# Acetylenic Ketones. Part IV (1). Reaction of *p*-Nitrobenzoylphenylacetylene with Nucleophilic Nitrogen Compounds

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*p*-Nitrobenzoylphenylacetylene (I) reacted with acylhydrazines (IIa-d) to give the corresponding hydrazones (VIa-d), which when treated with acetic anhydride, gave the same substituted pyrazole (VII). Hydrolysis of the latter with methanolic potassium hydroxide gave the pyrazole derivative (IX).

The reaction of I with ethyl and phenyl hydrazinecarboxylates (IIe,f) led to the formation of the hydrazones (VIe) and (VIf), respectively, whereas with methyl- and phenylhydrazines it produced the pyrazoles (X) and (XI), respectively. However, guanidine hydrochloride gave with acetylenic ketone (I), the pyrimidine (XV).

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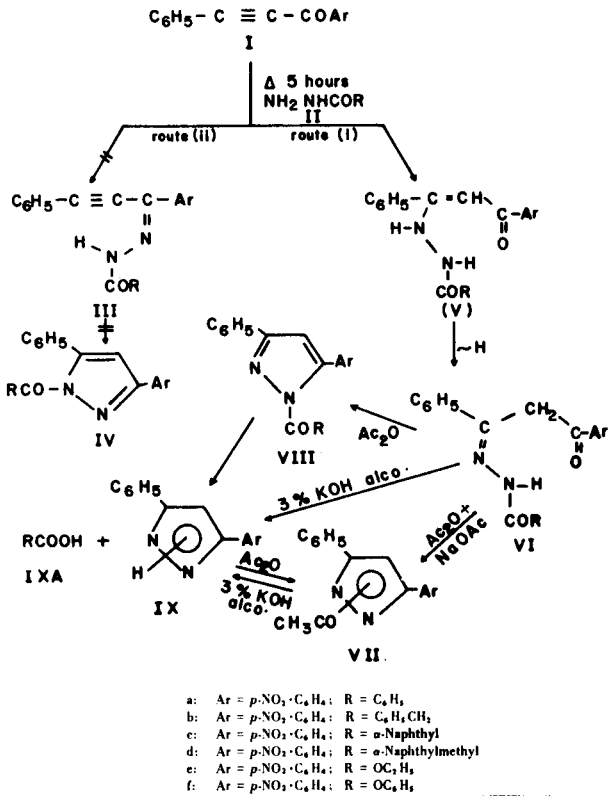
The goal of the present investigation was to prepare new substituted heterocyclic compounds and to shed further light on the reaction mechanisms of acetylenic ketones with nucleophilic nitrogen compounds. Thus, *p*-nitrobenzoylphenylacetylene (I) was allowed to react with acylhydrazines (IIa-d), ethyl and phenyl hydrazinecarboxylates (IIe,f), methylhydrazine, phenylhydrazine, *N,N*-dimethylhydrazine and guanidine hydrochloride.

When *p*-nitrobenzoylphenylacetylene (I) was refluxed with an alcoholic solution of acylhydrazines (IIa-d) and ethyl- and phenylhydrazinecarboxylates (IIe,f), it gave ω-(*p*-nitrobenzoyl)acetophenone-*N*-acyl hydrazones (VIa-d), ω-(*p*-nitrobenzoyl)acetophenone-*N*-ethoxycarbonyl- (VIe) and -*N*-phenoxycarbonyl- (VIf) hydrazones, respectively, (*cf.*, Scheme 1). The structure of the above products was established by spectral and chemical tools. Thus, the absence of $\nu$ (C≡C) and the presence of a sharp band in the region 3350-3520 $cm^{-1}$ [$\nu$ (NH)], excluded the possibility that the above compounds have either structure (III) or (IV) (*cf.*, Scheme 1). The ir spectra of compounds (VIa-f) also show a strong band in the region 1635-1728 $cm^{-1}$ [$\nu$ (C=O)] (2,3a) (*cf.*, Table I). Adequate evidence for the structure of VI is obtained from the nmr spectra (*cf.*, Table II) which show two doublets representing an AB system ($J_{AB}$ = 18-20 Hz) attributable to the methylene protons of the $CH_2COC_6H_4NO_2$-*p* group (2). Compound VIb shows, in addition, two doublets representing an AB system ($J_{AB}$ = 14.0 Hz) due to $COCH_2C_6H_5$ group (*cf.*, Table II). The fact that these methylene groups behave as an AB system can be interpreted by taking in consideration the restriction of rotation of the $CH_2COAr$ groups by the weak hydrogen bonding between the NH and the carbonyl group (2). The spectra also show (1H) broad signals, which do not exchange with deuterium oxide, in the region δ 4.73-6.87 due to NH groups (2).

**Scheme 1**



The electronic spectra of these compounds are identical which indicates their structural analogy. They show absorption maxima in the range 276-286 nm (*cf.*, Table I), which are slightly blue shifted with decrease in solvent polarity (*cf.*, VIb in Table I), indicating that they are $\pi$-$\pi^*$ transition bands (2).

Chemical reactions of these compounds give further evidence for the assigned structure. Thus, compounds VIa-d gave 1-acetyl-3(5)-*p*-nitrophenyl-5(3)phenylpyrazole (VII) by refluxing with acetic anhydride in the presence of sodium acetate. However, compounds (VIe,f) were easily cyclized by refluxing with acetic anhydride to the corresponding 5-*p*-nitrophenyl-1-ethoxycarbonyl- (VIIe) and 1-phenoxycarbonyl- (VIIIf) pyrazoles, respectively, (2). The formation of the acetyl pyrazole derivative (VII) can be explained on the premise that compounds VIa-d were hydrolyzed to 3(5)-*p*-nitrophenyl-5(3)phenylpyrazole (IX) followed by acetylation. This conclusion was hightened by the fact that VIa on boiling with sodium acetate in ethyl alcohol or with 3% methanolic potassium hydroxide gave the pyrazole (IX) and benzoic acid (IXA; R = $C_6H_5$). The ir spectra of these compounds VII, VIIIe and VIIIf show a strong band at 1740 $cm^{-1}$, 1768 $cm^{-1}$ and 1754 $cm^{-1}$ [$\nu$ (C=O)], respectively, (*cf.*, Table I) (2,4). Their nmr spectra (*cf.*, Table II) gave further support for the proposed structure, since they show a sharp signal at $\delta$ 6.80, 6.73 and 6.87, respectively, due to the olefinic protons (2). The structure of compounds VIIIe and VIIIf was rigidly confirmed by the fact that when refluxed with 3% methanolic potassium hydroxide they gave 3(5)-*p*-nitrophenyl-5(3)phenylpyrazole (IX).

Based on the above discussion, it was concluded that the reaction of *p*-nitrobenzoylphenylacetylene with acylhydrazines (IIa-d) and ethyl and phenylhydrazinecarb-

Table I

The Electronic and Infrared Spectral Data of Hydrazones (VIa-f) and Pyrazole Derivatives (VII), (VIIIe,f) and (IX)

| | Electronic Spectra (Ethanol) | | Infrared Spectra (Potassium bromide) | |
|---|---|---|---|---|
| Compound | $\lambda$ max (nm) | $\epsilon$ | $cm^{-1}$ | $\nu$ |
| VIa | 286 | 35,235 | 1523 (s) | $NO_2$ |
| | | | 1635 (s) | C=O |
| | | | 3520 (m) | NH |
| VIb | 283 | 34,650 | 1521 (s) | $NO_2$ |
| | In cyclohexane | | 1660 (s) | C=O |
| | 281 | 32,650 | 3350 (m) | NH |
| VIc | 286 | 32,435 | 1516 (s) | $NO_2$ |
| | | | 1642 (s) | C=O |
| | | | 3330 (m) | NH |
| VId | 281 | 38,120 | 1522 (s) | $NO_2$ |
| | ~288-294 | 34,780 | 1645 (s) | C=O |
| | | | 3200-3500 (br) | NH |
| VIe | 276 | 29,840 | 1520 (s) | $NO_2$ |
| | | | 1697 (s) | C=O |
| | | | 3240-3520 (br) | NH |
| VIf | 276 | 27,280 | 1520 (s) | $NO_2$ |
| | | | 1728 (s) | C=O |
| | | | 3240-3520 (br) | NH |
| VII | ~223-227 | 17,770 | 1515 (s) | $NO_2$ |
| | 291 | 21,130 | 1605 (s) | C=N |
| | | | 1740 (s) | C=O |
| VIIIe | 273 | 33,730 | 1513 (s) | $NO_2$ |
| | | | 1768 (s) | C=O |
| VIIIf | 275 | 28,240 | 1522 (s) | $NO_2$ |
| | | | 1754 (s) | C=O |
| IX | 236 | 18,610 | 1527 (s) | $NO_2$ |
| | ~255-265 | 16,210 | 1605 (s) | C=O |
| | 315 | 15,580 | 2800-3200 (br) | NH |

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Table II

Nuclear Magnetic Resonance Spectral Data of
Hydrazones (VIa-f) and Pyrazoles (VII), (VIIIe,f) and (IX) in Deuteriochloroform

| Compound | δ | Assignments (No. of Protons) | J (Hz) |
|---|---|---|---|
| VIa | 8.53-7.33 (m) | (14) Ar*H* | |
| | 5.6 (br) | (1) N*H* | |
| | 3.88 (d), 3.40 (d) | (2) -CH(H)-CO (AB system) | 18.5 |
| VIb | 8.53-7.57 (m) | (14) Ar*H* | |
| | 5.40 (br) | (1) N*H* | |
| | 4.58 (d), 4.25 (d) | (2) CO-CH(H)-$C_6H_5$ (AB system) | 14.0 |
| | 4.03 (d), 3.50 (d) | (2) -CH(H)-COC$_6$H$_4$·$NO_2$ (AB system) | 18.5 |
| VIc | 8.43-7.6 (m) | (16) Ar*H* | |
| | 6.87 (br) | (1) -*N*H | |
| | 4.02 (d), 3.55 (d) | (2) -CH(H)-CO (AB system) | 20 |
| VId | 8.27-7.35 (m) | (16) Ar*H* | |
| | 5.20 (br) | (1) -N*H* | |
| | 4.67 (s) | (2) -$CH_2$-$C_{10}H_7$ | |
| | 3.84 (d), 3.29 (d) | (2) -CH(H)-CO (AB system) | 19 |
| VIe | 8.40-7.37 (m) | (9) Ar*H* | |
| | 4.78 (br) | (1) -NH | |
| | 4.37 (q) | (2) -C*H*$_2$-$CH_3$ | 7 |
| | 3.88 (d), 3.38 (d) | (2) -CH(H)-CO (AB system) | 18 |
| | 1.50 (t) | (3) -$CH_2$C*H*$_3$ | 7 |
| VIf | 8.33-7.20 (m) | (14) Ar*H* | |
| | 4.73 (br) | (1) -N*H* | |
| | 3.85 (d), 3.36 (d) | (2) -CH(H)-CO (AB system) | 19 |
| VII | 8.43-7.27 (m) | (9) Ar*H* | |
| | 6.80 (s) | (1) -C*H*= | |
| | 2.80 (s) | (3) -COC*H*$_3$ | |
| VIIIe | 8.37-7.2 (m) | (9) Ar*H* | |
| | 6.73 (s) | (1) -C*H*= | |
| | 4.39 (q) | (2) -$CH_2$-$CH_3$ | 7 |
| | 1.52 (t) | (3) -$CH_2$-C*H*$_3$ | 7 |
| VIIIf | 8.25-7.25 (m) | (14) Ar*H* | |
| | 6.87 (s) | (1) -C*H*= | |
| IX | 8.57-7.53 (m) | (9) Ar*H* | |
| | 7.17 (s) | (1) -C*H*= | |
| | 2.90 (br) | (1) -N*H* | |

oxylates (IIe,f) appears to proceed by the initial attack of the amino group at the acetylenic bond [route (i) in Scheme 1] (2).

Authentic samples of VII and IX were obtained by reacting *p*-nitrobenzoylphenylacetylene with hydrazine hydrate to give IX which, upon treatment with acetic anhydride, gave the acetylated pyrazole (VII), as a single product (tlc).

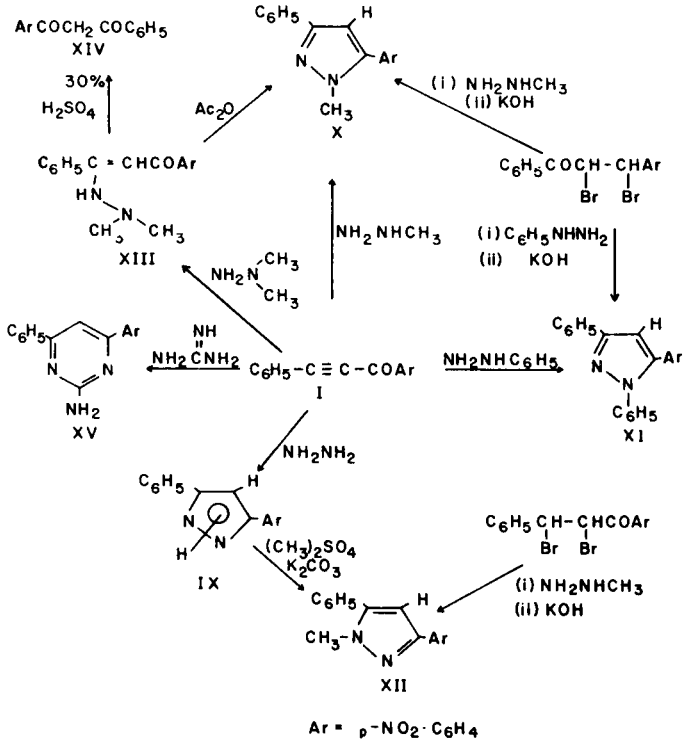
The reaction of methylhydrazine and phenylhydrazine with I gave 1-methyl-5-*p*-nitrophenyl-3-phenylpyrazole (X) and 1-phenyl-5-*p*-nitrophenyl-3-phenylpyrazole (XI), respectively, (*cf.*, Scheme 2). The structure of X and XI was established chemically and spectroscopically. Thus, the products were compared with authentic samples prepared by reacting the dibromides of *p*-nitrobenzalacetophenone and benzal-*p*-nitroacetophenone, respectively, with methylhydrazine and phenylhydrazine in methanolic potassium hydroxide (5) (*cf.*, Scheme 2). It is noteworthy to mention that the methylation of the pyrazole derivative (IX) with dimethyl sulfate and anhydrous potassium carbonate in acetone afforded 1-methyl-3-*p*-nitrophenyl-5-phenylpyrazole (XII) as a sole product. Non-identity of compounds X and XII was established by mixed m.p. and ir spectra. By studying the electronic spectra of X and XII (Table III) it was found that the latter absorbs at longer wave-length with a molar extinction coefficient greater than that of X. This may be attributed to steric interaction between the methyl and the *p*-nitrophenyl groups in X, which partially inhibits the planarity of the pyrazole and *p*-nitrophenyl rings.

The structure of methylpyrazoles (X) and (XII) was also inferred from their nmr spectra, which show a sharp signal at $\delta$ 3.93 ($NCH_3$) and a singlet at $\delta$ 6.73 and 6.72 (-CH=) (2), respectively (*cf.*, Table III).

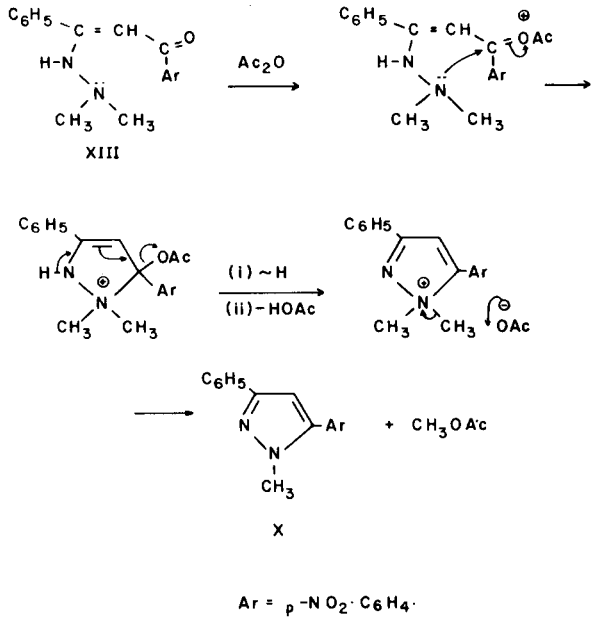
The reaction of *N,N*-dimethylhydrazine with *p*-nitrobenzoylphenylacetylene (I) gave 1,1-dimethyl-2-[$\beta$-($\alpha$-*p*-nitrobenzoylstyryl)]hydrazine (XIII) (6). The latter gave upon heating with acetic anhydride, 1-methyl-5-*p*-nitrophenyl-3-phenylpyrazole (X) (*cf.*, Scheme 2). The formation of the methylpyrazole (X) from XIII appears to proceed by an intramolecular nucleophilic displacement affected by the dimethylamino group (7) (*cf.*, Scheme 3). This view is corroborated by the observation that the nmr spectrum of the reaction mixture shows a singlet at $\delta$ 3.93 which can be attributed to ester group of methyl acetate (*cf.*, Scheme 3). A quite different behaviour has been noticed upon treatment of the hydrazine derivative (XIII) with acids. Thus, on refluxing with glacial acetic acid, the hydrazine derivative (XIII) was recovered unchanged. However, its treatment with sulfuric acid produced the corresponding $\beta$-diketone (XIV).

When *p*-nitrobenzoylphenylacetylene (I) was refluxed with an alcoholic solution of guanidine hydrochloride containing aqueous sodium carbonate solution, it gave 2-amino-6-*p*-nitrophenyl-4-phenylpyrimidine (XV) (*cf.*, Scheme 2) (2). The structure of this product was established spectroscopically. Thus, its ir spectrum (*cf.*, Table

**Scheme 2**




**Scheme 3**



III) shows two bands at 1632 $cm^{-1}$ and 1572 $cm^{-1}$ characteristic of the pyrimidine system (2,3b). It shows also three sharp bands at 3500 $cm^{-1}$, 3340 $cm^{-1}$ and 3200 $cm^{-1}$ [$\nu$ ($NH_2$) free and bonded] (2,8). However, the ir spectrum of a dilute chloroform solution of XV shows two bands at 3640 $cm^{-1}$ and 3440 $cm^{-1}$ corresponding to asymmetrical and symmetrical stretching frequencies of the free $NH_2$ group (2,9). The nmr spectrum of XV (*cf.*, Table IV) gave further support for the aminopyrimidine structure (2), since it shows a broad signal at $\delta$ 5.9 ($NH_2$) which disappeared when the deuteriochloroform solution was shaken with deuterium oxide. The electronic spectrum of XV gave two absorption maxima at 352 nm and 268 nm, characteristic of the pyrimidine system (2).

## EXPERIMENTAL

Melting points are uncorrected. Ir spectra were measured on Pye-Unicam SP 1000 and Beckman IR 12 spectrophotometers (Potassium bromide). Nmr spectra were measrued on a Varian T-60A spectrometer using TMS as internal standard. Electronic spectra were recorded on a Pye-Unicam SP 8000 spectrometer (ethyl alcohol). The purity of the analytical samples was checked by tlc (silica gel). Microanalyses were determined by Alfred Bernhardt, West Germany.

Reaction of *p*-Nitrobenzoylphenylacetylene (I) with acylhydrazines (IIa-d) and Ethyl and Phenyl Hydrazinecarboxylates (IIe,f).

A mixture of *p*-nitrobenzoylphenylacetylene (I) (0.01 mole) [prepared according to the method of Parker, Raphael and Wilkinson (10), m.p. 161-162° (from acetone) (11)] and acylhydrazine or ethyl or phenyl hydrazinecarboxylate (0.01 mole)

Table III

The Electronic, Infrared and Nuclear Magnetic Resonance Spectral Data of Compounds X, XI, XII and XV

| | Electronic Spectra (Ethanol) | | Infrared Spectra (Potassium bromide) | | Nmr (Deuteriochloroform) | |
|---|---|---|---|---|---|---|
| Compound | λ max (nm) | ε | $cm^{-1}$ | ν | δ | Assignments (No. of Protons) |
| X | 296 | 11,895 | 1525 (s) | $NO_2$ | 8.53-7.2 (m) | (9) Ar*H* |
| | 250 | 19,400 | 1600 (s) | C=N | 6.73 (s) | (1) -C*H*= |
| | | | | | 3.93 (s) | (3) NC$H_3$ |
| XI | 265 | 29,080 | 1520 (s) | $NO_2$ | 8.41-7.1 (m) | (14) Ar*H* |
| | ~233-237 | 24,265 | 1595 (s) | C=N | 7.19 (s) | (1) -C*H*= |
| XII | 320 | 16,220 | 1520 (s) | $NO_2$ | 8.40-7.30 (m) | (9) Ar*H* |
| | 229 | 20,720 | 1603 (s) | C=N | 6.72 (s) | (1) -C*H*= |
| | | | | | 3.95 (s) | (3) NC$H_3$ |
| XV | 352 | 11,035 | 1515 (s) | $NO_2$ | 8.43-7.67 (m) | (10) Ar*H* + |
| | 268 | 24,360 | 1550 (s) | C=C | | -C*H*= |
| | 231 | 21,070 | 1572 (s) | C=C | 5.9 (br) | (2) -N$H_2$ |
| | | | 1632 (s) | C=N | | |
| | | | 3200 (br) | $NH_2$ | | |
| | | | 3340 (s) | $NH_2$ | | |
| | | | 3500 (s) | $NH_2$ | | |

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Table IV

Hydrazone Derivatives (VIa-f)

| | Yield | | | Calcd. (%) | | | Found (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | (%) | M.p. °C | Formula | C | H | N | C | H | N |
| VIa | 96 | 217-218 (a) | $C_{22}H_{17}N_3O_4$ | 68.21 | 4.42 | 10.85 | 68.66 | 4.59 | 10.65 |
| VIb | 89 | 166-167 (a) | $C_{23}H_{19}N_3O_4$ | 68.82 | 4.77 | 10.47 | 68.79 | 4.84 | 10.45 |
| VIc | 88 | 206-207 (a) | $C_{26}H_{19}N_3O_4$ | 71.39 | 4.38 | 9.61 | 71.28 | 4.63 | 9.45 |
| VId | 88 | 140-141 (a) | $C_{27}H_{21}N_3O_4$ | 71.83 | 4.69 | 9.31 | 71.72 | 4.71 | 9.10 |
| VIe | 82 | 222-223 (b) | $C_{18}H_{17}N_3O_4$ | 60.85 | 4.75 | 11.88 | 61.26 | 4.85 | 11.61 |
| VIf | 86 | 202-203 (c) | $C_{22}H_{17}N_3O_5$ | 65.47 | 4.25 | 10.46 | 65.19 | 4.19 | 10.20 |

(a) Crystallized from benzene. (b) Crystallized from ethanol. (c) Crystallized from methanol.

was refluxed in ethyl alcohol (50 ml.) for 5 hours and then worked up as previously reported (2) to give the corresponding hydrazones (VIa-f). The results are reported in Table IV.

Action of Acetic Anhydride and Sodium Acetate on ω-(*p*-Nitrobenzoyl)acetophenone-*N*-acyl Hydrazones (VIa-d).

A mixture of the hydrazone derivative (VIa-d) (1.0 g.), anhydrous sodium acetate (0.2 g.) and acetic anhydride (5 ml.) was heated in an oil-bath at 125-130° for one hour. The cold reaction mixture was treated with cold 50% ethyl alcohol (25 ml.), and the precipitated solid was crystallized from cyclohexane to give in all cases 1-acetyl-3(5)-*p*-nitrophenyl-5(3)phenylpyrazole (VII), identified by authentic sample prepared from the reaction of acetic anhydride with 3(5)-*p*-nitrophenyl-5(3)phenylpyrazole (IX). The latter was prepared by leaving a mixture of *p*-nitrobenzoylphenylacetylene (I) (1.0 g.) and 99% hydrazine hydrate (5 ml.) at room temperature for 2-3 minutes (2). The solid was filtered and crystallized from acetone-benzene as yellowish-brown crystals, yield = 99%, m.p. 278-279° [reported m.p. 272-275° (12)].

*Anal.* Calcd. for $C_{15}H_{11}N_3O_2$: C, 67.92; H, 4.17; N, 15.84. Found: C, 67.92; H, 4.15; N, 15.84.

The 1-acetyl-3(5)-*p*-nitrophenyl-5(3)phenylpyrazole (VII) had m.p. and mixed m.p. 185-186° [reported m.p. 183-190° (12)], yield = 96%. Tlc gave only one spot indicating that the product (VII) was only one compound.

*Anal.* Calcd. for $C_{17}H_{13}N_3O_3$: C, 66.45; H, 4.26; N, 13.67. Found: C, 66.88; H, 4.53; N, 13.39.

Action of Acetic Anhydride on ω-*p*-Nitrobenzoylacetophenone-*N*-ethoxycarbonyl- (VIe) and *N*-phenoxycarbonyl- (VIf) Hydrazones.

The hydrazones (VIe,f) were treated with acetic anhydride as previously described (2) to give the corresponding pyrazoles (VIIIe,f).

1-Ethoxycarbonyl-5-(*p*-nitrophenyl)-3-phenylpyrazole (VIIIe).

This compound had m.p. 157-158°, yield = 82%.

*Anal.* Calcd. for $C_{18}H_{15}N_3O_4$: C, 64.05; H, 4.78; N, 12.51. Found: C, 63.83; H, 4.64; N, 12.32.

5-(*p*-Nitrophenyl)-1-phenoxycarbonyl-3-phenylpyrazole (VIIIf).

This compound had m.p. 152-153°, yield = 80%.

*Anal.* Calcd. for $C_{22}H_{15}N_3O_4$: C, 68.57; H, 3.92; N, 10.90. Found: C, 68.70; H, 4.12; N, 10.95.

Action of Alcoholic Potassium Hydroxide on ω-(*p*-Nitrobenzoyl)-acetophenone-*N*-acyl-(VIa-d),-*N*-ethoxycarbonyl- (VIe), -*N*-phenoxycarbonyl- (VIf) Hydrazones and 5-*p*-Nitrophenyl-1-ethoxycarbonyl- and 1-phenoxycarbonyl Pyrazoles (VIIIe,f).

The hydrazone derivatives (VIa-f) or the pyrazoles (VIIIe,f) (0.01 mole) were refluxed on a boiling water-bath with 3% methanolic potassium hydroxide (20 ml.) for 30 minutes. The reaction mixture was worked up as previously reported (2) to give 3(5)-*p*-nitrophenyl-5(3)phenylpyrazole (IX) in 95-97% yield; m.p. and mixed m.p. 278-279°.

The mother liquor obtained from the alkaline solution of VIa was acidified with dilute sulfuric acid to give the corresponding acid (IXA; R = $C_6H_5$) in 92% yield, identified by m.p. and mixed m.p. (121-122°) with pure benzoic acid.

The heating of ω-(*p*-nitrobenzoylacetophenone)-*N*-benzoyl hydrazone (VIa) with anhydrous sodium acetate in ethyl alcohol for 5 hours gave IX and the sodium salt of benzoic acid which after acidification gave benzoic acid, m.p. and mixed m.p. 121-122°.

Reaction of *p*-Nitrobenzoylphenylacetylene (I) with Methylhydrazine.

A mixture of the acetylenic ketone (I) (1.0 g.) and methylhydrazine (3 ml.) was left for 5 minutes at room temperature. The yellow solid was filtered and crystallized from cyclohexane to give 1-methyl-5-*p*-nitrophenyl-3-phenylpyrazole (X) as yellow leaflets, m.p. and mixed m.p. 129-130°, yield = 98%. The authentic sample was obtained from the reaction of dibromide of *p*-nitrobenzalacetophenone with methylhydrazine by the method outlined by Barnes and Dodson (5).

*Anal.* Calcd. for $C_{16}H_{13}N_3O_2$: C, 68.81; H, 4.69; N, 15.05. Found: C, 68.77; H, 4.87; N, 14.88.

Action of Dimethyl Sulfate on 3(5)-*p*-Nitrophenyl-5(3)phenylpyrazole (IX).

A mixture of dimethyl sulfate (8.0 ml.), anhydrous potassium carbonate (16.0 g.) and 3(5)-*p*-nitrophenyl-5(3)phenylpyrazole (IX) (1.0 g.) in dry acetone (60 ml.) was refluxed on a boiling water-bath for 12 hours. The solid separated after evaporation of the solvent was crystallized from cyclohexane to give 1-methyl-3-*p*-nitrophenyl-5-phenylpyrazole (XII) as yellow needles, m.p. and mixed m.p. 132-133°. An authentic sample was prepared from the reaction of methylhydrazine with the dibromide of benzal-*p*-nitroacetophenone (5), yield = 92%.

*Anal.* Calcd. for $C_{16}H_{13}N_3O_2$: C, 68.81; H, 4.69; N, 15.05. Found: C, 68.62; H, 4.72; N, 14.92.

Reaction of *p*-Nitrobenzoylphenylacetylene (I) with Phenylhydrazine.

A mixture of acetylenic ketone (I) (1.0 g.) and phenylhydrazine (0.45 g.) in ethanol was refluxed for 5 hours on a boiling water-bath. The brown solid separated after evaporation of the solvent was crystallized from petroleum-ether (60-80°) to give 1,3-diphenyl-5-*p*-nitrophenylpyrazole (XI) as brown crystals, m.p. and mixed m.p. 139-140° (13). The authentic sample was obtained from the reaction of the dibromide of *p*-nitrobenzalacetophenone with phenylhydrazine (5), yield = 81%.

*Anal.* Calcd. for $C_{21}H_{15}N_3O_2$: C, 73.89; H, 4.43; N, 12.31. Found: C, 73.96; H, 4.54; N, 12.56.

Action of Acetic Anhydride on 1,1-Dimethyl-2-[β-(α-*p*-nitrobenzoylstyryl)]hydrazine (XIII) (6).

The mixture of hydrazine derivative (XIII) (1.0 g.) and acetic anhydride (3 ml.) was heated on an oil-bath at 130-135° for 2 hours. The cold reaction mixture was treated with cold 50% ethanol (30 ml.), and the precipitated solid was crystallized from cyclohexane to give 1-methyl-5-*p*-nitrophenyl-3-phenylpyrazole (X) as yellow leaflets, m.p. and mixed m.p. 129-130°, yield = 96%.

When glacial acetic acid was used instead of acetic anhydride, the hydrazine derivative (XIII) was recovered unchanged.

Action of Dilute or Concentrated Sulfuric Acid on XIII.

A mixture of the hydrazine derivative (XIII) (0.5 g.) and 30% dilute sulfuric acid (15 ml.) was heated (120-125°) for 30 minutes. The reaction mixture was then cooled and the precipitated solid was crystallized from benzene-ethyl alcohol to give *p*-nitrodibenzoyl methane as brown crystals, m.p. 160-161° (14), yield = 78%. The same β-diketone (XIV) was obtained from the action of concentrated sulfuric acid on the hydrazine derivative (XIII) (15 ml./1 g.) for a period of 15 minutes (room temperature).

Reaction of *p*-Nitrobenzoylphenylacetylene (I) with Guanidine Hydrochloride.

A mixture of *p*-nitrobenzoylphenylacetylene (I) (6.3 g.) and

guanidine hydrochloride (2.25 g.) in ethanol (25 ml.) was refluxed, while a solution of sodium carbonate (1.4 g.) in water (5 ml.) was added portionwise during 2 hours. Refluxing was continued for a further 10 hours and worked up as previously reported (2) to give 2-amino-6-*p*-nitrophenyl-4-phenyl-pyrimidine (XV) as yellow crystals, m.p. 232-233° (from benzene), yield = 76%.

*Anal.* Calcd. for $C_{16}H_{12}N_4O_2$: C, 65.75; H, 4.14; N, 19.17. Found: C, 65.81; H, 4.16; N, 19.21.

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