

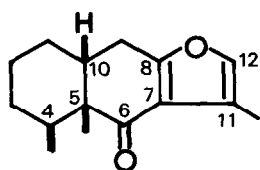
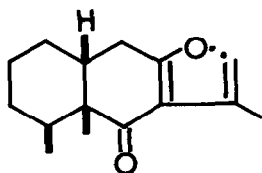
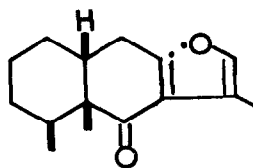
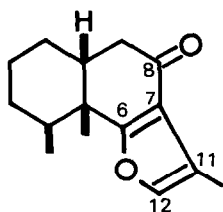
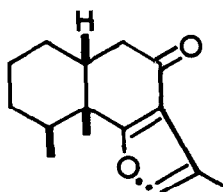
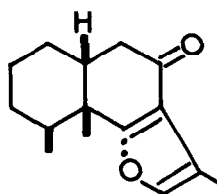
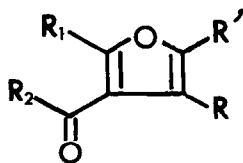
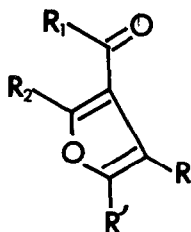
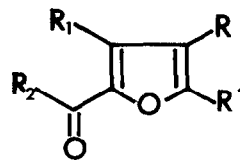
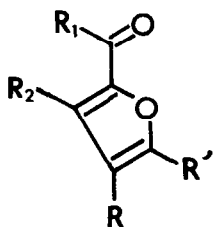
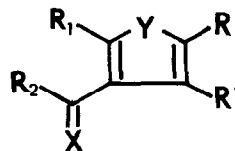
THERMAL ISOMERIZATION OF 3-ACYLFURAN TO ITS ISOMERIC 3-ACYLFURAN.
THERMAL INTERCONVERSION BETWEEN LIGULARONE AND ISOLIGULARONE.

Masahiro Tada and Takeyoshi Takahashi
Department of Chemistry, Faculty of Science,
The University of Tokyo, Bunyo-ku, Tokyo, Japan

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A number of studies on photochemical¹⁾ and thermal²⁾ valence bond isomerization of five-membered aromatic (or non-aromatic) heterocyclic compounds have been described. The photorearrangement of 2,5-di-tert-butylfuran to 2,4-di-tert-butylfuran and 2,2,7,7-tetramethylocta-4,5-dien-3-one was shown to proceed via tert-butylcyclopropenyl tert-butyl ketone.^{1f)} In a gas-phase thermal isomerization of acetylcyclopropane, this compound isomerized reversibly to 2,3-dihydro-5-methylfuran and irreversibly to cis- and trans-pent-3-en-2-ones and pent-4-en-2-one.²⁾ We wish to report the thermal interconversion between ligularone (1)³⁾ and isoligularone (2)⁴⁾.

A solution of ligularone (1)³⁾ (60 mg) in 1,6-dimethylnaphthalene was heated at 260-263° for 90 hr under a nitrogen atmosphere. The GLC analysis of the reaction mixture showed the presence of a product (2) and the starting material (1) in a ratio of about 1 : 1 ; no other product was detected. The product (2) was separated by silica gel column chromatography and purified by crystallization from light petroleum-ether to give pure isoligularone (2) (18 mg), m.p. 147-148°, IR (Nujol): 1660 and 1550 cm⁻¹; UV (EtOH): λ_{\max} 269 nm (ϵ 4800); PMR (CDCl₃): δ 0.90 (3H, d, J = 7 Hz ; C₍₄₎-CH₃), δ 1.28 (3H, s ; C₍₅₎-CH₃), δ 2.14 (3H, d, J = 1.5 Hz ; C₍₁₁₎-CH₃) and δ 7.02 (1H, q, J = 1.5 Hz ; C₍₁₂₎-H); MS : M⁺ at m/e 232 (C₁₅H₂₀O₂), which was found to be identical (IR, PMR, MS) with the authentic sample⁴⁾ of 2. Isoligularone (2) was then subjected to thermal isomerization under the same conditions as described above to yield a mixture of 1 (as a sole product) and 2. Irradiation of a solution of ligularone (1) in

(1)(A)(C)(2)(B)(D)(3) R = CH₃ , R' = H(5) R = CH₃ , R' = H(7) R = CH₃ , R' = H(4) R = H , R' = CH₃(6) R = H , R' = CH₃(8) R = H , R' = CH₃(9) R = CH₃ , R' = H(10) R = H , R' = CH₃For compounds 3 ~ 11 :R₁ , R₂ = alkyl groups(11) R , R' = H or alkyl groups

ether under a nitrogen atmosphere using a 160 W low pressure mercury-lamp with a quartz filter gave the product showing three spots on TLC. However, none of the compounds corresponding to these spots showed a signal due to a proton on a furan ring in its PMR spectrum.⁵⁾

On thermal or photochemical isomerization of 3-acylfuran (3), the formation of the isomeric 3-acylfurans (4 ~ 6) and 2-acylfurans (7 ~ 10) might be expected.⁶⁾ In our case, only a thermal interconversion between the compound of types 3 and 5 was observed. The equilibrium between ligularone (1) and isoligularone (2) can be plausibly explained by the O—C₍₁₂₎ bond cleavage, the rapid rotation about the C₍₇₎—C₍₁₁₎ bond of the intermediate diradical A or/and B, and the recyclization at the high temperature. No formation of the other isomers which were expected to be produced from the diradicals C and D were observed. This may be due to the difference in the reactivity of the two C—O bonds of a furan ring conjugated with a carbonyl group.

Studies on thermal and photochemical isomerization of the similar five-membered aromatic heterocyclic compounds (11 : X, Y = O, S, NH) are under way.

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a generous gift of 2 together with its spectral data.

5. Although these compounds have not yet been obtained in a pure state, they were different from the substances of types 4 ~ 10 (and 3) as shown by their PMR data. Further investigation is in progress.
6. These compounds could be derived from 3 via the diradicals or/and the cyclopropenyl intermediates analogous to those described in references 1 and 2.