

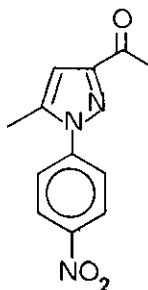
THE EASTMAN'S REACTION REVISITED

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In Memoriam of Professor Tetsuji Kametani

Abstract - Several previously unknown 3-acyl-5-alkyl-1-arylpyrazoles, differently functionalized in the 3- and 5- side chains, have been synthesized from appropriate 2,5-disubstituted furans by their reaction with p-nitrobenzenediazonium salts.

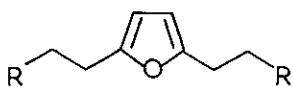
In 1948 Eastman and Detert¹ reported that 2,5-dimethylfuran reacts with p-nitrobenzenediazonium chloride in cold aqueous alcoholic solution and an excess of potassium acetate to give, after acidic hydrolysis, 3-acetyl-5-methyl-1-(4-nitrophenyl)pyrazole 1. After this observation the reaction has received hardly any further attention;² and, to the best of our knowledge, only Tedder *et al.*³ repeated and reproduced the same reaction. No other 2,5-disubstituted furyl derivatives different from 2,5-dimethylfuran have been tested.



1

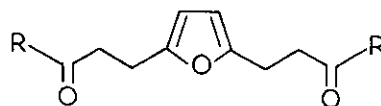
However, the method could show great use in order to prepare functionalized derivatives not easily available by classical synthetic methods⁴ involving ring construction and/or transformation of the pyrazole moiety. Thus, investigation of the afore-mentioned reaction with differently substituted 2,5-furyl derivatives appears to be convenient.

Three kinds of compounds have been chosen for this study: The reaction of derivatives 2 represents the extension of the procedure to higher homologues of 2,5-dimethylfuran; while, on the other hand, reactions of compounds 3 will permit the synthesis of the highly functionalized pyrazoles 4. Finally, the reaction of the unsymmetrical derivative 5 is interesting in connection with the regioselectivity of the process.⁵



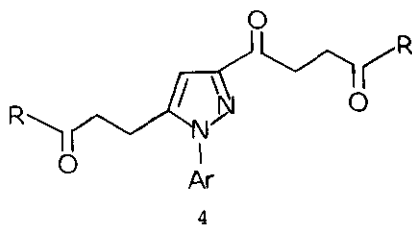
2

a) R = C₆H₅; b) R = OAc

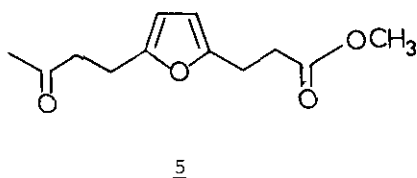


3

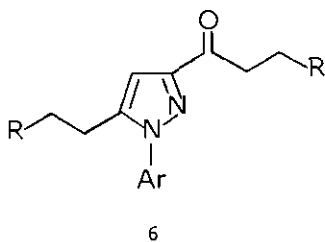
a) R = CH₃; b) R = OCH₃; c) R = C₆H₅



a) R = CH₃; b) R = OCH₃; c) R = C₆H₅



Following Eastman's conditions compounds 2a and 3a gave the expected pyrazoles 6a and 4a in 70% and 60% yields respectively, whereas compound 3c did not react, probably as a consequence of its low solubility



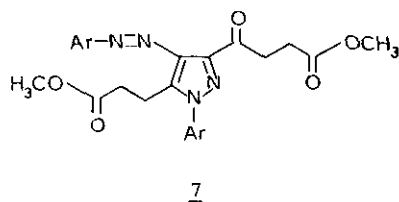
a) R = C₆H₅; b) R = OAc

in the reaction medium, and compound 2b gave a complex mixture of unidentified products. Nevertheless, the desired pyrazoles 4c and 6b can be obtained in 70% and 60% yields respectively if 4-nitrobenzenediazonium tetrafluoroborate in dioxane⁶ is used instead of the in situ prepared

p-nitrobenzenediazonium chloride. In our opinion, this procedure constitutes a valuable alternative to the original Eastman's one.

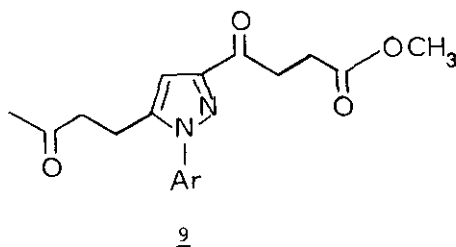
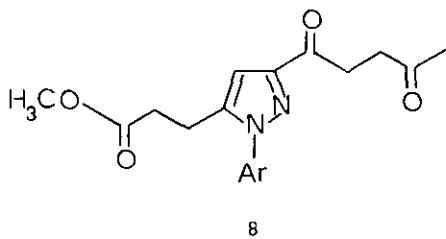
Conversely, the reaction of diester 3b with one equivalent of 4-nitrobenzenediazonium chloride (0°C, 3h) gives rise to a mixture of pyrazoles 4b and 7 in 20% and 40% yields, respectively.

However, the use of two equivalents of the diazonium salt and prolonged reaction times improve the yield of the desired pyrazole 4b up to 40% and 70%, respectively. It is worth

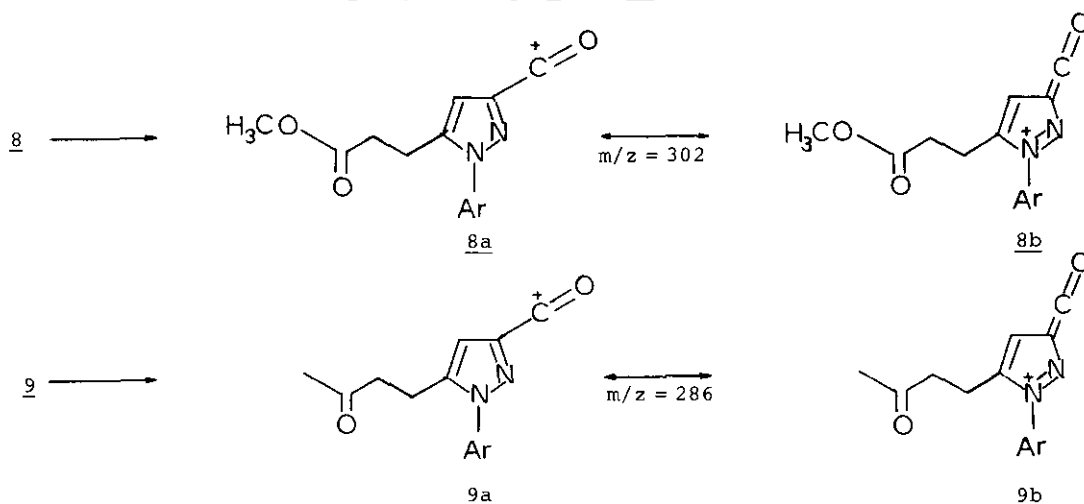


mentioning that the same results were obtained by using the tetrafluoroborate salt instead of the diazonium chloride.

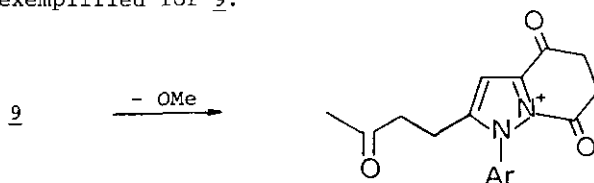
Reaction of compound 5 under Eastman's conditions gave a mixture of the structurally isomeric pyrazoles 8 and 9 in 30% and 55% yields respectively.



Structural assignation of both regioisomers was possible by the following way: The mass spectrum of pyrazole 8 contains the base peak at m/z 308. This fragment is formed by cleavage of the C-C bond adjacent to the carbonyl in position 3 of the heterocyclic moiety, with elimination of $\text{CH}_2\text{-CH}_2\text{-CO-CH}_3$ ($\underline{8} \longrightarrow \underline{8a} \longleftrightarrow \underline{8b}$). In a similar fashion, the base peak of the mass spectrum of structure 9 appears at m/z 286, with elimination of $\text{CH}_2\text{-CH}_2\text{-CO-OCH}_3$ ($\underline{9} \longrightarrow \underline{9a} \longleftrightarrow \underline{9b}$).



Furthermore, pyrazole 9 shows a much more intense M^+-31 than 8 (16.2 vs. 0.2%); whereas structure 8 shows a M^+-15 , which is not present in the spectrum of 9. These facts can be easily accounted for by the assistance of the pyridine-like nitrogen lone electron pair to the loss of CH_3O and CH_3 , respectively, forming a six-membered ring, as exemplified for 9:



In conclusion, Eastman's method constitutes an interesting and general procedure for the synthesis of functionalized pyrazoles not easily available by classical pyrazole synthesis.

ACKNOWLEDGEMENT

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EXPERIMENTAL PART

The evolution of the reactions was monitored by tlc, using silica gel plates 60 (Merck), grade II-III in the Brockmann scale. Melting points were taken in capillary tube using a Büchi 510 apparatus and are uncorrected. Ir spectra were recorded on a Perkin-Elmer 257 spectrophotometer. ^1H -Nmr and ^{13}C -nmr spectra were obtained using a Varian XL300 spectrometer at 300 MHz. Mass spectra were obtained using a MAT-711 spectrometer at 100 eV. p-Nitrobenzenediazonium tetrafluoroborate⁶ and furan derivatives⁵ were prepared following previously described procedures. Column chromatographies were carried out on silica gel 60 Merck.

REACTIONS WITH p-NITROBENZENEDIAZONIUM CHLORIDE. GENERAL PROCEDURE

To an ice-cold solution of the corresponding furan (1.97 mmol) and sodium acetate (494 mg, 6 mmol) in ethanol (10 ml) was added all at once the diazonium salt solution prepared from p-nitroaniline (276 mg, 2 mmol) in water (6 ml), 10% hydrochloric acid (1.2 ml), and sodium nitrite (138 mg, 2 mmol). The reaction mixture was kept in ice for 3 h and then poured into twice the volume of water, extracted with methylene chloride and dried on anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, a red oil was obtained which was dissolved in ethanol (5 ml). After addition of 6N hydrochloric acid (0.6 ml), the solution was refluxed for 5 min and then poured into water (5 ml), extracted with methylene chloride and dried on anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the crude product was chromatographed on a silica gel column, using a mixture of hexane - ethyl acetate (1:1) as eluent.

3-(1,4-Dioxopentyl)-5-(3-oxobutyl)-1-(4-nitrophenyl)pyrazole, 4a

Yield: 60%. mp 89-90°C (hexane-ethyl acetate). Ir(KBr): 1715, 1670, 1610, 1590, 1515, 1490 cm^{-1} . ^1H -Nmr(CDCl_3): δ 8.42, 8.38 (2H, d, $\text{H}_{3\text{nitrophenyl}}$, $J=8.2$); 7.80, 7.76 (2H, d, $\text{H}_{2\text{nitrophenyl}}$, $J=8.2$); 6.71 (1H, s, $\text{H}_{4\text{pyrazole}}$); 3.32 (2H, t, $-\text{CH}_2\text{-pyrazole}$, $J=5.2$); 2.99 - 2.82 (6H, m, $\text{CH}_2\text{-CO}$); 2.24 (3H, s, CH_3CO); 2.18 (3H, s, CH_3CO). ^{13}C -Nmr(CDCl_3): δ 206.71 (CO); 205.58 (CO); 193.99 (CO-pyrazole); 151.18 ($\text{C}_{3\text{nitrophenyl}}$); 146.62 ($\text{C}_{1\text{nitrophenyl}}$); 144.65 ($\text{C}_5\text{pyrazole}$); 143.75 ($\text{C}_3\text{pyrazole}$); 125.34 ($\text{C}_{4\text{nitrophenyl}}$); 124.41 ($\text{C}_{2\text{nitrophenyl}}$); 105.95 ($\text{C}_4\text{pyrazole}$); 41.26 (CO- $\text{CH}_2\text{-CH}_2\text{-pyrazole}$); 36.43, 32.10, 29.46 (CO- $\text{CH}_2\text{-CH}_2\text{-CO}$, $\text{CH}_2\text{-pyrazole}$); 19.95 (CH_3CO). Ms: m/z 357 (M^+ , 13.3); 314 ($\text{M}^+ - \text{MeCO}$, 100); 286 ($\text{M}^+ - \text{CH}_2\text{CH}_2\text{COMe}$, 93.3); 240 (286 - NO_2 , 17.7); 216 (314 - $\text{CH}_2=\text{CH}_2$ - $\text{CH}_2=\text{CH-CO-CH}_3$, 15.4).

1-(4-Nitrophenyl)-5-(2-phenylethyl)-3-(3-phenyl-1-oxopropyl)pyrazole, 6a

Yield: 70%. mp 84-85°C (hexane-ethyl acetate). Ir(KBr): 1690, 1600, 1530, 1500 cm^{-1} . $^1\text{H-Nmr}(\text{CDCl}_3)$: δ 8.27 (2H, d, $\text{H}^3_{\text{nitrophenyl}}$, $J=9.0$); 7.49 (2H, d, $\text{H}^2_{\text{nitrophenyl}}$, $J=9.0$); 7.27 - 7.16 (10H, m, phenyl); 6.86 (1H, s, $\text{H}^4_{\text{pyrazole}}$); 3.38 (2H, t, CH_2 -pyrazole, $J=5.9$); 3.09 - 2.90 (6H, m, CH_2). $^{13}\text{C-Nmr}(\text{CDCl}_3)$: δ 194.93 (CO); 151.62 ($\text{C}^4_{\text{nitrophenyl}}$); 146.67 ($\text{C}^1_{\text{nitrophenyl}}$); 145.09 ($\text{C}^5_{\text{pyrazole}}$); 143.84 ($\text{C}^3_{\text{pyrazole}}$); 141.00, 139.40 ($\text{C}^1_{\text{phenyl}}$); 128.38, 128.01 ($\text{C}^3_{\text{phenyl}}$); 128.14 ($\text{C}^4, \text{C}^1_{\text{phenyl}}$); 126.37, 125.72 ($\text{C}^2_{\text{phenyl}}$); 125.34 ($\text{C}^3_{\text{nitrophenyl}}$); 124.41 ($\text{C}^2_{\text{nitrophenyl}}$); 106.82 ($\text{C}^4_{\text{pyrazole}}$); 40.01 (CH_2CO); 34.69 ($\text{CO-CH}_2\text{-CH}_2\text{-Ph}$); 29.64, 28.12 ($-\text{CH}_2-$). Ms: m/z 425 (M^+ , 100); 397 ($\text{M}^+ - \text{CH}_2 = \text{CH}_2$, 50.3); 320 ($\text{M}^+ - \text{PhCH}_2\text{CH}_2$, 25.1); 293 ($297 - \text{CH}_2 = \text{CHPh}$, 75.2); 292 ($320 - \text{CO}$, 15.4).

REACTION OF 2-(2-METHOXYCARBONYLETHYL)-5-(3-OXOPROPYL)FURAN 5 WITH p-NITRO-BENZENEDIAZONIUM CHLORIDE

The same general procedure as for the syntheses of compounds 4a and 6a was followed. The crude product was chromatographed on a silica gel column, using a mixture of hexane-ethyl ether (1:10) as eluent.

3-(1,4-Dioxopentyl)-5-(2-methoxycarbonylethyl)-1-(4-nitrophenyl)pyrazole, 8

Yield: 30%. mp 70-71°C (hexane-ethyl acetate). Ir(KBr): 1720, 1680, 1610, 1590, 1530, 1510 cm^{-1} . $^1\text{H-Nmr}(\text{CDCl}_3)$: δ 8.40, 8.37 (2H, d, $\text{H}^3_{\text{nitrophenyl}}$, $J=9.0$); 7.76, 7.73 (2H, d, $\text{H}^2_{\text{nitrophenyl}}$, $J=9.0$); 6.75 (1H, s, $\text{H}^4_{\text{pyrazole}}$); 3.66 (3H, s, OMe); 3.31 (2H, t, $-\text{CH}_2$ -pyrazole, $J=5.9$); 3.04 (2H, t, $\text{CH}_2\text{-CO-pyrazole}$, $J=7.0$); 2.86 (2H, t, CH_2CO , $J=6.0$); 2.69 (2H, t, $\text{CH}_2\text{-COOMe}$, $J=7.0$); 2.22 (3H, s, CH_3CO). Ms: m/z 373 (M^+ , 32.1); 358 ($\text{M}^+ - 15$, 3.3); 342 ($\text{M}^+ - \text{OMe}$, 0.2); 330 ($\text{M}^+ - \text{CH}_3\text{CO}$, 13.6); 314 ($342 - \text{CO}$, 18.7); 302 ($\text{M}^+ - \text{CH}_2\text{CH}_2\text{COCH}_3$, 100); 298 ($330 - \text{MeOH}$, 5.4); 256 ($302 - \text{NO}_2$, 7.0); 216 ($314 - \text{CH}_2 = \text{CH}_2 - \text{CH}_2 = \text{CH-COMe}$, 8.8).

3-(3-Methoxycarbonyl-1-oxopropyl)-1-(4-nitrophenyl)-5-(3-oxopropyl)pyrazole 9

Yield: 55%. mp 67-68 °C (hexane-ethyl acetate). Ir(CCl_4): 1720, 1680, 1610, 1590, 1530, 1510 cm^{-1} . $^1\text{H-Nmr}(\text{CDCl}_3)$: δ 8.40, 8.37 (2H, d, $\text{H}^3_{\text{nitrophenyl}}$, $J=9.0$); 7.79, 7.76 (2H, d, $\text{H}^2_{\text{nitrophenyl}}$, $J=9.0$); 6.72 (1H, s, $\text{H}^4_{\text{pyrazole}}$); 3.67 (3H, s, OMe); 3.36 (2H, t, $-\text{CH}_2$ -pyrazole, $J=5.9$); 2.98 (2H, t, $\text{CH}_2\text{-CO-pyrazole}$, $J=6.8$); 2.87 (2H, t, CH_2CO , $J=6.0$); 2.73 (2H, t, $\text{CH}_2\text{-COOMe}$, $J=6.0$); 2.17 (3H, s, CH_3CO). Ms: m/z 373 (M^+ , 4.2); 342 ($\text{M}^+ - \text{OMe}$, 16.2); 330 ($\text{M}^+ - \text{CH}_3\text{CO}$, 66.5); 314 ($342 - \text{CO}$, 4.9); 302 ($\text{M}^+ - \text{CH}_2\text{CH}_2\text{COCH}_3$, 2.7); 298 ($330 - \text{MeOH}$, 65.6); 286 ($\text{M}^+ - \text{CH}_2\text{CH}_2\text{COOMe}$, 100); 256 ($302 - \text{NO}_2$, 1.2); 240 ($314 - \text{NO}_2$, 27.5); 216 ($330 - \text{CH}_2 = \text{CH}_2 - \text{CH}_2 = \text{CH-COOMe}$, 10.0).

REACTION OF 2,5-DI(2-METHOXYCARBONYLETHYL)FURAN 3b WITH p-NITROBENZENEDIAZONIUM CHLORIDE

To an ice-cold solution of 2,5-di-(2-methoxycarbonylethyl)furan 3b (260 mg, 1.08 mmol) and sodium acetate (290 mg, 3.54 mmol) in ethanol (13 ml) was added all at once the diazonium salt solution prepared from p-nitroaniline (152 mg, 1.1 mmol or 304 mg, 2.2 mmol) in water (3.3 ml or 6.6 ml), 10% hydrochloric acid (0.7 ml or 1.4 ml), and sodium nitrite (76 mg, 1.1 mmol or 152 mg, 2.2 mmol), as described for the synthesis of compounds 4a and 6a. The reaction mixture was kept in ice for the time shown in the following table, and then poured into twice the volume of water, extracted with methylene chloride and dried on anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, a red oil was obtained which was dissolved in ethanol (8 ml). After addition of 6N hydrochloric acid (0.8 ml), the solution was refluxed for 5 min and then poured into water (10 ml), extracted with methylene chloride and dried on anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the crude product was chromatographed on a silica gel column, using a mixture of hexane-ethyl acetate (1:1) as eluent.

Molar proportion furan/diazonium salt	Reaction time (h)	Yield (%)	
		<u>7</u>	<u>4b</u>
1:1	3	40	20
1:1	6	--	70
1:2	3	45	40
1:2	6	--	40

5-(2-Methoxycarbonylethyl)-1-(4-nitrophenyl)-4-(4-nitrophenylazo)-3-(3-methoxycarbonyl-1-oxopropyl)pyrazole, 7

mp 156-157°C (hexane-ethyl acetate). Ir(KBr): 1740, 1690, 1610, 1590, 1520 cm⁻¹. ¹H-Nmr(CDCl₃): δ 8.49, 8.46 (2H, d, H₃nitrophenyl, J=8.7); 8.39, 8.36 (2H, d, H₃nitrophenylazo, J=8.8); 8.02, 7.99 (2H, d, H₂nitrophenyl, J=8.7); 7.78, 7.75 (2H, d, H₂nitrophenylazo, J=8.8); 3.72 (3H, s, OMe); 3.64 (3H, s, OMe); 3.50 (2H, t, CH₂-pyrazole, J=6.6); 3.29 (2H, t, CH₂CO, J=7.7); 2.82 (2H, t, CO-CH₂-CH₂-COOMe, J=6.6); 2.73 (2H, t, CH₂-COOMe, J=7.9). ¹³C-Nmr(CDCl₃): δ 193.91 (CO); 172.91, 171.63 (COO); 155.77 (C₁nitrophenylazo); 148.60 (C₄nitrophenylazo); 147.80 (C₄nitrophenyl); 146.70 (C₁nitrophenyl); 142.92 (C₃pyrazole); 136.69, 136.39 (C₄, C₅pyrazole); 126.60, 124.85 (C₂, C₃nitrophenylazo); 124.64, 123.06 (C₂, C₃nitrophenyl); 51.85, 51.69 (CH₃O); 35.76 (CH₂CO); 31.89 (CH₂-CH₂-pyrazole); 27.45 (CH₂-CH₂CO); 21.42 (CH₂-pyrazole). Ms: m/z 538 (M⁺, 33.3); 521 (M⁺-OH, 5.4);

507 ($M^+ - OMe$, 15.1); 479 (507-CO, 12.1); 465 (507 - $CH_2=CO$, 100); 433 (479 - NO_2 , 2.6); 423 (479 - $CH_2=CH_2 - CO$, 6.1); 419 (465 - NO_2 , 36.4); 416 ($M^+ - C_6H_5NO_2$).

5-(2-Methoxycarbonylethyl)-3-(3-methoxycarbonyl-1-oxopropyl)-1-(4-nitrophenyl)-pyrazole, 4b

mp 123-124°C (ethyl acetate). Ir(KBr): 1730, 1690, 1600, 1530, 1500 cm^{-1} . 1H -Nmr($CDCl_3$): δ 8.44, 8.39 (2H, d, $H_{3nitrophenyl}$, $J=9.4$); 7.80, 7.75 (2H, d, $H_{2nitrophenyl}$); 6.69 (1H, s, $H_{4pyrazole}$); 3.69 (3H, s, OMe); 3.68 (3H, s, OMe); 3.39 (2H, t, CH_2 -pyrazole, $J=6.0$); 3.05 (2H, t, CH_2CO , $J=8.0$); 2.79 - 2.69 (4H, dt, $J=6.0$ and 8.0, 2 x CH_2COOMe). ^{13}C -Nmr($CDCl_3$): δ 193.83 (CO); 173.10, 171.82 (COO); 151.51 ($C_{4nitrophenyl}$); 147.05 ($C_{1nitrophenyl}$); 144.26 ($C_{5pyrazole}$); 143.89 ($C_{3pyrazole}$); 125.62, 124.75 ($C_{2,C3nitropyrazole}$); 106.39 ($C_{4pyrazole}$); 51.89, 51.62 (CH_3COO); 33.31 (CH_2CO); 32.30 (CH_2CH_2 -pyrazole); 27.57 (CH_2 -pyrazole); 21.62 (CH_2CH_2CO). Ms: m/z 389 (M^+ , 35.5); 358 ($M^+ - OMe$, 11.8); 330 (358-CO, 5.9); 302 ($M^+ - CH_2CH_2COOMe$, 100); 298 (330-MeOH, 23.5); 256 (302- NO_2 , 5.9); 216 (330 - $CH_2=CH_2 - CH_2=CHCOOMe$, 3.2).

REACTIONS WITH P-NITROBENZENEDIAZONIUM FLUOROBORATE. GENERAL PROCEDURE

4-Nitrobenzenediazonium fluoroborate (64 mg, 0.27 mmol) was added to a solution of the corresponding furan (0.27 mmol) and sodium acetate (216 mg, 2.6 mmol) in dioxan (2 ml). The reaction mixture was stirred at room temperature for 20 h (4c) or 5 h (6b) and then poured into twice the volume of water, extracted with methylene chloride and dried on anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the crude product was chromatographed on a silica gel column, using a mixture of hexane-ethyl acetate (1:1) as eluent.

5-(2-Benzoylethyl)-3-(3-benzoyl-1-oxopropyl)-1-(4-nitrophenyl)pyrazole, 4c

Yield: 70%. bp 130°C, 0.5 mmHg (Kugelrohr distillation). Ir(CCl_4): 1680, 1690, 1610, 1600, 1520 cm^{-1} . 1H -Nmr($CDCl_3$): δ 8.38, 8.35 (2H, d, $H_{3nitrophenyl}$, $J=9.1$); 7.99 - 7.90 (4H, m, $H_{2benzoyl}$); 7.83, 7.80 (2H, d, $H_{2nitrophenyl}$, $J=9.1$); 7.58 - 7.51 (2H, m, $H_{3benzoyl}$); 7.47 - 7.40 (4H, m, $H_{3benzoyl}$); 6.79 (1H, s, $H_{4pyrazole}$); 3.51 - 3.36 (6H, m, CH_2); 3.16 (2H, t, CH_2 -pyrazole, $J=6.9$). ^{13}C -Nmr($CDCl_3$): δ 198.32, 197.15, 194.49 (CO); 151.60 ($C_{4nitrophenyl}$); 146.89 ($C_{1nitrophenyl}$); 144.94 ($C_{5pyrazole}$); 144.02 ($C_{3pyrazole}$); 136.49, 135.95 ($C_{1benzoyl}$); 133.43, 132.93 ($C_{4benzoyl}$); 128.59, 128.38 ($C_{2benzoyl}$); 127.90, 127.79 ($C_{3benzoyl}$); 125.57 ($C_{1nitrophenyl}$); 124.69 ($C_{2nitrophenyl}$); 106.41 ($C_{4pyrazole}$); 36.82 (CO- CH_2-CH_2 -pyrazole); 32.46, 32.26 (CO- CH_2-CH_2-CO); 20.60 (CH_2 -pyrazole).

1-(4-Nitrophenyl)-3-(4-acetoxy-1-oxobutyl)-5-(3-acetoxypentyl)pyrazole, 6b

Yield: 60%. bp 110°C, 0.5 mmHg (Kugelrohr distillation). Ir(KBr): 1740, 1710, 1680, 1690, 1610, 1600, 1520 cm⁻¹. ¹H-Nmr(CDCl₃): δ 8.43, 8.40 (2H, d, H³nitrophenyl, J=9.0); 7.77, 7.74 (2H, d, H²nitrophenyl, J=9.0); 6.82 (1H, s, H⁴pyrazole); 4.14 (2H, t, CH₂OAc, J=6.0); 4.10 (2H, t, CH₂OAc, J=6.0); 3.13 (2H, t, CH₂-pyrazole, J=7.5); 2.86 (2H, t, CH₂CO, J=7.5); 2.10 - 1.99 (2H, m, CH₂); 2.01 (3H, s, CH₃CO); 2.00 (3H, s, CH₃CO). ¹³C-Nmr(CDCl₃): δ 194.84 (CO); 170.78, 170.54 (COO); 151.66 (C⁴nitrophenyl); 146.88 (C¹nitrophenyl); 144.77 (C⁵pyrazole); 143.87 (C³pyrazole); 125.38 (C³nitrophenyl); 124.64 (C²nitrophenyl); 106.66 (C⁴nitrophenyl); 63.54, 62.68 (CH₂OCOME); 34.77 (CH₂CO); 27.28 (CH₂CH₂-pyrazole); 23.01, 22.76 (CH₂-pyrazole, CH₂-CH₂CO); 20.67, 20.57 (CH₃COO).

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4. See: a) M. E. Grimmet, "Comprehensive Organic Chemistry", Vol.4, p. 400, P. G. Sammes, Ed., Wiley-Interscience, 1971.
 - b) A. N. Kost and I. I. Grandberg, Adv. Het. Chem., 1966, 6, 347.
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