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Reactions with Heterocyclic Diazonium Salts. Synthesis of Several New Fused Azolotriazine Derivatives

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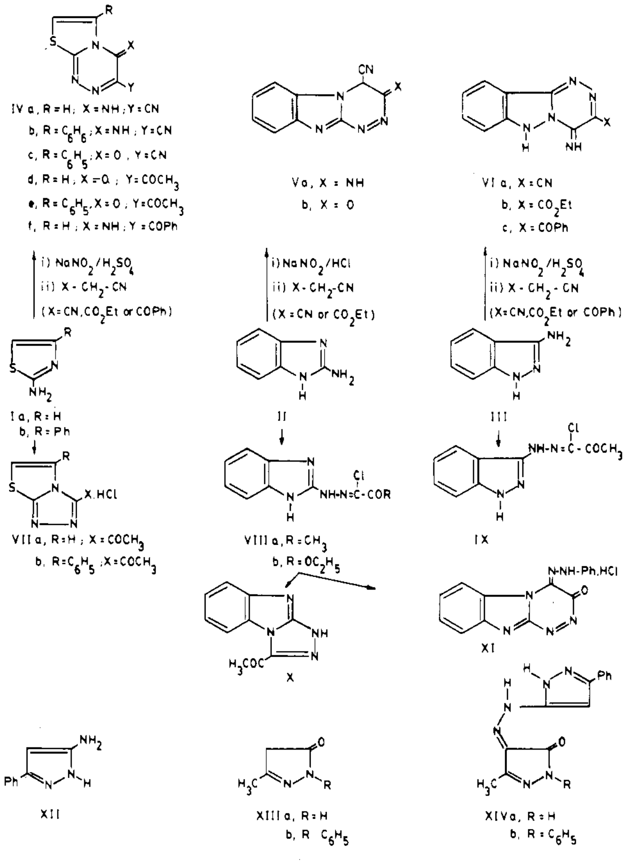
A variety of azolo-1,2,4-triazine derivatives were prepared via coupling diazotized aminoheterocyclic derivatives with activated nitriles. Coupling of diazotized amino heterocycles with α-chloroacetylacetone and/or ethyl α-chloroacetoacetate afforded fused 1,2,4-triazoles. The intermediately formed heterocyclic hydrazonyl halides could be isolated in some cases.

In continuation of our work aiming to explore the synthetic potentialities of heterocyclic diazonium salts (*1-3*), we report here our further results in this direction. Thus, the diazotized aminoheterocyclic derivatives Ia,b, II, and III coupled with activated nitriles to yield the azolotriazine derivatives IVa-f, Va,b, and VIa-c. Similarly diazotized Ia,b coupled with α-chloroacetylacetone to yield the thiazolo[3,2-*c*]-1,2,4-triazole derivatives VIIa,b. On the other hand, the hydrazonyl chlorides VIIIa,b were obtained on coupling diazotized II with α-chloroacetylacetone and with ethyl α-chloroacetoacetate. Also compound III coupled with α-chloroacetylacetone to yield the hydrazone IX. Compound VIIIa could be cyclized into the benzimidazo[1,2-*c*]-1,2,4-triazole derivative X. On the other hand, VIIIb cyclized into the benzimidazo[1,2-*c*]-*as*-triazine derivative XI by the action of phenylhydrazine.

Similar to previous work (*3*), diazotized 5-amino-3-phenylpyrazole (XII) coupled with the 2-pyrazolin-5-one derivatives XIIIa,b to yield the hydrazones XIVa,b. Compounds XIVa,b did not cyclize into pyrazolotriazines under conditions reported to effect cyclization of structurally related hydrazones.

The structures of the synthesized products were established on the basis of analytical and spectral data.



Experimental Section

All melting points are uncorrected. IR spectra were recorded (KBr) with a Beckman spectrophotometer. ^{1}H NMR spectra were obtained on an EM-390 90-MHz spectrophotometer using Me_4Si as internal indicator, and chemical shifts are expressed in ppm. Analytical data were obtained from the analytical data unit at Cairo University.

Reaction of Diazotized Ia,b, II, III, and XII with Active Hydrogen Compounds. A solution of 0.01 mol of diazotized Ia,b and III (prepared following the procedure described by

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Table I. List of the Products of Coupling Diazotized Ia,b, II, III, and XII with Active Hydrogen Compounds

compd[a]	mp, °C (crys solv)[b]	yield, %	IR, cm^{-1}	^1H NMR, ppm
IVa	280 (a)	80	1625 (C=N); 2240 (CN); 3270, 3140, 3100 (NH)	7.42 (d, 1 H, *J* = 6; thiazole H-5); 8.16 (d, 1 H, *J* = 6; thiazole H-4); 10.5 (s, br, 1 H, NH)
IVb	280 (b)	80	1650 (C=N); 2210 (CN); 3580, 3180 (NH)	7.4–7.8 (m, 6 H, aromatic and thiazole proton); 10.5 (s, br, 1 H, NH)
IVc	280 (c)	75	1700 (C=O); 2200 (CN)	7.2–7.8 (m, 6 H, aromatic and thiazole proton)
IVd	280 (d)	75	1600 (C=N); 1680–1720 (CO) br	7.38 (d, 1 H, *J* = 6; thiazole H-5); 8.12 (d, 1 H, *J* = 6; thiazole H-4); 2.1 (s, 3 H, $COCH_3$)
IVe	130 (a)	75	1580 (C=N); 1680–1720 (CO) br	7.4–8.0 (m, 6 H, aromatic and thiazole proton); 2.0 (s, 3 H, $COCH_3$)
IVf	200 (c)	70	1620 (C=N); 1720 (CO); 3400, 3290, 3190, 3360 (NH)	
Va	140 (e)	70	1680 (C=N); 2200 (CN); 3360 (NH)	7.2–8.0 (m, 4 H, aromatic protons); 10.2 (s, br, 1 H, NH)
Vb	250 (c)	70	1630 (C=N); 1680 (CO); 2200 (CN)	
VIa	300 (c)	70	1660 (C=N); 2240 (CN); 3360–3300, 3070–3000 (NH)	7.2–7.8 (m, 4 H, aromatic protons); 10.0 (s, br, 1 H, NH)
VIb	247 (c)	54	1630 (C=N); 1690 (CO); 3440 (NH)	1.3 (t, 3 H, CH_3); 4.3 (q, 2 H, CH_2; 7.2–8.0 (m, 4 H, aromatic protons); 11.2 (s, br, 1 H, NH)
VIc	274 (c)	50	1630 (C=N); 1660 (CO); 3480–3460 (NH)	7.1–8.2 (m, aromatic and NH protons)
VIIa	280 (b)	60	1650 (C=N); 1700 (CO)	
VIIb	280 (e)	60	1630 (C=N); 1670 (CO)	
VIIIa	279 (c)	60	1610 (δNH); 1640 (C=N); 1715 (CO)	2.1 (s, 3 H, CH_3); 7.2–7.6 (m, 4 H, aromatic protons); 11.0 (s, br, 2 H, NH protons)
VIIIb	146 (c)	60	1660 (CO); 3480–3460, 3140–3080 (NH)	1.3 (t, 3 H, CH_3); 4.2 (q, 2 H, CH_2); 7.2–7.7 (m, 4 H, aromatic protons); 10.9 (s, br, 2 H, NH, protons)
IX	185 (c)	50	1680 (CO), 3330 (NH)	2.0 (s, 3 H, $COCH_3$); 7.2–7.8 (m, 4 H, aromatic protons); 11.5 (br, 2 H, NH protons)
X	242 (c)	60	1640 (C=N); 1690 (CO)	2.2 (s, 3 H, $COCH_3$); 7.2–8.2 (m, 4 H, aromatic protons); 12.0 (s, br, NH)
XI	304 (c)	70	1630 (δNH); 1670 (C=N); 1710 (CO); 3480, 3380 (NH)	7.2–8.0 (m, 9 H, aromatic protons); 11.5 (m, br, 2 H, NH and HCl)
XIVa	260 (c)	60	1680 (CO); 3350 (NH)	
XIVb	255 (c)	50	1670 (CO); 3300–3330 (NH)	

[a] Satisfactory elemental analyses were found. [b] a = acetone–water, b = DMF–water, c = ethanol, d = acetone, e = ethanol–water.

Morgan and Morrow (*4*)) and II and XII (prepared following the procedure described by us (*2*)) was added to a solution of appropriate active hydrogen compound in ethanol. (The diazonium salts should be used directly. Gradual decomposition in solution takes place on standing. **Caution**: Care should be taken on attempted isolation of the diazonium salts or the diazo compounds in the solid state as some of these diazo compounds explode readily.) The solid product so formed on standing was collected by filtration and crystallized from the proper solvent (cf. Table I).

In the case of the products of coupling of diazotized Ia,b, the solution was concentrated to half its volume and left to cool. The solid product so formed was collected by filtration and crystallized from the proper solvent (cf. Table I).

3,4-Disubstituted Indazolo[3,2-c]-as-triazines (VIa-c). The experimental procedure described above for the reaction of diazotized III with malononitrile was adopted utilizing ethyl cyanoacetate and benzoylacetonitrile as coupling component, and the resulting coupling product was boiled in acetic acid under reflux for 4 h. The resulting solution was then evaporated and triturated with ethanol. The solid product so formed was collected by filtration and crystallized from the proper solvent (cf. Table I).

3-Phenylhydrazine-4-oxo-3,4-dihydrobenzimidazo[2,1-c]-as-triazine (XI). A solution of VIIIb (0.01 mol) in ethanol (50 mL) and phenylhydrazine (0.01 mol) was refluxed for 3 h. The reaction mixture was then evaporated under vacuum, and the remaining product was triturated with water. The solid product so formed was collected by filtration and crystallized from ethanol. (cf. Table I).

Benzimidazo[2,1-c]-1,2,4-triazole (X). A solution of VIIIa (0.01 mol) in benzene (50 mL) was treated with triethylamine (2.0 mL), and the reaction mixture was refluxed for 2 h. The solvent was then evaporated under vacuum, and the remaining solid product was then collected by filtration and crystallized from the proper solvent (cf. Table I).

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