A New Heterocyclic Structure. The [1,2,3]Triazolo[1,5-*d*][1,2,4]triazine

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The hydrazone derivatives of 4-benzoyl-1,2,3-triazole can easily be cyclised by reaction with various organic reagents (ortho esters, aldehyde and ketone compounds, phosgene, *etc*) which result in the incorporation of the introduced reagent's carbon atom into the new six membered ring. The newly created C-N bond of the resulting [1,2,3]triazolo[1,5-*d*][1,2,4]triazines displays a particular sensitivity due to the electron attracting effect of the triazole ring. Some mechanistic considerations are proposed to account for the observed results.

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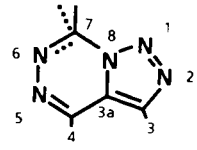
4-Benzoyl-1,2,3-triazole, **1**, can be obtained by various routes [1-3]. Amongst them the reaction of sodium azide with an acryloylphenyl substituted by a suitable leaving group at the γ position was the one used in this work.

The outstanding chemical feature of the 4-benzoyl-1,2,3-triazole molecule, **1**, is the acidic nature of the nitrogen bound triazole proton. This property is obviously exacerbated by the proximity of the benzoyl group and makes the assignment of the location of the acidic proton impossible.

For its part the ketone carbonyl behaves normally. For instance it condenses with hydrazines under classical conditions and provides hydrazone derivatives such as **2, 3, 4**. In these structures the vicinity of two nitrogen bound protons (the one on the triazole ring and the other on the hydrazone moiety) allows subsequent cyclisations into various derivatives with the [1,2,3]triazolo[1,5-*d*][1,2,4]-triazine nucleus.



[1,2,3]Triazolo[1,5-*d*][1,2,4]triazine

I. Cyclisation into [1,2,3]Triazolo[1,5-*d*][1,2,4]triazines, **5**.

The action of an orthoester on the unsubstituted hydrazone **2** results in the insertion of a trigonal carbon atom between the terminal hydrazone nitrogen atom and the closest of the triazolic ones. A 4-phenyl[1,2,3]triazolo-[1,5-*d*][1,2,4]triazine **5**, possibly substituted on the newly introduced 7 carbon atom, is obtained. The lack of any nitrogen bound proton in the resulting compounds is ascertained by ^{1}H nmr and, together with their empirical formulae, supports the structure **5**.

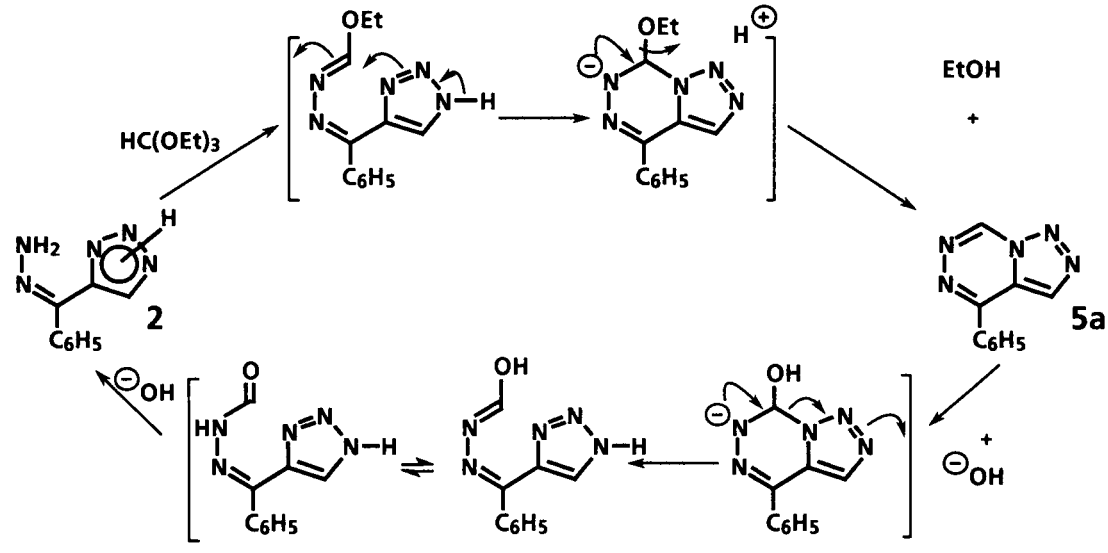
A putative ring closure mechanism could involve an ethoxy alkylidene derivative of **2** as a possible intermediate able to cyclise into an ethoxy dihydro derivative of **5**, by way of a nucleophilic attack of the ethoxy alkylidene moiety by the vicinal triazole nitrogen (Scheme 1a). The loss of an equivalent of ethanol completes the reaction and leads to the formation of the heteroaromatic derivative **5**. On the contrary the opening of the six membered ring can result from the nucleophilic attack on the amidinic 7 carbon atom by a hydroxide ion. The end product of the basic treatment (2*N* sodium hydroxide) is the starting hydrazone **2**, and it can be supposed that the representative scheme of the reaction (Scheme 1b) is formally the reverse of the previous one. That points out the sensitivity of the amidinic 7 carbon atom and the weakness of the newly formed 7C-8N bond, probably due, to a large extent, to the strong electron attracting effect of the triazole moiety.

It is likely for similar reasons that an acidic treatment gives the same ring opening. Cleavage of the 7C-8N bond and subsequent acidolysis of the hydrazone group degrade the molecule to finally give the initial benzoyltriazole **1**.

II. Cyclisations into 6,7-Dihydro[1,2,3]triazolo[1,5-*d*][1,2,4]-triazines **6,7**.

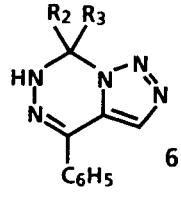
When the unsubstituted hydrazone **2** encounters a ketone or aldehyde compound, a cyclisation occurs spontaneously without any catalytic assistance. A 6,7-dihydro-[1,2,3]triazolo[1,5-*d*][1,2,4]triazine **6** is formed which may be unsubstituted, mono- or di-substituted at the 7 position, according to the type of the intervening carbonyl compound. The structure **6** is supported by the disappearance of the carbonyl group, the occasional concomitant appearance of the 7 substituents, the lack of an acidic triazolic NH hydrogen and the presence of a non acidic NH hydrogen (6 NH). The latter is supported by a ^{1}H nmr signal (δ = 8.6-9.5 ppm, DMSO-d_6) (Table VI) which differs markedly from that of the triazolic NH in **1, 2, 3** and **4** (δ = 15.3-15.7 ppm, DMSO-d_6) (Table IV). Moreover the

Scheme 1a



Scheme 1b

Table 1



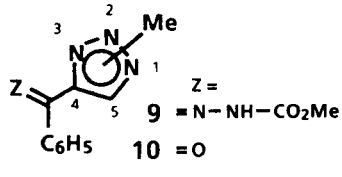
6

	R_2 =	R_3 =
a	H	H
b	CH_3	H
f	CH_3	CO_2Et

^{13}C NMR (DMSO; ppm)

	C3	C3a	C4	C7	Phenyl 1′	2′	3′	4′	7 CH_3	7 CO_2Et
6a	128.9 or 129.1	124.7	135.8	57.8	134.1	128.7	125.6	129.1 or 128.9		
6b	129.8	124.6	135.6	64.8	134.2	128.8	125.7	128.9	16.3	
6f	129.8	124.7	135.9	73.2	133.6	128.8	125.7	129.1	19.2	168.5 62.3 13.7

Table II



Z =
9 = N–NH–CO_2Me
10 = O

^{13}C NMR ($CDCl_3$; ppm)

	4CO	C4	C5	NMe	Phenyl 1′	2′	3′	4′	CO_2Me
10a (1Me)	185.6	148.4	129.1	36.9	136.6	130.6	128.4	132.2	
10b (2Me)	185.6	146.8	137.7	42.3	136.8	130.2	128.4	133.2	
10c (3Me)	184.2	133.4	138.8	37.8	137.3	129.2	128.9	133.9	
9		143.7	126	36.9	137.6	128.5 or	128.2	129.2	154.9 52.7

Table III

4-Benzoyl-1,2,3-triazole Hydrazones

Compound	R	Yield %	mp °C	Recrystallization solvent	Formula	Analyses, % Calcd./(Found) C	H	N
2	H	64	158-160	dil ethanol	$C_9H_9N_5$	57.74 (57.9)	4.84 (5.1)	37.41 (37.1)
3a	CH_3	45	138-140	dil ethanol	$C_{10}H_{11}N_5$	59.68 (59.8)	5.51 (5.5)	34.80 (34.6)
3b	CH_2CO_2Et	32	125-127	95% ethanol	$C_{13}H_{15}N_5O_2$	57.13 (57.4)	5.53 (5.7)	25.62 (25.8)
4a	CO_2Et	61	170-172	abs ethanol	$C_{12}H_{13}N_5O_2$	55.59 (55.6)	5.05 (5.0)	27.01 (26.9)

Table IV

^1H NMR (DMSO-d_6) ppm

Compound	H5 (s)	Arom H (m)	NH hydrazone	NH triazole	Others
2	7.80	7.12-7.40	7.63	15.30	
3a	7.80	7.10-7.42	8.13	15.23	3.05 (s, NCH_3)
3b	7.80	7.12-7.38	8.48	15.27	1.05 (t, OCH_2CH_3) 3.87-4.22 (m, OCH_2CH_3 and $-NCH_2-$)
4a	8.00	7.37	11.67	15.67	1.23 (t, OCH_2CH_3) 4.15 (q, OCH_2CH_3)

^{13}C nmr supports the presence of the 7 tetragonal carbon (Table I).

Dehydrogenation of the compound **6b** into the triazolotriazine **5b** can be carried out by means of a lead tetraacetate oxidation. This confirms the relationship between the structures **5** and **6** (Chart 1) that, on the other hand, are differentiated by their uv spectra [(absolute ethanol): **5a** λm 208 nm (ε 13300), 261 nm (ε 14200); **6a** λm 206 nm (ε 8470), 238 nm (ε 15400), 318 nm (ε 6300)].

CHART 1

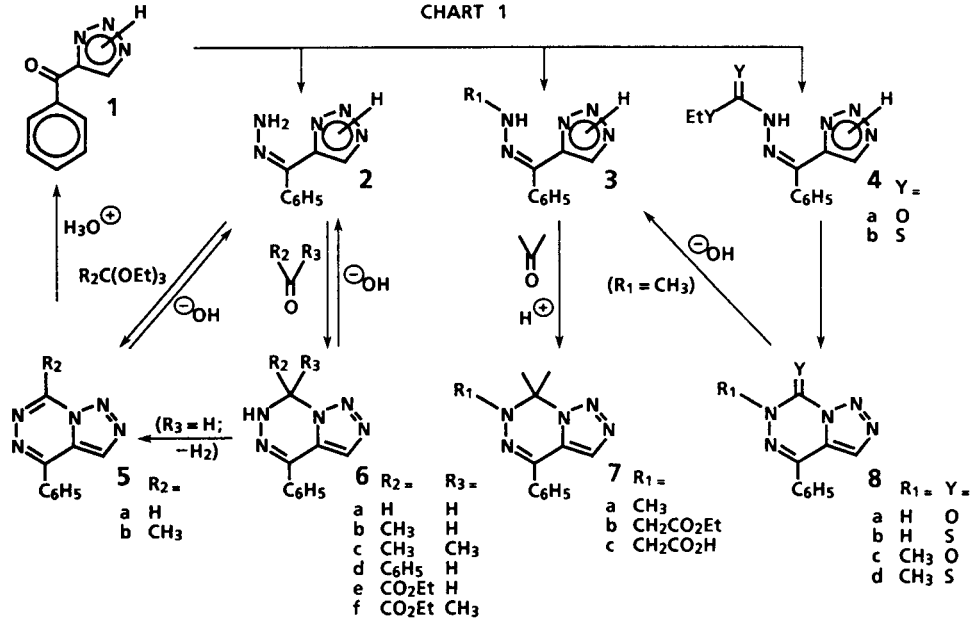


Table V

6,7-Dihydro-4-phenyl[1,2,3]triazolo[1,5-*d*][1,2,4]triazines

Compound	R1	R2	R3	Yield %	mp °C	Recrystallization solvent	Formula	Analyses, % Calcd./(Found) C	H	N
6a	H	H	H	70	188-190	95% ethanol	$C_{10}H_9N_5$	60.29	4.55	35.16
								(60.2)	(4.5)	(35.1)
6b	H	CH_3	H	59	187-189	95% ethanol	$C_{11}H_{11}N_5$	61.96	5.20	32.84
								(61.9)	(5.3)	(32.6)
6c [a]	H	CH_3	CH_3	62	164-166	95% ethanol	$C_{12}H_{13}N_5$	63.42	5.76	30.82
								(63.4)	(5.8)	(30.5)
6d	H	C_6H_5	H	71	172-174	dil ethanol	$C_{16}H_{13}N_5$	69.80	4.76	25.44
								(69.8)	(4.5)	(25.6)
6e [b]	H	$COOC_2H_5$	H	52	152-154	abs ethanol	$C_{13}H_{13}N_5O_2$	57.56	4.83	25.82
								(57.6)	(4.6)	(26.1)
6f [b]	H	$COOC_2H_5$	CH_3	43	127-129	95% ethanol	$C_{14}H_{15}N_5O_2$	58.93	5.30	24.55
								(58.5)	(5.5)	(24.4)
7a	CH_3	CH_3	CH_3	33	80-82	C_6H_6 + light petroleum	$C_{13}H_{15}N_5$	64.71	6.27	29.03
								(64.5)	(6.1)	(28.9)
7b	CH_2CO_2Et	CH_3	CH_3	67	111-113	dil acetone	$C_{16}H_{19}N_5O_2$	61.33	6.11	22.35
								(61.5)	(6.1)	(22.5)
7c	CH_2CO_2H	CH_3	CH_3	66	178-180	C_6H_6 + 95 % ethanol	$C_{14}H_{15}N_5O_2$	58.94	5.30	24.55
								(59.7)	(5.2)	(24.5)

[a] Excess acetone was used as solvent. [b] Sixteen hours under reflux.

Table VI

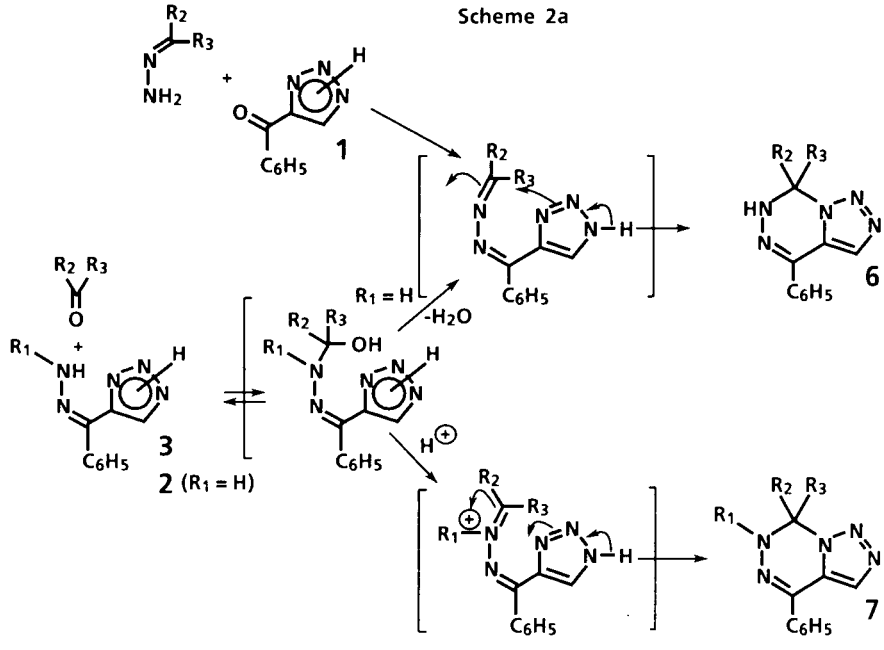
^{1}H NMR (DMSO-d_6) ppm

Compound	H3 (s)	Arom H (m)	NH6 or NCH_2-6	H7	$CH_3$7	Others
6a	7.98	7.28-7.77	8.63 (s, 1H)	5.58 (s, 2H)		
6b	7.97	7.28-7.77	8.71 (s, 1H)	5.57 (q, 1H)	1.78 (d, 1CH_3)	
6c	7.93	7.25-7.73	8.67 (s, 1H)		1.70 (s, 2CH_3)	
6d	8.47	7.30-7.80 (10H)	9.20 (s, 1H)	6.90 (s, 1H)		
6e	8.08	7.30-7.75	9.53 (s, 1H)	6.92 (s, 1H)		1.13 (t, OCH_2CH_3), 4.12 (q, OCH_2CH_3)
6f	8.05	7.27-7.75	9.53 (s, 1H)		2.13 (s, 1CH_3)	1.05 (t, OCH_2CH_3), 4.03 (q, OCH_2CH_3)
7a	7.96	7.27-7.77	3.20 (s, NCH_3)		1.75 (s, 2CH_3)	
7b	8.02	7.27-7.73	4.37 (s, NCH_2-)		1.77 (s, 2CH_3)	1.22 (t, OCH_2CH_3), 4.10 (q, OCH_2CH_3)
7c	8.03	7.30-7.77	4.32 (s, NCH_2-)		1.78 (s, 2CH_3)	12.53 (COOH)

The great ability of the structure **2** to entrap the carbonyl group of aldehyde and ketone compounds was highlighted when it was reacted with α-ketoesters. Only the carbonyl group of the latter was involved in the cyclisation to give dihydrotriazolotriazines, **6e**, **6f**, the structure of which was confirmed by ^{13}C nmr (Table I).

We were also inquisitive to know whether the monosubstituted hydrazones **3**, when treated with a ketone compound, were able to undergo the same ring closure. We observed that the cyclisation into *N*-substituted dihydrotriazolotriazines **7** does not in this instance occur spontaneously; it is fulfilled only when an acid is added to the reaction medium. It can be assumed that the first step of the reaction pathway, the nucleophilic attack on the carbonyl group by the end hydrazonic nitrogen, results in a kind of azahemiacetal (Scheme 2). In the case when the starting hydrazone derivative **2** is not *N*-substituted, the dehydration of this primary intermediate into an *N*-alkylidene derivative does not need any assistance and occurs spontaneously (Scheme 2a). [Such an *N*-alkylidene

Scheme 2a



Scheme 2b

derivative is also likely to be involved as an intermediate in the cyclisation with orthoesters (as supposed in Scheme 1a). However, in this case, the resulting alkoxy derivative of structure **6** (R_3 = OR) eliminates spontaneously an alcohol molecule to give the triazolotriazine **5**]. On the contrary, with the intermediates obtained from the *N*-substituted hydrazone derivatives **3**, a proton is required for the abstraction of the hydroxyl group (Scheme 2b). In any case, the resulting *N*-alkylidene derivative cyclises immediately and no intermediate could be isolated. Indeed, it was also possible to condense the isopropylidene hydrazine [4] with the benzoyltriazole **1** to give directly the cyclised derivative **6c** (Scheme 2a).

The reverse reaction of this cyclisation, the opening of the six membered ring, may be effected either by a basic treatment that leads to the starting hydrazone **2**, or by an acidic one which hydrolyzes the opened derivative to give the benzoyl triazole structure **1**. In both cases, either the abstraction of the 6 nitrogen bound proton by the hydroxyl ion, or the protonation of the 2-triazole nitrogen atom, initiate the same electronic shift, the reverse of that responsible for the cylisation, and so causes the ring opening (Figure 1).

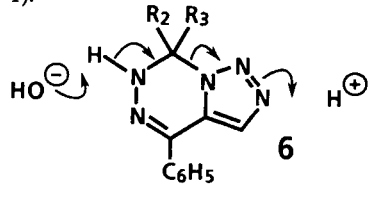


Figure 1

III. Cyclisation into 6*H*-[1,2,3]triazolo[1,5-*d*][1,2,4]triazin-7-one and 7-thione, **8**.

Reacting the unsubstituted hydrazone derivative **2** with phosgene does not permit the isolation of the intermediate isocyanate derivative, but leads directly to 4-phenyl-6*H*-[1,2,3]triazolo[1,5-*d*][1,2,4]triazin-7-one, **8a**, as expected. Another route to the same compound consists of the condensation of ethyl carbazate with the benzoyl triazole **1**, which results in the ethoxycarbonyl hydrazone derivative **4a**. Thermal treatment of the latter causes the ring closure with elimination of ethanol and provides the cyclic compound **8a**. Analogous cyclisations have been reported in the cases of the hydrazone derivatives resulting from the condensation of ethyl carbazate with the 4-formyl and 2-formylimidazoles [5] and 5-formylpyrazole [6]. However these examples show some differences. The ring closure of the ethoxycarbonyl hydrazone derivative of 5-formylpyrazole seems to require an alkaline treatment [6], whereas the cyclisations of the corresponding derivatives of 2-formyl and 4-formylimidazoles are apparently purely thermal reactions [5] and, in this respect, are more similar to the one that we have observed. It should be assumed that the easy elimination of the triazole proton - analogous to that of the imidazole NH proton - enables the triazole moiety to react with the carboxyl group. Such a property was also held to be responsible for the ready condensation reaction with the ketonic compounds (Scheme 2). It provides evidence for the acidic character of the nitrogen bound triazole proton, which is at least as reactive as that

of the imidazole nucleus, and it highlights the behavioural similarity between 1,2,3-triazole and imidazole structures.

The use of methyl dithiocarbazate [7] instead of ethyl carbazate leads through a similar thermal cyclisation to give the 7-thione derivative **8b**. The previously suggested mechanism can account for this ring closure.

Since the hydrazone derivatives **3b** and **3c** respectively with R_1 = *N*-ethoxycarbonylmethyl and *N*-carboxymethyl, were easily prepared, we tried to cyclise them. The nucleophilic attack of the ester or carboxylic carbonyl would have caused a seven membered ring cyclisation, providing a triazolotriazepinone. None of our attempts succeeded. However, when the hydrazone derivatives **3b** and **3c** were reacted with acetone, they underwent the six membered ring cyclisation and provided the *N*-substituted 6,7-dihydro[1,2,3]triazolo[1,5-*d*][1,2,4]triazines **7b** and **7c**.

Alkaline Transformations of the 6*H*-[1,2,3]Triazolo[1,5-*d*]-[1,2,4]triazin-7-ones, **8**.

The opening of the six membered ring of the triazolotriazinone **8a** can be provoked by basic treatment (sodium hydroxide). Once again the cleavage occurs between the 8 triazole nitrogen atom and the inserted 7 carbonyl. The unsubstituted hydrazone derivative **2** is obtained when the medium is alcohol free; whereas the ethoxycarbonylhydrazone derivative **4a** is formed in good yield when the reaction is carried out in an anhydrous ethanolic medium. A comparable ring opening, with the participation of an alcohol and formation of a *N*-alkoxycarbonyl derivative, has been described in the case of an imidazotetrazinone [8] and a mechanistic pathway, the reverse of that suggested for the formation of the cyclic derivatives **8**, was proposed.

We failed in our attempts to prepare the 7-methoxy and 7-methylthio[1,2,3]triazolo[1,5-*d*][1,2,4]triazines, **5** (R_2 = OMe or SMe), from the 7-one and 7-thione derivatives **8a** and **8b**, by means of an *O*- or *S*-methylation. We concluded that obtaining the anionic form at the oxygen or sulphur atom was impeded by the fragility of the 7C-8N bond.

However, using a slightly alkaline medium (potassium carbonate in acetone and dimethyl sulfate) we were able to methylate the triazolo triazinone **8a**, but the reaction was to cause an *N*-methylation yielding the triazolotriazinone **8c**. The location of the methyl group was demonstrated by the ir spectrum (carbonyl band at 1720 cm^{-1} still present) and the subsequent alkaline cleavage (under more basic conditions) which resulted in an opened derivative identical with the *N*-methylhydrazone **3a** prepared by condensation of methylhydrazine with the benzoyltriazole **1**.

These various results allow us to formulate assumptions explaining the behaviour of the triazolotriazinones **8** in alkaline conditions. Under mild conditions the first formed intermediate seems to be the anion resulting from the abstraction of the 6 nitrogen proton (Scheme 3a) (as indicated by the 6 nitrogen methylation which gives the *N*-methyl derivative **8c**). When this nitrogen anion is not immediately trapped by a methylating reagent, the negative charge cannot shift towards the oxygen atom but might be attracted by the farthest triazole nitrogen atom. The six membered ring opens with formation of an isocyanate group (Scheme 3a). If the alkaline agent is aqueous sodium hydroxide, the reaction results in carbon dioxide elimination and formation of the unsubstituted hydrazone derivative **2**. In the case of ethanolic sodium hydroxide, it leads to the ethoxycarbonyl derivative **4a**.

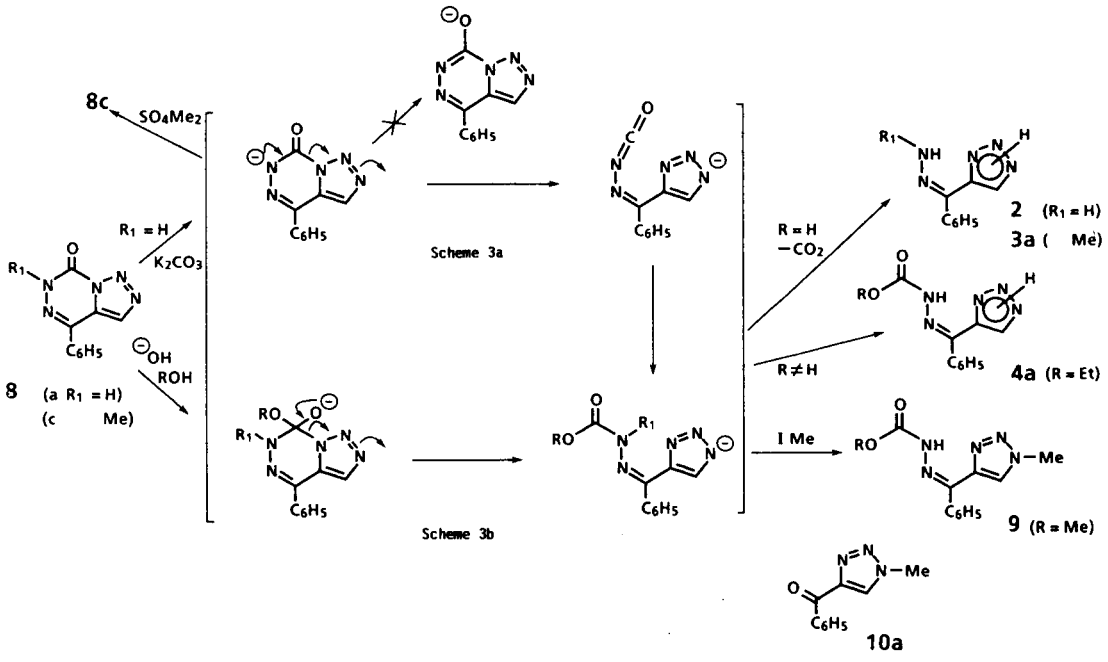
Another mechanistic pathway could be evoked. Its first step could be the nucleophilic attack at the 7 carbonyl group, as postulated in [8]. The electronic shift towards the farthest triazole nitrogen atom intervenes and breaks the ring. The resulting intermediate (Scheme 3b) is the same as that suggested from the putative isocyanate derivative. Both the pathways lead to the same results; however, only the abstraction of the 6 NH proton can explain the 6 *N*-methylation of **8a** into **8c**, whereas only the nucleophilic attack at the 7 carbonyl accounts for the alkaline hydrolysis of the *N*-methylated derivative **8c**.

The importance of the attracting effect of the farthest triazole nitrogen atom was highlighted by methylating (methyl iodide/methanol) the resulting intermediate anion. The reaction mixture contained the *N*-methyltriazinone **8c** together with the *N*-methoxycarbonyl derivative of the hydrazone of 4-benzoyl-*1-methyl*-1,2,3-triazole, **9**. No other methylation isomer was detectable. The location of the methyl group was ascertained by comparison of the ^{13}C nmr spectrum of **9** with those of the three pure isomers, **10a, 10b, 10c**, prepared by methylation of 4-benzoyl-1,2,3-triazole, **1**, (Table II).

Concluding Remarks.

Most of the reactions investigated in this work result from two important electronic effects. On one hand, in the hydrazone derivatives **2, 3, 4**, of 4-benzoyl-1,2,3-triazole, the noticeable electron donor property of the triazole system allows it to lose its acidic proton and is likely to be responsible for the six membered ring closure (Schemes 1a, 2a, 2b). This feature can be compared to that of some imidazole systems in analogous derivatives [5].

On the other hand the ease of the 6,7-dihydrotriazolotriazines, **6, 7, 8**, to be cleaved between the 7 carbon atom and the 8 nitrogen atom results presumably from the electron attracting effect of the triazole moiety (Schemes 1b, Figure 1). This reaction is formally the reverse of that producing the ring closure. Further comparative investigations with related heterobicyclic systems, such as dihydroimidazotriazines or -tetrazines, should make possible a generalization of their chemical behaviours.



EXPERIMENTAL

Melting points were determined with a Tottoli apparatus and are uncorrected. The ir spectra were recorded in Nujol on a Perkin Elmer 247 spectrophotometer, uv spectra on a Perkin Elmer model Coleman 575 spectrophotometer, ^{1}H nmr spectra on a Varian T-60A spectrometer, using TMS as internal standard and DMSO-d_6 as the solvent, and ^{13}C nmr spectra on a Brücker W. M. 250 spectrometer using TMS as internal standard, DMSO and deuteriochloroform as the solvents. Elemental analyses were performed by the Analytical Service of the Università degli Studi di Milano, Dipartimento di Chimica Organica e Industriale, via Venezian 21, Milan.

4-Benzoyl-1,2,3-triazole (**1**).

This compound was prepared from 3-chloro-1-phenyl-2-propen-1-one [9] and sodium azide in DMF as described in the literature [2], yield 60%, mp 118-120° (from benzene) [lit mp 122-123° (from acetic acid)]; ir: ν 1640 cm^{-1}; ^{1}H nmr: δ ppm 8.47 (s, H5), 7.42-8.17 (m, aromatic H), 15.53 (NH).

4-Benzoyl-1,2,3-triazole Hydrazones **2, 3, 4** (Tables III and IV).

General Procedure.

A solution of 0.05 mole of 4-benzoyl-1,2,3-triazole **1** [2] and 0.1 mole of the appropriate hydrazine in 150 ml of absolute ethanol was heated under reflux for 5-15 hours. The solvent was then removed under reduced pressure, the residue was taken up in water, the solid that formed was separated and recrystallized. Due to the presence of the triazolic nitrogen bound proton, the derivatives **1, 2, 3, 4** dissolve in aqueous solutions of sodium bicarbonate.

[Phenyl-(1,2,3-triazol-4-yl)methylene]hydrazinoacetic Acid (**3c**).

A mixture of 7.8 g (0.0285 mole) of **3b** and 50 ml of 2*N* sodium hydroxide was stirred at room temperature for 17 hours. The reaction mixture was then diluted with 50 ml of water, neutralized to *p*H 6 with 2*N* hydrochloric acid, filtered and acidified with 2*N* hydrochloric acid. The precipitate that slowly formed was separated after 6 hours and recrystallized from ethanol + light petroleum; yield 3.1 g (44%), mp 142-144°; ^{1}H nmr: δ ppm 7.83 (s, H5); 7.15-7.42 (m, aromatic H + NH); 4.03 (s, N-CH_2-); 8.65 (COOH); 12.12 (NH).

Anal. Calcd. for $C_{11}H_{11}N_5O_2$: C, 53.87; H, 4.52; N, 28.56. Found: C, 53.8; H, 4.4; N, 28.7.

4-Phenyl[1,2,3]triazolo[1,5-*d*][1,2,4]triazine (**5a**).

A mixture of 7 g (0.037 mole) of **2** and 80 ml of triethyl orthoformate was heated under reflux for 16 hours. On standing, crystals separated and the mixture was chilled, filtered and the crystals washed with ether + light petroleum, yield 4 g (55%), mp 175-177° (from 95% ethanol); ^{1}H nmr: δ ppm 8.88 (s, H3), 7.50-8.17 (m, aromatic H), 10.35 (s, H7).

Anal. Calcd. for $C_{10}N_7N_5$: C, 60.90; H, 3.58; N, 35.52. Found: C, 60.5; H, 3.6; N, 35.2.

In a similar way the 7-methyl-4-phenyl[1,2,3]triazolo[1,5-*d*][1,2,4]-triazine, (**5b**), was prepared from **2** and triethyl orthoacetate in absolute ethanol, yield 64%, mp 170-172°; ^{1}H nmr: δ ppm 8.80 (s, H3), 7.47-8.10 (m, aromatic H), 3.07 (s, $CH_3$7).

Anal. Calcd. for $C_{11}H_9N_5$: C, 62.55; H, 4.29; N, 33.16. Found: C, 62.4; H, 4.3; N, 33.0.

6,7-Dihydro[1,2,3]triazolo[1,5-*d*][1,2,4]triazine (**6**) (Tables V and VI).

General Procedure.

A mixture of **2** (1 mole) and the suitable aldehyde or ketone (1 mole) in absolute ethanol was stirred at room temperature for 1-2 hours. The compound precipitated, was separated and recrystallized.

6-Substituted-6,7-dihydro[1,2,3]triazolo[1,5-*d*][1,2,4]triazines (**7**) (Tables V and VI).

General Procedure.

A solution of **3** (0.01 mole) in 60 ml of acetone and 6 ml of 2*N* hydrochloric acid was stirred 2 hours at room temperature. The solvent was removed under reduced pressure, the residue was taken up in water, the compound precipitated, was separated, and recrystallized.

4-Phenyl-6*H*-[1,2,3]triazolo[1,5-*d*][1,2,4]triazin-7-one (**8a**).

Procedure 1.

To 0.2 g (0.011 mole) of **2** dissolved in 10 ml of dioxane a 20% toluene solution of phosgene was added and the reaction mixture was stirred for 5 hours at room temperature. The solvents were removed under reduced pressure, the residue was triturated with light petroleum and separated. The crude product amounted to 0.25 g (100%), mp 265-267° dec (from 95% ethanol).

Procedure 2.

A mixture of 5.19 g (0.03 mole) of **1** and 3.12 g (0.03 mole) of ethyl carbazate in 20 ml of absolute ethanol was gradually heated on an oil bath up to 240°, with solvent removing. After 1.5 hours the reaction was complete and the brown material triturated with hot ethanol. The crude product was separated and recrystallized from dilute ethanol with charcoal to yield 4.5 g (70%) of white needles, mp 268-270° dec; ir: ν cm^{-1} 1730 (C=O 7); ^1H nmr δ ppm 8.55 (s, H3), 7.37-7.90 (m, aromatic H), 13.23 (s, NH6).

Anal. Calcd. for $C_{10}H_7N_5O$: C, 56.33; H, 3.31; N, 32.85. Found: C, 56.2; H, 3.4; N, 32.5.

The product is the same as the one obtained by procedure 1.

In a similar way the 4-phenyl-6*H*-[1,2,3]triazolo[1,5-*d*][1,2,4]triazine-7-thione, (**8b**), was prepared starting from **1** and methyl dithiocarbazate [7], yield 65%, mp 282-284° dec (from 95% ethanol); ^1H nmr δ ppm 8.77 (s, H3), 7.43-7.95 (m, aromatic H), 14.67 (NH6).

Anal. Calcd. for $C_{10}H_7N_5S$: C, 52.39; H, 3.08; N, 30.55. Found: C, 52.2; H, 3.2; N, 30.3.

Alkaline Cleavage of **8a** into **4a**.

A mixture of 5.33 g (0.025 mole) of **8a** and 1 g (0.025 mole) of sodium hydroxide pellets in 150 ml of absolute ethanol was stirred 1 hour at room temperature and 2 hours under reflux. The reaction mixture was cooled, diluted with 1 l of water and acidified with 2*N* hydrochloric acid. The precipitate that formed was separated and recrystallized from absolute ethanol to give 4 g (62%) of **4a**, mp 170-172°. This material was identical with an authentic sample, obtained from **1** and ethyl carbazate, by mp, ir and nmr spectral comparison.

6-Methyl-4-phenyl-6*H*-[1,2,3]triazolo[1,5-*d*][1,2,4]triazin-7-one (**8c**).

To a suspension of 5.33 g (0.025 mole) of **8a** in 250 ml of acetone 1.75 g (0.013 mole) of anhydrous potassium carbonate were added. After 2 hours at room temperature 5.3 g (0.042 mole) of dimethyl sulfate were added. The resulting solution was stirred for 2 hours at room temperature and 2 hours under reflux. The solvent was removed under reduced pressure, the residue was taken up in water, separated and recrystallized from 95% ethanol, yield 68%, mp 215-217°; ^1H nmr: δ ppm 3.80 (s, $CH_3$6); 8.60 (s, H3); 7.40-7.88 (m, aromatic H).

Anal. Calcd. for $C_{11}H_9N_5O$: C, 58.14; H, 3.99; N, 30.82. Found: C, 57.8; H, 4.1; N, 30.7.

Similarly, the 6-methyl-4-phenyl-6*H*-[1,2,3]triazolo[1,5-*d*][1,2,4]triazine-7-thione, (**8d**), was prepared starting from **8b**, yield 45%, mp 194-196° (from 95% ethanol); ^1H nmr: δ ppm 4.18 (s, $CH_3$6), 8.78 (s, H3), 7.43-7.97 (m, aromatic H).

Anal. Calcd. for $C_{11}H_9N_5S$: C, 54.30; H, 3.73; N, 28.79. Found: C, 54.1; H, 3.7; N, 28.6.

[(1-Methyl-1*H*-1,2,3-triazol-4-yl)phenylmethylene]hydrazinecarboxylic Acid, Methyl Ester (**9**).

A mixture of 5.33 g (0.025 mole) of **8a** and 1 g (0.025 mole) of sodium hydroxide pellets in 150 ml of absolute methanol was stirred at room temperature until a solution was formed (1.5 hours). Methyl iodide (5.7 g, 0.04 mole) was added and stirring was continued for 4 hours at room temperature and 3 hours under reflux. After solvent removal, the residue was chromatographed on silica gel with benzene:ethyl acetate (1:1) as the solvent. After a mixture of **8a** and **8c**, 2 g (31%) of **9**, mp 200-202°, were collected; ^1H nmr: δ ppm 3.70 (s, COOMe), 4.10 (s, $CH_3$1), 8.17 (s, H5), 7.40-7.43 (m, aromatic H), 11.93 (s, NH).

Anal. Calcd. for $C_{12}H_{13}N_5O_2$: C, 55.59; H, 5.05; N, 27.01. Found: C, 55.9; H, 5.1; N, 27.1.

4-Benzoyl-1-(and 2)-methyl-1,2,3-triazoles (**10a** and **10b**).

A mixture of 12.2 g (0.06 mole) of **1** and 4.23 g (0.03 mole) of potassium carbonate in 300 ml of acetone and 18 ml of water was stirred at room temperature for 4 hours. Then 7.6 g (0.06 mole) of dimethyl sulfate were added and stirring was continued for 4 hours. After standing overnight, the acetone was removed under reduced pressure, water was added to the residue and the solution was extracted with chloroform. The organic layer was evaporated to dryness and the residue was triturated with ethyl ether and light petroleum. The insoluble material was separated and recrystallized from 95% ethanol to give 3.3 g (25%) of a product mp 150-152° which was identified [^{13}C nmr (Table II)] as **10a**; ^1H nmr (deuteriochloroform): δ ppm 4.13 (s, $CH_3$1), 8.10 (s, H5), 7.35-7.52 (m, aromatic H3', 4', 5'), 8.20-8.37 (m, aromatic H 2', 6').

Anal. Calcd. for $C_{11}H_{11}N_3O_2$: C, 60.82; H, 5.10; N, 19.34. Found: C, 61.1; H, 5.3; N, 19.0.

The mother liquor was evaporated and the residue chromatographed on silica gel with benzene:ethyl acetate (5:2) as the solvent. The eluate gave 5 g (38%) of pure **10b**, mp 70-72° (from 95% ethanol); ^1H nmr: δ ppm 4.28 (s, $CH_3$2), 7.33-8.20 (m, H5 + aromatic H).

Anal. Found: C, 60.9; H, 5.1; N, 19.1.

4-Benzoyl-3-methyl-1,2,3-triazole (**10c**).

To a stirred suspension of 5 g (0.025 mole) of **1** in 1500 ml of anhydrous methylene chloride, a solution of 5 g (0.034 mole) of trimethyloxonium tetrafluoborate in 300 ml of anhydrous methylene chloride was added during 30 minutes. Stirring was continued at room temperature for 7 hours. After standing overnight, an aqueous solution of potassium carbonate was added. The organic layer was evaporated to dryness and the residue chromatographed on silica gel with benzene:ethyl acetate (5:2) as the solvent. The eluate gave 2.6 g (49%) of **10c**, mp 101-103° (from 95% ethanol); ^1H nmr (deuteriochloroform): δ ppm 4.33 (s, $CH_3$3), 7.88 (s, H5), 7.37-7.85 (m, aromatic H).

Anal. Found: C, 61.0; H, 5.3; N, 19.1.

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