Ethyl 2-Diazoacetoacetate

Compiled by Flaviana Rodrigues Fintelman Dias

Flaviana Rodrigues Fintelman Dias was born in Muriaé, Brazil in 1985. She received her pharmacy degree from Universidade Federal Fluminense (UFF), Niterói, Brazil in 2010. She is currently in the final stages of her M.Sc. studies under the supervision of the Professors Anna Claudia Cunha and Vítor Francisco Ferreira in organic chemistry at Universidade Federal Fluminense. Her research interests are focused on the design and synthesis of new bioactive compounds, such as quinone and 1,2,3-triazole derivatives. By using ethyl 2-diazoacetoacetate and para-substituted aromatic hydrazine hydrochlorides several 1,2,3-triazoles have been prepared.

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Abstracts

(A) Cunha and co-workers\(^5\) showed that ethyl 2-diazoacetoacetate undergoes reaction with different phenylhydrazine hydrochlorides (route I) or arylsulfonylhydrazides (route II) to yield the corresponding 1,2,3-triazole derivatives in good yield. The intramolecular 1,5-electrocyclization of \(\beta\)-substituted-\(\alpha\)-diazocarbonyl compounds represents an efficient and flexible method for preparing various substituted 1,2,3-triazoles from easily available, properly functionalized carbonyl compounds and amine derivatives. The \(N\)-amino triazoles are easily converted into the corresponding 5-methyl-1\(H\)-[1,2,3]-triazole-4-carboxylic acid hydrazides, which exhibit in vitro antiplatelet profile against human platelet aggregation using arachidonic acid, adrenaline and ADP as agonists.\(^5\) The 1-arylsulfonylamino-5-methyl-1\(H\)-[1,2,3]-triazole-4-carboxylic acid ethyl esters were able to neutralize the hemolytic property of \(L.\) muta crude venom.\(^6\)

(B) Lacour et al.\(^7\) have reported that the unusual rhodium(II)-catalyzed condensation of oxetane with ethyl 2-diazoacetoacetate gives exclusively a rare type of functionalized 15-membered polyester macrocycle.

(C) Ferreira and co-workers\(^8\) used the rhodium-catalyzed decomposition of \(\alpha\)-diazocarbonyl compounds in the presence of butyl vinyl ether to produce ethyl 5-butoxy-2-methyl-4,5-dihydrofuran-3-carboxylate. The reaction of this intermediate with an excess of primary amine in the presence of glacial acetic acid afforded the corresponding substituted 4-acyl-2-methyl-1\(H\)-pyrrole in good yield.

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(D) [CpRu(CH3CN)3][PF6] and a diimine ligand catalyze the decomposition of ethyl 2-diazoacetoacetate leading to the O–H insertion (route I) and condensation (routes II and III) products with nitriles and ketones.9

(E) The reaction of ethyl 2-diazoacetoacetate with α-isocyanaoacetamides provided the corresponding polysubstituted 5-aminooxazoles in moderate to good yield. In the mechanism suggested by Yu and co-workers,16 ethyl 2-diazoacetoacetate is transformed into a ketene through the Wolff rearrangement. This intermediate reacts with isocyanamide to produce the nitrilium intermediate that is cyclized to the 2-keto-5-aminooxazole.

(F) Titanium(IV) enolates derived from ethyl 2-diazoacetoacetate add to TiCl4-activated N-tosylimines to give the α-N-tosylamino substituted α-diazo-β-keto carboxyl compounds. The diazo decomposition of the addition product under irradiation affords γ-lactam derivatives in good yield.11

(G) Lacour et al.12 reported a one-step catalytic asymmetric synthesis of ethano-Tröger’s base using ethyl 2-diazoacetoacetate and a rhodium(II)-catalyzed reaction. A new carbon quaternary stereogenic center was introduced. Ethano-Tröger’s base exhibits chirality, being the first chiral compound with two bridgehead stereogenic nitrogen atoms in its structure.

References