Synthesis of Furan Derivatives. XLV.\textsuperscript{1) A New Acid catalyzed
Cyclization of sterically Hindered cis Alkenals\textsuperscript{2)}

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(Received July 4, 1968)

Preparation of aryl 2,4-dialkyl-2,4-pentadienals (aryl is (5-nitro-2-furyl)- or (5-nitro-2-thienyl), alkyl is methyl or ethyl) by condensation of alkyl enol ether R-CH=CH-OR R=H with aryl-\alpha-alkylated acrolein acetics gave stereoselectively 2-cis-4-trans-2,4-dialkylated pentadienals. Driving force leading to above configuration is overcrawling control of the sterically hindered chain. The stereoselective formation of cis-alkenals was found to be applicable for aryl 2-cis-4-cis-6-trans-trialkylated heptatrienal. All hindered cis alkenals prepared in this paper cyclized to five or seven membered cyclic ketones in the presence of HCl or some organic acids.

A mechanism for the cyclization was proposed, that involves initial formation of oxocarbonium ion, which is later transformed by two of successive processes, i.e., the formation of bicyclo-[2.1.0] cyclopentanone derivative and its ring rupture by acid. Proposed mechanism was discussed from the result of deuterohydrochloric acid incorporated cyclization of IVa.

Earlier studies of the acid catalytic transformation\textsuperscript{4} of (5-nitro-2-furyl)-2,4-dimethyl-2-cis-4-trans-2,4-pentadienal (IVa) with hydrochloric or hydrobromic acid have shown that the compound is readily transformed to five membered conjugated ketone, 2-(5-nitro-2-furyl)-3,5-dimethyl-pent-2-en-1-one (Va). The present studies have been undertaken to examine whether this type cyclization may generally occur in 5-(5-nitro-2-furyl)-2-cis-4-trans-2,4-dialkylated pentadienals (IVa—d) and 7-(5-nitro-2-furyl)-2-cis-4-cis-6-trans-2,4,6-trimethylheptatrienal (VI).

At the onset of this work, the first requisite for the cyclization of the pentadienal is that the pentadienal is to have 2-cis-4-trans arrangement, and the second is that the use of hydrochloric or hydrobromic acid should be essential to lead the reaction to completion.

In the preparation of several pentadienals possessing above configuration IV, it was found the first requirement was fulfilled by the previously reported method involving the

\textsuperscript{2)} Presented at the 88th Annual Meeting of the Pharmaceutical Society of Japan at Tokyo, April 1968.
\textsuperscript{3)} Location: Katakasu, Fukuoka.
condensation of aryl α-alkylated acrolein acetals (R₁=N=H) (I) with alkyl enol ether (II) (R₃ =Me or Et) in the presence of boron trifluoride etherate, and subsequent dealkolation and acetal hydrolysis of the etheral acetal obtained III. The reaction scheme is shown in Fig. 1.

![Reaction Scheme](image)

Fig. 1. Preparation of Aryl-2,4-dialkylated-2-cis-4-trans-pentadienal

Although a number of pentadienals in furan derivatives⁵ have been reported, no systematic preparation of 2,4-di-substituted-2,4-pentadienals which might be expected considerable over-crawding caused by two alkyl substituents have been carried out yet.

Pentadienals (IVA—d) obtained from above method were found to have 2-cis-4-trans configuration as shown in Fig. 1. Gaschromatographic analysis of the hydrolysis aliquote of the etheral acetal (III, X=O, R₁=R₃=R₅=R₆=Me) did not show the appreciable amounts of other isomer than IVA. Substantiation of the configuration of IVA—in was drawn from the nuclear magnetic resonance (NMR) spectra, i.e., high field shift of the signal of 5-hydrogen of IVA—in makes marked

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contrast with the chemical shift of corresponding hydrogen in trans alkenals (see Fig. 2). The similar shift of 5-hydrogen of 2-cis pentadienal was already utilized to determine 2-cis-4-trans configuration of IVa, which was also ascertained by additional chemical evidence that dimethyl acetal of IVa easily eliminates one mole of methanol to give 1-methoxy-2-(5-nitro-2-furyl)-3,5-dimethylcyclopenta-2,4-diene. Scale drawing of IVb-c may also suggest the preference of 3-(S)-cis than 3-(S)-trans configuration, because van der Waals radius of ethyl may be considered as same as methyl group. The NMR properties and physical properties of some new pentadienals are shown in Fig. 2 and Table 1, respectively.

**Table I. Polyenals with cis Formyl Group**

<table>
<thead>
<tr>
<th>Dienal R</th>
<th>R1</th>
<th>R2</th>
<th>CHO</th>
<th>mp°C</th>
<th>UV absorption</th>
<th>IR absorption (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5-Nitro-2-furyl)-</td>
<td>Me</td>
<td>Me</td>
<td>(IVa)</td>
<td>113—114</td>
<td>221</td>
<td>12000</td>
</tr>
<tr>
<td>(5-Nitro-2-furyl)-</td>
<td>Me</td>
<td>Et</td>
<td>(IVb)</td>
<td>108—109</td>
<td>220</td>
<td>8800</td>
</tr>
<tr>
<td>(5-Nitro-2-furyl)-</td>
<td>Et</td>
<td>Me</td>
<td>(IVc)</td>
<td>101—102</td>
<td>221.5</td>
<td>11600</td>
</tr>
<tr>
<td>(5-Nitro-2-thienyl)-</td>
<td>Me</td>
<td>Me</td>
<td>(IVd)</td>
<td>150—152</td>
<td>222</td>
<td>7700</td>
</tr>
<tr>
<td>Trienal</td>
<td>Me</td>
<td>Me</td>
<td>(VI)</td>
<td>117—118</td>
<td>242</td>
<td>11200</td>
</tr>
</tbody>
</table>

![Diagram](image)

<table>
<thead>
<tr>
<th>Alkenal</th>
<th>Formula</th>
<th>Carbon (%)</th>
<th>Hydrogen (%)</th>
<th>Nitrogen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Calcd.</td>
<td>Found</td>
<td>Calcd.</td>
</tr>
<tr>
<td>IVb</td>
<td>C₁₆H₁₂O₃N₁</td>
<td>61.27</td>
<td>61.25</td>
<td>5.57</td>
</tr>
<tr>
<td>IVc</td>
<td>C₁₁H₁₀O₃N₁</td>
<td>61.27</td>
<td>61.20</td>
<td>5.57</td>
</tr>
<tr>
<td>IVd</td>
<td>C₁₁H₁₀N₃S₁</td>
<td>55.69</td>
<td>55.47</td>
<td>4.67</td>
</tr>
<tr>
<td>VI</td>
<td>C₁₆H₁₂O₃N₁</td>
<td>64.36</td>
<td>63.96</td>
<td>5.79</td>
</tr>
</tbody>
</table>

a) Recrystallized from 75% ethanol.

The 2-cis-4-trans configuration of obtained 2,4-di-alkyl-substituted pentadienal was also presented by the Wittig reaction, i.e., (5-nitro-2-furyl)-2,4-dimethyl-2-cis-4-trans-pentadienal (IVA) was obtained in approximately 5% yield, when (5-nitro-2-furyl)-x-methyl-acrolein (X) was treated with three molar formylethylidene triphenyolphosphorane (XI) in acetonitrile at 85° for 8 hours. Mixed melting point determination of the product with authentic IVa did not show any depression and both of them gave same Infrared (IR) spectrum. In this preparation, again no other appreciable stereoisomer have been detected.

From this result, stereochemistry of the formyl olefination is seemed to be determined by the stability of the betaine intermediate (XII). The initial combination of (5-nitro-2-furyl)-α-methyl-acrolein (X) with the phosphorane (XI) can occur in two ways to give either the erythro (XIIa) or threo (XIIb) betaine, which subsequently collapses with the formation of the 2-cis-4-trans isomer and 2,4-all trans isomer, respectively. In these conformations the erythro betaine (XIIa) is less sterically hindered than the threo betaine (XIIb), because in former conformation smaller formyl group is to place at the same side with larger 1-methyl-2-(5-nitro-2-furyl)vinyl group, and thus XIIa seems to more likely to form. As the phosphorane (XI) is resonance stabilized ylid\(^7\) owing to electron withdrawing effect of formyl group, betaine formation with aldehyde (X) is seemed to be reversible. Therefore the subsequent reaction would then be expected to proceed entirely through the erythro betaine (XIIa), and 2-cis-4-trans configuration favored for the resulting olefin (IVA). The stereochemical course above mentioned is shown in Fig. 3.

![Chemical Structure Diagram](image_url)

Fig. 3. Wittig Reaction of α-Formylethylidenetriphenylphosphorane with (5-Nitro-2-furyl)-α-methylacrolein

The 2-cis-4-trans pentadienones were now heated with dilute hydrochloric acid (0.5\%) in acetonitrile to see expected cyclization would generally take place. As the result of these experiment, the cyclization is found to occur entirely in good yields (70—80\% yields) to give 2-(5-nitro-2-furyl)-3,5-alkyl substituted-cyclopent-2-en-1-one (V). Structures of Va—d were shown in Table II.

TABLE II. Physical Properties of Cyclopentenone Derivatives

<table>
<thead>
<tr>
<th>Cyclopentenone derivative substituent</th>
<th>R</th>
<th>R₁</th>
<th>R₂</th>
<th>mp(°C)</th>
<th>UV absorption</th>
<th>IR absorption (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>λmax (nm)</td>
<td>εmax (L mol⁻¹ cm⁻¹)</td>
</tr>
<tr>
<td>5-Nitro-2-furyl-</td>
<td>Me</td>
<td>Me</td>
<td>(Va)</td>
<td>108—109</td>
<td>228</td>
<td>14000</td>
</tr>
<tr>
<td>5-Nitro-2-furyl-</td>
<td>Me</td>
<td>Et</td>
<td>(Vb)</td>
<td>61—62</td>
<td>225—227</td>
<td>14100</td>
</tr>
<tr>
<td>5-Nitro-2-furyl-</td>
<td>Et</td>
<td>Me</td>
<td>(Vc)</td>
<td>79—80</td>
<td>227</td>
<td>15200</td>
</tr>
<tr>
<td>5-Nitro-2-thienyl-</td>
<td>Me</td>
<td>Me</td>
<td>(Vd)</td>
<td>136—137</td>
<td>230</td>
<td>7700</td>
</tr>
<tr>
<td>(5-Nitro-2-furyl)-acryl-</td>
<td>Me</td>
<td>Me</td>
<td>(IX)</td>
<td>142—143</td>
<td>220</td>
<td>7800</td>
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</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Carbon (%)</th>
<th>Hydrogen (%)</th>
<th>Nitrogen (%)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Calc.</td>
<td>Found</td>
<td>Calc.</td>
</tr>
<tr>
<td>Vb</td>
<td>C₁₁H₁₉O₂N₁</td>
<td>61.27</td>
<td>61.20</td>
<td>5.57</td>
</tr>
<tr>
<td>Vc</td>
<td>C₁₁H₁₀O₂N₁</td>
<td>61.27</td>
<td>61.11</td>
<td>5.57</td>
</tr>
<tr>
<td>Vd</td>
<td>C₁₁H₁₁O₂N₁S</td>
<td>55.69</td>
<td>55.59</td>
<td>4.67</td>
</tr>
<tr>
<td>IX</td>
<td>C₁₁H₁₀O₂N₁</td>
<td>63.15</td>
<td>63.28</td>
<td>5.30</td>
</tr>
</tbody>
</table>

It was obtained that the condensation of aryl-α-alkyl-acrolein acetal (I) with alkenyl ether (II) (R–CH=CH–OR, R=H) never failed to give aryl 2-cis-4-trans-2,4-alkylated pentadienial (IV). If this stereochemical outcome is exactly retained in the attempted preparation of (5-nitro-2-furyl)-2,4,6-trimethyloctatrienial (VI), the configuration of this highhly hindered trienial should be 2-cis-4-cis-6-trans arrangement, and its zig-zag type conjugation might have a cyclization possibility which lead to seven membered cyclic ketone by acid (see Fig. 4). On the other hand, if R₁ is hydrogen, in stead of alkyl, expected stereochemistry of this trienal would be 2-cis-4-trans-6-trans arrangement, and subsequent cyclization might give five membersed cyclic ketone.

(5-Nitro-2-furyl)-2,4,6-trimethyl-2-cis-4-cis-6-trans-heptatrienial (VI) was obtained in the yield of 3—5% from concomitant reddish oily mixture which showed two peaks in gaschromatography. The configuration of the molecule was ascertained by its NMR spectrum, i.e., upfield shift of 7-vinylc proton appeared at 6.84 ppm gave a strong support to the configuration, whereas two hydrogens at 3 and 5 position showed singlet at 6.40 ppm. Assignable peaks for vinylc methyl at 2, 4 and 6 position were shown at 2.04, 2.26 and 2.31 ppm, respectively (see Fig. 2). VI showed carbonyl stretching band at 1671 cm⁻¹, and its UV and light absorption maxima showed at 242 nm (11200), 312.5 nm (14720) and 400 nm (28000). Low yield of VI is ascribed to the fact that facile cyclization of VI to give 2-(5-nitro-2-furyl)-3,5,7-trimethylcyclo-hepta-2,4-dien-1-one (VII) took place together with the hydrolysis of VI’s precursor, 7-(5-nitro-2-furyl)-1,1,3-trimethoxy-2,4,6-trimethylocta-4,6-diene under the similar condition used in the hydrolysis of etheral acetals (III). VII was obtained as red viscous oil, and its
structure was affirmed by its NMR spectrum, which showed doublet at 1.26 ppm ($J=7$ cps) due to 7-position secondary methyl group, and two singlets assigned for 3- and 5-vinylc methyl at 2.06 and 2.00 ppm, respectively. No other vinylic protons appeared except a singlet at 6.36 ppm which was assigned for 4-vinyl hydrogen, and another complex multiplets were appeared in the range of 2.0—3.2 ppm with three proton integration. Carbonyl stretching occurred at 1693 cm$^{-1}$ and UV absorption maximum occurred at 230 m$\mu$ (20700) and 370 m$\mu$ (12300) in ethanol. These values gave a reliable evidence of cyclization by losing one double bond from mother aldehyde (VI).

In contrast, cyclization of (5-nitro-2-furyl)-2,4-dimethyl-2-cis-4-trans-6-trans-heptatrienal (VIII) proceeded so easily that the alkenal could not isolated as pure form even in the use of weaker acid such as oxalic acid or $p$-toluenesulfonic acid. Hydrolysis of the corresponding etheral acetal which leads to VIII gave 2-(5-nitro-2-furyl)-acryl-3,5-dimethyl-cyclopet-2-en-1-one (IX). NMR spectrum of (IX) showed the presence of trans vinyl
Fig. 6. The Mechanism of Cyclization of Hindered cis-Pentadienal

Fig. 7. Infrared Spectra of Cyclization Mixture of 5-(5-Nitro-2-furyl)-2,4-dimethyl-3-methoxypent-4-en-1-ol in THF at 65°

The spectrum showed in solid line is obtained from oily residue which is obtained by evaporation of benzene elute in silicagel chromatofor of cyclization mixture after 4 hr.

Cyclization condition: 100 mg of 5-(5-nitro-2-furyl)-2,4-dimethyl-3-methoxypent-4-en-1-ol in 1 ml of THF is refluxed with 0.11 ml of 0.5 M HCl, in each run the reaction was stopped by the addition of sodium bicarbonate solution and the mixture was extracted with chloroform and dried with sodium sulfate. Evaporation of solvent yielded reddish oil, which was presented for analytical sample.

Fig. 8. The Comparison of NMR Spectrum of Va with that Deuterated 2-(5-Nitro-2-furyl)-3,5-dimethylpent-2-en-1-one

protons, which appeared as two doublets each centered at 7.00 (J=17 cps) and 7.70 ppm (J=17 cps). This is a strong support that (IX) is not seven membered but five membered cyclic ketone. The IR spectrum of (IX) showed carbonyl stretching at 1693 cm⁻¹ and double bond stretching at 1601 cm⁻¹. The UV maxima showed at 220 mμ (7800), 265 mμ (17600) and 383 mμ (18300) in ethanol (see Fig. 5).

The next step of this work was to investigate the reaction mechanism of the above cyclization. The reaction appears to involve initial ionization of carbonyl to form linear oxocarbonium ion (XIII). Ready loss of a proton from formyl group relieves the overcrowding of the molecule as shown in Fig. 6. Then the ion rearranged to the ketene intermediate (XIV) which is probably in equilibrium with oxocarbonium ion, and then the intermediate transformed successively to bicyclo[2.1.0]pentanone.

derivative (XV), which was converted to the cyclic ketone by subsequent acid cleavage of cyclopropane ring.

As one of the indirect supports of the intermediacy of above bicyclic ketone (XV), we can point out the presence of 1780 cm⁻¹ carbonyl stretching absorption which is assignable for cyclobutanone or ketene carbonyl from the cyclization reaction mixture of (5-nitro-2-furyl)-2,4-dimethyl-3-methoxy-pent-4-en-1-al (XVI) as shown in Fig. 7.

In order to examine the above reaction mechanism, deuterohydrochloric acid incorporated cyclization of IVa was then carried out in acetonitrile. Comparing with the NMR spectrum of the undeuterated ketone, the spectrum of the deuterated ketone showed following characteristics, i.e., (1) disappearance of complex multiplets in 2.0—3.3 ppm, (2) a singlet at 1.26 ppm ascribed to CH₃C=H, and (3) a singlet at 2.57 ppm having two proton integration due to vinylic CH₂D. The comparison of both spectrum is shown in Fig. 8.

The finding that all the moving hydrogens participated in the cyclization are readily replaced by deuterium is not inconsistent with above mechanism. The further examination of the proposed mechanism must be done from kinetic view point. This is in progress in our laboratories.

**Experimental**

**Alkyl Enol Ethers**

Methyl propenyl ether was prepared by the catalytic vapor phase decomposition of propionaldehyde dimethyl acetal by our previous paper.⁹ Ethyl butenyl ether was prepared according to M.G. Voronkov’s procedure,¹⁰ which boiled at 94—96.5⁰, n°² 1.40627.

(5-Nitro-2-furyl)-α-methyl-acrolein and (5-nitro-2-furyl)-α-ethyl-acrolein was prepared by our previous paper.⁹

(5-Nitro-2-thiethyl)-α-methylacrolein—(5-Nitro-2-thiethyl)-α-methylacrolein was prepared by following modification of G. Carrara, et al.’s procedure.¹¹

Ten grams of dry 5-nitro-2-thiophenecarboxaldehyde was placed in a flask fitted with a stirrer, dropping funnel, reflux condenser and thermometer. After cooling in an ice bath 30 ml of freshly distilled propionaldehyde was added at once at stirring. With caution, a 20% methanol solution of potassium hydroxide added dropwise until the temperature of the reaction mixture reaches to 30—35⁰. After rapid cooling 20 ml of acetic anhydride was added in one portion, the solution was boiled for 20 minutes and then cooled to 0⁰. After the addition of 50 ml of water and 3 ml of hydrochloric acid, the mixture was carefully warned to prevent sudden flashing of the contents and refluxed for 30 minutes, cooled, and the precipitates was collected and recrystallized from ethanol. It yielded 7.0 g of yellow prisms, mp 134⁰. UV λmax nmp (e): 249 (10200), 362 (22800). Anal. Calcd. for C₉H₆O₂N₂S: C, 48.74; H, 3.58; N, 7.11. Found: C, 48.55; H, 3.42; N, 6.98.

**Aryl-2,4-di-alkylated-2-cis-4-trans-pentadienals**

Since all preparations were essentially carried out in the same way, a typical experiment in the preparation of (5-nitro-2-furyl)-2-ethyl-4-methyl-2-cis-4-trans-pentadienal (IVb) is described.

(5-Nitro-2-furyl)-2-ethyl-4-methyl-2-cis-4-trans-pentadienal (IVb)—To a solution of 22.7 g (0.1 mole) of (5-nitro-2-furyl)-α-methylacrolein dimethyl acetal (mp 52—54⁰)⁶ in 50 ml of anhydrous chloroform was added a solution of 0.05 g of boron trifluoride etherate in 20 ml of anhydrous chloroform dropwise during the addition of 11 g (0.11 mole) of ethyl butenyl ether at 40—45⁰. The rate of addition was so controlled that the reaction temperature was maintained nearly constant. After the addition, the mixture was neutralized with a 2%aq. sodium acetate solution. The chloroform layer was separated and washed with water and dried over sodium sulfate. After evaporation a dark reddish oily residue was obtained, on which 100 ml of acetic acid, 35 ml of water and 3 gram of p-toluenesulfonylic acid were added, and the mixture was heated on a steam bath at 85—90⁰ for 1 hr. After cooling, yellow crystals was deposited, which were washed with water and recrystallized from 80% ethanol to give 19.5 g. of yellow prisms, mp 108—109⁰. Analysis and spectral data are shown in Table I.

**Reaction of α-Formylthiophenecarboxaldehyde (XI) with (5-Nitro-2-furyl)-α-methylacrolein (X)—**

A solution of (5-nitro-2-furyl)-α-methylacrolein (1.0 g, 5.5 mmole) and the phosphorane⁶ (5.2 g, 16.5 m

9) All melting points were not corrected.
mole) in acetonitrile was refluxed for 8 hr. The solvent was removed under reduced pressure, and the residue was extracted with three 25 ml portions of benzene. The combined extracts were evaporated up to give reddish oily gum which was adsorbed on to a column of silicagel (diameter 20 mm, height of packing 130 mm). The column was developed with benzene, and yellow prisms (50 mg) were obtained, which does not show any depression by mixed melting point determination with authentic (5-nitro-2-furyl)-2,4-dimethyl-2-cis-4-trans-pentadienal (IVA).

**Cyclization of Aryl-2,4-dialkylated 2-cis-4-trans-Pentadienal**

As the cyclization experiments were carried out in the same way, a typical experiment in the cyclization of (5-nitro-2-furyl)-2-methyl-4-ethyl-2-cis-4-trans-pentadienal is shown.

2-(5-Nitro-2-furyl)-3-ethyl-5-methyl-cyclopent-2-en-1-one (Vc)—In a flask, 2.3 g of (5-nitro-2-furyl)-2-methyl-4-ethyl-2-cis-4-trans,2,4-pentadienal, 30 ml of tetrahydrofuran and 5 ml of 0.5N hydrochloric acid were placed. The mixture was heated for 2 hr on a water bath. After cooling, the solvent was evaporated in vacuo. The residue obtained was recrystallized from 80% ethanol, it yielded 1.2 g of pale yellow needles, mp 79—80°. UV λ<sub>max</sub> m<sub>μ</sub> (ε): 227 (15200), 272 (6500), 352 (15000). IR cm<sup>-1</sup>: νC=O 1719 (KBr); δC=C 1639 (KBr). Analysis was shown in Table II.

Cyclization of (5-nitro-2-furyl)-2,4-dialkyl-2-cis-4-trans-pentadienals were carried out in the similar way, and corresponding cyclic ketones were obtained in 70—80% yields.

**Cyclization of (5-nitro-2-furyl)-2,4-dimethyl-2-cis-4-trans-pentadienal in the Presence of Deuterohydrochloric Acid**—The mixture of 1.5 g (6.8 mmole) of (5-nitro-2-furyl)-2,4-dimethyl-2-cis-4-trans-pentadienal (IVA), 25 ml of tetrahydrofuran and 2 ml of 20% deuterohydrochloric acid was heated for 2 hr on a steam bath. After cooling, the solvent was distilled off in vacuo. Yellow crystals thus obtained were collected, washed with several portions of small amount of carbon tetrachloride. Recrystallization from carbontetrachloride gave 1.0 g of deuterated 2-(5-nitro-2-furyl)-3,5-dimethylcyclopent-2-en-1-one, mp 108—109°. The NMR spectrum of this compound showed a characteristic peaks for secondary methyl protons \( \overset{1}{D}C\overset{2}{H}C\overset{\delta}{C} (1.25 \text{ ppm}) \) as a singlet with integrated intensity 3, vinyl methyl protons (2.57 ppm, integrated intensity 2). Complex multiplets which appeared in the spectrum of undeuterated (IVA) were lost. The spectrum was contrasted with that of undeuterated cyclic ketone in Fig. 8.

(5-Nitro-2-furyl)-2,4,6-trimethyl-2-cis-4-cis-6-trans-hepta-2,4,6-trienal (VI)—15 g (0.068 mole) of (5-nitro-2-furyl)-2,4-dimethyl-2-cis-4-trans-pentadienal (IVA), 8.7 g (0.0815 mole) of methyl orthoformate, 12.8 g of absolute methanol and a few mg of p-toluenesulfonic acid were placed in a three necked flask fitted with a stirrer, thermometer and dropping funnel. To the mixture 160 g of anhydrous chloroform was added and the solution was refluxed on a water bath. After 30 minutes, the mixture was fractionated through a 15 cm x 2 cm Widmer column to remove methyl orthoformate and methanol. Some 30 ml portions of chloroform was added in the course of fractionation. When the reading of thermometer reached to 62°, the mixture was cooled to 45°. After the fractionation, about 100 ml of chloroform solution of the acetal was obtained. To this solution 4.9 g (0.068 mole) of methyl propenyl ether was added dropwise at 35° in the presence of 50 mg of boron trifluoride etherate. Addition of propenyl ether was so controlled that the temperature of the reaction mixture was kept nearly constant. After the addition, stirring was continued for additional 1 hr, and then the mixture was neutralized with aqueous sodium bicarbonate and dried with anhydrous sodium sulfate. After evaporation of chloroform, 24 g of reddish oily substance obtained, and a half of the oil was dissolved into the mixture which contained 30 ml of acetic acid, 10 ml of water and 1 g of oxalic acid. The mixture was heated for 4 hours at 80°. After two days red prisms were separated, which were filtered, washed with water and recrystallized from 70% ethanol. It yielded 0.6 g of red prisms, mp 117—118°. Anal. Calcd. for C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>N: C, 64.36; H, 5.79; N, 5.36. Found: C, 63.96, H, 5.62, N, 5.20. The structural assignment for VI follows from their spectral data. IR cm<sup>-1</sup>: νC=O 1671 (KBr); νC=C 1620 and 1600 (KBr). UV λ<sub>max</sub> m<sub>μ</sub> (ε): 242 (11200), 312.5 (14700), 400 (28600). The NMR spectrum was strongly indicative of its structure. Each vinylic methyl at 2.4 and 6 position showed singlet at 2.04, 2.26 and 2.31 ppm, respectively. Two vinyl protons at 2 and 4 position absorbed at 6.40 ppm as singlet, one proton adjacent to 5-nitro-furan ring absorbed at 6.84 ppm, its high field shift of the proton confirmed the 2-cis-4-cis-6-trans structure. Gaschromatographic analysis of the mother liquid showed four peaks. Contamination of 2-(5-nitro-2-furyl)-3,5-dimethylcyclopent-2-en-1-one and 1-methoxy-2-(5-nitro-2-furyl)-3,5-dimethyl-pent-2,4-diene was detected. From the solution oily 2-(5-nitro-2-furyl)-3,5,7-tri-methyl-cyclohepta-2,4-dien-1-one (VII) was obtained as a major product, beside with the minor formation of an uncharacterized red oil which showed relative retention volume of 1.2 based on the retention volume of (VII).

2-(5-Nitro-2-furyl)-3,5,7-trimethyl-cyclohepta-2,4-dien-1-one (VII)—0.6 g of (5-nitro-2-furyl)-2,4,6-trimethyl-2-cis-4-cis-6-trans-2,4,6-heptatrienal (VI) was dissolved in 10 ml of acetonitrile containing 1.5 ml of 0.5N hydrochloric acid and refluxed for 2.5 hr on a water bath. After cooling, the solution was evaporated in vacuo. An oily residue thus obtained was fractionated by preparative gaschromatograph (0.5% SE-30, Shimadzu W, at 220°). From the first fraction, total 0.3 g of 2-(5-nitro-2-furyl)-3,5,7-trimethylcyclohepta-2,4-dien-1-one was obtained as a reddish oil, its structure was derived from the following spectral data. IR cm<sup>-1</sup>: νC=O 1694: νC=C 1654 and 1631. UV λ<sub>max</sub> m<sub>μ</sub> (ε): 230 (20700), 370 (12300). The NMR
spectrum was strongly indicative of its structure. It showed two singlets at 2.00 and 2.06 ppm ascribes to vinylic methyl group, one secondary methyl at 1.26 ppm as doublet (\(J=7\) cps), one vinylic proton at 6.36 ppm as singlet and complex multiplets in 2.0—3.4 ppm having intensity of three proton integration. Again, 0.1 g of uncharacterized reddish oil was obtained, and its UV spectrum in ethanol gave maxima at 228 m\(\mu\) and 370 m\(\mu\) which is nearly the same compared with that of VII. Whether the minor product is the stereoisomer of VII or double bond structural isomer of the cycloheptadienone is not fully certain.

**Acknowledgment** The authors wish to thank Dr. W. Kashihara, Ueno Chemical Research Laboratories and Department of Development, Mitsubishi Chemical Works, Kurosaki, for their contributions many helpful intermediates to this work.