

Note

Synthesis of 4-substituted-benzo[*h*]tetrazolo[1,5-*a*]-6,7-dihydroquinolines

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The chloroolefins **1** with potassium azide give title quinolines **2** through a substitution-intramolecular cycloaddition reaction sequence.

Ylidinemalononitriles are versatile synthons in heterocyclic synthesis^{1,2}. Both the olefinic bond and the nitrile functions have been reported as active sites for nucleophilic attack³. Under neutral condition, ylidinemalononitrile behaves as an electron deficient substrate. It however, exhibited nucleophilic character in base mediated reactions⁴. In general, nitriles are known as poor dipolarophiles in comparison to olefins. Although much emphasis have been devoted to electrophilic and nucleophilic studies involving olefinic and nitrile groups, their scope towards 1,3-dipoles has attracted least attention. The azides are important functional group and well known as a source of electron deficient nitrenes⁵. Further, alkyl and arylazides play key roles in the synthesis of nitrogen heterocycles via 1,3-dipolar reaction⁶.

In continuation of our efforts^{3,4} to diversify the scope of ylidinemalononitriles, we describe herein an efficient synthesis of benzo[*h*][1,2,3,4]tetra-

zolo[1,5-*a*]quinolines utilizing intramolecular 1,3-dipolar cycloaddition reaction of δ -azidocyanolefins.

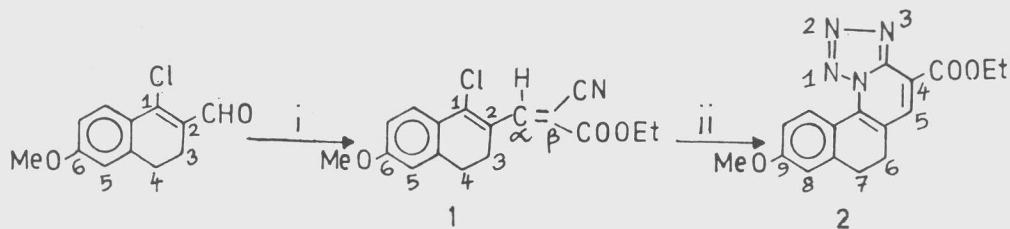
The cyanovinyl naphthalenes **1a-e** were prepared by Knoevenagel condensation of cyanomethylenes with 1-chloro-6-methoxy-3,4-dihydronaphthalene-2-carboxaldehyde⁷. The reaction of **1a** with potassium azide in refluxing ethanol underwent facile and *in situ* halide displacement to yield 4-carbomethoxy-9-methoxybenzo[*h*][1,2,3,4]tetrazolo[1,5-*a*]-6,7-dihydroquinoline **2a** (Scheme I) in 89% yield. The structure of the product **2a** was established by spectral data and elemental analysis.

The formation of the fused tetrazole **2a** clearly revealed an intramolecular 1,3-dipolar cycloaddition reaction of azide group on the neighbouring C \equiv N group. Our attempts to isolate any other side products were unsuccessful and **2a** was obtained as the sole product, supporting selective 1,3-dipolar cycloaddition of the azide on nitrile group and discarded the generation of the nitrene intermediate.

In conclusion, the nitrile functional group despite poor dipolarophilicity, behaves as better dipolarophile than olefinic group and preferably undergoes 1,3-dipolar cycloaddition reaction with azides. Further work on the mechanism and generalization of this reaction is in progress.

Experimental

All melting points were taken in open capillaries and are uncorrected. IR spectra were recorded on a Perkin Elmer 580B infrared spectrometer in KBr disks; ¹H NMR spectra on Varian T-60 or Jeol



i, RCH₂CN/EtOH/Et₃N

ii, KN₃/EtOH-H₂O/80°C

Scheme I

JNM-FX90Q spectrometer using TMS as internal standard and mass spectra on a AEIMS-30 spectrometer. Purity of the samples were checked by TLC.

1-Chloro-6-methoxy-2- $[\beta$ -cyano- β -carboethoxyvinyl]-3,4-dihydronaphthalene 1a. To a solution of 1-chloro-6-methoxy-3,4-dihydronaphthalene-2-carboxaldehyde (1.11 g, 0.005 mole) and ethyl cyanoacetate (0.57 g, 0.005 mole) in 30 mL ethanol was added triethylamine (0.60 g, 0.006 mole) and the reaction mixture was refluxed for 1 hr/or 2 hr (see Table I) under casual stirring. The solution was poured onto 200 mL of water, filtered, washed with cold water and dried. Recrystallisation from methanol afforded **1a**, 86% yield, m.p. 190-92°C; IR(KBr): 2225, 1712, 1600, 1565 cm^{-1} ; Mass: m/z 317 (M^+), 288 (M^+ -Et); ^1H NMR (90 MHz, CDCl_3): δ 1.3 (t, 3H), 2.6-3.2 (m, 4H), 3.7 (s, 3H), 4.1-4.5 (q, 2H), 6.75 (d, 1H, aromatic), 7.60 (dd, 1H, aromatic), 7.80 (dd, 1H, aromatic), 8.5 (s, 1H).

Compounds **1b-e** were prepared similarly and their characterization data are given in Table I.

4-Carboethoxy-9-methoxy-benzo[*h*][1, 2, 3, 4]-tetrazolo[1, 5-*a*]-6, 7-dihydroquinoline 2a. Compound **1a** (1.05 g, 0.003 mole) and potassium azide (0.54 g, 0.006 mole) were taken in a mixture of ethanol and water (20 mL, 4:1 ratio) and refluxed for 4.5 hr at 80°C. The reaction mixture was concentrated under reduced pressure and cooled to obtain solid product. Recrystallisation from ethyl acetate afforded **2a** as off-white crystals, yield 0.96 g (89%), m.p. 160-62°C; IR(KBr): 1690, 1595, 1560 cm^{-1} ; Mass: m/z 324 (M^+) and 296 (M^+ - N_2); ^1H

Table I—Characterization data of compounds 1 and 2

Compd	R	Reaction time (hr)	Yield (%)	m.p. °C	Mass spectra (M^+)
1a	COOEt	1.0	82	110-12	317
1b	CN	0.5	92	190-92	270
1c	CONH ₂	1.5	80	200-2	288
1d	COOH	2.0	75	194-96	289
1e	COOMe	1.2	85	126-27	303
2a	COOEt	4.5	89	160-62	324
2b	CN	4.0	70	221-23	277
2c	CONH ₂	6.0	62	246-48	295
2d	COOH	7.0	56	276-78	296
2e	COOMe	4.5	63	175-77	310

NMR (90 MHz, CDCl_3): δ 1.3 (t, 3H), 2.6-3.35 (m, 4H), 3.7 (s, 3H), 4.13-4.50 (q, 2H), 6.75 (d, 1H, aromatic), 7.60 (d, 1H, aromatic), 7.86 (dd, 1H, aromatic), 8.0 (s, 1H).

Compounds **2b-e** were prepared similarly from compounds **1b-e** and their characterization data are given in Table I.

References

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