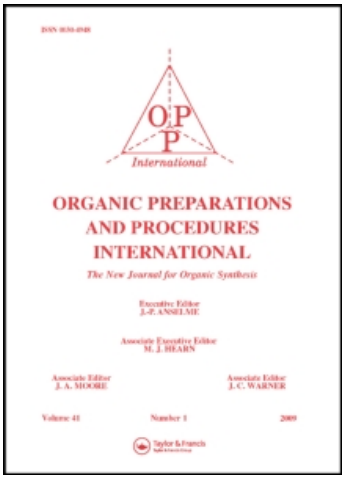

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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To cite this Article Rao, A. K. S. Bhujanga , Radhakrishna, Arakali S. , Rao, C. Gundu , Singh, Bajrang Bali and Bhatnagar, Surendra P.(1988) 'AN IMPROVED PROCEDURE FOR THE PREPARATION OF ETHYL α-CARBETHOXY-β-(ARYLAMINO)ACRYLATES', Organic Preparations and Procedures International, 20: 1, 93 — 95
To link to this Article: DOI: 10.1080/00304948809355873
URL: http://dx.doi.org/10.1080/00304948809355873

ORGANIC PREPARATIONS AND PROCEDURES INT. 20(1), 93-103 (1988)

OPPI BRIEFS

AN IMPROVED PROCEDURE FOR THE PREPARATION OF ETHYL α-CARBETHOXY-β-(ARYLAMINO)ACRYLATES†

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Ethyl α-carbethoxy-β-(arylamino) acrylates are valuable intermediates for the synthesis of biologically important quinoline derivatives. These acrylates have been prepared by a variety of methods.[1-4] A recent publication[5] on the synthesis of these acrylates describes a method similar to that published by Levai et al.[6] and uses zinc chloride as a catalyst based on a Hungarian patent.[7] In this method the reaction is carried out in stages and the reactants, triethyl orthoformate and diethyl malonate are added in strict proportions at definite intervals to the arylamine, making the procedure somewhat cumbersome; furthermore, the reaction times are also quite long (22 hrs). We now report a method using a superior catalyst where all the reactants are mixed together and heated for 6-8 hrs giving quantitative yields of the desired acrylates without any work-up.

$$\underset{\text{I}}{ArNH_2} + \underset{\text{II}}{CH(OEt)_3} + \underset{\text{III}}{CH_2(CO_2Et)_2} \xrightarrow[\Delta,\,6\text{-}8\ h]{FeCl_3} \underset{\text{IV}}{ArNHCH{=}C(CO_2Et)_2}$$

Thus, a mixture of arylamine, triethyl orthoformate and diethyl malonate was heated in the presence of catalytic amount of ferric chloride at 100-110° for 3 hrs and for a further period of 3 to 5 hrs at 130-140°. The completion of the reaction was indicated by the distillation of the theoretical amount of ethanol from the reaction mixture. The residue on

cooling solidifies and is identical to the product obtained from the reaction of the arylamine with diethyl ethoxymethylenemalonate (TLC, IR and mixture mp.). The crude product did not require any purification and was used as such for further reactions. The reaction has been successfully applied to a representative set of arylamines (Table).[8] The use of zinc chloride as catalyst in place of ferric chloride gave much lower yields (approx. 80%) of the acrylate.

EXPERIMENTAL SECTION

Ethyl α-Carbethoxy-β-anilinoacrylate (IV). General Procedure.- In a 500 ml round bottom flask, equipped with a distillation unit and stirring arrangement, was taken aniline (74.4 g, 0.8 mole), triethyl orthoformate (118.4 g, 0.8 mole), diethyl malonate (128 g, 0.8 mole) and anhydrous ferric chloride (0.150 g). The mixture was stirred well and heated at 100-110° for 3 hrs. During this period, the ethanol generated in the reaction was removed by distillation. At the end of this time, a further amount of triethyl orthoformate (11.8 g, 0.8 mole) was added and heating continued at 130-140° for 5 hrs. By the end of this time, a total of 140 ml (2.4 moles) of ethanol had been collected. The reaction mixture was then poured into a glass dish. The solidified mass was collected and powdered. This product was identified as ethyl α-carbethoxy-β-anilinoacrylate (212 g, 100%), mp. 44-46°, which was recrystallized from hexane to recover pure acrylate (200 g, 94%), mp. 47-48°. This product was identical in all respects to the authentic sample prepared from aniline and diethyl ethoxymethylenemalonate.

TABLE. Ethyl α-Carbethoxy-β-(arylamino)acrylate

Compound IV Ar	Yield (%) Crude	Yield (%) Pure[a]	mp. (°C) Crude	mp. (°C) Pure	mp. (°C) authentic[b] sample
C_6H_5	100	94	44-46	47-48	47-48
p-$NO_2C_6H_4$	100	96	136-38	142	141-43
m-$NO_2C_6H_4$	100	96	72-76	80	79-81
m-ClC_6H_4	100	93	52-54	56	56-57
2,5-$(CH_3O)_2C_6H_3$-	100	96	70-72	73	73-75

a) Recrystallized from hexane. b) Authentic samples were prepared by the reaction of arylamine with diethyl ethoxymethylenemalonate (EMME) and recrystallization of the crude product with hexane.

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† Publication was delayed at the request of the authors. An application has been filed for obtaining an Indian Patent.

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