

The Reactions of 2,4-Dinitrobenzenediazonium Ions with Furans

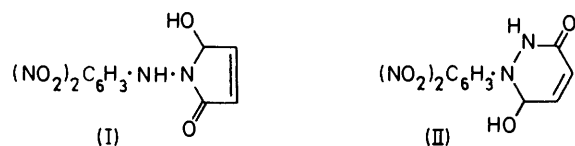
By Michael G. Bartle, Suresh T. Gore, Raymond K. Mackie, Sushila Mhatre, and John M. Tedder,
Department of Chemistry, University of St. Andrews, St. Andrews KY16 9ST, Scotland

The reaction of 2,4-dinitrobenzene ions with furans has been investigated. The course of the reaction is very dependent on the reaction conditions. Furan and 2-methyl- and 3-methyl-furan in an aqueous acetic acid medium undergo ring opening to yield an *N*-(2,4-dinitroanilino)-5-hydroxypyrrol-2(5*H*)-one (I), but in acetic anhydride-sodium acetate medium undergo arylation. 2,5-Dimethylfuran undergoes coupling at the 3-position in aqueous acetic acid, coupling at the 2-methyl group in acetic anhydride-sodium acetate and ring opening in ethanol. The reactions with benzo[*b*]furan, and 2,5-diphenylfuran were also studied and both arylation and coupling reactions were observed.

In two earlier papers we have described the reaction of 2,4-dinitrobenzenediazonium ions with thiophen and its alkyl derivatives.^{1,2} We found that thiophen itself and the two monomethyl thiophens underwent arylation by an unexpected acidic Gomberg reaction. The more highly substituted alkylthiophens underwent coupling reactions, either nuclear coupling or side-chain coupling in another unexpected process. Although a well known student text describes the coupling of diazonium salts with furans, very little evidence for such reactions appears in the literature.³ A study of the reaction of 2,4-dinitrobenzenediazonium ions with furans was, therefore, a logical extension of our earlier work.

Previously reported reactions of furans with diazonium salts are mainly arylation reactions carried out under Gomberg reaction conditions.⁴⁻⁶ Acetamidofuran will couple to yield azo-dyes⁷ and Eastman and Detert have⁸ reported a reaction which appears to involve coupling with 2,5-dimethylfuran which will be discussed below.

Treatment of furan with a solution of 2,4-dinitrobenzenediazonium sulphate in aqueous acetic acid (*cf.* ref. 1) yielded a yellow crystalline compound which analysis and mass spectra showed to have the molecular formula C₁₀H₈N₄O₆ and with spectral properties (¹H n.m.r., i.r., u.v., and mass) consistent with either structure (I) or (II). Evidence supporting structure (I) comes from the oxidation of the product with



chromic acid which yielded *N*-(2,4-dinitrophenylamino)-maleimide (III) identical to a sample prepared from the reaction of 2,4-dinitrophenylhydrazine with maleic anhydride.⁹ The five-membered structure of the maleimide (rather than a six-membered pyridazinedione ring) was confirmed by the single ¹³C n.m.r. absorption for the

¹ M. G. Bartle, S. T. Gore, R. K. Mackie, and J. M. Tedder, *J.C.S., Perkin I*, 1976, 1636.

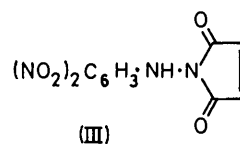
² S. T. Gore, R. K. Mackie, and J. M. Tedder, *J.C.S., Perkin I*, 1976, 1639.

³ J. D. Roberts and M. C. Caserio, 'Basic Principles of Organic Chemistry', W. A. Benjamin, Inc. New York 1964, 989.

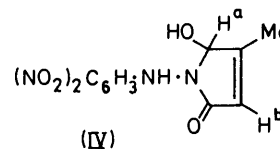
⁴ A. W. Johnson, *J. Chem. Soc.*, 1946, 895.

⁵ K. B. L. Mathur and H. S. Mehra, *J. Chem. Soc.*, 1961, 2576.

carbonyl carbon atoms ($\delta = 168.02$ p.p.m.) and also for the olefinic carbons ($\delta = 134.24$ p.p.m.).



Similar reactions were observed when 2-methyl- and 3-methyl-furan were treated with 2,4-dinitrobenzenediazonium sulphate in the same way. The product from 3-methylfuran (IV) had a 4- rather than a 3-methyl group in the pyrrol-2(5*H*)-one ring since protons a and b gave a singlet at δ 5.52 and 6.95 when the ¹H n.m.r. was run in Me₂SO-D₂O.



In an attempt to elucidate the mechanism of the ring opening, the reaction was repeated using crystalline 2,4-dinitrobenzenediazonium fluoroborate in acetic anhydride and in the presence of sodium acetate. Under these conditions nitrogen was evolved and the product after a reaction of 2 h at room temperature proved to be 2-(2,4-dinitrophenyl)furan. Treatment of 2-methylfuran in the same way likewise yielded 2-methyl-5-(2,4-dinitrophenyl)furan.

The reaction of 2,4-dinitrobenzenediazonium ions with 2,5-dimethylfuran is even more solvent dependent. Reaction with the diazonium sulphate in aqueous acetic acid yielded a deep red 'resinous' solid which was recrystallised with difficulty to yield 2,4-dinitrobenzeneazo-3'-(2',5'-dimethylfuran). This was identified by its analysis and the absence of any NH absorption in its i.r. spectrum. When the reaction was repeated using the diazonium fluoroborate in acetic anhydride with 1 mol. equiv. of sodium acetate, or the diazonium fluoroborate in dioxan solution coupling occurred at

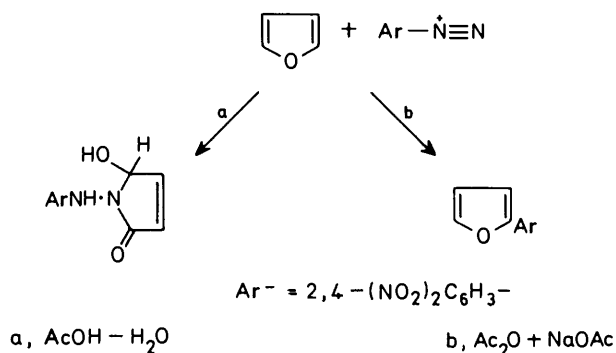
⁶ W. Freund, *J. Chem. Soc.*, 1952, 3073.

⁷ R. K. Kuhn and G. Kruger, *Chem. Ber.*, 1957, 90, 264.

⁸ R. H. Eastman and F. L. Detert, *J. Amer. Chem. Soc.*, 1948, 70, 962.

⁹ H. Rubinstein, J. E. Skarbek, and H. Feur, *J. Org. Chem.*, 1971, 36, 3372.

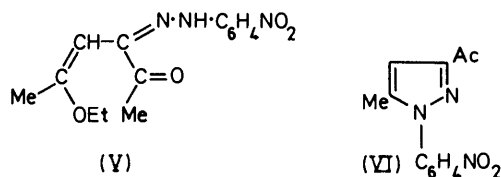
the 2-methyl group to yield the 2,4-dinitrophenylhydrazone of 5-methylfuran-2-carbaldehyde (with the identical molecular formula to the azo-compound) whose structure was confirmed by the presence of an NH



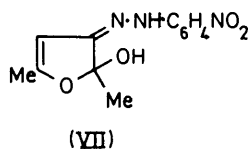
SCHEME 1

absorption in its i.r. spectrum and by comparison with an authentic specimen. However when 2,5-dimethylfuran in acetic anhydride was treated with the diazonium fluoroborate and an excess of sodium acetate, ring opening occurred and the isolated product was 2,4-dinitrophenylhydrazone of hexane-2,3,5-trione.

Eastman and Detert had previously investigated the reaction of 2,5-dimethylfuran with *p*-nitrobenzenediazonium chloride in aqueous alcohol in the presence of an excess of potassium acetate.⁸ They reported ring opening to yield compound (V) which when treated under reflux with hydrochloric acid gave 3-acetyl-5-methyl-1-(*p*-nitrophenyl)pyrazole (VI). Repetition of their



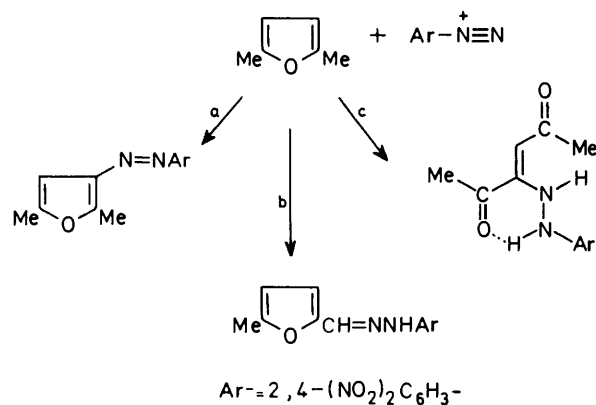
work confirmed their structure of the final product, but the intermediate product isolated in the present study had characteristics which were more consistent with structure (VII). In order to compare this earlier study



with the present work the reaction with *p*-nitrobenzenediazonium chloride was repeated in aqueous acetic acid and a resinous product was obtained from which *p*-nitrobenzeneazo-3'-(2',5'-dimethylfuran) could be isolated. To complete the series the reaction of 2,4-dinitrobenzenediazonium ions in ethanol was investigated and the dinitrophenylhydrazone of hexane-2,3,5-trione was obtained (*i.e.* the same product as in acetic anhydride in the presence of an excess of sodium acetate).

Reaction of 2,4-dinitrobenzenediazonium ions with benzo[*b*]furan, either the sulphate in aqueous acetic-sulphuric acid mixture or the anhydrous fluoroborate in acetic anhydride and an excess of sodium acetate, only yielded 3-(2,4-dinitrophenyl)benzo[*b*]furan together with some bis(dinitrophenyl)benzo[*b*]furan. 2-Methylbenzo[*b*]furan reacted with the 2,4-dinitrobenzenediazonium sulphate in the acetic acid-sulphuric acid medium to yield principally the arylated product 3-(2,4-dinitrophenyl)-2-methylbenzo[*b*]furan but also some of the azo-dye {2,4-dinitrobenzeneazo-3'-(2'-methylbenzo[*b*]furan)}. 2,5-Diphenylfuran also yielded mainly 'Gomberg' products with 2,4-dinitrobenzenediazonium sulphate although a trace of azo-dye appears to have been formed.

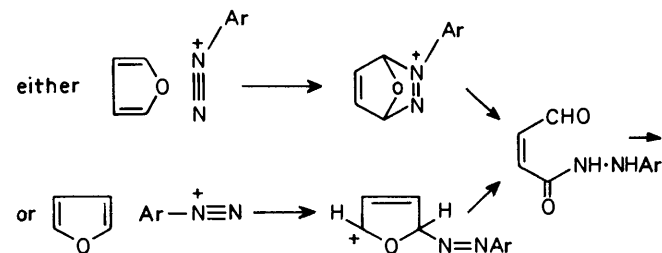
It is impossible to elucidate completely the mechanism of the various reactions described on present evidence.



a, $\text{AcOH} + \text{H}_2\text{O}$; b, dioxan or $\text{Ac}_2\text{O} + \text{NaOAc}$ (1equiv.)
c, EtOH or $\text{Ac}_2\text{O} + \text{NaOAc}$ (excess)

SCHEME 2

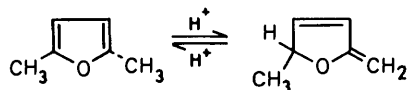
The ring-opening reactions of furan and the monomethylfurans could involve cycloaddition reactions, as have been recently established for diazonium salts with powerful electron-withdrawing substituents,¹⁰ or normal electrophilic substitution. The failure of benzo[*b*]furan



to couple provides some support for the cycloaddition mechanism and further support comes from the rapidity of the reaction with furans compared with the much slower coupling reactions. The reactions with 2,5-

¹⁰ B. A. Carlson, W. A. Sheppard, and O. W. Webster, *J. Amer. Chem. Soc.*, 1975, **97**, 5291.

dimethylfuran to form the phenylhydrazone of hexanetrione clearly involve electrophilic attack at the 3-position followed by the formation of the analogue of (VII). The more electron-withdrawing nature of the 2,4-dinitrophenyl group facilitates further nucleophilic attack with the resultant ring opening. The side-chain attack observed when there is no nucleophile present must involve the similar methylene intermediate observed in the thiophen studies.²



The ready Gomberg arylation also remains unexplained although compared with the thiophens which underwent arylation in a very acidic media, the arylation of furan itself involves less acidic conditions. However benzo[*b*]-furan arylates in the aqueous sulphuric acid-acetic mixture under conditions very similar to benzo[*b*]-thiophen.

EXPERIMENTAL

2,4-Dinitrobenzenediazonium Sulphate Solution.—This solution was made up according to the method described in ref. 1.

Reaction of Furan with 2,4-Dinitrobenzenediazonium Sulphate in Acetic Acid Solution.—A solution of furan (1.36 g, 0.02 mol) in glacial acetic acid (25 ml) was added to the 2,4-dinitrobenzenediazonium sulphate solution (0.02 mol). The reaction mixture was stirred at room temperature for 15 min and the yellow precipitate formed was filtered off, washed with water, once with aqueous methanol, and then ether. The dried product was recrystallised from benzene-acetone, m.p. 193—194 °C (Found: C, 42.8; H, 2.9; N, 19.8. $C_{10}H_8N_4O_6$ requires C, 42.9; H, 2.9; N, 20.0%), $M^+ = m/e$ 280, λ_{max} 332 nm ($\epsilon = 1.54 \times 10^4$), ν_{max} 3 310, 1 690, 1 620, 1 590, 1 515, 1 495, 1 340, 1 310, 1 110, 925, 915, 870, 830, 800, 740, and 700 cm^{-1} ; $\delta([^2H_6]Me_2SO)$ 5.6 (1 H, d, 8 Hz), 6.34 (1 H, d, 6 Hz), 6.88 (1 H, d, 8 Hz), 7.28 (1 H, dd, 6 Hz, 1.5 Hz), 7.4 (1 H, d, 9 Hz), 8.34 (1 H, dd, 9 and 2 Hz), 8.88 (1 H, d, 2 Hz), and 10.16 (1 H, s); $\delta([^2H_6]Me_2SO + ^2H_2O)$ 5.6 (1 H, s), 6.3 (1 H, d, 6 Hz), 7.26 (1 H, dd, 6 Hz, 1.5 Hz), 7.38 (1 H, d, 9 Hz), 8.32 (1 H, dd, 9 Hz, 1 Hz), and 8.88 (1 H, d, 1 Hz). The yield of *N*-(2,4-dinitroanilino)-5-hydroxypyrrrol-2(5H)-one (I) was 4.03 g (72%). Treatment of (I) with benzoyl chloride in pyridine give a dibenzoyl derivative, m.p. 164 °C, m/e 488 (M^+) (Found: C, 60.6; H, 3.2; N, 11.3. $C_{24}H_{16}N_4O_8$ requires C, 59.3; H, 3.3; N, 11.5%).

Oxidation of the Product from the Furan Reaction.—A chromic acid solution was made by dissolving sodium dichromate (0.60 g) in concentrated H_2SO_4 (3 ml) and then adding dilute H_2SO_4 (5M; 2 ml) to it. The solution was cooled (0 to 5 °C) and added dropwise with stirring to an ice-cold solution of compound (I) (0.560 g; 0.002M) in acetone (25 ml). The addition took place in 2—3 min after which the green solution was stirred for further 5 min before being poured into water (200 ml). The yellow precipitate which formed was filtered off and washed with water, a small amount of ice-cold methanol, and ether. The dried product was purified by re-precipitation from a benzene solution (100 ml) by addition of petroleum (b.p.

40—60 °C) to give *N*-(2,4-dinitrophenylamino)maleimide (III) (0.34 g, 61%), m.p. 233 °C (decomp.), mixed m.p. with authentic sample 232—234 °C (decomp.); $M^+ = m/e$ 278 (Found: C, 43.5; H, 2.1; N, 19.9. Calc. for $C_{10}H_6N_4O_6$: C, 43.2; H, 2.2; N, 20.2%); i.r. and 1H and ^{13}C n.m.r. spectra were identical with those of the *N*-(2,4-dinitrophenylamino)maleimide (III) made by an unambiguous route.

***N*-(2,4-Dinitrophenylamino)maleimide.**^{9,11} 2,4-Dinitrophenylhydrazine (20 g) was added at room temperature to a solution of maleic anhydride (9.8 g) in glacial acetic acid (200 ml). The reaction was stirred for 6 h and then filtered to give a yellow solid (28 g). This was dried over P_2O_5 and NaOH to give 1-(2,4-dinitrophenyl)-2-(3-carboxyacryloyl)hydrazine, m.p. 190—192 °C, 1.5 g of which was heated under reflux in glacial acetic acid (50 ml) for 5 h. A yellow product was obtained when the reaction was poured into water. The solid was filtered off and purified by dissolution in hot benzene and reprecipitation with petroleum (b.p. 40—60 °C) to give *N*-(2,4-dinitrophenylamino)maleimide (III), m.p. 231—232 °C (decomp.) [lit., m.p. 232 °C (decomp.)], $M^+ = m/e$ 278, $\delta([^2H_6]Me_2SO - ^2H_2O)$ 7.24 (2 H, s), 7.4 (1 H, d, 9 Hz), 8.4 (1 H, dd, 9 and 2 Hz), 8.92 (1 H, d, 2 Hz); ν_{max} 3 380, 1 740, 1 620, 1 595, 1 520, 1 500, 1 340, 1 320, 1 060, 1 050, 825, 740, and 715 cm^{-1} (Found: C, 43.3; H, 2.15; N, 20.0. Calc. for $C_{10}H_6N_4O_6$: C, 43.2; H, 2.2; N, 20.2%), ^{13}C n.m.r. spectra of *N*-(2,4-dinitroanilino)-5-hydroxydihydropyrrole-2(5H)-one (I) and *N*-(2,4-dinitrophenylamino)maleimide (III), were obtained on their 1M-solution in $Me_2SO - [^2H_6]Me_2SO$ (20%). The values are collected in the Table.

No.	(I)		(III)	
	Peak height	δ^*	Peak height	δ
1	14	168.50	45	168.01
2	19	149.31	24	147.45
3	24	148.96	14	138.21
4	11	137.19	76	134.16
5	30	129.86	12	130.89
6	24	125.63	31	130.27
7	22	122.80	25	122.91
8	24	116.34	26	115.50
9	21	84.58		

* Chemical shifts are downfield from internal tetramethylsilane.

Reaction of 2-Methylfuran with 2,4-Dinitrobenzenediazonium Sulphate in Acetic Acid Solution.—A solution of 2-methylfuran (0.82 g, 0.01 mol) in glacial acetic acid (30 ml) was added to the diazonium solution (0.01 mol) and the reaction stirred at room temperature. A yellow precipitate was formed immediately and the reaction was stopped after 5 min; the solution was poured into cold water (200 ml) and the precipitate was filtered off. It was washed with water (3 times) and dried over P_2O_5 *in vacuo* to give a yellow powder. After recrystallisation in aqueous dimethylformamide and drying, *N*-(2,4-dinitroanilino)-5-hydroxy-5-methylpyrrrol-2(5H)-one was obtained as a yellow powder, m.p. 205 °C (decomp.) (1.9 g, 64%), $M^+ = m/e$ 294 (Found: C, 44.7; H, 3.5; N, 18.9. $C_{11}H_{10}N_4O_6$ requires C, 44.9; H, 3.4; N, 19.0%), ν_{max} 3 200—3 380 (br, NH), 1 710 (C=O), 1 620, 1 595, 1 500m, 1 350 (NO₂), 1 315, 1 270, 1 230, 1 155, 1 140, 1 120, 820, and 740 cm^{-1} ; λ_{max} 328 ($\epsilon = 1.43 \times 10^4$) and 260 nm (7.62 $\times 10^3$); $\delta([^2H_6]Me_2SO)$ 1.52 (3 H, s), 6.7 (1 H, d, 6 Hz), 7.3—7.5 (2 H,

¹¹ H. Feuer and J. P. Asunskis, *J. Org. Chem.*, 1962, **27**, 4684.

m), 8.3 (1 H, dd, 9 and 2 Hz), 8.9 (1 H, d, 2 Hz), and 9.9 (1 H, br); δ ($^2\text{H}_6$]Me₂SO-²H₂O) 1.54 (3 H, s), 6.8 (1 H, d, 6 Hz), 7.3—7.5 (2 H, m), 8.34 (1 H, dd, 9 and 2 Hz), and 8.92 (1 H, d, 2 Hz).

Reaction of 3-Methylfuran with 2,4-Dinitrobenzenediazonium Sulphate in Acetic Acid Solution.—A solution of 3-methylfuran^{12,13} (0.125 g, 0.05 ml) in glacial acetic acid (10 ml) was added with stirring to the diazonium solution (0.05 mol) at room temperature. A further 10-ml portion of glacial acetic acid was added and the red reaction mixture stirred for 16 h (when a test for diazonium ions was negative) before being poured into ice-cold water (100 ml). The red precipitate formed was filtered off, washed with water and dried *in vacuo* over P₂O₅. The red powder was purified by dissolution in hot benzene and reprecipitation with petroleum (b.p. 40—60 °C) to give *N*-(2,4-dinitroanilino)-5-hydroxy-4-methylpyrrol-2(5H)-one (0.14 g, 32%) as a chrome yellow powder, m.p. 193—194 °C (Found: C, 44.6; H, 3.2; N, 18.9. C₁₁H₁₀N₄O₆ requires C, 44.9; H, 3.4; N, 19.0%), $M^+ = m/e$ 294; ν_{max} 3 200—3 300br (NH), 1 685, 1 615, 1 585, 1 500, 1 340, 1 285, 975, 870, 830, and 740 cm⁻¹; λ_{max} 330 ($\epsilon = 1.465 \times 10^4$) and 255 nm (1 020 $\times 10^4$); δ ($^2\text{H}_6$]Me₂SO) 1.87 (3 H, s), 5.46 (1 H, d, 8 Hz), 6.6—7.0 (2 H, m), 7.4 (1 H, d, 9.5 Hz), 8.3 (1 H, dd, 9.5 and 2 Hz), 8.87 (1 H, d, 2 Hz), and 10.2 (1 H, br); δ ($^2\text{H}_6$]Me₂SO-²H₂O) 1.9 (3 H, s), 5.52 (1 H, s), 6.95 (1 H, s), 7.4 (1 H, d, 9.5 Hz), 8.3 (1 H, dd, 9.5 and 2 Hz), and 8.9 (1 H, d, 2 Hz).

Reaction of 2,5-Dimethylfuran with 2,4-Dinitrobenzenediazonium Sulphate in Acetic Acid Solution.—The 2,4-dinitrobenzenediazonium sulphate solution (0.05 mol) was added to a solution of 2,5-dimethylfuran¹⁴ (4.8 g, 0.05 mol) in glacial acetic acid (200 ml) and stirred at room temperature for 50 h. Dilution with water produced a dark red gummy precipitate, which was collected. Attempts to purify the precipitate by recrystallisation failed and it was chromatographed on an alumina column using chloroform. A deep red 'glassy' solid (3.8 g) was obtained which was precipitated from carbon tetrachloride to yield 2,4-dinitrobenzeneazo-3'-(2',5'-dimethylfuran), m.p. 172 °C (decomp.) (Found: C, 50.1; H, 3.6; N, 18.4%; m/e 290.0652. C₁₃H₁₀N₄O₅ requires C, 49.7; H, 3.5; N, 19.3%; m/e 290.0651); the i.r. spectrum showed the absence of OH and C=O groups, λ_{max} 340 ($\epsilon = 1.02 \times 10^4$), 470 nm (3.70 $\times 10^4$). The compound could not be properly crystallised or purified further. The aqueous layer was extracted with chloroform and the extract was washed with water, aqueous sodium hydrogen carbonate solution until neutral, and water, and then dried over magnesium sulphate. Evaporation of the solvent gave a red oil (3.8 g) which was chromatographed on an alumina column. Chloroform eluted a deep red compound which was found to be more (2.8 g) of the azo-compound. No arylated derivatives were found and the total yield of the 2,4-dinitrobenzeneazo-3'-(2',5'-dimethylfuran) was 5.6 g (40%).

Reaction of 2,5-Dimethylfuran with 2,4-Dinitrobenzenediazonium Fluoroborate in Dioxan.—2,4-Dinitrobenzenediazonium fluoroborate was added to a solution of 2,5-dimethylfuran (0.29 g, 0.003 mol) in dioxan (20 ml). The reaction was stirred at room temperature for 2 h, when its colour changed from yellow to deep red. At the end of the reaction period it was poured into cold water, and the red precipitate was filtered off, washed several times with

water, and then dried over P₂O₅ to give 0.60 g of a red powder. This was put on a short silica column. The orange red fraction eluted by a mixture of benzene and chloroform (3 : 1) gave a red solid. After recrystallisation from ethanol the 2,4-dinitrophenylhydrazone of 5-methylfuran-2-carbaldehyde was obtained as deep red needles (0.1 g, 11%), m.p. 208 °C, $M^+ = m/e$ 290; ν_{max} 3 280 (NH) 1 610, 1 510, 1 330, 1 130, 1 020, 830, and 795 cm⁻¹ (Found: C, 49.2; H, 3.9; N, 19.1. Calc. for C₁₃H₁₀N₄O₅: C, 49.7; H, 3.5; N, 19.3%). An authentic sample prepared from 5-methylfuran-2-carbaldehyde had m.p. 210—211 °C (lit., 212 °C); ν_{max} 3 280 (NH), 1 600, 1 510, 1 330 (NO₂), 1 130, 1 020, 830, and 795 cm⁻¹ (Found: C, 49.8; H, 3.4; N, 19.1. Calc. for C₁₂H₁₀N₄O₅: C, 49.7; H, 3.5; N, 19.3%). Mixed m.p. with the above compound was 208 °C.

Reaction of Furan with 2,4-Dinitrobenzenediazonium Fluoroborate in Acetic Anhydride and 1 Mole Equivalent of Sodium Acetate.—Furan (0.41 g) was added to a solution of sodium acetate (0.49 g) in acetic anhydride (20 ml) and 2,4-dinitrobenzenediazonium fluoroborate (1.68 g) was then added to it. The mixture was stirred for 2 h and then washed with a saturated solution of sodium hydrogen carbonate and then with water. It was extracted with chloroform, and the extract dried, evaporated, and purified by chromatography on a silica column (benzene). The first yellow fraction on evaporation gave yellow crystals of 2-(2,4-dinitrophenyl)furan (0.3 g, 21%). Recrystallised from light petroleum (b.p. 60—80 °C) it had m.p. 64 °C; $M^+ = m/e$ 234; δ [(CD₃)₂SO] 8.51 (1 H, d, 2 Hz), 8.42 (1 H, dd, 2 and 9 Hz), 7.95 (1 H, d, 9 Hz), 7.64 (1 H, dd, 0.7 and 1.7 Hz), 6.92 (1 H, dd, 0.7 and 3.7 Hz), 6.60 (1 H, dd, 1.7 and 3.7 Hz); the i.r. spectrum showed an absence of C=O, OH, and NH groups (Found: C, 51.4; H, 2.6; N, 11.7. C₁₀H₆N₂O₅ requires C, 51.3; H, 2.6; N, 12.0%).

By repeating the experiment using a large excess of sodium acetate (5 g) the yield of 2-(2,4-dinitrophenyl)furan was increased to 0.45 g (32%).

Reaction of 2,5-Dimethylfuran with 2,4-Dinitrobenzenediazonium Fluoroborate in Acetic Anhydride and 1 Mole Equivalent of Sodium Acetate.—2,5-Dimethylfuran (0.58 g) was added to a solution of sodium acetate (0.49 g) in acetic anhydride (20 ml). 2,4-Dinitrobenzenediazonium fluoroborate (1.68 g) was then added to it. The mixture was stirred for 2 h and then washed with a saturated solution of sodium hydrogen carbonate and then with water. It was extracted with chloroform, dried, evaporated, and purified by chromatography on silica (benzene). The first red fraction yielded the dinitrophenylhydrazone of 5-methylfuran-2-carbaldehyde identical to that obtained in the experiment performed in dioxan; ν_{max} 3 280 cm⁻¹ (NH) (Found: C, 49.4; H, 3.4; N, 19.1%; M , 290.066 1. Calc. for C₁₂H₁₀N₄O₅: C, 49.7; H, 3.5; N, 19.3%; M , 290.065 1).

Reaction of 4-Nitrobenzenediazonium Chloride with 2,5-Dimethylfuran in Ethanol (Eastman and Detert⁸).—4-Nitroaniline (7.0 g) was slurried with sodium nitrite (3.5 g) in ice-water (100 ml) and concentrated hydrochloric acid (20 ml) was added to it with stirring and external cooling. The resultant solution was added to a mixture of 2,5-dimethylfuran (4.8 g) and sodium acetate (15 g) in ethanol (150 ml) and stirred at 0 °C for 3 h. The mixture was poured into water and an orange oil solidified slowly and

¹² J. W. Cornforth, *J. Chem. Soc.*, 1958, 1019.

¹³ J. W. Cornforth, *J. Chem. Soc.*, 1958, 1310.

¹⁴ R. Gaertner and R. G. Tonkyn, *J. Amer. Chem. Soc.*, 1951, 73, 5872.

was filtered off. It was recrystallised from benzene–light petroleum (b.p. 60–80 °C) to give the orange intermediate compound (VII), m.p. 125 °C; $M^+ = m/e$ 263; ν_{\max} 3 400s cm^{-1} (NH, OH, but no C=O absorption). A portion was refluxed in a mixture of ethanol–5N-hydrochloric acid (1 : 1) for 5 min and then poured into water. The orange solid was filtered off and recrystallised from ethanol–water to give pale orange needles of compound (VI), m.p. 133 °C; $M^+ = m/e$ 245 (Found: C, 58.2; H, 4.5; N, 16.8. Calc. for $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_3$: C, 58.8; H, 4.5; N, 17.1%); ν_{\max} 1 680 cm^{-1} (no NH or OH absorption); λ_{\max} 295 nm ($\epsilon = 1.38 \times 10^4$).

Reaction of p-Nitrobenzenediazonium Chloride with 2,5-Dimethylfuran in Acetic Acid.—*p*-Nitroaniline (7.0 g) was diazotised with sodium nitrite (3.5 g) and concentrated hydrochloric acid (20 ml) as above and was added to a solution of 2,5-dimethylfuran (4.8 g) in glacial acetic acid (150 ml); the mixture was stirred at 0 °C for 20 h during which time it became dark red. The solution was diluted with water and extracted with chloroform; the extract was washed with water, aqueous sodium bicarbonate solution until neutral, and then water; it was then dried over magnesium sulphate. Evaporation of the solvent gave a dark red oil (4.0 g) which crystallised with time. The product was extremely difficult to recrystallise and was purified by chromatography on a silica column using chloroform to give *p*-nitrobenzeneazo-3'-(2',5'-dimethylfuran), m.p. 222 °C, $M^+ = m/e$ 245 (Found: C, 59.0; H, 4.6%; M , 245.0795. $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_3$ requires C, 58.8; H, 4.5%; M , 245.0800); λ_{\max} 378 nm ($\epsilon = 9.9 \times 10^3$).

Reaction of 2,5-Dimethylfuran with 2,4-Dinitrobenzenediazonium Sulphate in Ethanol.—2,4-Dinitrobenzenediazonium sulphate solution (0.05 mol) was added to a solution of 2,5-dimethylfuran (4.8 g, 0.05 mol) in ethanol (600 ml required to maintain solution) and stirred at 0 °C for 3 h. The solution was diluted and then set aside overnight when the orange oil solidified and was filtered off (7.0 g). It was recrystallised from benzene–light petroleum (b.p. 60–80 °C) to yield *hexane-2,3,5-trione 3-(2,4-dinitrophenylhydrazone)* (see below), m.p. 132 °C, $M^+ = m/e$ 308; ν_{\max} 1 685 cm^{-1} (no NH or OH absorption) (Found: C, 47.0; H, 4.0; N, 17.9. $\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}_6$ requires C, 46.8; H, 3.9; N, 18.2%).

Reaction of 2,5-Dimethylfuran with 2,4-Dinitrobenzenediazonium Fluoroborate in Acetic Anhydride in the Presence of an Excess of Sodium Acetate.—2,5-Dimethylfuran (0.59 g) was added to a solution of sodium acetate (5 g) in acetic anhydride (10 ml) followed by 2,4-dinitrobenzenediazonium fluoroborate (1.68 g). The mixture was stirred for 2 h, cooled in ice, and poured into water (50 ml); the mixture was stirred vigorously and solid sodium hydrogen carbonate was added to it until the pH was 6.5. The precipitate which formed was filtered off, washed with water, and dried (0.96 g, 50%). Recrystallisation from aqueous ethanol yielded *hexane-2,3,5-trione 3-(2,4-dinitrophenylhydrazone)*, m.p. 138 °C; m/e (M^+) 308; $\delta(\text{CDCl}_3)$ 10–11 (1 H, br), 8.92 (3 H, m), 2.35 (3 H, s), 2.55 (3 H, s), 3.9 (2 H, s); ν_{\max} 1 690 (C=O) (Found: C, 46.8; H, 3.8; N, 18.2%. $\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}_6$ requires C, 46.8; H, 3.9; N, 18.2%).

Reaction of 2-Methylfuran with 2,4-Dinitrobenzenediazonium Fluoroborate in Acetic Anhydride and an Excess of Sodium Acetate.—2-Methylfuran (0.49 g) was added to a solution of sodium acetate (5 g) in acetic anhydride (20 ml).

2,4-Dinitrobenzenediazonium fluoroborate (1.68 g) was then added to the mixture which was then stirred for 2 h, cooled in ice, and poured into water (50 ml); this was then stirred vigorously and solid sodium hydrogen carbonate was added until the pH was 6.5. Granules of product were filtered off, washed with water, and dried (1.1 g, 78%). 5-(2,4-Dinitrophenyl)-2-methylfuran was purified by passage down a short, silica column (chloroform) and evaporation of the yellow fraction (0.65 g), m.p. 98 °C; $M^+ = m/e$ 248; $\delta(\text{CDCl}_3)$ 8.48 (1 H, d, 2 Hz), 8.38 (1 H, dd, 2 and 9 Hz), 7.95 (1 H, d, 9 Hz), 6.83 (1 H, d, 3.7 Hz), 6.20 (1 H, d, 3.7 Hz), and 2.38 (3 H, s); the i.r. spectra showed an absence of C=O, OH, and NH groups (Found: C, 53.3; H, 3.1; N, 11.4. $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_5$ requires C, 53.0; H, 3.6; N, 11.2%). The same compound was obtained in lower yield using an equimolar quantity of sodium acetate.

The Reaction of 2,4-Dinitrobenzenediazonium Sulphate with Benzo[b]furan in Acetic Acid Solution.—A solution of benzo[b]furan¹⁵ (1.18 g, 0.01 mol) in glacial acetic acid (40 ml) was added to the freshly prepared solution of 2,4-dinitrobenzenediazonium sulphate (0.01 mol). The reaction was stirred at room temperature for 24 h. An orange–red precipitate was filtered off, washed with water, and chromatographed on an alumina column. The first fraction eluted by benzene gave a yellow solid on evaporation of the solvent, and this was recrystallised from benzene–light petroleum to give 3-(2,4-dinitrophenyl)benzo[b]furan as fine yellow needles (0.75 g, 26%), m.p. 138 °C; $M^+ = m/e$ 284 (Found: C, 59.2; H, 2.7; N, 9.7. $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_5$ requires C, 59.2; H, 2.8; N, 9.9%); the i.r. spectrum showed the absence of OH or C=O groups; λ_{\max} 366 nm ($\epsilon = 1.7 \times 10^4$). A further red fraction eluted by chloroform gave an orange yellow solid. This was recrystallised from benzene–light petroleum to give 2,3-bis-(2,4-dinitrophenyl)benzo[b]furan, m.p. 100 °C; $M^+ = m/e$ 450; the i.r. spectrum showed the absence of OH or C=O groups; λ_{\max} 358 nm ($\epsilon = 1.6 \times 10^4$) (Found: C, 53.1; H, 2.4; N, 12.1. $\text{C}_{20}\text{H}_{10}\text{N}_4\text{O}_9$ requires C, 53.3; H, 2.2; N, 12.5%).

The Reaction of Benzo[b]furan with 2,4-Dinitrobenzenediazonium Fluoroborate in Acetic Anhydride Solution.—Identical products to the above reaction were obtained when the reaction was repeated using the diazonium fluoroborate in acetic anhydride with 1 mol. equiv. of sodium acetate. An excess of acetate simply reduced the yield.

The Reaction of 2-Methylbenzo[b]furan with 2,4-Dinitrobenzenediazonium Sulphate in Acetic Acid Solution.—A solution of 2-methylbenzo[b]furan¹⁶ (1.32 g, 0.01 mol) in glacial acetic acid (30 ml) was added to a freshly prepared solution of 2,4-dinitrobenzenediazonium sulphate (0.01 mol). A further 30 ml of glacial acetic acid was added to make the reaction homogeneous. After being stirred at room temperature for 44 h, the solution was diluted with cold water and extracted with chloroform. The chloroform extract was washed successively with water, sodium hydrogen carbonate solution, and water, before being dried over Na_2SO_4 . The red oil obtained after evaporation of the solvent was chromatographed on an alumina column. The first colourless fraction eluted by benzene was unchanged 2-methylbenzo[b]furan (0.27 g). The next yellow fraction eluted by benzene gave 3-(2,4-dinitrophenyl)-2-methylbenzo[b]furan as a viscous oil (0.55 g, 23%), b.p.

¹⁵ W. Burgstahler and L. R. Worden, *Org. Synthesis*, 1966, **46**, 28.

¹⁶ E. Baciocchi, S. Clementi, and G. V. Sebastiani, *J.C.S. Perkin II*, 1974, 1882.

260—265 °C/1 mmHg; $M^+ = m/e$ 298 (Found: C, 60.2; H, 3.4; N, 9.2. $C_{15}H_{10}N_2O_5$ requires C, 60.4; H, 3.4; N, 9.4%); ν_{\max} 1600, 1520, 1335, 900, 830, and 740 cm^{-1} ; 1H n.m.r. $\delta(CDCl_3)$ 2.37 (3 H, s), 7—7.7, and 7.9—9.0 (7 H, complex multiplets). The next fraction eluted by benzene gave 2,4-dinitrobenzeneazo-3'-(2'-methylbenzo[b]furan) as an orange yellow solid (0.2 g, 8%), m.p. 189 °C, $M^+ = m/e$ 326 (Found: C, 55.0; H, 3.0; N, 17.1. $C_{15}H_{10}N_4O_5$ requires C, 55.2; H, 3.1; N, 17.2%), i.r. spectrum showed an absence of NH absorption; λ_{\max} 356 nm. Further elution by chloroform gave a resinous red solid, which was difficult to purify.

Reaction of 2,5-Diphenylfuran with 2,4-Dinitrobenzene-diazonium Sulphate.—The diazonium sulphate solution (0.05 mol) was added to a solution of 2,5-diphenylfuran¹⁷ (11 g, 0.05 mol) in glacial acetic acid (400 ml). The solution immediately became deep green and some precipitation of 2,5-diphenylfuran occurred; this was corrected by the addition of more glacial acetic acid. After 1 h the colour gradually turned to a dark red; the mixture was stirred for 70 h. Although a slight precipitate had formed, the

¹⁷ R. E. Lutz and R. J. Rowlett, *J. Amer. Chem. Soc.*, 1948, **70**, 1359.

mixture was extracted with chloroform without filtration and the extract was washed with aqueous sodium hydrogen carbonate solution until no longer acidic and then water; it was then dried over magnesium sulphate. Evaporation of the solvent gave a dark red oil (16 g) which was chromatographed on a silica column. Benzene eluted a yellow fraction which gave a red oil (11 g). This was purified using a further silica column and recrystallised from benzene–light petroleum (b.p. 70—80 °C) to yield 3-(2,4-dinitrophenyl)-2,5-diphenylfuran as orange needles, m.p. 165 °C, $M^+ = m/e$ 386 (Found: C, 68.3; H, 3.7; N, 7.0. $C_{22}H_{10}N_2O_5$ requires C, 68.4; H, 3.6; N, 7.3%); the i.r. spectrum showed no C=O absorption; λ_{\max} 322 ($\epsilon = 2.90 \times 10^4$) and 376 nm (1.74×10^4). A benzene–chloroform mixture next eluted 3,4-bis-(2,4-dinitrophenyl)-2,5-diphenylfuran as an orange solid (1.1 g), m.p. 114 °C, $M^+ = m/e$ 552 (Found: C, 59.4; H, 2.9; N, 9.8. $C_{28}H_{16}N_4O_6$ requires C, 60.9; H, 2.9; N, 10.2%), λ_{\max} 305 ($\epsilon = 2.04 \times 10^4$) and 380 nm (8.8×10^3). Finally chloroform eluted a small amount of a red oil (0.2 g) which could not be purified but appeared to contain 2,4-dinitrobenzeneazo-3'-(2',5'-diphenylfuran) (m/e 414.0963. $C_{22}H_{15}N_4O_5$ requires m/e 414.0964).

[7/982 Received, 9th June, 1977]