

During the course of our investigation to see if the extrusion of a substituted sulfur moiety would occur in sulfoxide, sulfone, and sulfilimine of 2,5-diphenyl-1,4-dithiin we found a variety of novel rearrangements involved in thermolysis as well as photolysis of these dithiin derivatives.

Sulfoxide 1 upon heating in acetonitrile at 70 °C afforded rearranged 1,3-dithiole 2 along with thiophene 3 due to the extrusion of SO. When irradiated in methanol with a high pressure mercury lamp, 1 gave 2, 4, and 5 as well which was not obtained in the thermolysis.

\[
1 \xrightarrow{\Delta} 2 + 3
\]

Photolysis of sulfilimine 6 gave rearranged product 7 and dithiin 4, while thermolysis led to the elimination of both S=N-Tos and N-Tos fragments and no rearrangement was observed.

Sulfone 8 showed quite an unusual photochemical behaviour. Upon irradiation in methanol 8 gave rise to 2,5-diphenylthiophene 9 in a low yield other than 2,4-diphenylthiophene 3 solely due to the loss of sulfur dioxide. The formation of 9 most likely proceeds via the valence isomerization to thioketone 10.

This mechanism was supported by the photolysis in n-butylamine, which resulted in the formation of isomeric 1-butylpyrroles, 11 and 12.

\[
8 \xrightarrow{hv} 9 + 2 + 3
\]

\[
8 \xrightarrow{MeOH} 9 + 2
\]

\[
8 \xrightarrow{n-BuNH_2} 10 + 11 + 12
\]