Competitive [3+2] and [4+2] Cycloaddition Reactions of 2-Furaldehyde Phenylhydrazone with Alkenes[1]

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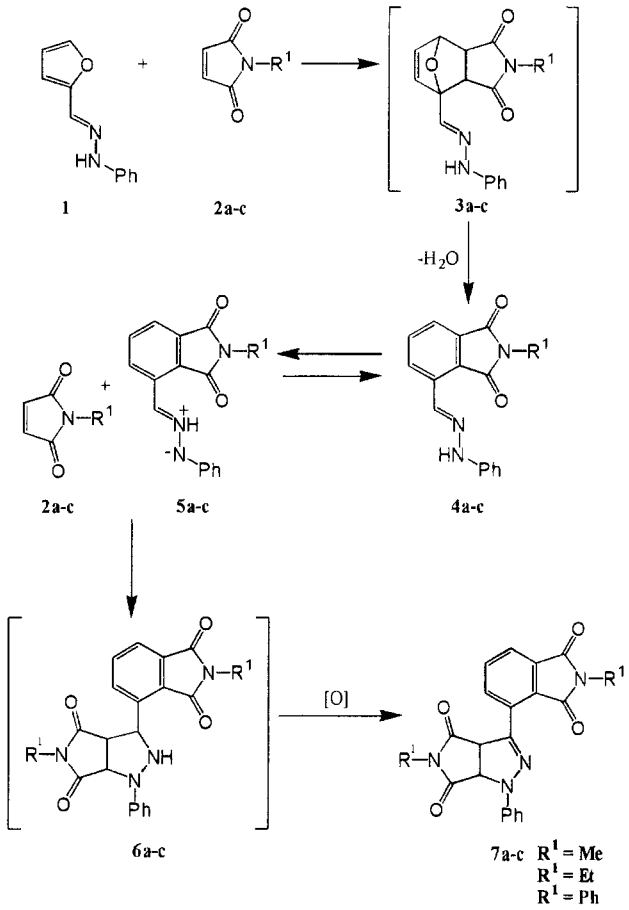
Maleimides react with 2-furaldehyde phenylhydrazone **1** at the furan ring to give 4-(phenylhydrazono)methyl-1*H*-isoindole-1,3(2*H*)-diones when equimolar mixtures are refluxed in benzene for shorter reaction times. Excess maleimides and longer reaction times give mixtures of 4-(phenylhydrazono)methyl-1*H*-isoindole-1,3(2*H*)-diones and 3-(1,3-dihydro-1,3-dioxo-4-isoindolyl)-1,6a-dihydropyrrolo[3,4-*c*]pyrazolo-4,6(3a*H*,5*H*)-diones resulting from [4+2] and [3+2] double-cycloaddition. Reactions of **1** with dimethyl acetylene dicarboxylate give the double-cycloaddition product dimethyl-3[4-hydroxy-2,3-bis(methoxycarbonyl)phenyl]-1-phenylpyrazole-4,5-dicarboxylate. Methyl acrylate and acrylonitrile gives only the [3+2] cycloaddition products, 3-(2-furyl)-1-phenyl-4,5-dihydropyrazole-4-carboxylic methyl ester and 3-(2-furyl)-1-phenyl-4,5-dihydropyrazole-4-carbonitrile, respectively.

Diels–Alder-type cycloadditions of the furan ring are well known reactions,[2] and the dienophilic activity of the furan ring can be enhanced by some substituents, like acetals[3] and amines.[4] However, *N,N*-dimethylhydrazone of 2-furaldehyde is known to react with two moles of methyl propiolate to give dimethyl-2-dimethylaminopyridine-3,5-dicarboxylate via a double conjugate addition of methyl propiolate and subsequent elimination of dimethyl amine.[5] Diethyl azodicarboxylate reacts with the same hydrazone to give a 1 : 1 adduct via a conjugate addition on the furan ring.[5] On the other hand dimethyl acetylenedicarboxylate[6] and maleimides[7] have been found to react with *N,N*-dimethylhydrazone of 2-furaldehyde on the furan ring in the [4+2] cycloaddition. The initial cycloadducts were not isolated in these cases and concurrent cycloaromatization led to dimethyl 3-hydrazonomethylphthalate and phthalimide derivatives, respectively. Furaldehyde-*N,N*-dimethylhydrazones do not show any azadiene activity[8] towards a hetero Diels–Alder reaction, as found with common α,β-unsaturated aldehyde hydrazones. The only reaction reported of a furaldehyde derivative showing the azadiene activity is the [4+2] cycloaddition of furaldehyde oxime with acrylates and maleic anhydride.[9]

Aromatic aldehyde phenylhydrazones, such as benzaldehyde phenylhydrazone, can exist as an azomethine imine tautomeric form as well; this 1,3-dipolar species undergoes [3+2] cycloaddition with alkenes to give pyrazolidines; ready air oxidation of these compounds gives pyrazolines as products with a less rigorous exclusion of oxygen.[10] Aromatic aldehyde phenylhydrazones react with dimethyl acetylenedicarboxylate to give pyrazoline directly. Inter and intra molecular hydrazone-alkene cycloadditions[11] have been used in the preparation of a variety of fused pyrazolidines and pyrazolines. Thiophene-2-carbaldehyde phenylhydrazone and pyridine-2-carbaldehyde phenylhydrazone are also known[10] to react similarly in this [3+2] cycloaddition. It is interesting to note that 2-furaldehyde has not been utilized in these cycloadditions and one can expect phenylhydrazone to behave differently from the corresponding *N,N*-dimethylhydrazone due to the existence of the azomethine imine–hydrazone tautomerism in the phenylhydrazones. This [3+2] cycloaddition makes the 2-furaldehyde a molecule with at least two cycloaddition sites, and hence possible multiple additions; we report here on the reactivity patterns of these sites with a variety of electron-deficient alkenes and dimethyl acetylenedicarboxylate.

Results and Discussion

2-Furaldehyde phenylhydrazone (**1**) was found to react with maleimides **2a—c** when an equimolar mixture was refluxed in benzene. A TLC analysis of the reaction mixture showed the formation of a single product and complete disappearance of the starting materials after 8—12 h. The product was isolated in 59% yield from the reaction between *N*-methylmaleimide (**2a**) and **1**, which showed three adjacent protons in a benzene nucleus at δ = 7.72 (d, J = 7.3 Hz), 7.64 (dd, J = 7.3, 7.9 Hz), 8.38 (d, J = 7.9 Hz), showing a 1,2,3-trisubstitued aromatic nucleus; also, two amide carbonyl signals were seen at δ = 168.2 and 169.1 in the ^{13}C spectrum. The CI mass spectrum showed the M+1 peak at 280 as the molecular-ion peak, showing the loss of a water molecule from the primary 1 : 1 adduct. This compound was identified as the 2-methyl-4-(phenylhydrazono)methyl-1*H*-isoindole-1,3(2*H*)-dione (**4a**). Similar products, **4b** and **4c**, were isolated in 52 and 42% yields, respectively, from reactions with maleimides **2b** and **2c** as well (Scheme 1). These products resulted from the initial [4+2] cycloaddition at the furan ring to give epoxy intermediates **3a—c** and the fragmentation of this with the elimination of water to give the aromatized products. The reactions carried out with two molar amounts of *N*-methylmaleimide gave two products in



Scheme 1.

1.2 : 1 ratio after prolonged heating of 24—48 h. The major product was found to be identical to the product found in the 1 : 1 reaction, which is **4a** (25% yield), and the minor product (21% yield) showed two methyl signals at δ = 2.98 (3H, s) and 3.20 (3H, s) in the ^{1}H NMR spectrum and four carbonyl signals at δ = 167.7, 168.4, 172.4, and 172.9 in the ^{13}C NMR; the molecular ion peak at 391 supported the fact that this product arises from a 1 : 2 addition and was identified as a 3-(2,3-dihydro-2-methyl-1,3-dioxo-1*H*-isoindol-4-yl)-1,6a-dihydro-5-methylpyrrolo[3,4-*c*]pyrazolo-4,6(3a*H*,5*H*)-dione (**7a**). The formation of this product can be explained as a second mole of *N*-methyl maleimide addition to the azomethine imine tautomeric form **5a** in a [3+2] dipolar cycloaddition to give a pyrazolidine **6a**, which undergoes air oxidation to give the pyrazoline **7a**.

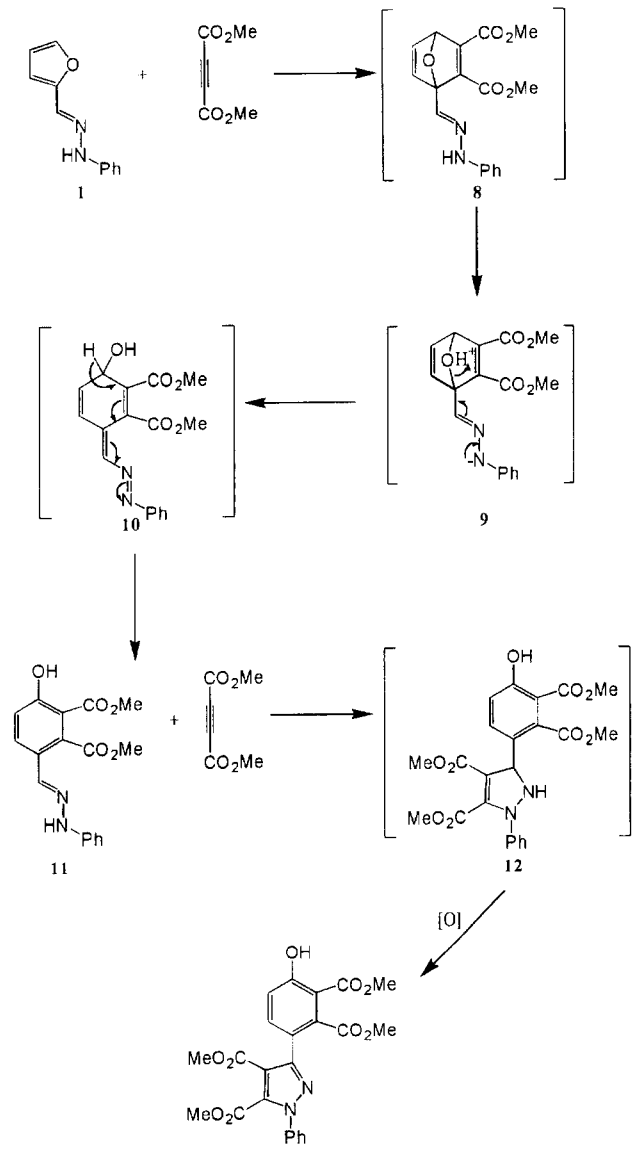
Similar results were observed with two other maleimides, **2b** and **2c**, with two equivalent reactions and longer reaction times, producing the double-cycloaddition compounds **7b** and **7c** (Scheme 1). In order to see the sequence of this double-cycloaddition compound, **4a** was heated with *N*-methylmaleimide in refluxing benzene and the NMR analysis of the reaction mixture after 12 h showed the formation of 25% of the second product **7a**, confirming that the [3+2] cycloaddition occurs at the azomethine-imine form **5a**. In attempts to achieve complete conversion of **4a** to **7a**, it was found that considerable decomposition occurred during heating in high boiling solvents, such as toluene, giving very long reaction times.

The reaction of **1** with dimethyl acetylenedicarboxylate was studied with both 1 : 1 and 1 : 2 molar ratios in refluxing benzene; in both reactions the formation of a single product **13** was observed, and was identified as the 2 : 1 cycloaddition product resulting from [4+2] and [3+2] tandem cycloaddition. Shorter reaction times and lower temperatures failed to yield the 1 : 1 adduct **11** in this reaction, suggesting that the initial adduct reacts rapidly with the more reactive acetylenic dienophile to give the pyrazoline **12**, which upon air oxidation gives the pyrazole **13**. Bighelli et al. reported that the adduct formed by the reaction of *N*,*N*-dimethylhydrazone of 2-furaldehyde with dimethyl acetylenedicarboxylate does not open directly to the phenol.[12] In our case the formation of the phenol directly could be explained as a result of transfer of the acidic hydrazone proton in the adduct **8** to oxygen in the epoxy intermediate **9**. It is very likely that **9** will rearrange to give the intermediate **10** during the ring-opening aromatization, as shown in the Scheme 2. As far as we are aware, this is the first example of such an intramolecular acidic hydrogen assisted ring opening in the oxabicycloheptadiene system. 2-Furaldehyde phenylhydrazone (**1**) reacts with methyl acrylate (**14a**) to give a 1 : 1 adduct in low yield when heated in refluxing methyl acrylate for 24 h; no evidence was found for the formation of multiple adducts when the reaction was carried out for 3 d.

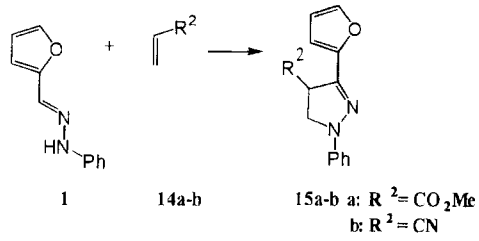
The product isolated after chromatography showed high-field ^{1}H NMR signals of the pyrazoline ring at δ = 3.38 (1H, dd, J = 6.8, 17.5 Hz), 3.63 (1H, dd, J = 13.0, 17.5 Hz) and 4.81 (1H, dd, J = 6.8, 13.0 Hz) corresponds to a three-proton ABX pattern, which has been confirmed by the COSY experiment. Regiochemistry of the addition of acrylate is similar to the pyrimidine carbaldehyde hydrazone–acrylate reactions reported by Noguchi et al.[13] The mass spectrum of **15a** showed a molecular ion peak at 270, indicating the loss of two mass units from a 1 : 1 adduct, which is typical of azomethine imine cycloaddition followed by air oxidation to give the pyrazoline **15a**. A reaction with acrylonitrile (**14b**) also gave a similar 3-(2-furyl)pyrazoline product (**15b**) (Scheme 3).

1,4-Naphthoquinone when reacted in 1 : 1 and 2 : 1 molar ratios with 2-furaldehyde phenylhydrazone in refluxing toluene for 36 h gave the 1 : 1 adduct and no multiple additions were observed in 2 : 1 molar ratios and longer reaction times, in contrast to maleimides. The reaction occurs only at the furan ring, resulting in 9,10-anthraquinone-1-carbaldehyde phenylhydrazone (**16**) (Scheme 4). This is in contrast to the Potts results[7] on *N*,*N*-dimethylhydrazones; we believe that the initial [4+2] adduct undergoes rapid dehydrative aromatization before any air oxidation, again suggesting the role of acidic hydrazone hydrogen in the aromatization.

Reactions attempted with **1** and maleic anhydride gave polymers and tars, but failed to yield any isolable products. 2-Furaldehyde phenylhydrazone (**1**) failed to react with less-reactive dienophiles, nitrostyrene and norbornene, even under forcing conditions. In conclusion, these studies

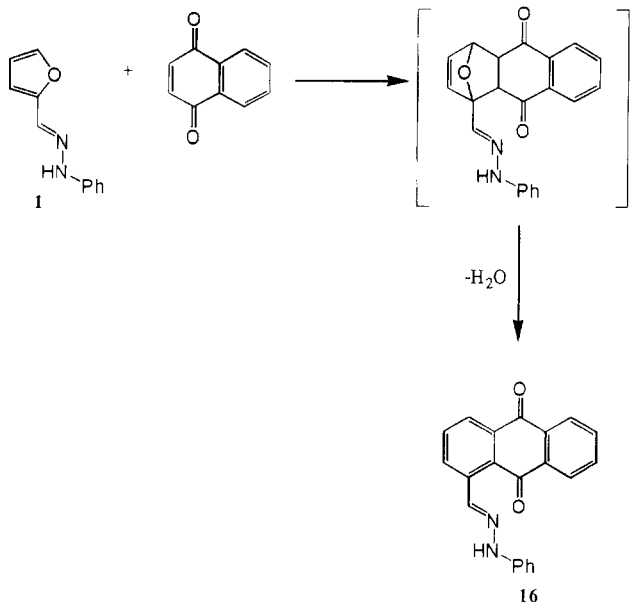


Scheme 2.



Scheme 3.

show that strongly activated symmetrical dienophiles, such as maleimides and 1,4-naphthoquinone, react on the furan ring in [4+2] cycloaddition. Unsymmetrical alkenes, such as acrylates, react via dipolar cycloaddition on the hydrazone in contrast to the Abraca's results[5] on *N,N*-dimethylhydrazones. Excess maleimides and longer reaction times can produce double cycloadditions. As far as we are aware, this is the first example of the use of a tandem [4+2] and [3+2]



Scheme 4.

process in the synthesis of substituted pyrazolines and pyrazoles; these results extend the scope of the hydrazone-alkene cycloaddition and furan-alkene addition in synthesis.

Experimental

Melting points were determined in open capillary tubes and are uncorrected. ^{1}H NMR spectra were recorded in a Bruker AC-F 200 spectrometer operating at 200.132 MHz in $CDCl_3$ and chemical shifts are given in parts per million down field from tetramethylsilane (δ = 0.00). ^{13}C NMR spectra in $CDCl_3$ solutions were recorded in the same spectrometer operating at 50.323 MHz; the chemical shifts were measured relative to $CDCl_3$ and converted to δ (TMS) using δ ($CDCl_3$) = 77.00. Mass spectra were obtained in a Hewlett–Packard 5890 GC/MS in the EI mode or CI mode using CH_4 ionization. IR spectra were recorded on a JASCO 5300 FT-IR spectrometer or on a Perkin–Elmer 1420 spectrometer in $CHCl_3$ solutions. UV-vis spectra were obtained using a JASCO V-560 spectrometer, using 1 cm cells. All solvents were distilled before use. Preparative thin layer chromatography was carried out using BDH G6 silica gel coated on 20×20 cm glass plates.

General Procedure for the Reaction of 2-Furaldehyde Phenylhydrazone (1) with Maleimides (2a—c), 1 : 1 Molar Ratio Reactions. A mixture of 2-furaldehyde phenylhydrazone (2 mmol) and maleimide (2 mmol) in dry benzene (5 cm^3) was refluxed for 6—12 h. The solvent was evaporated under reduced pressure and the residue was purified by preparative thin-layer chromatography, eluting with 1 : 1 dichloromethane/hexane. The products were further purified by recrystallization with ethyl acetate, methanol.

2-Methyl-4-(phenylhydrazono)methyl-1*H*-isoindole-1,3(2*H*)-dione (4a). Yield 59%, mp 205—207 °C. Found: C, 68.80; H, 4.81%. Calcd for $C_{16}H_{13}N_3O_2$: C, 68.81; H, 4.69%. UV (MeOH) λ_{max}/nm 374 (ε/dm^3 mol^{-1} cm^{-1} 11399), 233 (15225), 195 (12355), 192 (11638); IR, ν_{max} 3025, 2350, 1704, 1222, 1217, 1212, 788, 783, 776 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 3.12 (3H, s), 6.94 (1H, t, J = 8.3 Hz), 7.15 (2H, t, J = 7.7 Hz), 7.31 (2H, dt, J = 7.7, 8.3 Hz), 7.72 Hz (1H, d, J = 7.3 Hz), 7.64 (1H, dd, J = 7.3, 7.9 Hz), 8.15 (1H, brs), 8.38 (1H, d, J = 7.9 Hz), 8.72 (1H, s); ^{13}C NMR ($CDCl_3$) δ = 23.9, 113.1, 121.1, 122.1, 126.1, 129.4, 129.7, 130.9, 132.6, 133.4, 134.4, 143.8, 168.2, 169.2; MS *m/z* (CI) 280 (100%),

279 (34), 187 (61), 108 (15), 158 (9), 93 (24), 92 (18), 77 (56), 65 (34).

2-Ethyl-4-(phenylhydrazono)methyl-1*H*-isoindole-1,3(2*H*)-dione (4b). Yield 52%, mp 168—169 °C. Found: C, 69.50; H, 5.12%. Calcd for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15%. UV (MeOH) λ_{max}/nm 369 (ε/dm^3 mol^{-1} cm^{-1} 18547), 233 (25813), 203 (22356), 197 (21506); IR, ν_{max} 3022, 1765, 1702, 1600, 1563, 1445, 1352, 1253, 1222, 1169, 1037, 875 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.27 (3H, t, J = 7.0 Hz), 3.73 (2H, q, J = 7.0 Hz), 6.93 (1H, t, J = 7.0 Hz), 7.15 (2H, t, J = 7.5 Hz), 7.30 (2H, dt, J = 7.0, 7.5 Hz), 7.61 (1H, d, J = 7.6 Hz), 7.69 (1H, dd, J = 7.6, 7.7 Hz), 8.21 (1H, brs), 8.36 (1H, d, J = 7.7 Hz), 8.72 (1H, s); ^{13}C NMR ($CDCl_3$) δ = 14.0, 32.9, 113.1, 114.5, 121.1, 122.1, 129.4, 131.0, 132.6, 133.6, 134.4, 143.8, 167.8, 167.9, 168.9; MS *m/z* (CI), 294 (46), 293 (55), 237 (33), 209 (48), 159 (29), 107 (99), 105 (99), 77 (99), 65 (47), 46 (69), 39 (51), 28 (100).

2-Phenyl-4-(phenylhydrazono)methyl-1*H*-isoindole-1,3(2*H*)-dione (4c). Yield 42%, mp 194—196 °C. Found: C, 73.95; H, 4.23%. Calcd for $C_{21}H_{15}N_3O_2$: C, 73.89; H, 4.43%. UV (MeOH) λ_{max}/nm 376 (ε/dm^3 mol^{-1} cm^{-1} 11519), 242 (13591), 203 (13570), 197 (12714), 193 (12993); IR, ν_{max} 2927, 2360, 1713, 1600, 1222, 1213, 1208, 789, 773, 766 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 6.94 (1H, dd, J = 7.1, 7.6 Hz), 7.16 (1H, d, J = 7.5 Hz), 7.25—7.55 (8H, m), 7.73 (1H, dd, J = 7.5, 7.7 Hz), 7.83 (1H, d, J = 7.3 Hz), 8.17 (1H, brs), 8.47 (1H, d, J = 7.9 Hz), 8.77 (1H, s); ^{13}C NMR ($CDCl_3$) δ = 113.2, 121.2, 122.7, 125.5, 126.7, 128.1, 129.1, 130.3, 130.9, 131.7, 132.1, 133.9, 134.9, 143.7, 167.0, 167.9; MS *m/z* (CI), 342 (22), 252 (18), 224 (100), 179 (43), 167 (12), 76 (43).

1 : 2 Molar Ratio Reactions; A procedure similar to the 1 : 1 reaction was used, except 4 mmols of maleimides (**2a**—**c**), were used and refluxed for 24—48 h.

***N*-Methylmaleimide Reaction; Reaction Time 24 h; 4a : 7a = 1.2 : 1. 3-(2,3-Dihydro-2-methyl-1,3-dioxo-1*H*-isoindol-4-yl)-1,6a-dihydro-5-methylpyrrolo[3,4-*c*]pyrazole-4,6(3*aH*,5*H*)-dione (7a).** **4a**: 25% yield, **7a**: 21% yield, mp 201—203 °C. Found: C, 64.99; H, 4.30%. Calcd for $C_{21}H_{16}N_4O_4$: C, 64.94; H, 4.15%. UV (MeOH) λ_{max}/nm 595 (ε/dm^3 mol^{-1} cm^{-1} 1474), 539 (1630), 352 (6907), 203 (21030), 192 (18236); IR, ν_{max} 2928, 1768, 1709, 1599, 1501, 1439, 1381, 1287, 1219, 1145 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.98 (3H, s), 3.20 (3H, s), 5.27 (1H, d, J = 11.4 Hz), 6.36 (1H, d, J = 11.4 Hz), 7.04 (1H, dd, J = 7.3, 7.3 Hz), 7.37 (2H, dd, J = 7.4, 8.6 Hz), 7.60 (2H, d, J = 7.8 Hz), 7.70 (1H, dd, J = 7.6, 7.7 Hz), 7.86 (1H, dd, J = 7.9, 1.0 Hz), 8.15 (1H, dd, J = 7.3, 1.0 Hz); ^{13}C NMR ($CDCl_3$) δ = 24.2, 29.7, 54.3, 65.6, 114.5, 122.1, 123.7, 128.0, 128.8, 129.3, 133.3, 133.7, 134.7, 141.2, 143.6, 167.7, 168.4, 172.4, 172.9; MS *m/z* (CI), 389 (11), 376 (24), 358 (51), 349 (24), 330 (28), 111 (21), 91 (34), 84 (57), 77 (45).

***N*-Ethylmaleimide Reaction; Reaction Time 32 h; 4b : 7b = 1.2 : 1. 3-(2,3-Dihydro-2-ethyl-1,3-dioxo-1*H*-isoindol-4-yl)-1,6a-dihydro-5-ethylpyrrolo[3,4-*c*]pyrazole-4,6(3*aH*,5*H*)-dione (7b).** **4b**: 26% yield, **7b**: 22% yield, mp 214—215 °C. Found: C, 66.48; H, 4.74%. Calcd for $C_{23}H_{20}N_4O_4$: C, 66.34; H, 4.84%. UV (MeOH) λ_{max}/nm 593 (ε/dm^3 mol^{-1} cm^{-1} 1129), 538 (1307), 339 (15095), 205 (23383); IR, ν_{max} 3029, 1768, 1717, 1599, 1444, 1400, 1379, 1227, 1222, 1144, 874 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.14 (3H, t, J = 7.0 Hz), 1.28 (2H, t, J = 7.0 Hz), 3.53 (2H, q, J = 7.0 Hz), 3.76 (2H, q, J = 7.0 Hz), 5.25 (1H, d, J = 11.3 Hz), 6.33 (1H, J = 11.3 Hz), 7.05 (1H, dd, J = 7.5, 7.6 Hz), 7.37 (2H, dd, J = 7.5, 7.6 Hz), 7.59 (2H, d, J = 7.6 Hz), 7.69 (1H, dd, J = 7.5, 7.5 Hz), 7.87 (1H, dd, J = 1.2, 7.5 Hz), 8.13 (1H, dd, J = 1.2, 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ = 12.7, 13.8, 33.1, 34.5, 54.3, 65.6, 113.0, 114.5, 122.1, 123.7, 128.8, 129.2, 133.3, 133.6, 134.6, 141.4, 243.7, 167.5, 168.1, 172.1, 172.8; MS *m/z* (CI), 417 (41), 343 (72), 316 (51), 296 (23), 288 (18), 77 (68), 65 (44), 44 (52), 28 (100).

***N*-Phenylmaleimide Reaction; Reaction Time 48 h; 4c : 7c = 1.1 : 1. 3-(2,3-Dihydro-2-phenyl-1,3-dioxo-1*H*-isoindol-4-yl)-1,6a-dihydro-5-phenylpyrrolo[3,4-*c*]pyrazole-4,6(3*aH*,5*H*)-dione (7c).** **4c**: 22% yield, **7c**: 20% yield, mp 137 °C. Found: C, 72.50; H, 3.82%. Calcd for $C_{31}H_{20}N_4O_4$: C, 72.65; H, 3.93%. UV (MeOH) λ_{max}/nm 594 (ε/dm^3 mol^{-1} cm^{-1} 1459), 539 (1536), 524 (1336), 358 (11597), 203 (24468); IR, ν_{max} 3022, 2361, 1716, 1599, 1500, 1379, 1222, 1218, 1212, 1191, 1120, 879 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 5.22 (1H, d, J = 11.5 Hz), 6.39 (1H, d, J = 11.5 Hz), 7.04 (1H, dd, J = 7.5, 7.6 Hz), 7.20 (2H, d, J = 7.5 Hz), 7.31—7.50 (10H, m), 7.61 (2H, d, J = 7.5 Hz), 7.72 (1H, dd, J = 7.6, 7.8 Hz), 7.93 (1H, dd, J = 1.2, 7.6 Hz), 8.24 (1H, dd, J = 1.2, 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ = 54.0, 65.4, 114.6, 122.2, 124.2, 126.0, 126.7, 127.5, 128.8, 129.0, 129.2, 131.0, 131.4, 132.7, 134.0, 135.1, 141.2, 143.5, 166.4, 167.4, 171.3, 171.8; MS *m/z* (CI), 356 (9), 172 (12), 91 (7), 84 (7), 77 (11), 44 (27), 28 (100).

Reaction of 2-Furaldehyde Phenylhydrazone with Dimethyl Acetylenedicarboxylate. A mixture of 2-furaldehyde phenylhydrazone (2 mmol) and dimethyl acetylenedicarboxylate (4 mmol) was refluxed in benzene (5 cm^3). The reaction was monitored using TLC; complete disappearance of the starting compounds was observed after 18 h. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography; after eluting with 15 : 85 acetone/hexane, dimethyl-3-[4-hydroxy-2,3-bis(methoxycarbonyl)phenyl]-1-phenylpyrazole-4,5-dicarboxylate (**13**) was obtained as a yellow powder.

Dimethyl-3-[4-hydroxy-2,3-bis(methoxycarbonyl)phenyl]-1-phenylpyrazole-4,5-dicarboxylate (13). Yield 35%, mp 157—159 °C. Found: C, 59.20; H, 4.52%. Calcd for $C_{23}H_{20}N_2O_9$: C, 58.98; H, 4.30%. IR, ν_{max} 3034, 1736, 1680, 1597, 1541, 1498, 1444, 1267, 1169, 1078 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 3.70 (3H, s), 3.73 (3H, s), 3.88 (3H, s), 3.92 (3H, s), 7.13 (1H, d, J = 8.0 Hz), 7.41—7.55 (6H, m), 11.20 (1H, s); ^{13}C NMR ($CDCl_3$) δ = 51.9, 52.1, 52.9, 53.3, 109.7, 114.4, 118.6, 121.4, 123.8, 129.1, 129.3, 134.8, 135.7, 137.6, 138.7, 149.9, 160.9, 161.8, 162.2, 168.0, 169.3, MS *m/z* (CI), 440 (14), 295 (34), 286 (20), 279 (40), 263 (100), 222 (31), 190 (38).

General Procedure for the Reaction of 1 with Acrylates 14a and 14b. A solution of 2-furaldehyde phenylhydrazone (1 mmol) in acrylate (10 cm^3) was heated under reflux. The reaction was monitored using TLC, and stopped after the complete disappearance of 2-furaldehyde phenylhydrazone (20—24 h). The excess acrylate was evaporated under reduced pressure and the residue was purified by preparative thin-layer chromatography, eluting with 10 : 1 hexane/ethyl acetate.

Methyl-3-(2-furyl)-1-phenyl-4,5-dihydropyrazole-4-carboxylate (15a). Yield 18%, mp 126—127 °C. Found: C, 66.45; H, 5.36%. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22%. ^{1}H NMR ($CDCl_3$) δ = 3.38 (1H, dd, J = 6.8, 17.5 Hz), 3.63 (1H, dd, J = 13.0, 17.5 Hz), 3.70 (3H, s), 4.81 (1H, dd, J = 6.8, 13.0 Hz), 6.47 (1H, dd, J = 1.8, 3.4 Hz), 6.64 (1H, d, J = 3.4 Hz), 6.88, (1H, m), 7.10 (2H, t, J = 8.1 Hz), 7.28 (2H, m), 7.49 (1H, d, J = 1.8 Hz); ^{13}C NMR ($CDCl_3$) δ = 38.1, 52.5, 109.8, 111.7, 113.3, 119.9, 129.1, 139.3, 144.3, 144.6, 171.7; MS *m/z* (EI) 270 (M^+; 100), 211 (78), 183 (25), 156 (8), 104 (8), 77 (26).

3-(2-Furyl)-1-phenyl-4,5-dihydropyrazole-4-carbonitrile (15b). Yield 16%, mp 135—137 °C. Found: C, 70.65; H, 4.71%. Calcd for $C_{14}H_{11}N_3O$: C, 70.87; H, 4.67%. ^{1}H NMR ($CDCl_3$) δ = 2.83 (1H, dd, J = 8, 15.0 Hz), 2.96 (1H, dd, J = 10.2,

15.0 Hz), 4.21 (1H, dd, J = 6.8, 10.2 Hz), 6.45 (1H, dd, J = 1.8, 3.4 Hz), 6.62 (1H, d, J = 3.4 Hz), 6.90 (1H, m), 7.10 (2H, t, J = 8.1 Hz), 7.28 (2H, m), 7.40 (1H, d, J = 1.8 Hz); ^{13}C NMR ($CDCl_3$) δ = 34.7, 52.8, 110.7, 111.7, 112.9, 113.6, 119.9, 120.4, 128.3, 129.3, 142.2, 142.7; MS m/z (EI) 237 (M^+; 65), 210 (100), 182 (12), 155 (8), 77 (35).

Reaction of 2-Furaldehyde Phenylhydrazone with 1,4-Naphthoquinone. A mixture of 2-furaldehyde phenylhydrazone (1 mmol) and 1,4-naphthoquinone (2 mmol) was refluxed in toluene (5 cm^3). The reaction was monitored using TLC and the complete disappearance of the 2-furaldehyde phenylhydrazone was observed after 40 h. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography; eluting with 15 : 85 ethyl acetate/hexane, yielded 1-(phenylhydrazonomethyl)anthraquinone (**16**) as brown crystals.

1-(Phenylhydrazonomethyl)anthraquinone (16). Yield 32%, mp 157—158 °C. Found: C, 77.41; H, 4.21%. Calcd for $C_{21}H_{14}N_2O_2$: C, 77.29; H, 4.32%. ^{1}H NMR ($CDCl_3$) δ = 7.02 (1H, d, J = 7.2 Hz), 7.20 (2H, t, J = 8.5 Hz), 7.42 (2H, m), 7.43 (1H, s), 7.52 (2H, m), 7.62—7.75 (4H, m), 8.05—8.15 (2H, m); ^{13}C NMR ($CDCl_3$) δ = 112.8, 120.3, 122.4, 125.9, 127.1, 127.6, 128.5, 128.7, 129.3, 129.4, 130.0, 132.5, 133.8, 135.3, 136.2, 142.6, 142.9, 184.4, 185.2; MS m/z (EI), 326 (14), 234 (100), 207 (65), 179 (56).

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