Accepted Manuscript

The reaction of 2-amino-N'-arylbenzamidines with tetracyanoethene reinvestigated: Routes to imidazoles, quinazolines and quinolino[2',3':4,5]imidazo[1,2-c]quinazoline-8-carbonitrile

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PII: S0040-4020(15)30077-6

DOI: 10.1016/j.tet.2015.09.049

Reference: TET 27146

To appear in: *Tetrahedron*

Received Date: 22 July 2015

Revised Date: 9 September 2015

Accepted Date: 21 September 2015

Please cite this article as: Mirallai SI, Manoli M, Koutentis PA, The reaction of 2-amino-N'-arylbenzamidines with tetracyanoethene reinvestigated: Routes to imidazoles, quinazolines and quinolino[2',3':4,5]imidazo[1,2-c]quinazoline-8-carbonitrile, Tetrahedron (2015), doi: 10.1016/j.tet.2015.09.049.

The reaction of 2-amino-*N′*-arylbenzamidines with tetracyanoethene reinvestigated: Routes to imidazoles, quinazolines and quinolino[2',3':4,5]imidazo[1,2-*c*]quinazoline-8-carbonitrile

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2-Amino-*N′*-phenylbenzamidine (**1a**) reacts with tetracyanoethene (TCNE) to give 2-[2-(2-aminophenyl)-5-imino-1-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**11a**), 4-(phenylamino)quinazoline-2-carbonitrile (**5a**) and 4-imino-3-phenyl-3,4-dihydroquinazoline-2-carbonitrile (**9a**). By optimizing the reaction conditions each of the compounds can be isolated as the main product and seven examples of these reactions are described. The [1*H*-imidazol-4(5*H*)-ylidene]malononitrile **11a** was also independently synthesized in three steps from 2-amino-*N′*-(2-nitrophenyl)benz-amidine (**25**) and TCNE in an overall yield of 56%. Dimroth rearrangement of either 2-aminophenyl- or 2-nitrophenyl-substituted [1*H*-imidazol-4(5*H*)-ylidene]malono-nitriles **11a** or **27** with DBU in hot DCM gave the 2-[2-(2-aminophenyl)- and 2-[2-(2-nitrophenyl)-5-(phenylimino)-3*H*-imidazol-4(5*H*)-ylidene]malononitriles **28** (71%) and **34** (59%), respectively. Treatment of the [3*H*-imidazol-4(5*H*)-ylidene]malono-nitrile **28** with ethyl orthoformate in DMA at 165 ^{o}C gave (*Z*)-2-[3-(phenylimino)-imidazo[1,2-*c*]quinazolin-2(3*H*)-ylidene]malononitrile (**36**) (70%), thermolysis of which gave quinolino[3',2':4,5]imidazo[1,2-*c*]quinazoline-13-carbonitrile (**30**) (97%).

Keywords: Heterocycles; quinazolines; imidazoles; tetracyanoethylene; amidines; cyclization reactions.