Ethyl 2-Diazoacetoacetate

Compiled by Flaviana Rodrigues Fintelman Dias

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Introduction

α-Diazocarbonyl compounds have attracted great attention because of their versatile, synthetically useful transformations.1 Their most important reactions are those that involve loss of molecular nitrogen induced by thermolytic, catalytic, and photolytic conditions.1,2 Conventional synthetic methods for diazo carbonyl compounds include diazotization of amines, dehydrogenation of hydrazones and diazo transfer reactions.3 The diazo transfer donor is invariably a sulfonyl azide such as tosyl azide, p-carboxybenzenesulfonyl azide, p-dodecylbenzenesulfonyl azide and methanesulfonyl azide. This Spotlight focusses on ethyl diazoacetatoacetate, a yellow oil (1.131 g/mL at 25 °C).3 The general method for the construction of this reagent involves diazo-transfer reaction to the α-methylene position of ethyl acetoacetate in the presence of a base such as Et3N.4

Abstracts

(A) Cunha and co-workers5,6 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 β-substituted-α-diazocarbonyl compounds represents an efficient and flexible method for preparing various substituted 1,2,3-triazoles from easily available, properly functionalyzed carbonyl compounds and amine derivatives. The N-amino triazoles are easily converted into the corresponding 5-methyl-1H-[1,2,3]-triazole-4-carboxylic acid hydrazides, that exhibited in vitro antiplatelet profile against human platelet aggregation using arachidonic acid, adrenaline and ADP as agonists.5 The 1-arylsulfonylamino-5-methyl-1H-[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 polymer ether macrocycle.

(C) Ferreira and co-workers8 used the rhodium-catalyzed decomposition of α-diazo-β-ketoester in the presence of butyl vinyl ether to produce ethyl 5-butoxy-2-methyl-4,5-dihydropyrano-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-1H-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.³

(E) The reaction of ethyl 2-diazoacetoacetate with N-tosylimines gives the N-tosylamino-substituted δ-diazo-δ-keto carbonyl compounds. The diazo decomposition of the addition product under irradiation affords γ-lactam derivatives in good yield.¹¹

(F) Titanium(IV) enolates derived from ethyl 2-diazoacetoacetate add to TiCl₄-activated N-tosylimines to give the δ-N-tosylamino substituted δ-diazo-δ-keto carbonyl 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