Alkalische Verseifung von II——2.0 g (II) wurden mit 20 ml 30% KOH 15-minutenlang auf dem Wasserbade stark erhitzt, wobei der Solid in ein bei Erkalten fest werdendes Öl überging.

Nach Abkühlung wurde es abgesaugt, in Wasser gelöst und mit AcOH neutralisiert. Das dabei abgeschiedene Präzipitat wurde getrennt, an 100 Mesch Silicagel mit Chloroform zweimal chromatographiert. Die hauptsächliche homogene Fraktion wurde aus wenig Äther umgefällt, wobei sich schwach gelben sandartigen Kristallen von Schmp. 142～143° erhalten ließen.

Auf Grund der Molekulargewichtsmessung nach der Rastschen Methode für $C_{13}H_{11}N_3$ analysiert: Gef.: C, 74.77; H, 5.05; N, 19.63. Ber.: C, 74.62; H, 5.30; N, 20.08.

Herrn Prof. Dr. Kamura und seiner Assistanten danken wir für die Leitung der Dipolmomentmessungen.

Zusammenfassung

Im Rahmen der Untersuchungen der Synthesemöglickeit von *as*-Triazin-N-oxyden, oxydierten wir 3-Amino-5,6-diphenyl-*as*-triazin, 5,6-Diphenyl-*as*-triazin-3(2*H*)-on und ihre einfache Derivate durch Persäure, wobei sich einige entsprechenden 1-N-Oxyde erhalten ließen, deren Konstitutionen spektroskopisch sowie dipolmomentmetrisch diskutiert wurden.

(Eingegangen am 15, Februar 1965)

[Chem. Pharm. Bull. 13(10)1177～1182(1965)]

UDC 547.722.5.07

151. Akio Fujita, Jun-ichi Matsumoto, Shinsaku Minami, and Hideji Takamatsu: Studies on Nitrofuran Derivatives. III.[*1] Novel Self-condensations of 5-Nitro-2-furaldehyde and 5-Nitro-2-thenaldehyde.[*2]

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During the course of synthetic studies of 2-(5-nitro-2-furyl)vinyl heterocyclic compounds it has been observed[*1] that 5-nitro-2-furaldehyde, when treated with the equimolar amount of 3-pyridineacetonitrile, 3-pyridineacetamide, ethyl 3-pyridineacetate, or 4-picoline N-oxide in acetic anhydride, always gave unexpectedly the same neutral compound (I), decomposing at 253～255° without melt, as a major product. The present study was undertaken to elucidate the structure of the compound (I), which consequently was established to be 1,2-diacetoxy-1,2-bis(5-nitro-2-furyl)ethene (I′), and to test the generality of this condensation reaction for other aromatic aldehydes.

It was subsequently found that the reaction was also catalysed by 4-picoline, 3-acetylpyridine,[*4] and 3-methylpyridazine[1)] and that it was conveniently effected only by mixing equimolar amounts of 5-nitro-2-furaldehyde and pyridine in acetic anhydride at room temperature to afford the compound (I) in a 60% yield along with a small amount of 5-nitro-2-furfurylidene diacetate[2)] (Table I).

[*1] Part II. A. Fujita, T. Yamamoto, J. Matsumoto, S. Minami, H. Takamatsu: Yakugaku Zasshi, 85, 565 (1965).

[*2] This work was presented at Kinki branch meeting of Pharmaceutical Society of Japan, held on May, 1964.

[*3] Ebie, Fukushima-ku, Osaka (藤田昭夫, 松本純一, 南 新作, 高松秀二).

[*4] The commercially available material (Cilag Chemie Co., Switzerland) was used.

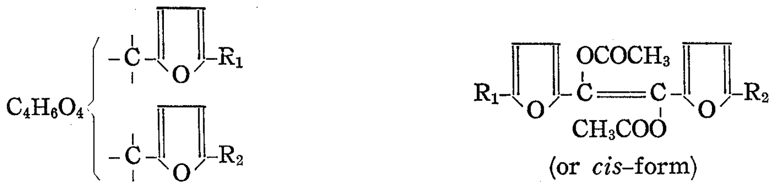
1) W.G. Overend, L.M. Turton, L.F. Wiggins: J. Chem. Soc., **1950**, 3500.

2) H. Gilman, G.F. Wright: J. Am. Chem. Soc., **52**, 2550 (1930).

The compound (I), yellow colored, is sparingly soluble in the most of organic solvents and in water and shows the characteristic infrared absorption bands (in KBr) at 1520, 1353 (nitro group), 3130, 1033, 975, 963, 872, 818, 759, and 738 cm^{-1} (furan ring[3]) together with the strong absorption at 1768 cm^{-1} suggesting the presence of an enol acetate[4] in the molecule. The ultraviolet absorption maximum (in dioxane) at 286 $m\mu$ ($\log \varepsilon$ 4.07) agreed to the presence of the conjugated nitrofuran group. The analytical data, coupled with the formation of a derivative (II) discussed below, allowed us to formulate I as $C_{14}H_{10}O_{10}N_2$, although the attempts of the molecular-weight determination were unsuccessful owing to the decomposition of I on Rast's method and to its limited solubility.

The compound (I) did not react with any carbonyl reagents and profoundly decomposed on alkaline hydrolysis to give a water soluble substance which had no ultraviolet absorption maximum above 220 $m\mu$. The compound (I) was recovered unchanged under reflux with 10% hydrochloric acid in ethanol, whereas drastic hydrolysis of I with 20% hydrochloric acid in acetic acid under nitrogen furnished 5-nitro-2-furoic acid[5] as a major product.

In order to convert the nitro group into the acetamido group, which might cause to increase the solubility of the compound, I was subjected to catalytic reduction over palladized charcoal in acetic anhydride. Thus the reaction produced two products, $C_{16}H_{14}O_9N_2$ (II), m.p. 225~227° (decomp.), and $C_{18}H_{18}O_8N_2$ (III), m.p. 271~273°. The former showed still the presence of the high frequency carbonyl group (1785 cm^{-1}, broad) and nitro group (1540, 1353 cm^{-1}), and a new band ascribable to an amido group at 1675 cm^{-1} in the infrared spectrum (in KBr). Further reduction of II under the same conditions converted it into III which had no longer infrared absorption bands arising from the nitro group but the characteristic amide bands at 1695 and 1533 cm^{-1} and an NH strong absorption band at 3305 cm^{-1} besides the sharp band at 1750 cm^{-1}. The compound (III) was also obtained by the reduction of I with zinc dust and acetic anhydride,[6] though the yield was very poor. The treatment of II with 10% hydrochloric acid in ethanol gave ethyl 5-nitro-2-furoate[7] as expected, but 5-aminofuran analog was not able to isolate, probably because of its instability.[8]



IVa : $R_1=R_2=NO_2$
IVb : $R_1=NO_2$, $R_2=NHCOCH_3$
IVc : $R_1=R_2=NHCOCH_3$

I′ : $R_1=R_2=NO_2$
II′ : $R_1=NO_2$, $R_2=NHCOCH_3$
III′ : $R_1=R_2=NHCOCH_3$

Chart 1.

Both formation of II and conversion of II into III suggested the molecular formula of I $C_{14}H_{10}O_{10}N_2$ rather than $C_7H_5O_5N$ and led to the partial structure (IVb) for II, and hence IVa and IVc for I and III, respectively. The correctness of this assignment was

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[3] *a*) A.H.J. Cross, *et al.*: J. Appl. Chem., **7**, 562 (1957). *b*) K. Takano: Nippon Kagaku Zasshi, 82, 373 (1961), and references cited.

[4] L.J. Bellamy: "The Infrared Spectra of Complex Molecules," 2nd Ed., 182 (1958). John Wiley and Sons, Inc., New York.

[5] B.T. Freuer, J.R. Johnson: J. Am. Chem. Soc., **53**, 1142 (1931).

[6] Cf. M. Kohn, O. Krasso: J. Org. Chem., **13**, 329 (1948).

[7] R. Marquis: Anal. Chim., **4** (8), 196 (1905).

[8] Cf. F.F. Ebetino, J.J. Carroll, G. Gever: J. Med. Pharm. Chem., **5**, 513 (1962).

supported by the nuclear magnetic resonance spectrum[*5] of II, which showed the presence of the acetamido group (2.10 δ, 3H, singlet), two protons on the acetamidofuran ring (6.43 and 6.89 δ, each doublet J=3.5 c.p.s.) and two protons on the nitrofuran ring (6.87 and 7.54 δ, each doublet J=4.0 c.p.s.). Furthermore, the peaks at 2.43 and 2.46 δ (each 3H), coupled with the infrared evidences, revealed the $C_4H_6O_4$ moiety to consist of two enol acetate groupings.

All these facts are best summarized in the structures (I′, II′, and III′ for I, II, and III), respectively, regardless of their geometrical isomerisms. Conclusive proof of the structure (I) was obtained by an independent synthesis of 1,2-diacetoxy-1,2-bis(5-nitro-2-furyl)ethene (I′). 1,2-Diacetoxy-1,2-di(2-furyl)ethene[9] (VI) was subjected to nitration with fuming nitric acid in acetic acid and acetic anhydride to afford I′ identical in all respects with the compound (I).

There was an additional observation that the treatment of I with either hot glacial acetic acid or acetic anhydride resulted in a formation of $C_{14}H_{10}O_{10}N_2$ (V) melting at 185~187°, isomeric with I, and it showed the infrared absorption bands at 1795 (enol ester[4]), 1530, 1348 (nitro group), 3100, 1021, 968, 854, 832, 810, and 739 cm^{-1} (furan ring[3]) and the ultraviolet absorption maximum at 295 mμ (log ε 4.13) in dioxane. It was reasonably considered to be the geometrical isomer of I, but the treatment of V under the same reaction conditions with hot glacial acetic acid failed to regenerate the compound (I) and it was recovered unchanged.

To test the generality of this condensation reaction for some other aldehydes was then examined under the similar conditions. 5-Nitro-2-thenaldehyde[10] afforded 1,2-diacetoxy-1,2-bis(5-nitro-2-thienyl)ethene (VIII), which was identical in all respects with that prepared by nitration of 1,2-diacetoxy-1,2-di(2-thienyl)ethene (VII) *via* acetylation of authentic 2,2′-thenoin.[11] 2-Furaldehyde, 2-thenaldehyde,[12] benzaldehyde, *p*-hydroxy-, and *p*-nitrobenzaldehyde, however, did not give any condensation product. The reaction of an equimolar mixture of 5-nitro-2-furaldehyde and 5-nitro-2-thenaldehyde was expected to produce an unsymmetrically condensed product, but the only isolable product was found to be I.

It is now obvious from the above evidences that pyridine and its equivalents act as a catalyst for the benzoin-type condensation of certain aldehydes. Some thiazolium and imidazolium salts[13,14] have been reported to effect the benzoin condensation just as cyanide ion. Breslow[14] has suggested that the catalytic action occurs *via* a zwitter-ion derived from the loss of a proton at C-2 of the positively charged thiazolium (or imidazolium) ring. In addition, there are brief reports that certain heterocycles with a "reactive" methyl group, such as quinaldine, catalysed a self-condensation[15] of quinaldaldehyde to 1,2-di(2-quinolyl)-1,2-ethendiol and, on the other hand, 2-picolinaldehyde, when treated with acetic acid at room temperature, underwent a condensation to 1,2-di(2-pyridyl)-1,2-ethendiol.[16]

[*5] The NMR spectrum was determined in hexadeuterioacetone at 50° on Varian A-60 spectrometer; chemical shifts are expressed as δ values (p.p.m.) from tetramethylsilane as an internal standard. Although the signal at 2.10 δ was overlapped to one of signals arising from partly deutrated acetone(s) contaminated in CD_3COCD_3, the subtraction of the latter from the spectrum of the compound allowed the unequivocal assignment of the signal intensity.

9) F. Cramer, W. Krum : Ber., **86**, 1586 (1953).
10) T.M. Patrick, W.S. Emerson : J. Am. Chem. Soc., **74**, 1356 (1952).
11) S. Z. Cardon, H.P. Lankelma : *Ibid.*, **70**, 4248 (1948).
12) E. Campaigne, W.L. Archer : *Ibid.*, **75**, 989 (1953).
13) T. Ugai, R. Tanaka, T. Dokawa : Yakugaku Zasshi, **63**, 296 (1943); T. Ugai, T. Dokawa, S. Tsubokawa : *Ibid.*, **64** (7A), 3 (1944).
14) R. Breslow : J. Am. Chem. Soc., **80**, 3719 (1958).
15) H. Andrews, S. Skidmore, H. Suschitzky : J. Chem. Soc., **1962**, 3827.
16) H.R. Hensel : Angew. Chem., **65**, 491 (1953).

The condensation reactions in our present study have a close relationship to those precedents. Though the factors to influence the reaction must be settled, the intermediacy of the by-product in the reaction, 5-nitro-2-furfurylidene diacetate, was obviously eliminated since the diacetate did not give any condensation product under the same reaction conditions. Further work on the mechanism is in progress.

Experimental[*6]

Reaction of 5-Nitro-2-furaldehyde with Base in Acetic Anhydride——In a typical run, 1.58 g. (0.02 mole) of dry pyridine was added to a solution of 2.8 g. (0.02 mole) of 5-nitro-2-furaldehyde in 6 ml. (ca. 0.06 mole) of Ac_2O and the mixture was allowed to stand at room temperature with occasional shaking. After 3 hr., during which time a crystalline substance precipitated, H_2O was added under cooling to decompose the excess of Ac_2O, and the resulting solid was collected, washed with H_2O, then with EtOH giving 2.5 g. of yellow crystals. Recrystallization from acetone, AcOH, acetonitrile, or dioxane gave 2.2 g. of 1,2-diacetoxy-1,2-bis(5-nitro-2-furyl)ethene (I=I′), decomposing at 253∼255° without melt. *Anal.* Calcd. for $C_{14}H_{10}O_{10}N_2$: C, 45.91; H, 2.75; N, 7.65. Found : C, 46.12; H, 2.83; N, 7.86.

The cold filtrate and washings afforded 0.75 g. of another crystals, which were recrystallized from aq. MeOH to form colorless needles, m.p. 90∼92°, identical with the authentic specimen of 5-nitrofurfrylidene diacetate[2] (IX) by mixed melting point and IR comparison.

The results in other runs with pyridine, 4-picoline, 3-acetylpyridine,[*4] and 3-methylpyridazine[*7,1] are listed in Table I (and see also Part II[*1]).

TABLE I. The Reaction of 5-Nitro-2-furaldehyde with Base in Acetic Anhydride[a]

Base	Mole	Reaction time (hr.)	Temp.[b] (°C)	Yield[d] (%)	
				I	IX
Pyridine	0.02	0.5	45∼50	46	0.54
〃	0.02	3	R.t.[c]	60	14
〃	0.002	17	〃 [c]	33	14
4-Picoline	0.02	1	50∼60	58[e]	—[f]
3-Acetylpyridine	0.02	8	50∼60	44	—[f]
3-Methylpyridazine	0.02	0.5	80∼90	46	—[f]

a) The aldehyde (0.02 mole) and Ac_2O (0.06 mole) were used.
b) Bath temperature. c) Room temperature.
d) The yields represent purified products and were calculated on basis of the aldehyde.
e) Accompanied with 4-[2-(5-nitro-2-furyl)vinyl]pyridine[17] (0.4 g.).
f) No attempts of the isolation.

Reaction of 5-Nitro-2-thenaldehyde with Pyridine in Acetic Anhydride——A mixture of 1.57 g. (0.01 mole) of 5-nitro-2-thenaldehyde[10] and 0.79 g. (0.01 mole) of pyridine in 3 ml. of Ac_2O was allowed to stand at room temperature for 3 hr. The resulting solid was collected, and washed with H_2O, then with EtOH giving 220 mg. of yellow crystals, m.p. 230∼235° (decomp.). Recrystallization from acetonitrile gave yellow prisms, m.p. 257∼260° (decomp.), identical with 1,2-diacetoxy-1,2-bis(5-nitro-2-thienyl)ethene (VIII) resulted from nitration of 1,2-diacetoxy-1,2-di(2-thienyl)ethene (VII) as described bellow. *Anal.* Calcd. for $C_{14}H_{10}O_8N_2S_2$: C, 42.12; H, 2.53; N, 7.03; S, 16.09. Found : C, 42.23; H, 2.57; N, 7.11; S, 15.86. IR ν_{max}^{KBr} cm^{-1} : 1790 (C=O).

From the above EtOH washings 10 g. (63.7%) of 5-nitro-2-thenaldehyde was recovered on distillation.

Reaction of 5-Nitro-2-furaldehyde and 5-Nitro-2-thenaldehyde with Pyridine in Acetic Anhydride——A mixture of 705 mg. (5 mmoles) of 5-nitro-2-furaldehyde and 785 mg. (5 mmoles) of 5-nitro-2-thenaldehyde and 395 mg. (5 mmoles) of pyridine in 3 ml. (ca. 30 mmoles) of Ac_2O was allowed to stand at room temperature for 3 hr. After the resulting precipitate was worked up as described above, 430 mg. of I was obtained,

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[*6] All melting points were taken on a hot stage and are uncorrected. Extracts were dried over anhyd. $MgSO_4$.

[*7] The experiments in the last three were carried out by Mr. M. Nakata in our laboratory.

[17] Belg. Pat., 615319 (1962) (Boehringer & Soehne).

Hydrogenation of I to 1-(5-Acetamido-2-furyl)-2-(5-nitro-2-furyl)-1,2-diacetoxyethen (II=II′) and 1,2-Diacetoxy-1,2-bis(5-acetamido-2-furyl)ethene (III=III′)——A suspension of 1.0 g. of I and 1.0 g. of 10% Pd-C in 200 ml. of Ac_2O and 10 ml. of AcOH was subjected to hydrogenation at 3 kg./cm^2 pressure and room temperature until the absorption of hydrogen ceased. The reaction mixture was filtered to remove the catalyst and undissolved crystals which gave 550 mg. of unreacted I after extraction with acetone and evaporation of the solvent. The resulting filtrate was concentrated to about 70 ml. *in vacuo* yielding the additional 30 mg. of I and further concentrated to dryness. The residue was extracted with $CHCl_3$ under slight warming, and the extract filtered to remove an insoluble substance which was recrystallized from EtOH to afford 50 mg. of Ⅲ, colorless prisms, m.p. 271～273°. *Anal.* Calcd. for $C_{18}H_{18}O_8N_2$: C, 55.38; H, 4.65; N, 7.18. Found : C, 55.44; H, 4.77; N, 7.26.

The above $CHCl_3$ solution was washed with dil. aq. NH_4OH, then with H_2O, and dried. The solvent was evaporated to leave 290 mg. of crude crystals, which were chromatographed on silica gel (20 g., Merck) from $CHCl_3$-acetone (9:1, v/v) to give 230 mg. of Ⅱ, m.p. 223～225° (decomp.), and subsequently from $CHCl_3$-EtOH (9:1, v/v) to give additional 5 mg. of Ⅲ. Recrystallization of Ⅱ from MeOH afforded analytically pure, yellow needles, m.p. 225～227° (decomp.). The thin-layer chromatograms (Kieselgel G nach Stahl) of Ⅱ in two systems (EtOH and $CHCl_3$-acetone (10:5, v/v)) had a single spot in each case. *Anal.* Calcd. for $C_{16}H_{14}O_9N_2$: C, 50.80; H, 3.73; N, 7.41. Found : C, 50.78; H, 3.64; N, 7.54.

Hydrogenation of II to III——A mixture of 100 mg. of Ⅱ and 100 mg. of 10% Pd-C in 50 ml. of Ac_2O and 5 ml. of AcOH was subjected to hydrogenation at atmospheric pressure until the absorption of hydrogen ceased. After removal of the catalyst, the resulting solution was concentrated to a small volume *in vacuo* to separate a white solid which was washed with H_2O, and recrystallized from EtOH to afford 60 mg. of colorless prisms, m.p. 271～273°, identical with Ⅲ described above.

Reduction of I with Zinc Dust and Acetic Anhydride⁶⁾——Zinc dust (3.0 g.) was added portionwise with shaking to a suspension of 3.0 g. of I in 22 ml. of Ac_2O and 5 ml. of AcOH. The mixture was refluxed for 0.5 hr., cooled to room temperature and followed by addition of another 1.0 g. of zinc dust. After refluxing for additional 0.5 hr. and cooling, the mixture was filtered to remove the separated crystals and an excess of zinc dust which were extracted with hot acetone to afford the unchanged I. The resulting filtrate was concentrated to dryness *in vacuo* and the residue dissolved in ca. 500 ml. of $CHCl_3$. The $CHCl_3$ solution was washed with H_2O, dried, and concentrated to leave 270 mg. of a dark red oil. The oil was chromatographed on neutral alumina (5 g., Woelm activ. grade 1) from $CHCl_3$ to give ca. 100 mg. of a reddish brown oil failed to crystallize, and subsequently from $CHCl_3$-EtOH (50:1, v/v) to give 25 mg. of a white solid. Recrystallization of the solid from EtOH formed colorless prisms, m.p. 271～273°, identical with Ⅲ described previously.

Hydrolysis of I; 5-Nitro-2-furoic Acid——A suspension of 1.0 g. of I in a mixture of 23 ml. of conc. HCl and 30 ml. of AcOH was gently refluxed under nitrogen for 1.5 hr., during which time it turned to the yellowish red colored, clear solution. After removal of a trace of insoluble material the resulting solution was concentrated to dryness *in vacuo* and the residue was dissolved in $CHCl_3$. The $CHCl_3$ solution was washed with H_2O, dried, and the solvent evaporated leaving 500 mg. of an oily residue which crystallized partially on standing; the IR spectrum of the crystals whithout purification was essentially identical with that of 5-nitro-2-furoic acid. Distillation of the oil and recrystallization from hexane-MeOH afforded 150 mg. of 5-nitro-2-furoic acid, m.p. 185～186°, identical with an authentic specimen.⁵⁾

An alternative isolation procedure involved chromatography of the oily residue on neutral alumina with $CHCl_3$ as eluent.

Hydrolysis of II in EtOH; Ethyl 5-Nitro-2-furoate——A solution of 225 mg. of Ⅱ in 3 ml. of conc. HCl and 7 ml. of EtOH was gently refluxed for 1 hr. After removal of EtOH *in vacuo* the resulting acidic solution was diluted with H_2O, extracted with $CHCl_3$, the extract washed with H_2O, and dried. The solvent was evaporated to leave a viscous oil, which gave a crystalline substance on distillation at 90～100°/2 mm. (bath temp.) and a viscous brown oil at 135～140°/2 mm. (bath temp.). The first distillate on recrystallization from MeOH gave 25 mg. of colorless scales, m.p. 99～101°. IR ν_{max}^{KBr} cm^{-1} : 1727 (C=O). *Anal.* Calcd. for $C_7H_5O_5N$: C, 45.41; H, 3.83; N, 7.57. Found : C, 45.46; H, 3.97; N, 7.67. It was identified as ethyl 5-nitro-2-furoate,⁷⁾ derived from ethyl 5-nitro-2-furylimidate melting at 72～73° (reported¹⁸⁾ m.p. 73～74°). The second distillate was not investigated further.

Isomerization of I to V——A mixture of 1.0 g. of I and ca. 100 ml. of AcOH (or Ac_2O) was refluxed for 1 hr., cooled to room temperature and filtered to yield ca. 0.9 g. of the starting I. The filtrate was concentrated to dryness *in vacuo*, the resulting solid dissolved in acetone, and treated with charcoal to give yellow crystals (V, 30 mg.), m.p. 180～185°. Recrystallization from MeOH afforded analytically pure, yellow prisms (17 mg.), m.p. 185～187°. *Anal.* Calcd. for $C_{14}H_{10}O_5N_2$: C, 45.91; H, 2.75; N, 7.65. Found : C, 46.36; H, 2.75; N, 7.70. On thin-layer chromatography (Kieselgel G nach Stahl, EtOH system) V was lesser polar than the isomeric I and showed a single spot.

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18) U. S. Pat. : 964233 (1964) (Abbott Lab.).

Nitration of 1,2-Diacetoxy-1,2-di(2-furyl)ethene (VI)——Ⅵ, m.p. 202~204° (reported9) m.p. 204°), was prepared *via* condensation of furfural to 2,2′-furoin according to the procedure of Hartman, *et al.*,19) followed by acetylation with pyridine–Ac_2O.

To a solution of 1.66 g. (0.006 mole) of Ⅵ in 5 ml. of Ac_2O cooled to below −5° was added dropwise with stirring a cold mixture of 0.948 g. (0.015 mole) of fuming HNO_3 and 6.5 ml. of AcOH. After stirring for 2 hr. at −5~−10° the reaction mixture was poured onto ice to result in a sepaeration of a gum, which was collected, washed with H_2O, then with MeOH, and recrystallized from acetone to yield 0.16 g. of 1,2-diacetoxy-1,2-bis(5-nitro-2-furyl)ethene (I′), decomposing at 252~255° without melt, indentical in all respects with I. *Anal.* Calcd. for $C_{14}H_{10}O_{10}N_2$: C, 45.91; H, 2.75; N, 7.65. Found : C, 46.35; H, 2.89; N, 7.68.

From the MeOH washings and mother liquor the other crystals were obtained and recrystallization from MeOH gave 15 mg. of needles, m.p. 166~167°. IR ν_{max}^{KBr} cm^{-1} : 1643 (C=O). *Anal.* Calcd. for $C_{10}H_6O_4$: C, 63.16; H, 3.18. Found : C, 63.33; H, 3.06. It was identified as furil (reported m.p. 165~166.5°,20) IR ν_{max}^{KBr} cm^{-1} : 1640.3b)).

1,2-Diacetoxy-1,2-di(2-thienyl)ethene (VII)——2,2′-Thenoin (2.0 g.), prepared by the procedure of Cardon, *et al.*,11) was acetylated with 2.0 g. of pyridine and 15 ml. of Ac_2O on heating to 80~90° for 1 hr. Work up as usual and recrystallization from acetone gave 2.2 g. of the acetate, needles, m.p. 264~265°. *Anal.* Calcd. for $C_{14}H_{12}O_4S_2$: C, 54.52; H, 3.92; S, 20.79. Found : C, 54.79; H, 3.98; S, 21.06.

Nitration of VII——According to the above procedure, nitration was carried out by treating 295 mg. of Ⅶ in 2.5 ml. of Ac_2O with a mixture of 443 mg. of fuming HNO_3 and 3.5 ml. of AcOH. Recrystallization of the crude product from acetonitrile gave 70 mg. of Ⅷ, m.p. 257~260° (decomp.), identical with the sample described previously. *Anal.* Calcd. for $C_{14}H_{10}O_8N_2S_2$: C, 42.21; H, 2.53; N, 7.03; S, 16.09. Found : C, 42.62; H, 2.72; N, 6.84; S, 16.22.

The authors wish to express their gratitude to Dr. S. Ose, Director of this laboratory, for his interest and encouragement throughout this work. Thanks are also due to the members of the Analytical Center of this laboratary for elemental analyses and NMR spectral measurements.

Summary

An unusual product, resulted from the reaction of 5-nitro-2-furaldehyde with pyridine or its equivalents in acetic anhydride, was established to be 1,2-diacetoxy-1,2-bis(5-nitro-2-furyl)ethene. Similarly, 1,2-diacetoxy-1,2-bis(5-nitro-2-thienyl)ethene was obtained from the self-condensation reaction of 5-nitro-2-thenaldehyde. Attempts to prepare the corresponding condensation products of some other aromatic aldehydes, however, failed under the similar reaction conditions.

(Received March 27, 1965)

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19) W. W. Hartman, J. B. Dickey : J. Am. Chem. Soc., **55**, 1228 (1933).

20) B. B. Corson, R. W. McAllister : *Ibid.*, **51**, 2822 (1929).