NOTES

The Thermal Dimerization of 2-Vinylfuran*

By Chuji Aso, Toyoki KUNITAKE and Yoshinari TANAKA

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2-Vinylfuran was found to undergo a rather facile thermal polymerization1) during the course of the study of its free radical polymerization.2)

Since the thermal dimerization of styrene has been studied in connection with the elucidation of the initiation mechanism of thermal polymerization,3) similar experiments were carried out for 2-vinylfuran.

Results

The monomer prepared in a manner described previously2) was dissolved in purified toluene or bromobenzene (molar ratio 1 : 10) in an ampule. After it had been sealed under reduced nitrogen pressure, the ampule was allowed to stand at 130°C for 300 hr. After the insoluble fraction in methanol had been removed and the solvents had been evaporated at a reduced pressure, viscous oil was obtained. The gas chromatogram of the distillable portion of the oil (ca. 100°C/4 mmHg) consisted of one major peak, and its yield was 10 to 20% with a toluene solvent and 30 to 50% in bromobenzene. Elementary analysis: Found: C, 75.65; H, 6.40. Calcd. for C_6H_6O: C, 76.57; H, 6.43%. The molecular weight determination (Vapor Pressure Osmometer, Model 301A, Mechrolab. Inc.) showed the portion to be a dimer (Found: 175, 198. Calcd. for dimer: 188). The residues of the distillation had molecular weights from that of a trimer to that of a hexamer, depending on the solvent used. Thus, the distillate was concluded to be a dimer of 2-vinylfuran. Subsequent measurements of infrared, ultraviolet and NMR spectra gave the following results:

a) IR data. Characteristic bands for furans4) observed at 3150, 1595, 1500, 1006, 881 and

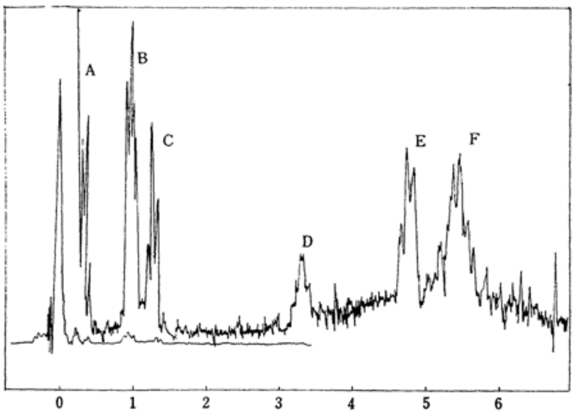

Fig. 1. NMR spectrum of the dimer.

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Part II of "The Polymerization of Vinyl Compounds with Heterocyclic Groups."

1) Y. Tanaka, Master's thesis. Kyushu Univ., 1964.

2) C. Aso and Y. Tanaka, *Chem. High Polymers, Japan*, **27**, 373 (1964).

3) F. Mayo, *J. Am. Chem. Soc.*, **75**, 6133 (1953).

4) Kagaku-no-ryoiki. Special Issue, No. 28. "Infrared Absorption Spectroscopy," Vol. III, Nanko-do, Tokyo (1961), p. 108.

$796\ \text{cm}^{-1}$. No vinyl absorption. Characteristic bands for aliphatic C–H bonds at 2948, 2866, 1450 and $1380\ \text{cm}^{-1}$.

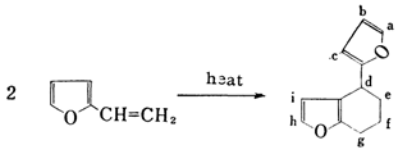
b) UV data. No double bond conjugated with the furan ring present.

c) NMR data (in benzene, Varian A 60). The NMR assignment shown in the table is consistent with the chemical shifts for other furan derivatives[5] and with the other data obtained for the dimer, although no detailed analysis of spin-spin coupling has yet been carried out.

TABLE I. NMR ASSIGNMENTS

Peak	A	B	C	D	E	F
Area ratio	2	2	1	1	2	4
Assignment	a, h	b, i	c	d	g	e, f

$J_{de} \fallingdotseq 5$ c. p. s. $J_{fg} \fallingdotseq 5$ c. p. s.



The dimer may be formed either by a Diels-Alder type reaction, followed by isomerization, or by a coupling of biradicals. Although it is not clear whether this compound can be related with the thermal initiation of polymerization, the contrast should be interesting between this compound and the cyclobutane derivative obtained thermally from styrene.[3]

We wish to express our thanks to Professor Taku Matsuo of our department for his helpful discussions.

Department of Organic Synthesis
Faculty of Engineering
Kyushu University
Hakozaki, Fukuoka

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[5] R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 905 (1961); G. S. Reddy and J. H. Goldstein, *J. Phys. Chem.*, **65**, 1539 (1961).