# Reactions of 3-Diazo-1,3-dihydro-2*H*-indol-2-one Derivatives with Enaminones. A Novel Synthesis of 1,2,3-Triazoles

Rodinei Augusti and Concetta Kascheres*

*Universidade Estadual de Campinas, Instituto de Química, Caixa Postal 6154, 13081 Campinas, São Paulo, Brazil*

*Received June 2, 1993*•

A new and efficient method of 1,2,3-triazole synthesis is described in which these heterocyclics are formed through a novel nitrogen transfer from diazocarbonyl compounds to enaminones. Thus, the reaction of 3-diazo-1,3-dihydro-2*H*-indol-2-one derivatives **1** (X = NR[3]) and 3-diazobenzo[*b*]thiophen-2(3*H*)-one **5** (X = S) with enaminones **2** and **7** leads to the formation of mainly 1,2,3-triazoles **4** and pyrazoloquinazolinones **3**. Both the phenyl substituents (Y and Z in **1**) and the nature of the X group affects the reaction rate and product distribution. Rate increases with an increase in the electron-withdrawing ability of the substituents Y and Z. The dinitro derivative **1g** is shown to be the most efficient in promoting 1,2,3-triazole **4** formation while pyrazoloquinazolinones **3** are often competitively formed when other derivatives of **1** are employed.

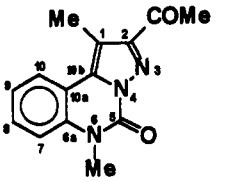
## Introduction

Recent examples of the applications of diazocarbonyl compounds in synthesis have involved the use of these systems as carbenoid sources which can undergo a variety of reactions. Thus, ylides are generated by these electrophilic intermediates through interaction with nonbonding electron pairs on heteroatoms,[1] indenones from intramolecular addition onto acetylenic $\pi$ bonds,[2] cyclopentanes by intramolecular C–H insertion,[3] and cyclopropanes by intramolecular alkene addition.[4]

Diazodiphenylethanone reacts with enaminones via its copper (II)-stabilized carbene to form pyrroles[5] or via diphenylketene under noncatalytic thermal conditions to form nucleophilic addition products.[6] Our continuing interest in the reactivity of diazocarbonyl compounds with enaminones led us to study the behavior of 3-diazo-1,3-dihydro-2*H*-indol-2-one (**1a**) for which ketene formation is not favored under thermal conditions.[7]

## Results and Discussion

The reaction of **1a** with 4-(methylamino)-3-penten-2-one **2a**, in refluxing toluene for 7 days, led to the formation of the pyrazoloquinazolinone **3a** in 60% yield and the triazole **4a** as a minor product (Table I, entry 1). Structural elucidation was based on spectroscopic data. Thus, the mass spectrum of **3a** shows a molecular ion at *m/z* 241 which corresponds to (**1a** + **2a** – $NH_2Me$), and the $^1H$ NMR spectrum (in $CDCl_3$–TFA) shows two singlets at 2.80 and 2.81 ppm as well as signals in the aromatic region. The correct regioisomer was confirmed by the COLOC spectrum of its N-methylated derivative **3c** which shows a $^3J$ correlation between the 1-methyl hydrogen and carbon at position **10b**.




**3c**

The mass spectrum of **4a** shows a molecular ion at *m/z* 139 which corresponds to (**2a** + $N_2$ – $H_2$), and the $^1H$ NMR spectrum ($CCl_4$) shows three singlets of equal intensity at 2.53, 2.57, and 3.94 ppm with no signals in the aromatic region. These data indicate that the only portion of **1a** that is incorporated in this product is $N_2$. Therefore, the minor product formed involves a novel nitrogen transfer to form a heterocyclic system. While nitrogen-transfer reactions from azides are well documented,[8,9] the same is not true of diazocarbonyl systems.[10]

Reactions of **1a** or its N-methylated analog **1b** with other enaminones did not give very favorable results. Thus, **1a** reacts with the enamino ester **2b** to form triazole **4b** and pyrazoloquinazolinone **3b** both in relatively low yields (Table I, entry 2). When **1b** was used with **2a** or with 4-amino-3-penten-2-one (**2c**) small amounts of the corresponding pyrazoloquinazolinone **3c** were obtained (Table I, entries 3 and 4) as the only isolable product.

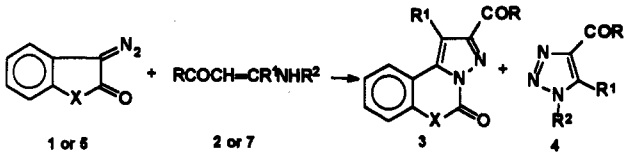
At this stage it was difficult to understand why such minor structural changes in the reagents should cause such differences. Both classes of compounds are of synthetic interest. Many pyrazoloquinazolinone derivatives are antiallergy and antiinflamatory agents,[11] and 1,2,3-triazoles have found industrial and medicinal applications.[12] In comparison with the usual routes to these compounds, which normally use acetylenes,[12,13] the present reagents

• Abstract published in *Advance ACS Abstracts*, October 15, 1993.

(1) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263.
(2) Padwa, A.; Krumpe, K. E.; Gareau, Y.; Chiachio, U. *J. Org. Chem.* **1991**, *56*, 2523.
(3) Taber, D. F.; Henessy, M. J.; Louey, J. P. *J. Org. Chem.* **1992**, *57*, 436.
(4) Maas, G. *Top. Curr. Chem.* **1987**, *137*, 77, Chapter 2.
(5) Eberlin, M. N.; Kascheres, C. *J. Org. Chem.* **1988**, *53*, 2084.
(6) Eberlin, M. N.; Takahata, Y.; Kascheres, C. *J. Org. Chem.* **1990**, *55*, 5150.
(7) Moriconi, E. J.; Murray, J. J. *J. Org. Chem.* **1964**, *29*, 3577.
(8) Regitz, M.; Maas, G. In *Diazo Compounds: Properties and Synthesis*; Academic: Orlando, FL, 1986.
(9) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*(9), 733.
(10) (a) Schollkopf, U.; Tonne, P.; Schafer, H.; Markush, P. *Liebigs Ann. Chem.* **1969**, *722*, 45. (b) Schollkopf, U.; Wiskott, E.; Riedel, K. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 138.
(11) Vogt, R. B. U.S. Pat. 4,112,098, 1978.
(12) (a) Sainsbury, M. In *Rodd's Chemistry of Carbon Compounds*; Ansell, M. F., Ed.; Elsevier: New York, 1984; Vol. IV (D), Chapter 18. (b) Wamhoff, H. In *Comprehensive Heterocyclic Chemistry*; Potts, K. T., Ed.; Pergamon Press: Oxford, 1984; Vol. 5, p 669.
(13) Yamazaki, T.; Schechter, H. *Tetrahedron Lett.* **1973**, *16*, 1417.

0022-3263/93/1958-7079$04.00/0 

**Table I. Reactions of 3-Diazo-1,3-dihydro-2*H*-indol-2-one (1a), its N-Methylated Derivative (1b), and 3-Diazobenzo[*b*]thiophen-2(3*H*)-one (5) with Enaminones 2 and 7**



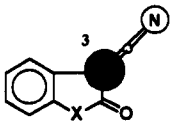

| entry | 1 or 5 | 2 or 7 | 3 (% yield) | 4 (% yield) | reactn time[a] (h) |
|---|---|---|---|---|---|
| 1 | 1a (X = NH) | 2a (R = R¹ = R² = Me) | 3a (60) | 4a (6) | 168 |
| 2 | 1a | 2b (R = OEt, R¹ = R² = Me) | 3b (28) | 4b (16) | 168 |
| 3 | 1b (X = NMe) | 2a | 3c (12) | | 192 |
| 4 | 1b | 2c (R = R¹ = Me, R² = H) | 3c (9) | | 192 |
| 5 | 5 (X = S) | 2a | 3j (7) | 4a (32) | 120 |
| 6 | 5 | 2b | | 4b (58) | 120 |
| 7 | 5 | 2d (R = R¹ = Me, R² = *t*-Bu) | | 4d (47) | 120 |
| 8 | 5 | 2e (R = OEt, R¹ = Me, R² = *t*-Bu) | | 4e (77) | 120 |
| 9[b] | 5 | 7a (R,R¹ = $-CH_2C(Me)_2CH_2-$, R² = H) | | 4f (59) | 360 |
| 10[b] | 5 | 7b (R,R¹ = $-CH_2C(Me)_2CH_2-$, R² = Me) | | 4g (19) | 240 |

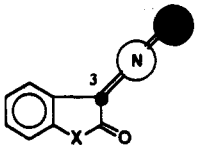
[a] Reaction times were established by following the disappearance of the $N_2$ band at 2100 $cm^{-1}$ at the IR spectrum. [b] In refluxing benzene.

**Table II. Frontier Orbital Energies (eV) of the Diazocarbonyl Compounds 1 and 5 Calculated by AM1**

| compd | 1a | 1b | 1c | 1d | 1e | 1f | 1g | 5 |
|---|---|---|---|---|---|---|---|---|
| HOMO | −8.56 | −8.51 | −8.50 | −8.43 | −9.20 | −9.12 | −9.72 | −8.88 |
| LUMO | −0.58 | −0.54 | −0.55 | −0.59 | −1.36 | −1.31 | −1.95 | −0.83 |

would lead to more diversified systems if the reactions were general enough. Therefore, a systematic study was undertaken in order to understand the factors governing the formation of both types of compounds. We began by preparing 3-diazobenzo[*b*]thiophen-2(3*H*)-one (**5**), the sulfur analog of 1. The results obtained in the reactions




of **5** with various enaminones (Table I, entries 5–10) show that triazoles are the major products. AM1 molecular orbital calculations show that the diazocarbonyl compounds 1 and **5** have LUMOs with large coefficients on the two diazo nitrogens and HOMOs with large coefficients on both the C3 and the terminal diazo nitrogen as shown.

These calculations also show that, of the three diazocarbonyl compounds used thus far, **5** has the lower energy LUMO (Table II). Considering that triazole formation involves reaction on two of the nucleophilic sites of the enaminones (C$\alpha$ and N) and that their yields in reactions with **2** are approximately proportional to the HOMO energy of the enaminone reagent used[6] and are not subject to steric effects (as can be seen by the yields involving N-*tert*-butyl enaminones **2d** and **2e**), we felt that the reaction might be frontier orbital controlled. Thus, electron-withdrawing groups should increase the reactivity of 1 toward triazole formation.

The question which remained concerned the formation of the pyrazoloquinazolinones. It is known that **1a** reacts with electrophilic acetylenes[13] to form pyrazoloquinazolinone derivatives through a 1,3 dipolar cycloaddition (which, according to Huisgen, would be controlled by the LUMO of the dipolarophile and the HOMO of the dipole[14]) followed by a [1,5] sigmatropic shift mechanism. The possibility that the formation of the pyrazoloquinazolinones would also involve this frontier orbital interaction in our case led us to investigate the effect of electron-releasing groups on **1a**.

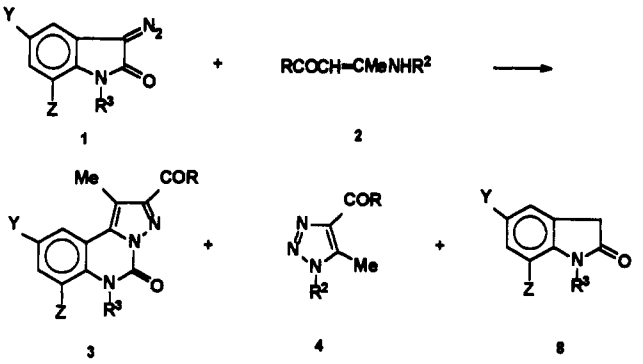
Reactions of the 5-methyl- and 5-methoxy-3-diazo-1,3-dihydro-2*H*-indol-2-ones (**1c** and **1d**, respectively), whose frontier orbital energies are presented in Table II, led to poor turnover to either of the corresponding pyrazoloquinazolinones or triazoles (Table III, entries 1–3) with total yields of products varying from 15% to 35%.

Much better results were obtained with the 5-nitro derivative **1e**. Although the low solubility of **1e** in refluxing toluene made it necessary to run the reaction as a suspension, the reaction time was considerably shorter. Reaction with the enamino ketones **2a** and **2d** led to formation of pyrazoloquinazolinone **3g** in approximately 40% yield and the triazoles **4a** and **4d** in approximately 25% yields (Table III, entries 4 and 6). These results indicate that formation of **3** does not require that the diazo compound have a high-energy HOMO and suggests that it acts as an electrophile in the formation of this compound as well as in the formation of **4**. If this is the case, a cycloaddition mechanism to form pyrazoloquinazolinones does not seem reasonable because of the small coefficients on C3 in the LUMO of **1** (as shown before). It is interesting to note that the reaction of **1e** with the enamino ester **2b** furnishes the corresponding pyrazoloquinazolinone (**3h**) in low yield and that this product is not detected at all in the reaction with **2e**. Instead, the triazoles **4b** and **4e** are formed in 54% and 73% yield, respectively (Table III, entries 5 and 7).

The *N*-methyl derivative **1f** was prepared to improve solubility properties. No reduction of reaction time in comparison with **1e** was observed. However, pyrazoloquinazolinone formation was completely suppressed in reactions with **2a** and **2d** and, at the same time, the yields of the corresponding triazoles doubled (Table III, entries 8 and 10). As expected, molecular orbital considerations (Table II) show very little difference in frontier orbital energies between **1e** and **1f**. Therefore, we assume that the difference in behavior does not involve the initial approximation of the reagents. One possibility is that a common intermediate is responsible for formation of both products.

(14) Huisgen, R.; Bihlmaier, W.; Reissig, H. U.; Voss, S. *Tetrahedron Lett.* **1979**, *28*, 2621.

**Table III. Reactions of Substituted 3-Diazo-1,3-dihydro-2*H*-indol-2-one (1) with Enaminones 2**




| entry | 1 | 2 | 3 (1% yield) | 4 (% yield) | 8 (% yield) | reactn time (h) |
|---|---|---|---|---|---|---|
| 1 | 1c (Y = Me, Z = R³ = H) | 2a (R = R² = Me) | 3d (35) | trace | | 168 |
| 2 | 1c | 2b (R = OEt, R² = Me) | 3e (17) | 4b (10) | | 168 |
| 3 | 1d (Y = OMe, Z = R³ = H) | 2b | 3f (4) | 4b (11) | | 168 |
| 4 | 1e (Y = $NO_2$, Z = R³ = H) | 2a | 3g (39) | 4a (27) | | 72 |
| 5 | 1e | 2b | 3h (8) | 4b (54) | 8a (11) | 42 |
| 6 | 1e | 2d (R = Me, R² = *t*-Bu) | 3g (38) | 4d (25 | | 48 |
| 7 | 1e | 2e (R = OEt, *R*² = *t*-Bu) | | 4e (73) | | 36 |
| 8 | 1f (Y = $NO_2$, Z = H, R³ = Me) | 2a | | 4a (55) | 8b (23) | 80 |
| 9 | 1f | 2b | | 4b (59) | 8b (17) | 42 |
| 10 | 1f | 2d | | 4d (59) | | 56 |
| 11 | 1f | 2e | | 4e (82) | | 36 |
| 12[a] | 1f | 2a | 3i (18) | 4a (35) | | 80 |
| 13 | 1g (Y = Z = $NO_2$, R³ = H) | 2a | | 4a (55) | 8c (8) | 6 |
| 14 | 1g | 2b | | 4b (67) | 8c (21) | 2 |
| 15 | 1g | 2d | | 4d (61) | | 3 |
| 16 | 1g | 2e | | 4e (81) | | 1.5 |

[a] In the presence of a catalytic amount of *p*-toluenesulfonic acid.

We suggest initial nucleophilic attack of the enaminone at the C$\alpha$ position on the terminal nitrogen of 1 (or 5) to form adduct A (Scheme I). Cyclization to B, either directly or through the azo intermediate C (which can exist in various tautomeric and geometric forms) with subsequent loss of amine followed by a [1,5 → N²] sigmatropic rearrangement,[13] would lead to 3. Formation of this product would be favored by an increase in nucleophilicity at C3, in electrophilicity at C$\beta$, and in facility of amine elimination which can be accomplished by equilibria involving the acidic N–H proton of the isatin portion of the intermediate. In fact, when the reaction of **1f** with **2a** was repeated using catalytic amounts of *p*-toluenesulfonic acid, pyrazoloquinazolinone **3i** (Table III, entry 12) was obtained in 18% yield and triazole **4a** in 35% yield. A comparison of entries 8 and 12 shows that **3i** is formed at the expense of **4a**, consistent with competitive formation of these products. Perhaps enamino esters show much less tendency to form pyrazoloquinazolinone because the lower electrophilicity at the C$\beta$ position makes this reaction slow with respect to the competitive cyclization and elimination of an oxindole derivative to form triazole.

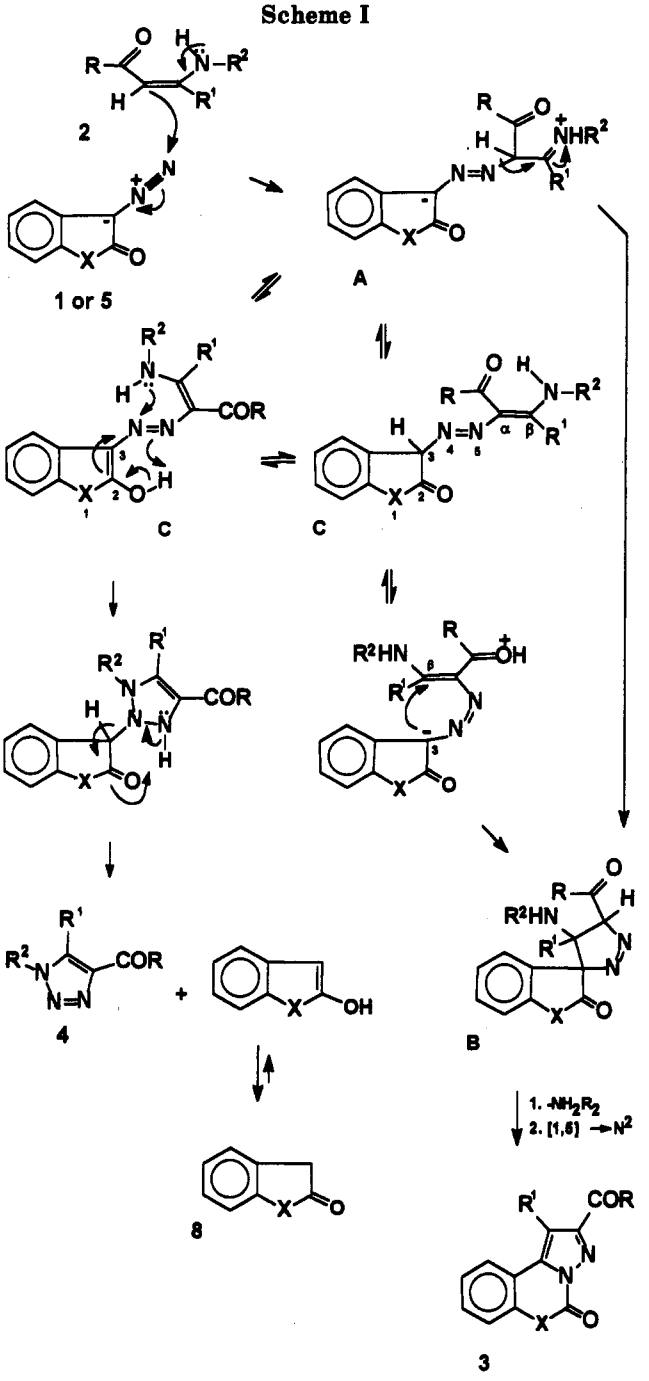
The isolation of the respective oxindole is accomplished in some cases. However, as can be seen in Table III, the yield is never equal to that of triazole. Two control experiments show that oxindole decomposes during work-up. Thus, when equimolar quantities of **4b** and **8a** were placed on a Florisil column (used in all separations) approximately 50% of **8a** decomposed forming polar complex mixtures which were also formed in the reactions. In the second study the crude mixture from reaction of **2e** with **1f** (in which triazole formation yield was the greatest) was analyzed by $^1$H NMR ($CDCl_3$). The relative intensities of the signals at $\delta$ 2.77 and 3.63 showed that triazole **4e** and oxindole **8b** were present in a 3:2 relative proportion, respectively, at the end of the reaction time. However, after column chromatography (Florisil), no **8b** was recovered.

The above results show that an electron-withdrawing group on 1 favors reaction. To obtain an even better diazocarbonyl reagent we prepared **1g** by dinitrating isatin[15] followed by reaction with tosylhydrazine which in this case formed **1g** directly without base addition.[16] This compound's lower melting point with respect to **1e** and its solubility in refluxing toluene under the reaction conditions suggest intramolecular hydrogen bonding between the N1 proton and the 7-$NO_2$ group. Reaction times decreased by a factor of approximately 10–20 forming triazoles in yields that are approximately the same as when **1f** was used. We have not been able to detect any pyrazoloquinazolinone product in the reactions with **1g** perhaps because intramolecular hydrogen bonding makes the N1 proton less available for forming species that are more reactive toward formation of **3** as mentioned above. Another possibility is that the corresponding C3 position of the intermediate formed is not nucleophilic enough (Scheme I).

In conclusion, we have been able to direct this reaction toward the formation of triazoles by use of the appropriately substituted 3-diazo-1,3-dihydro-2*H*-indol-2-one under neutral conditions using readily available reagents. In spite of their simplicity, none of the triazoles formed in this study have been previously reported. The most important method of 1,2,3-triazole synthesis involves reactions of azides with acetylenes.[12] The triazoles prepared in this project would require the use of N-alkyl azides

(15) Menon, K. N.; Perkin, W. H.; Robinson, R. *J. Chem. Soc.* **1930**, 830.
(16) Creger, P. L. *J. Org. Chem.* **1965**, *30*, 3610.
(17) Grundmann, C.; Haldenwanger, H. *Angew. Chem.* **1950**, *62*, 410.

**Scheme I**



which are hazardous to work with.[17] It is expected that this novel reaction will prove to be a useful synthetic procedure and lead to formation of triazoles which would be difficult to prepare from other routes. At this time the use of these reagents to form pyrazoloquinazolinones seems to be of limited synthetic utility because of the low yields that are generally obtained. However, studies are under way using different acid catalysts to determine if the reaction can be directed to their formation in high yields.

## Experimental Section

Melting points are uncorrected. Proton and carbon chemical shifts were measured relative to internal tetramethylsilane. The electron impact mass spectra were obtained at 70 eV.

The enaminones **2** and **7**[18] were prepared according to reported methods. Diazocarbonyl compounds **1** and **5** were prepared from the corresponding 1,3-dihydro-2*H*-indole-2,3-diones; thus, **1a**, **1c**, **1d**, and **1e** were obtained according to Creger[16] while the obtention of **1b**[7] and **5**[19] followed the cited references.

**3-Diazo-1,3-dihydro-1-methyl-5-nitro-2*H*-indol-2-one (1f).** Compound **1f** was prepared following the same procedure described for the synthesis of its analog **1b**.[7] The product formed yellow crystals, mp 225–6 °C dec: IR (KBr) 2110, 1700, 1520, 1330 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 3.41 (s, 3H), 6.99 (d, 1H, $J$ = 8.7 Hz), 8.14 (d, 1H, $J$ = 2.2 Hz), 8.18 (dd, 1H, $J$ = 8.7, 2.2 Hz); MS $m/z$ (relative intensity) 218 (70), 190 (46), 116 (100).

**3-Diazo-1,3-dihydro-5,7-dinitro-2*H*-indol-2-one (1g).** Tosylhydrazine (0.45 g, 2.4 mmol) in 5 mL of methanol was added slowly to a solution of 1,3-dihydro-5,7-dinitro-2*H*-indole-2,3-dione[15] (0.58 g, 2.4 mmol) in 10 mL of hot methanol. A yellow solid precipitated immediately, and the resulting suspension was refluxed for 16 h. After filtration, **1g** was obtained directly as yellow crystals (76% yield), mp 233–6 °C dec: IR (KBr) 3450, 2120, 1700, 1520, 1380 cm$^{-1}$; $^1$H NMR (DMSO-$d_6$) $\delta$ 8.58 (d, 1H, $J$ = 2.0 Hz), 8.79 (d, 1H, $J$ = 2.0 Hz), 12.05 (s, 1H); MS $m/z$ (relative intensity) 249 (48), 221 (100), 147 (29), 101 (30), 100 (26), 74 (39). Anal. Calcd for $C_8H_3N_5O_5$: C, 49.54; H, 2.75; N, 25.69. Found: C, 49.28; H, 2.69; N, 25.42.

**General Procedure for Reactions of Diazocarbonyl Compounds 1 and 5 with Enaminones 2 and 7.** A mixture of diazocarbonyl compounds **1** and **5** (1 mmol) and enaminones **2** and **7** (1 mmol) in dry toluene (or benzene) (30 mL) was refluxed until the disappearance of the $N_2$ absorption band at 2100 cm$^{-1}$ in the IR spectrum. Compounds **3a** and **3g** precipitated, while the other reaction products remained in solution. After filtration of these insoluble products, the solvent was evaporated, and the crude material was submitted to column chromatography (Florisil) using mixtures of hexane, $CH_2Cl_2$, and methanol as eluents. All the products obtained were further purified by preparative thin-layer chromatography (TLC). It was carried out on silica using MeOH/$CHCl_3$ solution (1:100) as eluent.

**2-Acetyl-1-methylpyrazolo[1,5-*c*]quinazolin-5(6*H*)-one (3a).** The product formed colorless crystals, mp 320–5 °C dec: IR (KBr) 3440, 1735, 1690 cm$^{-1}$; $^1$H NMR ($CDCl_3$–TFA) $\delta$ 2.80 (s, 3H), 2.81 (s, 3H), 7.39 (d, 1H, $J$ = 8.0 Hz); 7.47 (t, 1H, $J$ = 8.0 Hz), 7.60 (t, 1H, $J$ = 8.0 Hz), 8.16 (d, 1H, $J$ = 8.0 Hz); MS $m/z$ (relative intensity) 241 (84), 226 (17), 198 (100), 172 (7). Anal. Calcd for $C_{13}H_{11}N_3O_2$: C, 64.72; N, 17.41; H, 4.60. Found: C, 64.39; N, 17.22; H, 4.55.

**2-Carbethoxy-1-methylpyrazolo[1,5-*c*]quinazolin-5(6*H*)-one (3b).** The product eluted with MeOH/$CH_2Cl_2$ (1:10) and formed colorless crystals, mp 270–2 °C: IR (KBr) 3200, 1740 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.45 (t, 3H, $J$ = 7.0 Hz), 2.80 (s, 3H), 4.48 (q, 2H, $J$ = 7.0 Hz), 7.33 (t, 1H, $J$ = 7.7 Hz), 7.48 (m, 2H), 8.02 (d, 1H, $J$ = 7.7 Hz), 10.71 (b, 1H); MS $m/z$ (relative intensity) 271 (100), 199 (87), 198 (55), 197 (29), 196 (80), 170 (45). Anal. Calcd for $C_{14}H_{13}N_3O_3$: C, 61.98; H, 4.83; N, 15.49. Found: C, 61.81; H, 4.44; N, 15.16.

**2-Acetyl-1,6-dimethylpyrazolo[1,5-*c*]quinazolin-5(6*H*)-one (3c).** The product eluted with MeOH/$CH_2Cl_2$ (1:100) and formed colorless crystals, mp 288–9 °C: IR (KBr) 1720, 1690, 1485, 1340 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.78 (s, 3H), 2.79 (s, 3H), 3.82 (s, 3H), 7.39 (m, 2H), 7.58 (dt, 1H, $J$ = 8.0, 1.5 Hz), 8.11 (dd, 1H, $J$ = 8.0, 1.5 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 10.4, 28.4, 31.5, 114.6, 114.9, 115.1, 123.8, 124.0, 129.9, 135.4, 136.5, 145.6, 151.2, 196.9; MS $m/z$ (relative intensity) 255 (84), 240 (7), 212 (100), 186 (7), 184 (3). Anal. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46. Found: C, 65.40; H, 4.92; N, 16.62.

**2-Acetyl-1,9-dimethylpyrazolo[1,5-*c*]quinazolin-5(6*H*)-one (3d).** The product eluted with MeOH/$CH_2Cl_2$ (5:100) and formed colorless crystals, mp 331–5 °C dec: IR (KBr) 3200, 1735, 1695 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.48 (s, 3H), 2.81 (s, 6H), 7.25 (d, 1H, $J$ = 8.0 Hz), 7.33 (dd, 1H, $J$ = 8.0, 1.5 Hz), 7.88 (s, 1H), 9.60 (b, 1H); MS $m/z$ (relative intensity) 255 (87), 240 (16), 212 (100). Anal. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46. Found: C, 65.21; H, 4.68; N, 16.12.

**2-Carbethoxy-1,9-dimethylpyrazolo[1,5-*c*]quinazolin-5(6*H*)-one (3e).** The product eluted with MeOH/$CH_2Cl_2$ (1:10) and formed colorless crystals, mp 266–8 °C: IR (KBr) 3230, 1735

(18) Greenhill, J. V. *Chem. Soc. Rev.* **1977**, *6*, 277.

(19) Ried, W.; Dietrich, R. *Chem. Ber.* **1961**, *94*, 387.

cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.44 (t, 3H, $J$ = 7.0 Hz), 2.45 (s, 3H), 2.77 (s, 3H), 4.47 (q, 2H, $J$ = 7.0 Hz), 7.27 (d, 1H, $J$ = 8.0 Hz), 7.35 (d, 1H, $J$ = 8.0 Hz), 7.79 (s, 1H); 10.79 (b, 1H); MS $m/z$ (relative intensity) 285 (100), 213 (95), 212 (57), 211(37), 210 (76),184 (34). Anal. Calcd for $C_{15}H_{15}N_3O_3$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.60; H, 5.26; N, 14.29.

**2-Carbethoxy-9-methoxy-1-methylpyrazolo[1,5-*c*]quinazolin-5(6*H*)-one (3f).** The product eluted with MeOH/$CH_2Cl_2$ (1:10) and formed colorless crystals, mp 268–9 °C: IR (KBr) 3450, 1735 cm$^{-1}$; $^1$H NMR ($CDCl_3$–TFA) $\delta$ 1.41 (t, 3H, $J$ = 7.0 Hz), 2.92 (s, 3H), 3.96 (s, 3H), 4.43 (q, 2H, $J$ = 7.0 Hz), 7.24 (d, 1H, $J$ = 8.9 Hz), 7.33 (d, 1H, $J$ = 8.9 Hz), 7.66 (s, 1H); MS $m/z$ (relative intensity) 301 (16), 256 (20), 255 (20), 229 (48), 226 (40), 213 (32), 127 (100), 77 (76).

**2-Acetyl-1-methyl-9-nitropyrazolo[1,5-*c*]quinazolin-5(6*H*)-one (3g).** The product formed colorless crystals, mp 363–8 °C dec: IR (KBr) 1715, 1695, 1535, 1335 cm$^{-1}$; $^1$H NMR ($CDCl_3$–TFA) $\delta$ 2.86 (s, 3H), 2.90 (s, 3H), 7.59 (d, 1H, $J$ = 9.0 Hz), 8.50 (dd, 1H, $J$ = 9.0, 2.3 Hz), 9.05 (d, 1H, $J$ = 2.3 Hz); MS $m/z$ (relative intensity) 286 (100), 271 (33), 242 (74), 197 (25). Anal. Calcd for $C_{13}H_{10}N_4O_4$: C, 54.55; H, 3.52; N, 19.57. Found: C, 54.23; H, 2.98; N, 19.02.

**2-Carbethoxy-1-methyl-9-nitropyrazolo[1,5-*c*]quinazolin-5(6*H*)-one (3h).** The product eluted with MeOH/$CH_2Cl_2$ (1:5) and formed colorless crystals, mp > 300 °C: IR (KBr) 1755, 1535, 1345 cm$^{-1}$; $^1$H NMR ($CDCl_3$–TFA) $\delta$ 1.47 (t, 3H, $J$ = 7.0 Hz), 2.89 (s, 3H), 4.53 (q, 2H, $J$ = 7.0 Hz), 7.56 (d, 1H, $J$ = 9.0 Hz), 8.48 (dd, 1H, $J$ = 9.0, 2.3 Hz), 9.03 (d, 1H, $J$ = 2.3 Hz); MS $m/z$ (relative intensity) 316 (100), 271 (23), 270 (50), 244 (67), 241 (75), 198 (25). All attempts to obtain a pure sample of this material failed.

**2-Acetyl-1,6-dimethyl-9-nitropyrazolo[1,5-*c*]quinazolin-5(6*H*)-one (3i).** The product eluted with MeOH/$CH_2Cl_2$ (1:50) and formed colorless crystals, mp 295–6 °C dec: IR (KBr) 1735, 1690, 1520, 1345, 1310 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.81 (s, 3H), 2.88 (s, 3H), 3.91 (s, 3H), 7.51 (d, 1H, $J$ = 9.0 Hz), 8.45 (dd, 1H, $J$ = 9.0, 2.5 Hz), 9.00 (d, 1H, $J$ = 2.5 Hz); MS $m/z$ (relative intensity) 300 (100), 285 (11), 258 (82), 241 (9), 211(24). Anal. Calcd for $C_{14}H_{12}N_4O_4$: C, 56.00; H, 4.03; N, 18.66. Found: C, 55.52; H, 3.95; N, 18.49.

**2-Acetyl-1-methyl-5*H*-pyrazolo[1,5-*c*][1,3]benzothiazin-5(6*H*)-one (3j).** The product eluted with MeOH/$CH_2Cl_2$ (2:100) and formed colorless crystals, mp 190–1 °C: IR (KBr) 1690, 1280 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.78 (s, 3H), 2.82 (s, 3H), 7.45 (m, 3H), 8.22 (d, 1H, $J$ = 8.0 Hz); MS $m/z$ (relative intensity) 258 (34), 230 (6), 215 (16), 187 (46), 43 (100). Anal. Calcd for $C_{13}H_{10}N_2O_2S$: C, 60.45; N, 10.85; H, 3.90. Found: C, 60.81; N, 10.42; H, 3.85.

**4-Acetyl-1,5-dimethyl-1*H*-1,2,3-triazole (4a).** The product eluted with MeOH/$CH_2Cl_2$ (1:100) and formed colorless crystals, mp 102–3 °C: IR (KBr) 1680 cm$^{-1}$; $^1$H NMR ($CCl_4$) $\delta$ 2.53 (s, 3H), 2.57 (s, 3H), 3.94 (s, 3H); MS $m/z$ (relative intensity) 139 (100), 124 (10), 111 (13), 96 (28), 68 (40), 56 (79). Anal. Calcd for $C_6H_9N_3O$: C, 51.79; N, 30.20; H, 6.52. Found: C, 52.02; N, 30.49; H, 6.29.

**4-Carbethoxy-1,5-dimethyl-1*H*-1,2,3-triazole (4b).** The product eluted with MeOH/$CH_2Cl_2$ (1:100) and formed a colorless oil: IR (neat) 1720 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.41 (t, 3H, $J$ = 7.0 Hz), 2.49 (s, 3H), 3.92 (s, 3H), 4.30 (q, 2H, $J$ = 7.0 Hz); MS $m/z$ (relative intensity) 169 (12), 124 (20), 113 (58), 112 (10), 97 (38), 96 (23), 68 (42), 56 (100). Anal. Calcd for $C_7H_{11}N_3O_2$: C, 49.70; N, 24.84; H, 6.55. Found: C, 50.00; N, 24.62; H, 6.50.

**4-Acetyl-1-(1,1-dimethylethyl)-5-methyl-1*H*-1,2,3-triazole (4d).** The product eluted with MeOH/$CH_2Cl_2$ (1:100) and formed colorless crystals, mp 62–3 °C: IR (KBr) 1680 cm$^{-1}$; $^1$H NMR ($CCl_4$) $\delta$ 1.74 (s, 9H), 2.55 (s, 3H), 2.72 (s, 3H); MS $m/z$ (relative intensity) 181 (25), 110 (12), 97 (45), 96 (39), 57 (100), 43 (75). Anal. Calcd for $C_9H_{15}N_3O$: C, 59.64; N, 23.18; H, 8.34. Found: C, 59.91; N, 23.60; H, 8.26.

**4-Carbethoxy-1-(1,1-dimethylethyl)-5-methyl-1*H*-1,2,3-triazole (4e).** The product eluted with MeOH/$CH_2Cl_2$ (1:100) and formed a colorless oil: IR (neat) 1710 cm$^{-1}$; $^1$H NMR ($CCl_4$) $\delta$ 1.42 (t, 3H, $J$ = 7.0 Hz), 1.74 (s, 9H). 2.72 (s, 3H), 4.31 (q, 2H, $J$ = 7.0 Hz); MS (relative intensity) 211 (28), 196 (34), 127 (18), 110 (23), 57 (100), 43 (22). Anal. Calcd for $C_{10}H_{17}N_3O_2$: C, 56.85; N, 19.89; H, 8.11. Found: C, 56.88; N, 19.56; H, 8.09.

**6,6-Dimethyl-4,5,6,7-tetrahydro-1*H*-benzotriazol-4-one (4f).** The product eluted with MeOH/$CH_2Cl_2$ (1:20) and formed colorless crystals, mp 139–40 °C: IR (KBr) 3220, 1680 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.14 (s, 6H), 2.53 (s, 2H), 2.89 (s, 2H), 13.4 (b, 1H); MS $m/z$ (relative intensity) 165 (29), 150 (59), 122 (25), 109 (100), 94 (25), 57 (20). Anal. Calcd for $C_8H_{11}N_3O$: C, 58.17; N, 25.44; H, 6.71. Found: C, 58.43; N, 25.02; H, 6.61.

**1,6,6-Trimethyl-4,5,6,7-trihydro-1*H*-benzotriazol-4-one (4g).** The product eluted with MeOH/$CH_2Cl_2$ (1:40) and formed colorless crystals, mp 131–2 °C: IR (KBr) 1680 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.16 (s, 6H), 2.49 (s, 2H), 2.75 (s, 2H), 4.03 (s, 3H); MS (relative intensity) 179 (12), 136 (4), 108 (6), 67 (100), 66 (23), 55 (14). Anal. Calcd for $C_9H_{13}N_3O$: C, 60.32; N, 23.45; H, 7.31. Found: C, 60.75; N, 23.00; H, 7.17.

**5-Nitro-1,3-dihydro-2*H*-indol-2-one (8a).** The product eluted with MeOH/$CH_2Cl_2$ (1:50) and formed colorless crystals, mp 240–1 °C (lit.[20] 241–2 °C).

**1-Methyl-5-nitro-1,3-dihydro-2*H*-indol-2-one (8b).** The product eluted with MeOH/$CH_2Cl_2$ (1:100) and formed colorless crystals, mp 191–2 °C (lit.[21] 194–5 °C).

**5,7-Dinitro-1,3-dihydro-2*H*-indol-2-one (8c).** The product eluted with MeOH/$CH_2Cl_2$ (1:100) and formed colorless crystals, mp 247–8 °C (lit.[22] 248– 50 °C).

**Acknowledgment.** R.A. thanks FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) for financial support.

**Supplementary Material Available:** COLOC NMR data for **3c** (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(20) Sumpter, W. C.; Miller, M.; Magan, M. E. *J. Am. Chem. Soc.* **1945**, *67*, 499.
(21) Kisteneva, M. S. *J. Gen. Chem. USSR (Engl. Transl.)* **1956**, *26*, 2251.
(22) Coretts, R. T.; Hindmarsh, K. W.; Mah, E. *Can. J. Chem.* **1970**, *48*, 3747.