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1,3-DIPOLAR CYCLOADDITION AND NUCLEOPHYLIC SUBSTITUTION REACTIONS OF C-ACETYL AND C-ETHOXYCARBONYL DERIVATIVE OF HYDRAZIDOYL BROMIDES

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Abstract—1,3-Dipolar cycloaddition as well as nucleophilic substitution reactions of c-acetyl and c-ethoxycarbonyl derivatives of hydrazidoyl bromides with a variety of dipolarophiles viz., alkenes, alkynes, α,β-unsaturated ketones, aldehydes azomethines and selected nucleophiles have been investigated. The analytical and spectral data of the resulting products are consistent with the proposed structures.

The chemistry of N-(α-chlorobenzylidene) N-phenylhydrazine has been undoubtedly a major point of attraction in as far as 1,3-dipolar cycloaddition reactions are concerned.[1-4] However, the marked superiority of c-acetyl and c-ethoxycarbonyl derivatives of hydrazidoyl halides[5-7] over their aromatic counterparts may have immense synthetic utility in the preparation of heterocyclic and acyclic products. Which have been relatively little explored until recently. Early developments in the cycloaddition reaction have been mainly reported by Huisgen[1-3] *et al.* but no systematic work on the cycloaddition of c-acetyl and c-ethoxycarbonyl derivatives of hydrazidoyl halides with dipolarophiles, has so far appeared in the literature. In continuation of our previous studies[8,9] directed towards exploring the synthetic potentialities of hydrazidoyl halides we have now prepared a series of c-acetyl and c-ethoxycarbonyl derivatives of hydrazidoyl halides and investigated their 1,3-dipolar cycloaddition as well as nucleophilic substitution reactions. Exploration of the studies is principally directed towards the synthesis of new heterocyclic and acyclic products.

RESULTS AND DISCUSSION

Bromination of hydrazones (**1a–f**), prepared by the coupling of diazonium salt solution with active methylene compounds, afforded corresponding hydrazidoyl bromide[10] (**2a–f**) at 0–5°. Reaction usually carried out in hydrous condition using sodium acetate in the mixture of glacial acetic acid and acetic anhydride. Structural assignments for these hydrazidoyl halides are based on their elemental and spectral analyses. NMR spectra of these compounds are characterised by the presence of a N–H singlet at a very down field. IR spectra displaced a wide range of peaks characteristic of N–H, C=N, NO_2 and C=O groups in their specific range.

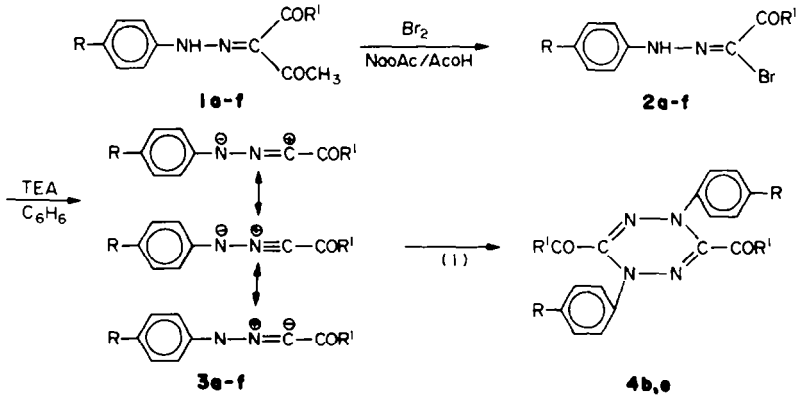
Dehydrobromination of these hydrazidoyl halides with triethylamine in any organic solvents, led to the formation of corresponding nitrile imines, (**3a–f**), as evident from appearance of intense bright colouration. Lack of stabilizing factors, and sensitivity towards atmospheric components were the major factors which precluded the isolation of these nitrile imines and therefore, these species generated in solution and undergo cycloaddition with dipolarophiles *in situ*. The enhanced reactivity of these species may also have been supported from the fact that nitrile imine, in absence of any suitable dipolarophile, dimerizes to 1,4-dihydro 1,2,4,5-tetrazine (**4b,e**).

Δ^2-Pyrazolines. The reaction of nitrile imines (**3a–d**) was carried out with allylamide in equimolar amounts for 2 hr, to give Δ^2-pyrazoline (**5a–d**) exclusively in 78–89% yields (Scheme 2). The products having certain and unique regioselectivity, i.e. addition takes place at ethylenic double bond of allylamide. Interestingly, it was observed that reaction takes place with exceptional ease, probably due to the pronounced activating influence of the neighbouring amide function and thus required cycloadducts are obtained in appreciable yields. All the products are bright coloured, crystalline, high melting stuff. Compound **5b** and **5d** are not melted even at 200° but sublime at 220° and 200° respectively and thus capable of being purified by sublimation.

Similarly, the reaction of nitrile imine (**3e**) with maleic anhydride afforded the Δ^2-pyrazoline (**6**) in approximately 40% yield. This reaction, and even reaction with allylamide is not facile because the nucleophilicity of the nitrogen of nitrile imine (**3e**) is so diminished by the deactivating influence of *p*-nitro group that the compound reacts sluggishly with dipolarophiles: head-to-tail dimerization of the 1,3-dipole to a dihydrotetrazine derivatives (**4e**) then takes place as a competing reaction (Scheme 2).

The reactivity of dipolarophiles in such addition is strongly controlled by the substituents. In general, all the substituents in the dipolarophile (relative to H) strongly accelerate 1,3-dipolar cycloadditions. α,β-Unsaturated ketones are highly reactive dipolarophiles, and thus reacted smoothly with nitrile imines (**3a–d**) afforded corresponding 1,3,4,5-tetrasubstituted Δ^2-pyrazoline (**7a–j**) in 45–80% yields (Scheme 2).

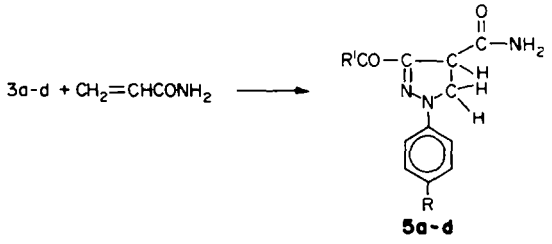
1,3,4-Oxadiazolines. Although the dipolarophilic activity of carbonyl compounds is of little worth as evidenced by the fact that normal ketones, such as, acetophenone and benzophenone do not respond cycloaddition reaction with nitrile imines. Contrary electron-deficient CO groups of benzil or of diethylmesoxalate afforded adduct with diphenyl nitrile imine in 75 and 73% respectively. However, it was observed during course of these investigations that nitrile imine **5b** and **5e** on treatment with 4-hydroxy-3-ethoxy-benzaldehyde and 3-



1a-f 2a-f 3a-f 4b,e

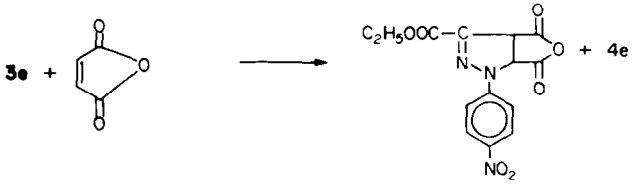
	R	R'
2,3a	Br	OC_2H_5
b	Br	CH_3
c	CH_3	OC_2H_5
d	CH_3	CH_3
e	NO_2	OC_2H_5
f	NO_2	CH_3

Scheme 1.



5a-d

Scheme 2.



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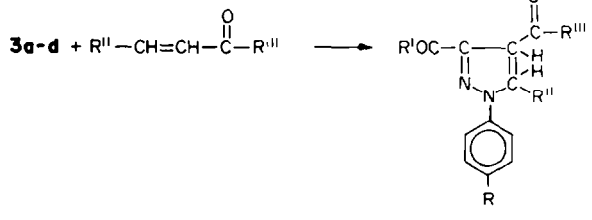
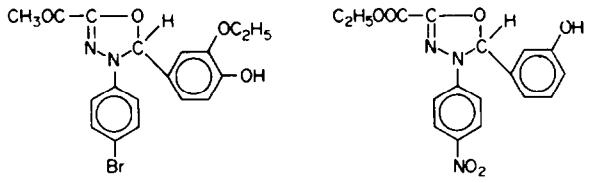


7a-j

	R	R'	R''	R'''
7a	Br	C_2H_5O	C_6H_5	C_6H_5
b	Br	C_2H_5O	4-OCH_3-C_6H_3	4-Cl-C_6H_4
c	Br	C_2H_5O	3,4(OCH_3)$_2C_6H_3$	4-CH_3O C_6H_4
d	"	"	3,4-$OCH_2C_6H_3$	4-CH_3O C_6H_4
e	"	CH_3	3,4-$O_2CH_2C_6H_3$	4-Cl-C_6H_4
f	"	CH_3	C_6H_5	C_6H_5
g	"	"	3,4-$O_2CH_2C_6H_3$	4-OCH_3 C_6H_4
h	CH_3	C_2H_5O	C_6H_5	OC_2H_5
i	CH_3	C_2H_5O	3,4-(OCH_3)$_2C_6H_3$	4-OCH_3 C_6H_4
j	CH_3	CH_3	C_6H_5	C_6H_5



8 **9**

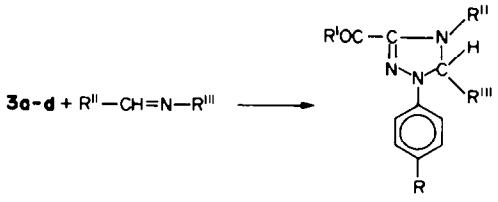
Scheme 3.

hydroxybenzaldehyde, afforded 1,3,4-oxadiazolines **8** and **9** respectively in quantitative yields (Scheme 3).

1,2,4-Δ^2-*Triazolines.* Both aliphatic and aromatic azomethines are liable to add on nitrile imine, their dipolarophilic character is considerably more pronounced than that of the parent carbonyl compounds. Thus, when nitrile imines (**3a–d**) were allowed to react with azomethine afforded corresponding Δ^2-triazolines (**10a–g**) exclusively in 45–62% yields (Scheme 4).

Pyrazoles. Alkynes with C≡C triple bond, are well known and possess marked dipolarophilic activity and afford the aromatic pyrazole derivatives on direct reaction with nitrile imine. Furthermore, conjugation increases the activity of these dipolarophiles which, in turn enhance the yield of the products. The reaction of nitrile imine (**3c**) with dimethylacetylenedicarboxylate, afforded pyrazole (**11**) as the exclusive product in 90% yield (Scheme 5).

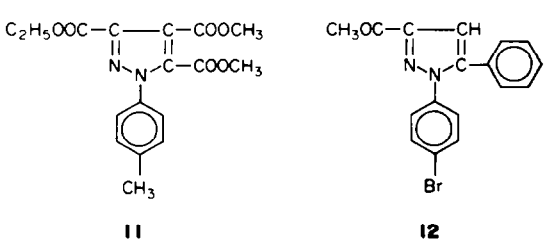
On the other hand, it also offers a versatile method for preparing 5-substituted pyrazoles, by the making use of mono-substituted acetylenes. Thus, when phenyl acetylene was reacted with nitrile imine (**4b**), it afforded 1-(4-bromophenyl)-3-acetyl-5-phenyl pyrazole (**12**) in 60% yield (Scheme 5).



10a–g

	R	R'	R''	R'''
10a	Br	OC_2H_5	C_6H_5	C_6H_5
b	Br	OC_2H_5	$C_{10}H_7$	C_6H_5
c	Br	CH_3	$C_{10}H_7$	C_6H_5
d	CH_3	OC_2H_5	C_6H_5	C_6H_5
e	"	OC_2H_5	C_6H_5	$4-OH-C_6H_4$
f	"	OC_2H_5	$C_{10}H_7$	C_6H_5
g	"	CH_3	$C_{10}H_7$	C_6H_5

Scheme 4.



11 **12**

Scheme 5.

The structures of all these monoadducts follows from their elemental and spectral analyses (Tables 1 and 2). Experimental results indicate that the cycloadducts (**5–12**) are supposed to be formed by the 3+2→5 addition of dipolarophiles on to the nitrile imines intermediate (**3a–f**) generated *in situ* from hydrazidoyl bromide (**2a–f**). The orientation of the cycloaddition can be interpreted in a manner similar to that proposed for other 1,3-dipolar intermediates, which seems to be influenced more strongly by steric than by electronic factors.

Our interest is now turned to the synthesis of acyclic systems. Like their alkyl and aryl halides, hydrazidoyl bromides (**2a–f**) also undergo nucleophilic substitution reactions with selected nucleophiles. Although deactivating influence of the neighbouring CO group renders the Cl atom less reactive towards incoming nucleophiles, but, in some cases it is reported to have been displaced by strong nucleophilic reagents, for e.g. when hydrazidoyl bromides (**2c,e,f**) were treated with a calculated amount of sodium azide in aq. dioxane, hydrazidoyl azide (**13,e,f**) were formed in 56–60% yields. Similarly, bromides **2e** and **2f** were reacted with phenyl hydrazine and hydrazidine **14e** and **14f** were obtained in 68 and 62% yield respectively as a bright crystalline compound. The reaction of hydrazine hydrate with hydrazidoyl bromide (**2c**) also afforded hydrazidine (**15c**) in 50% yield (Scheme 6).

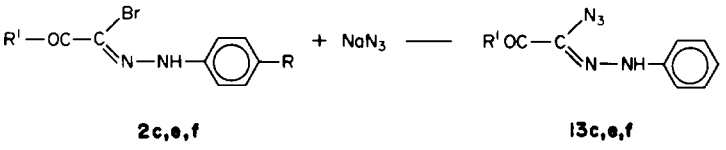
Reaction of hydrazidoyl bromides with heterocycles like pyridine, quinoline, and isoquinoline represent yet another example of intermolecular reaction and the substitution products so obtained may undergo cyclization affording cyclic products under different conditions. Hydrazidoyl bromide (**2e**) on treatment with quinoline or isoquinoline afforded their corresponding salts (**16** and **17**) respectively, at 40–50°. On the other hand, if the hydrazidoyl bromide (**2e**) was allowed to reflux with quinoline at 160–70°, complex decomposition reaction occurred yielding 2-quinolinium derivative (**18**) in 80% yield (Scheme 6).

EXPERIMENTAL

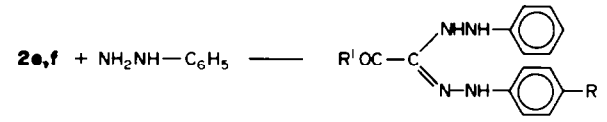
Uncorrected m.ps were determined on a Gallen-Kamp apparatus. The products were separated and purified by column chromatography using neutral alumina and purity checked by tlc. The IR spectra were recorded on Perkin–Elmer infracord instrument, NMR spectra ($CDCl_3$, $CDCl_3+D_2O$ or DMSO) were run on a Varian A-60 and A-90 spectrometer using TMS as an internal standard. Unless otherwise stated all reactions were run under strictly anhydrous conditions.

Preparation of 1,4-*dihydro*-1,2,4,5-*tetrazine* (**4b,e**)

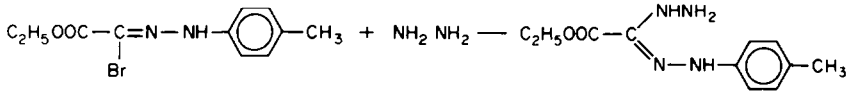
Compounds **2b,c** (0.005 mol) were suspended in 95% alcohol (25.0 ml) and triethylamine (0.01 mol) in 5 ml of the same solvent was then added dropwise with constant stirring. Some time it is



2c,e,f 13c,e,f

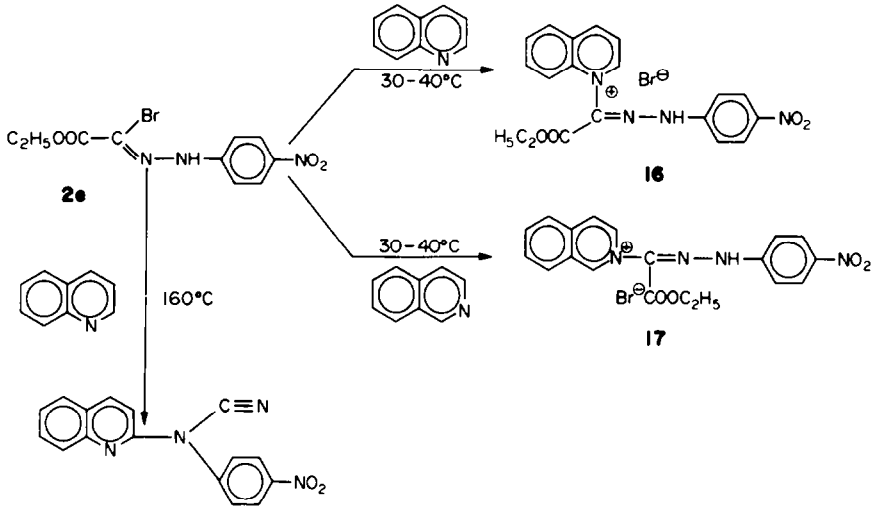


14e,f



2c 15c

Scheme 6.



18

slightly heated and then left overnight at room temp. The resulting brown mass was filtered, washed with water and alcohol and then dried. Finally products are purified by chromatography and recrystallized with proper solvents (Table 1).

Preparation of Δ^2*-pyrazolines*

(i) *Reactions with ethylenic compounds.* A soln of **2a–e** (0.005 mol) and olefinic dipolarophiles *viz* allyl amide (0.005 mol, 0.35 g) or maleic anhydride (0.005 mol, 0.49 g) in anhyd chloroform (60 ml) was allowed to reflux in an oil bath at 80°. When a clear soln was obtained, an equivalent amount of triethylamine was added. The mixture was further refluxed for 10 hr. Pyrazoline **5a** and **5d** are separated out from the chloroform simply on cooling. Whereas compounds **5b**, **5c** and **6** remain in the solution. Chloroform was removed by distillation and residue taken in dry benzene (20 ml). On cooling triethylamine-hydrobromide was precipitated out as white gelatinous mass, which was filtered off and filtrate gives Δ^2-pyrazolines. Compounds are purified and then recrystallized with proper solvents.

(ii) *Reaction with* α,β*-unsaturated ketones.* To a soln of **2a–d** in dried benzene (60 ml) was added α,β-unsaturated ketones (0.005 mol). The soln was refluxed with a constant stirring, while triethylamine (0.005 mol) was then added dropwise, mixture was refluxed for further 10–12 hr and left overnight at room temp. Conventional work up of the mixture afforded **7a–j** in good yields (Table 1). Spectral data of the compounds are given in Table 2.

Preparation of 1,3,4*-oxadiazolines* (**8**, **9**)

A soln of (0.005 mol) hydrazidoyl bromides, 0.005 mol of aromatic aldehydes and approximately ice of triethylamine in 40 ml of dry MeOH was stirred at room temp overnight under N_2 and then refluxed for 10–20 hr. The mixture was cooled and shaken slightly for some time. The precipitated chloride was filtered off and compounds crystallised from appropriate solvents.

Preparation of Δ^2*-triazolines*

A soln of triethylamine (0.01 mol) in chloroform was added dropwise over a period of 30 min, to a well stirred soln of **2a–d** and azomethine (0.005 mol) in 50 ml chloroform. The mixture was further heated under reflux for 30–40 hr. The solvent was then evaporated and finally taken in 15 ml benzene to precipitate triethylamine hydro bromide, which was filtered off and filtrate was distilled off under pressure. The products are purified by column chromatography and recrystallised from appropriate solvents.

Preparation of pyrazoles

Pyrazoles are prepared by the reaction of **2b,c** and acetylenic compounds in equimolar amount, in presence of base. Benzene was generally used as a solvent and soln was refluxed for 16 hr and then followed the above procedure.

Preparation of hydrazidoyl azide (**13,c, e, f**)

A soln of **2c,e,f** (0.01 mol) in 40–60% dioxane-water was slightly heated to dissolve the solid materials. To this soln was added a soln of sodium azide dissolved in 5 ml of the same solvent. The hydrazidoyl azides are precipitated after ½ hr on cooling at room temp. The products were filtered washed with water and dried and then thrice recrystallised from suitable solvents.

Preparation of hydrazidines (**14e, f and 15c**)

Compound **2e,f,c** was stirred as a slurry with 95% EtOH (20 ml) at room temp, while a soln of hydrazine in 3 ml alcohol was

Table 1. Physical characteristics of the products

Compd. No.	M.p.°	Yield %	Recrystallizing solvent	Molecular formula	Elemental analysis calc (found)		
					C %	H %	N %
4b	70–71	52	Aq. MeOH	$C_{18}H_{14}Br_2N_4O_2$	45.18 (45.20)	2.92 (2.90)	11.71 (11.78)
4e	232–33	89	EtOH	$C_{20}H_{18}N_6O_8$	51.06 (51.12)	3.72 (3.64)	17.87 (17.92)
5a	195	78	DMF–H_2O	$C_{13}H_{14}BrN_3O_3$	45.88 (45.80)	4.11 (4.21)	12.35 (12.30)
5b	220 (Sublime)	80	DMF–MeOH	$C_{12}H_{12}BrN_3O_2$	46.45 (46.42)	3.87 (3.81)	13.54 (13.62)
5c	159	89	MeOH	$C_{14}H_{17}N_3O_3$	61.09 (61.12)	6.18 (6.20)	15.27 (15.22)
5d	200 (Sublime)	78	DMF–MeOH	$C_{13}H_{15}N_3O_2$	63.67 (63.59)	6.12 (6.20)	17.10 (17.00)
6	212–13	40	$CHCl_3$	$C_{14}H_{11}N_3O_7$	50.45 (50.40)	3.30 (3.18)	12.61 (12.64)
7a	136	48	MeOH	$C_{25}H_{21}BrN_2O_3$	62.89 (62.91)	4.40 (4.32)	5.87 (5.91)
7b	172	80	EtOH	$C_{26}H_{22}BrClN_2O_4$	57.61 (57.64)	4.06 (4.01)	5.17 (5.20)
7c	182	58	MeOH	$C_{28}H_{27}BrN_2O_6$	59.25 (59.18)	4.76 (4.68)	4.93 (5.01)
7d	119	60	MeOH	$C_{27}H_{23}BrN_2O_6$	58.80 (58.82)	4.17 (4.19)	5.08 (5.01)
7e	121	50	$CHCl_3$–MeOH	$C_{25}H_{18}BrClN_2O_4$	57.08 (57.12)	3.42 (3.18)	5.32 (5.36)
7f	72–3	45	MeOH	$C_{24}H_{19}BrN_2O_2$	64.42 (64.40)	4.25 (4.12)	6.26 (6.32)
7g	129–30	54	EtOH	$C_{26}H_{21}BrN_2O_5$	59.88 (59.80)	4.03 (4.14)	5.29 (5.18)
7h	112–14	70	$CHCl_3$–EtOH	$C_{22}H_{24}N_2O_4$	69.47 (69.42)	6.31 (6.42)	7.36 (7.42)
7i	169–70	70	EtOAc–EtOH	$C_{29}H_{30}N_2O_6$	69.32 (69.14)	5.97 (5.89)	5.57 (5.58)
7j	180	62	EtOH	$C_{25}H_{22}N_2O_2$	78.53 (78.50)	5.75 (5.71)	7.32 (7.40)
8	242–3	50	$CHCl_3$–EtOH	$C_{18}H_{17}BrN_2O_4$	53.33 (53.21)	4.19 (4.21)	6.91 (6.80)
9	225–26	52	EtOH	$C_{17}H_{15}N_3O_6$	57.14 (57.20)	4.20 (4.21)	11.76 (11.68)
10a	236–37	60	EtOAc–EtOH	$C_{23}H_{20}BrN_3O_2$	61.33 (61.40)	4.44 (4.40)	9.33 (9.39)
10b	150	45	MeOH	$C_{27}H_{22}BrN_3O_2$	64.80 (64.79)	4.40 (4.32)	8.40 (8.42)
10c	220–22	52	C_6H_6	$C_{26}H_{20}BrN_3O$	66.38 (66.41)	4.25 (4.28)	8.93 (8.81)
10d	122–23	62	EtOH	$C_{24}H_{23}N_3O_2$	74.80 (74.84)	5.97 (5.89)	10.99 (10.89)
10e	152–53	45	$CHCl_3$–MeOH	$C_{24}H_{23}N_3O_3$	71.82 (71.80)	5.73 (5.64)	10.47 (10.49)
10f	226–27	40	$CHCl_3$–EtOH	$C_{28}H_{25}N_3O_2$	77.24 (77.10)	5.74 (5.81)	9.65 (9.70)
10g	241–42	50	C_6H_6	$C_{27}H_{23}N_3O$	80.00 (80.01)	5.67 (5.62)	10.37 (10.41)
11	91	90	P.E. (60–80)	$C_{17}H_{18}N_2O_6$	58.95 (58.90)	5.20 (5.18)	8.09 (8.15)
12	76–78	60	EtOH	$C_{17}H_{13}BrN_2O$	59.82 (59.89)	3.81 (3.84)	8.21 (8.10)

Table 1. (*Contd*)

Compd. No.	M.p.°	Yield %	Recrystallizing solvent	Molecular formula	Elemental analysis calc (found) C %	H %	N %
13c	99–100	60	Aq. MeOH	$C_{11}H_{13}N_5O_2$	53.84 (53.72)	5.26 (5.32)	28.34 (28.18)
13e	133	56	EtOH	$C_{10}H_{10}N_6O_4$	43.16 (43.20)	3.59 (3.42)	30.21 (30.10)
13f	180–82	60	Acetone–H_2O	$C_9H_8N_6O_3$	43.54 (43.59)	3.23 (3.20)	33.87 (33.79)
14e	185	68	EtOH	$C_{16}H_{17}N_4O_4$	55.97 (55.90)	4.95 (4.89)	23.32 (23.41)
14f	227	62	EtOH	$C_{15}H_{15}N_5O_3$	57.50 (57.42)	4.79 (4.81)	22.36 (22.28)
15c	170	50	Acetone	$C_{11}H_{16}N_4O_2$	55.97 (55.84)	6.77 (6.88)	23.72 (23.81)
16	170	60	EtOH	$C_{19}H_{17}N_4O_4$	62.63 (62.58)	4.65 (4.72)	15.34 (15.41)
17	185	70	EtOH	$C_{19}H_{17}N_4O_4$	62.63 (62.61)	4.65 (4.60)	15.34 (15.21)
18	190–91	80	EtOH	$C_{16}H_{10}N_4O_2$	66.20 (66.25)	3.44 (3.49)	19.31 (19.22)

Table 2. Spectral studies of the products

Compd. No.	^{1}H-NMR Spectral data (δ ppm)	Number of protons	Assignment	Compd. No.	IR (KBr) data (cm^{-1})	Assignment
4e	($CDCl_3$)					
	1.20, t, J = 7.2 Hz	3H + 3H	Methyl	**5b**	3290, 3240	NH_2-Amide
	4.26, q, J = 7.2 Hz	2 H + 2 H	Methylene		2940, 1300, 1460	CH-Aromatic
	7.27, 8.33, m	8 H	Aromatic		1680	C=O-Acetyl
					1610	C=O-Amide
5a	(DMSO-d_6)					
	1.30, t, J = 7.0 Hz	3 H	Methyl		1590	C=N
	4.30, q, J = 7.0 Hz	2 H	Methylene		1430, 1550	C–N
	3.31, q, J = 7.0 Hz	2 H	Methylene			
	4.96, q, J = 7.0 Hz	1 H	Methine	**8**	3280	OH
	6.88–7.66, m	4 H	Aromatic		1620	C=O
	7.91, s	2 H	Amide		1590	C=N
					1420, 1305	C–N
5d	(DMSO-d_6)					
					1540, 1500, 1450	C=C-Aromatic
	2.25, s	3 H	Methyl			
					3100, 880	CH-Aromatic
	2.42, s	3 H	Methyl			
					2940	CH-Aliphatic
	3.07, q, J = 7.0 Hz	2 H	Methylene			
	4.90, q, J = 7.0 Hz	1 H	Methine	**10b**	1670	C=O
	7.10–7.30, m	4 H	Aromatic		1560	C=N
	7.80, s	2 H	Amide		1449, 1100	C–N
					1590, 1565, 1485	C=C-Aromatic
7a	($CDCl_3$)				3040, 870, 830	CH-Aromatic
	1.09, t, J = 7.2 Hz	3 H	Methyl			
	4.01, q, J = 7.2 Hz	2 H	Methylene	**10e**	2990	OH
	4.31, d, J = 7.2 Hz	1 H	Methine		1700	C=O
	5.64, d, J = 7.2 Hz	1 H	Methine		1620	C=N
	6.78–7.78, m	14 H	Aromatic		1608, 1570, 1510, 1470	C=C-Aromatic
					2940, 795, 830	CH-Aromatic
7b	1.21, t, J = 7.0 Hz	3 H	Methyl	**10f**	2930–3040 (broad)	CH-Nephthyl
	3.83, s	3 H	Methoxy		1680	C=O
	4.11, q, J = 7.0 Hz	2 H	Methylene		1530	C=N
	4.40, d, J = 5.0 Hz	1 H	Methine		1480, 980	C–N
	5.70, d, J = 5.0 Hz	1 H	Methine		1550	C=C-Aromatic
	6.83–7.97, m	12 H	Aromatic			
7c	1.10, t, J = 7.2 Hz	3 H	Methyl	**10g**	2940–3040 (broad)	CH-Nephthyl

Table 2. (*Contd*)

Compd. No.	^{1}H-NMR Spectral data (δ ppm)	Number of protons	Assignment	Compd. No.	IR (KBr) data (cm^{-1})	Assignment
	3.68, s	3 H	Methoxy			
					1670	C=O
	3.74, s	3 H + 3 H	Methoxy			
					1530	C=N
	4.02, q, J = 7.2 Hz	2 H	Methylene			
					1485, 985	C–N
	4.25, d, J = 7.2 Hz	1 H	Methine			
					1400	C=C-Aromatic
	5.54, d, J = 7.2 Hz	1 H	Methine			
	6.52–7.75, m	11 H	Aromatic	**13e**	3280, 1560	NH
					2125, 1150	N_3
7h	1.05–1.33, m	3 H + 3 H	Methyl			
					1720	C=O
	2.15, d, J = 7.2 Hz	3 H	Methyl			
					1600	C=N
	3.91–4.53, m	2 H + 2 H	Methylene			
					1500, 1330	NO_2
	4.70, d, J = 7.2 Hz	1 H	Methine			
					1480, 1100	C–N
	5.54, d, J = 7.2 Hz	1 H	Methine			
	6.88–7.75	9 H	Aromatic	**13f**	3100, 1560	NH
					2120, 1240	N_3
7i	1.09, t, J = 7.2 Hz	3 H	Methyl			
					1670	C=O
	2.12, s	3 H	Methyl			
					1590	C=N
	3.64, s	3 H	Methoxy			
					1500, 1330	NO_2
	3.71, s	3 H + 3 H	Methoxy			
					1360, 1150	C–N
	4.01, q, J = 7.2 Hz	2 H	Methylene			
	4.24, d, J = 7.2 Hz	1 H	Methine			
	5.55, d, J = 7.2 Hz	1 H	Methine			
	6.52–7.74, m	11 H	Aromatic			
7j	2.25, s	3 H	Methyl			
	2.43, s	3 H	Acetyl			
	4.43, d, j = 5.0 Hz	1 H	Methine			
	5.71, d, J = 5.0 Hz	1 H	Methine			
	6.95–7.90, m	14 H	Aromatic			
10a	1.20, t, J = 7.0 Hz	3 H	Methyl			
	2.16, s	3 H	Methyl			
	4.43, q, J = 7.0 Hz	2 H	Methylene			
	6.83, s	1 H	Methine			
	6.75–7.41, m	14 H	Aromatic			
10c	1.28, t, J = 7.2 Hz	3 H	Methyl			
	2.21, s	3 H	Methyl			
	1.15, s	1 H	Hydroxyl			
	4.28, q, J = 7.2 Hz	2 H	Methylene			
	6.96–7.79, m	13 + 1 H	Aromatic + Methine			
11	1.28, t, J = 7.2 Hz	3 H	Methyl			
	2.30, s	3 H	Methyl			
	3.66, s	3 H	Methoxy			
	3.81, s	3 H	Methoxy			
	4.27, q, J = 7.2 Hz	2 H	Methylene			
	7.14, s	4 H	Aromatic			
14e	1.10–1.36, m	3 + 1 H	Methyl + Imino			
	4.26, q, J = 7.0 Hz	2 H	Methylene			
	5.36, q	1 H	Imino			
	7.00–8.23, m	9 H	Aromatic			
14f	0.74, d, J = 7.2 Hz	1 H	Imino			
	1.14, d, J = 7.2 Hz	1 H	Imino			
	2.08, s	3 H	Acetyl			
	6.01–8.08, m	9 H	Aromatic			

s = singlet, d = doublet, t = triplet, q = quartet.

added dropwise with vigorous stirring. The soln soon became deep red and a brown red solid precipitated. It was collected after further 8 hr stirring and recrystallized thrice with proper solvents.

Reaction of quinoline and isoquinoline with hydrazidoyl bromide

On warming, **2e** (1.0 g) with a mixture of quinoline or isoquinoline and alcohol (5.0 ml) for 10–20 min, the corresponding salts **16** and **17** were obtained in excellent yield. On the other hand, when the soln of **2e** with quinoline was allowed to reflux in an oil bath at 160–70° for 4 hr, compound **18** was obtained as a creamy white product, which was further recrystallized from EtOH into crystalline pure material.

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REFERENCES

[1]R. Huisgen, *Angew. Chem.* Int. ed. **2**, 565 (1963).
[2]R. Huisgen, *Proc. Chem. Soc.* 357 (1961).
[3]R. Huisgen, *J. Org. Chem.* **33**, 2291 (1968).
[4]R. A. Firestone, *Ibid.* **33**, 2285 (1968).
[5]L. Garanti, A. Sala and G. Zecchi, *Ibid.* **42**, 1389 (1977).
[6]R. N. Butler and F. L. Scott, *Chem. & Ind.* 1216 (1970).
[7]D. A. Bowack and A. Lapworth, *J. Chem. Soc.* 1854 (1905).
[8]R. S. Tewari and P. Parihar, *Indian J. Chem.* **19B**, 218 (1980).
[9]R. S. Tewari and P. Parihar, *Z. Naturforsch.* **35B**, 99 (1980).
[10]D. B. Sharp and C. S. Hamilton, *J. Am. Chem. Soc.* **68**, 588 (1946).
[11]R. Huisgen, E. Aufderhaar and G. Wallbillich, *Chem. Ber.* **98**, 1476 (1965).
[12]R. Fusco, P. D. Croce and A. Salvi, *Tetrahedron Letters* 3071 (1967).