BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1658—1664 (1968)

Studies of Heteroaromaticity. IX.[1] Stability and Reactivity of 5-Nitro-2-furyl Diazo Compounds

Tadashi SASAKI, Shoji EGUCHI and Atsuyuki KOJIMA

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya

(Received December 23, 1967)

(5-Nitro-2-furyl)diazomethane (2), 3-(5-nitro-2-furyl)diazopropene (4), and 1-(5-nitro-2-furyl)diazoethane (6) were prepared by the oxidation of the corresponding hydrazones with active manganese dioxide. The relative stabilities of these diazo compounds were then compared with *p*-nitrophenyldiazomethane in their ethanolic solutions and in their solid states by measuring their decomposition rates spectroscopically; it was found that the stability decreased in the following order:

$6 \simeq p$-nitrophenyldiazomethane $> 2 \simeq 4$ in ethanol

p-nitrophenyldiazomethane $> 2 > 4 > 6$ in the solid state.

The reactivities of these diazo compounds were also investigated in the decomposition reactions; the thermal and photolytic decomposition of 2 afforded 1,2-di(5-nitro-2-furyl)ethylene (7) in a low yield, but 4 cyclized readily to 3-(5-nitro-2-furyl)pyrazole (8) in a good yield and 6, to an azine (9) even upon standing at room temperature. 2 was treated with benzoic acid in ether to give 5-nitro-2-furfuryl benzoate (10) in a quantitative yield, and with triphenylphosphine in the same solvent to afford the triphenylphosphazine (13) in a 75% yield; this last substance liberated nitrogen very easily in the presence of cuprous ions to give the phosphonium ylid (14), one of the Wittig reagents. 14 was then considered as a possible starting material for preparing (5-nitro-2-furyl)ethylenic compounds. Similarly, 3-(5-nitro-2-furyl)acrolein triphenylphosphazine (17) was prepared from 4 and triphenylphosphine.

Although the preparation[2] and chemical properties[3] of aromatic diazo compounds have been studied extensively, little is known about heterocyclic diazo compounds, among which 2-furyl-,[4] 2-thienyl-,[4b] phenyl-2-thienyl-[5] and di-2-thienyl diazomethane[5] have been reported.

In this paper we wish to describe the preparation of 5-nitro-2-furyldiazomethane (2), 3-(5-nitro-2-furyl)diazopropene (4), and 1-(5-nitro-2-furyl)-diazoethane (6), and some reaction thereof, from the viewpoint of their chemical reactivities and their antibacterial activity.[6]

Results and Discussion

Of the several methods for the preparation of aromatic diazo compounds, the best way is by the oxidation of the corresponding hydrazones; the choice of the oxidation reagent is known to play a very important role with respect to the yields of the diazo compounds.[2b,7]

5-Nitro-2-furfural hydrazone (1a) was oxidized with active manganese dioxide in ether at 0°C to afford a diazo compound 2 in over an 80% yield, though the oxidation with yellow mercuric oxide or lead tetraacetate, which is known to be very effective reagent for the preparation of dicyanodiazomethane from the corresponding hydrazone,[8] gave 2 in yields of less than 10%. The pyrolytic decomposition[2c] of the sodium salt of 5-nitro-2-furfural tosylhydrazone (1b) afforded 2 in around a 50% yield:

$$1a \longrightarrow 2 \longleftarrow 1b$$

The similar oxidation of the corresponding

1) Part VIII of this series: T. Sasaki and T. Yoshioka, This Bulletin, **40**, 2608 (1967).

2) a) A. Hantzsch and M. Lehmann, *Ber.*, **35**, 897 (1902); b) H. Staudinger and A. Gaule, *ibid.*, **49**, 1897 (1916); c) G. M. Kaufman, J. A. Smith, G. G. Van der Stouw and H. Shechter, *J. Am. Chem. Soc.*, **87**, 935 (1965), and the references cited therein.

3) a) C. D. Gutsche, G. L. Bachman and R. S. Coffey, *Tetrahedron*, **18**, 617 (1962); b) H. Nozaki, R. Noyori and K. Sisido, *ibid.*, **20**, 1125 (1964).

4) a) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, **1935**, 286; b) J. B. F. N. Engerts, G. van Bruggen, J. String and H. Wynberg, *Rec. trav. chim.*, **84**, 1610 (1965).

5) H. Reimlinger, *Chem. Ber.*, **97**, 3493 (1964).

6) The pharmacological findings on the compounds in this paper will be published elsewhere.

7) W. Schroeder and L. Katz, *J. Org. Chem.*, **19**, 718 (1954).

8) E. Ciganek, *ibid.*, **30**, 4198 (1965).

TABLE 1. PROPERTIES OF NITROFURYL DIAZO COMPOUNDS: 2, 4 and 6

Compound	2			4			6		
Appearance	Red prisms			Reddish violet plates			Red plates		
Mp °C	86—88 dec. (from ether)			94—95 (from ether)			69—70 dec. (from ether)		
Formula	$C_5H_3O_3N_3$			$C_7H_5O_3N_3$			$C_6H_5O_3N_3$		
Anal. %	C	H	N	C	H	N	C	H	N
Calcd	38.66	1.98	27.45	46.93	2.81	23.46	43.12	3.02	25.15
Found	38.94	1.87	27.68	47.00	2.54	23.35	43.87	3.02	24.69[a]
Infrared data (KBr) cm^{-1}	2110(diazo), 1529 and 1357 (nitro), 1574, 1512, 1175, 1035 and 803(furyl)			2100(diazo), 1608(C=C), 1519 and 1358(nitro), 1560, 1500, 1193, 1036 and 807(furyl)			2070(diazo), 1519 and 1353(nitro), 1570, 1506, 1178, 1015 and 803(furyl)		
Ultraviolet data (EtOH)[b] $m\mu$ ($\varepsilon \times 10^{-2}$)	244(87.3), 300(104) and 406 (26.3)			220(110), 289(200) and 440 (248)			250(86.5), 292(109) and 423(111)		
NMR data ($CDCl_3$) τ, cps	2.64[c] (1 H, d, J=4.0), 3.83[c] (1 H, d, J=4.0) and 4.67(1 H, s)			2.70[c] (1 H, d, J=4.0), 3.78[c] (1 H, d, J=4.0), 4.07[d] (1 H, d, J=16), 3.13[e] (1 H, q, J=16 and 9.0) and 5.09[f] (1 H, d, J=9.0)					

a) Compound 6 was too unstable to obtain satisfactory values of the microanalysis, presumably by loosing nitrogen. b) See also Fig. 1. c) Nitrofuran ring protons signal. d) C-3-H signal. e) C-2-H signal. f) C-1-H signal.

hydrazones, 3 and 5, derived from 3-(5-nitro-2-furyl)acrolein and 5-nitro-2-furyl methyl ketone with active manganese dioxide afforded the corresponding diazo compounds, 4 and 6, in the good yields of 70 and 62% respectively:

$$3 \longrightarrow 4 \qquad 5 \longrightarrow 6$$

The structure of 2, 4, and 6 were confirmed by the analytical and spectral data which are summarized in Table 1. Judging from the data shown in this table ($J_{C-2-H,C-3-H}$=16 cps), 4 may be regarded as having a *trans*-configuration.

The relative stabilities of 2, 4, and 6 to *p*-nitrophenyldiazomethane[9] were measured in their ethanolic solutions from their ultraviolet spectra and in their solid states from their infrared spectra, both as a function of the time at 20°C. The half-lives and the rate constants of their decompositions are summarized in Table 2. From this table, it can be concluded that, in ethanol, 2 has nearly the same stability as 4, but only about a quarter that of 6 or of *p*-nitrophenyldiazomethane, while 2-furyldiazomethane has been reported to be a very unstable red oil.[4] In the solid state, the stability decreased in the following order: *p*-nitrophenyldiazomethane>2>4>6.

In both states, *p*-nitrophenyldiazomethane is the most stable except in the case of 6 in ethanol, where some solvent effects might be expected. This result is in good accordance with our expectations based on the resonance stability of each compound in the ground state. The facts that the final absorption maxima in ethanol were located at 300 $m\mu$ (from 406 $m\mu$) for 2, at 354 $m\mu$ (from 440 $m\mu$) for 4, and at 305 $m\mu$ (from 423 $m\mu$) for 6 showed that the final decomposition products of 2, 4, and 6 were 5-nitro-2-furfuryl ethyl ether (11), 3-(5-nitro-2-furyl)-pyrazole (8), and, presumably, α-(5-nitro-2-furyl)ethyl ethyl ether (12) respectively.

In order to attempt a carbenoid reaction, 2 was decomposed in carbenophilic cyclohexene in the presence of copper powder by heating it until nitrogen gas evolution had ceased; the products were then purified by column chromatography. The only crystalline product isolated was 1,2-di-(5-nitro-2-furyl)ethylene (7); neither insertion- nor addition-products to cyclohexene could be separated. The photolysis of 2 in the presence of a carbenophile, such as cyclohexene, styrene, or α-morpholinostyrene, led to the formation of 7 in a low yield, and in all cases a large amount of an intractable, dark brown mass was produced. These results indicate that 5-nitro-2-furylcarbene, even if produced from 2, is too stable to react further with those carbenophiles, but, rather, affords the dimer 7; consequently, 2 may be concluded to be an unsuitable precursor for the carbenoid reaction.

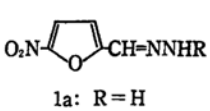
When 4 was heated over its melting point or was kept standing in ether in the presence of a catalytic amount of triethylamine, intramolecular cyclization occurred to give 8 in a good yield. The structure of 8 was confirmed from the following spectral data: the infrared spectrum showed no diazo-band, but it did show an NH-band at 3165 cm^{-1}, and the nmr spectrum in $CDCl_3$ had signals due to two protons of a pyrazole ring at 2.08 τ (1H, d, J=2.5 cps) and 3.17 τ (1H, d, J=2.5 cps), none of which disappeared on deuteration; a signal due to an NH proton of a pyrazole ring

9) T. Curtius and A. Lublin, *Ber.*, **33**, 2490 (1900).

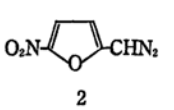
Table 2. Relative stabilities of nitrofuryl diazocompounds and *p*-nitrophenyl diazomethane[a)]

	Compound	2	4	6	O_2N-⟨⟩-CHN_2
In EtOH	Initial concentration (mmol)	0.536	0.0458	0.109	0.0459
	Rate constant, $k_1\times10^{-4}$ (sec^{-1})	1.72	2.27	0.494	0.520
	Half-life (min)	67	51	234	222
At Solid[b)]	Rate constant, $k_1\times10^{-7}$ (sec^{-1})	1.34	6.70	22.9	0.803
	Half-life (day)	60	12	3.5	100

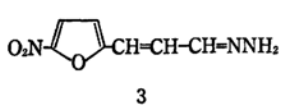
a) Measurements were carried out at 20°C. b) In potassium bromide pellet.



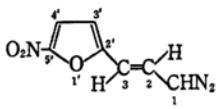
1a: R=H
b: R=Tosyl



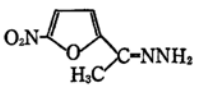
2



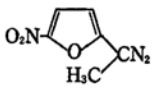
3



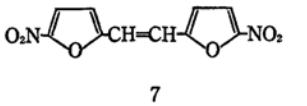
4



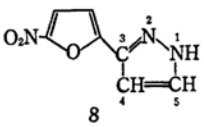
5



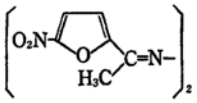
6



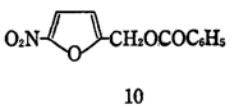
7



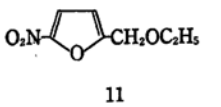
8



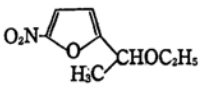
9



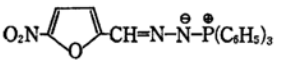
10



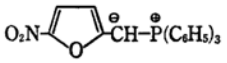
11



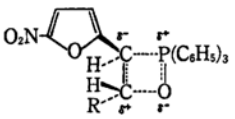
12



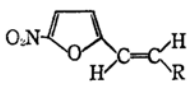
13



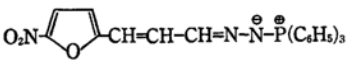
14



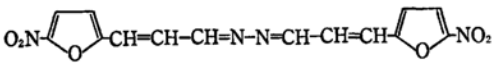
15



16a: R=$-C_6H_5$
b: R=$-CH=CH-C_6H_5$
c: R=$-C_4H_3O$



17



18

may be expected to be located in the lower field of around $-3.0\,\tau$,[10] besides those due to two protons of a nitrofuran ring at 2.21 τ (1 H, d, J= 3.8 cps) and at 2.87 τ (1 H, d, J=3.8 cps)[11] and the ultraviolet spectrum in ethanol had an absorption maximum at 354 mμ.[12] Such a facile intramolecular cyclization of unsaturated diazo compounds has also been reported with vinyldiazomethanes:[4a,13]

2 ⟶ 7 4 ⟶ 8

Compound 6 also decomposed very easily either in the solid state or as a benzene solution on only standing at room temperature; it gave an azine derivative 9 as the main product. A similar azine

10) C. L. Habraken, H. J. Munter and J. C. P. Westgest, *Rec. trav. chim.*, **86**, 56 (1967).
11) T. Sasaki and T. Yoshioka, This Bulletin, **40**, 2604 (1967).
12) Part XV of this series: T. Sasaki, S. Eguchi and A. Kojima, *J. Heterocyclic Chem.*, **5**, 243 (1968).
13) a) C. D. H. Hurd and S. C. Lui, *J. Am. Chem. Soc.*, **57**, 2656 (1935); b) A. Ledwith and D. Parry, *J. Chem. Soc., (B)*, **1967**, 41.

formation by the decomposition of diaryldiazomethane has also been reported.[14] This shows that nitrofurylcarbene, even if produced from 6, is a rather stable and unreactive species, similar to that produced from 2 described above:

$$6 \longrightarrow 9$$

By far the most common reactions of diazoalkanes are those in which they act as nucleophiles, the α-carbon being most often the nucleophilic center. It is generally believed[15] that the case of reaction decreases with a decrease in the basicity of the α-carbon and that it is affected by the steric effects as well, while the behavior of diazoalkanes as electrophiles is much less pronounced. As an example of a nucleophile, 2 was treated with benzoic acid in ether at room temperature; it afforded the corresponding benzoate, 10, in a quantitative yield. This reaction proceeded very slowly; it took about three days for 2 to be consumed completely even in the presence of an excess amount of benzoic acid, though 2-furyldiazomethane gives the corresponding benzoate in only 30 min.[4b] These results show that the presence of a nitro group in a furan ring causes an increase in the diazomethane stability because of the resonance stabilization and a lowering in the nucleophilicity of 2. Another example is given by the formation of 11 when 2 is left to stand in ethanol, as has been described above. As an example of 2 as an electrophile, 2 was treated in ether with triphenylphosphine at room temperature to afford 5-nitro-2-furfural triphenylphosphazine (13) in a 75% yield. 13 liberated nitrogen readily in the presence of cuprous ions to give 5-nitro-2-furfurylidene triphenylphosphorane, a phosphonium ylid (14) and one of the Wittig reagents;[16] this provides a novel preparative method for (5-nitro-2-furfuryl)ethylenic compounds, for which the condensation of 5-nitro-2-furfural with active methylene and methyl compounds is the general procedure.[17] A Wittig reaction using 14 is interesting because the preparation of the Wittig reagent by the usual method from 5-nitro-2-furfuryl halides and triphenylphosphine, followed by base-treatment, was unsuccessful because of the facile furan-ring cleavage by a base, though the reaction of 5-nitro-2-furfural with the Wittig reagents has been reported.[18]

Thus, on the treatment of 2 with carbonyl compounds such as benzaldehyde, furfural, and cinnamaldehyde in the presence of triphenylphosphine and cuprous chloride, the corresponding (5-nitro-2-furyl)ethylenic compounds, 16a, b, and c, were obtained, but in low yields. A similar reaction with *p*-nitrobenzaldehyde 5-nitro-2-furfural resulted only in the formation of intractable masses, while that with acetophenone and acetone afforded small amounts of 7 and 5-nitro-2-furfural azine,[19a] with the ketones mostly recovered. The reactivity of the Wittig reaction is known to depend mainly on the charge on the α-carbon atom, and the most stable phosphinemethylenes are completely unreactive; thus, the *p*-nitrophenylmethine triphenylphosphonium ylid gives no olefins at all with benzaldehyde and cinnamaldehyde because of the resonance stabilization.[20]

The above results indicate that nitrofurfuryl phosphobetaine (15) is more basic—in other words, more reactive—than the corresponding *p*-nitrophenyl compound.

The diazo compound 4 reacted similarly with triphenylphosphine in ether to give the corresponding phosphazine (17), which was more labile than 13. Thus, 17 afforded the known β-(5-nitro-2-furyl)acrolein azine[19b] in a good yield upon only being warmed in acetone. Such a facile formation of an azine from phosphazine can be explained by the instability of 17; the decomposition of 17 may afford the corresponding phosphonium ylid, which will be attacked by 4 as an electrophile, this attack to be followed by the elimination of triphenylphosphine from the primary adduct to give an azine.

Experimental[21]

5-Nitro-2-furfural Tosylhydrazone (1b). This was prepared by the usual method from 5-nitrofurfural[22] and tosylhydrazine in a quantitative yield as yellow needles, mp 155—156°C (from methanol): λ_{max}^{EtOH} 352 mμ (ε 15000); ν(KBr) 3170, 1614, 1593, 1528, 1352, 1318 and 1168 cm^{-1}.

14) W. Kirmse, L. Horner and H. Hoffmann, *Liebigs Ann.*, **614**, 19 (1958).
15) C. G. Overberger, J-P. Anselme and J. G. Lombardino, "Organic Compounds with Nitrogen-Nitrogen Bonds," The Ronald Press Company, New York (1966), p. 51.
16) G. Wittig and M. Schlosser, *Tetrahedron*, **18**, 1023 (1962).
17) T. Sasaki, unpublished data.
18) H. Saikachi, private communication.
19) a) K. Miyake, *Yakugaku Zasshi (J. Pharm. Soc. Japan)*, **72**, 1162 (1952); b) H. Saikachi and H. Hoshida, *ibid.*, **71**, 982 (1951).
20) a) S. Fliszar, R. F. Hudson and G. Salvadori, *Helv. Chim. Acta*, **46**, 1580 (1963); b) F. Krohnke, *Chem. Ber.*, **83**, 291 (1950).
21) The microanalyses were carried out on a Yanagimoto C. H. N. Corder Model MT-1. All the melting-points were determined on a Yanagimoto micro-melting-point apparatus and have not been corrected. The ultraviolet spectra were run on a JASCO Model ORD/UV-5 spectrophotometer; the infrared spectra, on a JASCO Model IR-S infrared spectrophotometer, and the NMR spectra, on a Varian A-60 spectrometer, in which the chemical shifts are described in τ-values relative to tetramethylsilane as an internal standard and the singlet peaks are designated as s; the doublet, as d; the triplet, as t; the quartet, as q; and the multiplet, as m.
22) H. Gilman and G. F. Wright, *J. Am. Chem. Soc.*, **52**, 2550, 4165 (1930); *ibid.*, **53**, 1923 (1931).

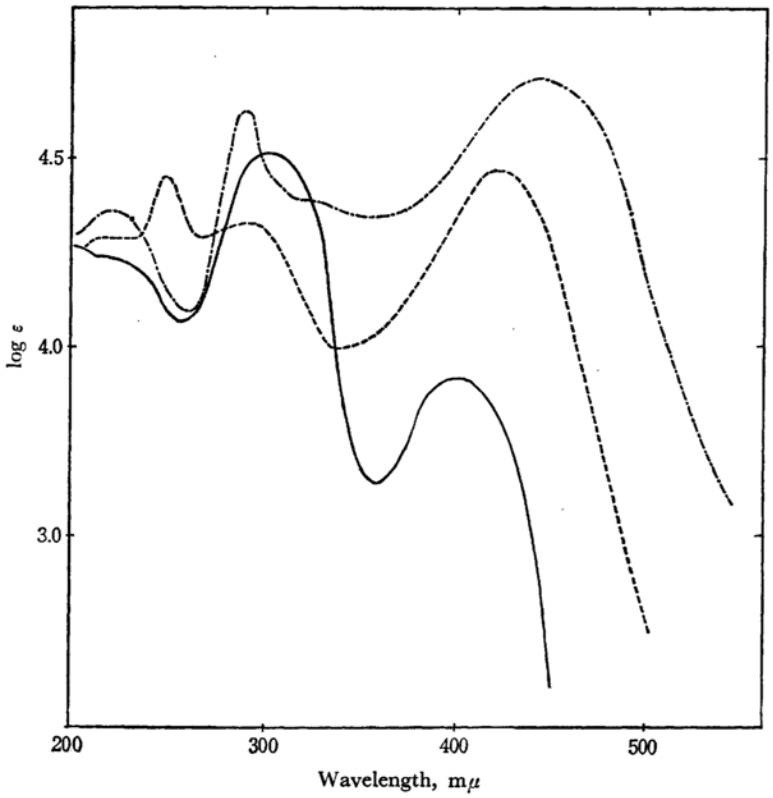


Fig. 1. Ultraviolet absorption spectra of nitrofuryldiazomethane, 2 (——), 4 (-·-·) and 6 (- - -) in ethanol.

Found: C, 46.60; H, 3.35; N, 13.36%. Calcd for $C_{12}H_{11}O_5N_3S$: C, 46.61; H, 3.59; N, 13.59%.

3-(5-Nitro-2-furyl)acroleinhydrazone (3). This was prepared similarly from 5-nitro-2-furylacrolein[23] and 80% hydrazine hydrate in a 52% yield as red needles, mp 150—151°C (from methanol): λ_{max}^{EtOH} 400 mμ (ε 17200): ν(KBr) 3375, 1609, 1572, 1555, 1490, 1356 and 807 cm^{-1}.

Found: C, 46.19; H, 3.95; N, 23.04. Calcd for $C_7H_7O_3N_3$: C, 46.41; H, 3.90; N, 23.20%.

5-Nitro-2-furyl Methyl Ketonehydrazone (5). This was prepared similarly from 5-nitro-2-furyl methyl ketone[24] and hydrazine hydrate in a 35% yield as red needles, mp 162—164°C (from methanol): λ_{max}^{EtOH} 384 mμ (ε 13600); ν(KBr) 3440, 3325, 3240, 1687, 1637, 1580, 1504, 1052 and 810 cm^{-1}; NMR ($CDCl_3$) τ 2.30 (1H, d, J=4.0 cps), 2.57 (2H, s, it disappeared on deuteration), 3.17 (1H, d, J=4.0 cps) and 8.00 (3H, s).

Found: C, 43.05; H, 3.62; N, 24.40%. Calcd for $C_6H_7O_3N_3$: C, 42.60; H, 4.17; N, 24.85%.

Preparation of 5-Nitro-2-furyl Diazo Compounds, 2, 4, and 6. *By Oxidation of the Hydrazones.* A mixture of 1.55 g (0.01 mol) of 1a, mp 162—164°C (dec.) (lit.[25] 164°C (dec.)), 6.20 g (0.07 mol) of active manganese dioxide,[26] and 3 g of anhydrous sodium sulfate in 40 m*l* of dry ether was stirred for 1 hr under ice cooling. The inorganic materials were then removed by filtration and washed with 100 m*l* of ether. The combined ethereal filtrate and washings were evaporated to dryness under reduced pressure to give 1.25 g (81.6%) of 2. The similar oxidation of 3 and 5 gave 4 in a 70% yield and 6 in a 62% yield. The appearance, melting point, and analytical and spectral data of these diazo compounds are summarized in Table 1, and their UV spectra, in Fig. 1.

By Pyrolysis of 1b. Sodium salt of 1b was pyrolyzed by the known procedure[2c] under the reduced pressure of 10^{-3} mmHg at 120—140°C to give 2 in a 50% yield from a sublimed portion.

Stability Measurement of 2, 4, and 6. The decreasing rates of the UV maximum absorption at 406 mμ for 2, at 440 mμ for 4, and 423 mμ for 6 in ethanol were followed as a function of the time at 20°; the half-life of the change and each rate constant were calculated, the results being as given in Table 2. Similarly, the decreasing rates of each diazo absorption band of these diazo compounds at 2110 for 2, at 2100 for 4, and at 2070 cm^{-1} for 6, together with that of *p*-nitrophenyldiazomethane at 2100 cm^{-1}, were followed to give each decomposition half-life in a KBr pellet and each rate constant (*cf.* Table 2).

Identification of the Final Products in Ethanol. After 2 had been kept standing in ethanol at room temperature for several hours, the ethanol was removed under reduced pressure; the residual red oil was identified as 11 spectroscopically (infrared and ultraviolet

23) H. Saikachi and H. Ogawa, *ibid.*, **80**, 3642 (1958).
24) I. J. Rinkes, *Rec. trav. chim.*, **50**, 834 (1931).
25) R. Hull, Brit. Pat. 816886 (1959); *Chem. Abstr.*, **55**, 24791 (1961).
26) J. Attenburrow, *J. Chem. Soc.*, **1952**, 1094.

spectra) by comparison with a specimen prepared by the known method.[27] Similarly, 4 was left in ethanol at room temperature for a while, and then, after the ethanol had been removed, the residual yellow solid, mp 199°C was identified as 8 by the comparison of the infrared spectra and by a mixed-melting-point determination. The similar treatment of 6 afforded a red oil, the amount of which was too small to be purified by distillation; in view of the similarity of the ultraviolet and infrared data to those of 11, we assumed this red oil to be 12.

Decomposition of 2 in Cyclohexene. *By Pyrolysis.* A mixture of 0.5 g (0.003 mol) of 2, and 0.2 g of copper powder in 16 m*l* of cyclohexene was heated at 70° for 40 min; during that time the nitrogen-gas evolution amounted to almost 100% of the theoretical yield. After the excess cyclohexene had been removed under reduced pressure, the oily residue, which showed two spots (R_f=0.50 and 0.01) on a silica-gel TLC*1 (benzene-methanol 95 : 5 vol% as the solvent and iodine as the developer), was chromatographed on a silica-gel (Mallinckrodt, 100 mesh) column, using benzene as the eluent, to give 22 mg (5.8%) of 7 as brownish yellow needles (mp 251—252°C (from benzene)), corresponding to the upper spot on TLC. λ_{max}^{EtOH} 242 mμ (ε 14300), 282 (7950), 406 (38000) and 424 (30400); ν(KBr) 1583, 1533, 1497, 1354, 1250, 1164, 960 and 820 cm^{-1}.

Found: C, 47.77; H, 2.34; N, 10.85%. Calcd for $C_{10}H_6O_6N_2$: C, 48.01; H, 2.42; N, 11.20%.

The fraction corresponding to the lower spot on TLC was eluted with methanol and a methanolic eluate was condensed to give a dark brown, intractable oil as the main product.

The decomposition of 2 in styrene, α-morpholinostyrene, tetrahydrofuran, and benzene as a carbenophile afforded only 7 in 4—6% yields after the purification of the products by silica-gel column chromatography; the main product was always an intractable, dark brown oil.

By Photolysis. A solution of 2 in cyclohexene or styrene was irradiated at room temperature through a Pyrex jacket with a 100-watt, high-pressure mercury lamp (UM-102, Ushio Denki Co., Tokyo, Japan) until nitrogen-gas evolution had ceased; when the products were then examined on TLC, they showed several spots, most of them seeming to originate from the decomposition products, including the nitrofuran-ring cleavage.

After the removal of the solvent, the crude product was purified by silica-gel column chromatography; this gave 7 in 3—5% yields.

3-(5-Nitro-2-furyl)pyrazole (8). A solution of 0.5 g (0.003 mol) of 4 and a few drops of triethylamine in 30 m*l* of ether was kept standing at room temperature for 18 hr. The yellow needles that were thus precipitated were filtered, washed with ether, and recrystallized from ethanol to give 0.26 g (51%) of 8 as faintly yellow needles, mp 199—200°C: λ_{max}^{EtOH} 354 mμ (ε 15300), 230 (11500); ν (KBr) 3165, 1604, 1538, 1500, 1348, 1020 and 810 cm^{-1}.

Found: C, 47.05; H, 3.17; N, 21.71%.[28] Calcd for $C_7H_5O_3N_3$: C, 46.93; H, 2.81; N, 23.46%.

5-Nitro-2-furyl Methyl Ketone Azine (9). A solution of 0.05 g (0.03 mol) of 6 in 20 m*l* of benzene was refluxed for 30 min. The precipitated crystals were filtered with cooling and recrystallized from acetone to give 25 mg (50%) of 9 as yellow needles, mp 189—190°C: λ_{max}^{EtOH} 223 mμ (ε 12000), 367 (32000); ν (KBr) 1610, 1568, 1514, 1473, 1350, 1035 and 812 cm^{-1}.

Found: C, 47.03; H, 3.27; N, 17.92%. Calcd for $C_{12}H_{10}O_6N_4$: C, 47.06; H, 3.29; N, 18.30%.

5-Nitro-2-furfuryl Benzoate (10). A solution of 0.26 g (0.002 mol) of 2 and 0.72 g (0.006 mol) of benzoic acid in 50 m*l* of ether was stirred at room temperature for 3 days, by which time 2 disappeared on TLC. The mixture was then evaporated to dryness to give yellow solids, which were recrystallized from ether to give 0.42 g (99%) of crude 10. Three recrystallizations from ether gave an analytical sample, mp 90—91°C: $\lambda_{max}^{Et_2O}$ 299 mμ (ε 8170); ν(KBr) 1719, 1597, 1533, 1348, 1242, 1021, 810, 749 and 710 cm^{-1}.

Found: C, 58.24; H, 3.50; N, 5.52%. Calcd for $C_{12}H_9O_5N$: C, 58.30; H, 3.67; N, 5.67%.

5-Nitro-2-furfural Triphenylphosphazine (13). To a solution of 0.015 g (0.001 mol) of 2 in 20 m*l* of ether, 0.29 g (0.001 mol) of triphenylphosphine in 10 m*l* of ether was added. After standing for 30 min at room temperature, the mixture was evaporated to dryness under reduced pressure, and the residue was recrystallized from an acetone - *n*-hexane mixture to give 0.31 g (75%) of 13 as deep red plates, mp 159—161°C: λ_{max}^{EtOH} 237 mμ (ε 11600) and 427 (21600); ν (KBr) 1598, 1542, 1500, 1368, 1062, 1026, 815, 736 and 700 cm^{-1}; NMR ($CDCl_3$) τ 1.77—2.52 (16 H, m, phenyl protons and –N=CH–), 2.69 (1H, d, J=3.8 cps, a furan-ring proton) and 3.49 (1 H, d, J=3.8 cps, a furan-ring proton).

Found: C, 65.02; H, 4.40; N, 9.85%. For an aged sample after one month: C, 63.91; H, 4.24; N, 9.57%. Calcd for $C_{23}H_{18}O_3N_3P$: C, 66.55; H, 4.38; N, 10.13%.

1-(5-Nitro-2-furyl)-2-phenylethylene (16a). A mixture of 0.5 g (0.003 mol) of 2, 0.35 g (0.0033 mol) of benzaldehyde, 0.86 g (0.0033 mol) of triphenylphosphine, and 15 mg of cuprous chloride in 30 m*l* of tetrahydrofuran was refluxed for 20 hr. The solvent was then removed under reduced pressure to give a brownish, sticky residue which was dissolved in benzene and chromatographed on a silica-gel column, using benzene as the eluent. The removal of the solvent from the eluate afforded yellow crystals, which were then recrystallized from ethanol to give 0.26 g (36%) of 16a as yellow needles, mp 109—110°C (lit.[29] 111—112°C): NMR ($CDCl_3$) τ 2.68 and 3.48 (each 1H, d, J=3.8 cps, nitrofuran-ring protons), 2.56—2.64 (5H, m, phenyl protons), 2.67 and 3.10 (each 1H, d, J=16.5 cps, olefinic protons).[30]

1-(5-Nitro-2-furyl)-4-phenylbutadiene (16b). A mixture of 0.538 g (0.0035 mol) of 2, 1.0 g (0.0076 mol) of cinnamaldehyde, 0.925 g (0.0035 mol) of

27) K. Kawabe, T. Suzuki and M. Iguchi, *Yakugaku Zasshi (J. Pharm. Soc. Japan)*, **80**, 62 (1960).

*1 Thin-layer Chromatography.

28) The smaller value of nitrogen analysis might be explained by the facile decomposition of 8, even at room temperature; the structural elucidation of this compound was done mainly on the basis of the spectral data.

29) I. Hirao and Y. Kitamura, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **85**, 506 (1964).

30) This coupling constant shows a *trans*-configuration of the olefin protons for 16a, as expected from the four-centered transition state, keeping bulky phenyl and nitrofuran rings in a *trans*-configuration, as has been shown in 15.

triphenylphosphine, and 16 mg of cuprous chloride in 30 m*l* of tetrahydrofuran was refluxed for 40 hr. After the removal of the solvent, a brownish residue was chromatographed on a silica-gel column, using benzene as the eluent. The eluant was condensed to give yellowish-brown crystals, which were then recrystallized from ethanol to give 0.152 g (18%) of 16b as brownish-yellow needles, mp 137—139°C: λ_{max}^{EtOH} 228 mμ (ε 14100), 300 (24300) and 410 (29300); ν(KBr) 1612, 1593, 1560, 1517, 1506, 1390, 1355, 1246, 1174, 1070 and 809 cm^{-1}; NMR ($CDCl_3$) τ 2.39—3.39 (9H, m, phenyl protons and three olefinic protons), 3.52 (1 H, d, J=3.8 cps, C-3-H) and 3.60 (1 H, d, J=15 cps, C-1-H).

Found: C, 69.40; H, 4.42; N, 5.68%. Calcd for $C_{14}H_{11}O_3N$: C, 69.70; H, 4.59; N, 5.80%.

1-(5-Nitro-2-furyl)-2-furylethylene (16c). A mixture of 0.502 g (0.0033 mol) of 2, 0.312 g (0.0033 mol) of furfural, 0.86 g (0.0033 mol) of triphenylphosphine, and 20 mg of cuprous chloride in 30 m*l* of tetrahydrofuran was refluxed for 20 hr. The reaction mixture was then worked up as above to give 55 mg (10%) of 16 c as reddish-brown prisms, mp 94—96°C (from ethanol): λ_{max}^{EtOH} 208 mμ (ε 12300), 235 (8150), 294 (17600) and 409 (23400); ν(KBr) 1625, 1587, 1554, 1516, 1492, 1395, 1354, 1240, 1020 and 804 cm^{-1}.

Found: C, 58.37; H, 3.49; N, 6.39%. Calcd for $C_{10}H_7O_4N_2$: C, 58.54; H, 3.44; N, 6.83%.

3-(5 - Nitro - 2 - furyl) acrolein Triphenylphosphazine (17). To a solution of 0.22 g (0.00084 mol) of triphenylphosphine in 5 m*l* of ether, a solution of 0.156 g (0.00087 mol) of 4 in 20 m*l* of ether was added. After standing for 1 hr at room temperature, the mixture was concentrated to a volume of about 10 m*l*, thus giving red prisms which were collected to give 0.268 g (72.5%) of 17 with a mp of 144—146°C: λ_{max}^{EtOH} 219 mμ (ε 33500); 314 (19900), and 443 (24500); ν(KBr) 1610, 1592, 1562, 1537, 1504, 1487, 1350, 1254, 1024, 970, 812 and 721 cm^{-1}.

Found: C, 64.72; H, 4.29; N, 8.72%. Calcd for $C_{25}H_{22}O_4N_3P$: C, 65.30; H, 4.83; N, 9.14%.

3-(5-Nitro-2-furyl)acrolein Azine (18). A solution of 61 mg (0.00014 mol) of 17 in 10 m*l* of acetone was warmed at 50—60°C for several hours. After cooling, the precipitated solid was collected to give 12 mg (52%) of the azine as yellow powders, mp 226—228°C (dec.) (lit.[18b] mp 227—228°C (dec.)).

The authors wish to express their thanks to the Ueno Pharmaceutical Co. for kindly supplying the nitrofurfural and to the Dainippon Pharmaceutical Co. for the NMR measurements. The microanalyses were done by Mr. Akiho Ishihara at their laboratories; to him especially the authors are much obliged.