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An Unusual Reaction Between Coumarin and Diethylmalonate, Catalyzed in the Heterogeneous Phase

Short Communication

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In the reaction of diethylmalonate and coumarin catalyzed by an activated barium hydroxide catalyst (C-200) in a solid liquid system an unusual nucleophilic addition-elimination to the lactonic $C=O$ bond occurs.

(Keywords: Basic catalyst; Barium hydroxide catalyst; Coumarin)

Eine ungewöhnliche in heterogener Phase katalysierte Reaktion zwischen Cumarin und Diethylmalonat (Kurze Mitteilung)

Bei der Reaktion von Diethylmalonat und Cumarin, die mit einem aktivierten Bariumhydroxid-Katalysator (C-200) in einem Fest-Flüssig-System katalysiert wird, ergab sich eine ungewöhnliche Addition-Eliminierung an der laktonischen $C=O$-Bindung.

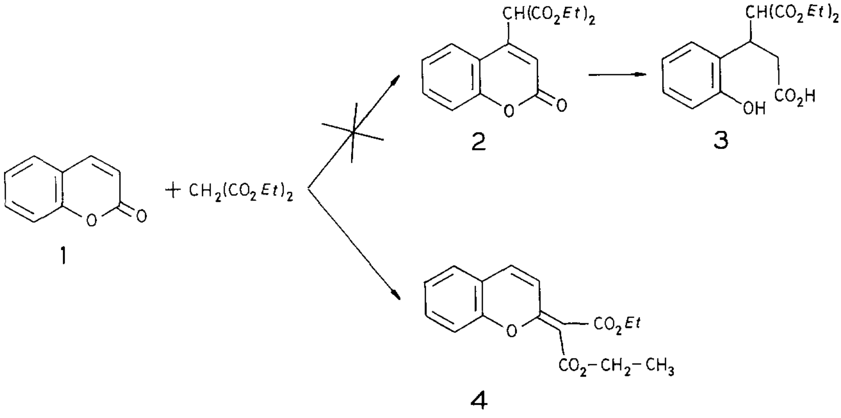
Coumarins are widely distributed in plants particularly in the "*Umbelliferae*" and "*Rutaceae*" families. On the other hand the coumarinic skeleton is related to many drugs e.g.: antifungi, anticoagulatives etc. Consequently the reactivity of the coumarinic skeleton has been extensively studied in the literature[1].

Recently a new barium hydroxide catalyst (C-200) has been described as a catalyst for the *Michael* addition in the heterogeneous phase[2].

When the *Michael* addition of diethylmalonate to coumarin (**1**) was catalyzed by the C-200 catalyst, no *Michael* adduct **2** was obtained. The new product was not the open product **3** produced by alcaline hydrolisis of **2** since no OH group was observed in the IR spectrum.

The analysis of the only reaction product obtained in 30% yield indicated the molecular formula $C_{16}H_{16}O_5$ or $C_{16}H_{18}O_5$ which eliminates **2**.

In the IR spectrum no γ, δ-unsaturated δ-lactone band was present coumarin exhibits a C=O band at $1\,700\,cm^{-1}$ but a $1\,730\,cm^{-1}$ band is observed. This can be attributed to an α,β-unsaturated ester. No OH group was observed, hence no alcaline hydrolisis was caused by the solid C-200 catalyst. This is due to the fact that this catalyst only hydrolizes the salicylic esters[3].



In the PMR spectrum, peaks at 7.85 (d) and 6.45 (d) ppm (J = 9.8 Hz) are due to the two protons of the lactonic ring of coumarin. Since a CH_2-signal is absent in the appropriate region, structure **4** was assigned to the reaction product. Similar products were obtained with $CH_2(CN)_2$ and $CN-CH_2-CO_2Et$ with similar pK_a-values to diethylmalonate[4]. When the active methylene compound has a high C–H-acitity e.g.: acetylacetone, ethylacetoacetate etc. the expected Michael reaction is produced[4].

The mechanism of this unusual reaction may be explained according to the microcrystalline structure of the active site of the catalyst[5]. The reaction of coumarin with diethylmalonate takes place in the crystalline structure of the catalyst. This structure renders impossible a *Michael* addition to the rigid coumarin molecule that interacts with the Ba(II) by the lone pairs of the oxygens, but the 1,2-addition can occur quite easily.

The fact that the carbanion remains on the catalytic surface was proved using a polymeric supported reagent. When Ⓟ $-CH=CH-CO-Ph$ (obtained from a polystyrene resin Ⓟ $-CHO$[6] by the *Claisen-Schmidt* reaction) is added to a mixture of diethylmalonate and the C-200 catalyst, no *Michael* addition to "supported chalcone" was observed. Thus it may be concluded that the process takes place on the solid surface. When the

CH_2 of the active methylene compound has a great acidity ($pK_a \leqslant 10$), the carbanion is trapped by the polymer. Consequently the process takes place in the homogeneous phase and a *Michael* addition is produced.

Experimental

The Catalyst

The activated barium hydroxide catalyst C-200 was prepared by calcination of commercial barium hydroxide octahydrate as described previously[3]. The surface area ($1.9 \pm 0.1\,m^2\,g^{-1}$) was determined by *BET* method.

Synthesis of **4**

The barium hydroxide catalyst is added to a stirred solution of coumarin (1.46 g, 0.01 mol) and diethylmalonate (1.52 ml, 0.01 mol) in *Et*OH (96%, 50 ml). The mixture is stirred at reflux for 4 h. Then cold $HCl-H_2O$ solution was added until $pH = 6$ to destroy the catalyst. The mixture is cooled to 4 °C and the product (**4**) is filtered and washed with cold water. No recrystallization is necessary. Yield 30%; m.p. 56 °C.

IR KBr (cm^{-1}) = 1 730 (−CO−O*Et*), 1 200 broad band (−O*Et*), 1 260 (v) (arylic ether), 760 (ortho subst.).

PMR ($CDCl_3$) $\delta = 1.22$ (t, 6 H), 4.25 (q, 4 H), 6.45 (d, 9.8 Hz, 1 H), 7.3–7.6 (m, 4 H), 7.85 (d, 9.8 Hz, 1 H).

$C_{16}H_{16}O_5$. Found C 66.9 ± 0.4 H 5.9 ± 0.2.
Calc C 66.6 H 5.6.

Reaction with Polymeric Supported Reagent

The Ⓟ−CH=CH−CO−*Ph* resin was obtained by the reaction of P−CHO[6] ($1.3\,meq\,g^{-1}$) with acetophenone in the presence of NaOH under standard *Claisen-Schmidt* conditions.

This "supported chalcone" was added to a mixture of diethylmalonate and C-200 catalyst (this mixture was equilibrated for 10 h) and the mixture stirred for 24 h. The resin was washed and dried and the IR spectrum was recorded. No ester band was observed indicating that no reaction took place.

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