

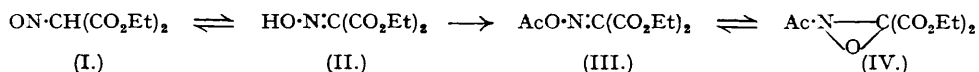
490. *The Reductive Acetylation of Aliphatic Nitro-compounds.*

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The reductive acetylation of ethyl nitromalonate and ethyl nitrocyanoacetate has been effected in low yield. This may throw some light on the enolisation of nitromalonic esters.

THE reductive acetylation of aromatic nitro-compounds is known (*e.g.*, Kohn and Krasso, *J. Org. Chem.*, 1948, **13**, 329) and also that of aliphatic oximino-compounds (B.P. 583,307). Ethyl nitromalonate and ethyl nitrocyanoacetate have been successfully reduced in this laboratory in 30% yield by zinc, acetic acid, and acetic anhydride to ethyl acetamidomalonate and acetamidocyanoacetate. The low yield may be due to the ease with which the malonic ester, for example, enolises on the carbon atom.

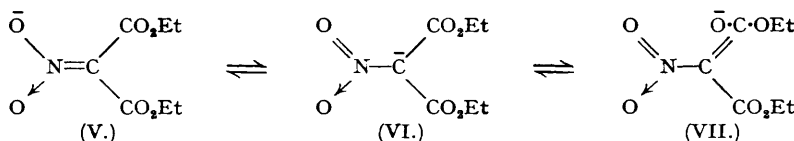
In the case of the oximino-esters, Cerchez and Collesiu (*Compt. rend.*, 1932, **194**, 1954) described the formation of the oxime acetate and its subsequent reduction. They postulated its existence in two forms (III and IV) :



The existence of (IV) or an analogue would seem to be essential for reduction to ethyl acetamidomalonate.

If nitromalonic ester (VI) may be compared with *o*-nitrophenol, enolisation would afford the

aci-nitro-compound (V). It can also be substituted in sodium ethoxide solution (cf. Weisblat and Lyttle, *J. Amer. Chem. Soc.*, 1949, **71**, 3079) and this probably proceeds through (VII).



[Where (V)—(VII) are some of the canonical forms of the resonating enol ion.]

Thus nitromalonic ester might exist mainly in form (VII). This aspect was discussed by Arndt and Rose (*J.*, 1935, **7**). Meyer (*Ber.*, 1914, **47**, 2380) suggested that with compounds of the type $\text{R}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NO}_2$ enolisation is on the carbon and not on the nitrogen atom; this was supported by Kuhn and Albrecht (*Ber.*, 1927, **60**, 1297). Arndt and Rose, disputing this, based their conclusions on esterification of the nitronic acid with diazomethane and claimed nitronic esters of type (V); they disagreed with the conclusions of Steinkopf (*Annalen*, 1923, **434**, 29), who claimed the preparation of nitronic esters from methyl iodide and the silver salt. It must be noted that the properties of these esters differed.

Weisblat and Lyttle (*loc. cit.*) prepared ethyl α -nitro- α -carbethoxy- β -3-indolylpropionate from ethyl nitromalonate and gramine, but reduction with zinc and acetic acid only gave 56% of ethyl α -hydroxylamino- β -3-indolylpropionate.

One possible explanation of the fact that nitromalonic ester is reduced under the conditions described below only to about one-third of the extent that oximinomalonic ester is reduced may be that steps corresponding to (III)—(IV) are lacking, owing to enolisation on the carbon and not on the nitrogen atom.

EXPERIMENTAL.

Ethyl Acetamidocyanoacetate.—Ethyl nitrocyanoacetate (Conrad and Schulze, *Ber.*, 1909, **42**, 740) (10 g.), acetic acid (40 ml.), acetic anhydride (40 ml.), and a trace of copper powder were mechanically stirred at 50° with addition of zinc dust. The rate of addition was decreased and the temperature allowed to rise to 80° and kept there until 25 g. of zinc had been added. The mixture was cooled, filtered, and washed with acetic acid. The filtrates were evaporated in a vacuum and the syrup was diluted with water. Crystals (3 g.) were deposited, having m. p. 131—134° alone or mixed with an authentic sample (Found: N, 15.7; Ac, 25.7. Calc. for $\text{C}_7\text{H}_{10}\text{O}_5\text{N}_2$: N, 16.5; Ac, 25.3%).

Ethyl Acetamidomalonate.—Ethyl nitromalonate (Wahl, *Bull. Soc. chim.*, 1901, [iii], **25**, 926; Arndt and Rose, *loc. cit.*) was treated in an analogous fashion, affording a 30% yield of ethyl acetamidomalonate, m. p. and mixed m. p. 94° (Found: N, 6.4. Calc. for $\text{C}_9\text{H}_{15}\text{O}_5\text{N}$: N, 6.5%). The oil remaining after removal of the crystals was unchanged starting material.

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