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A NOVEL, MILD PREPARATION OF THE 2H-1-BENZOPYRAN-2-ONE (COUMARIN) RING SYSTEM

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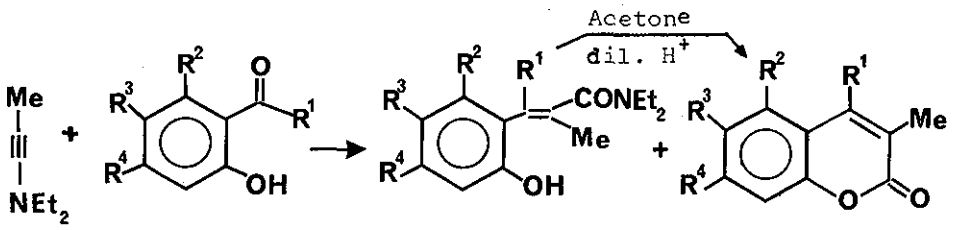
A facile synthesis of coumarins from o-hydroxycarbonyl compounds and 1-diethylaminopropyne is described. The reaction takes place under very mild conditions, giving coumarins in 38-47% yield. The unwanted sideproducts, the (E)-isomers, produced more coumarins after treatment the reaction mixture with acid, thus bringing the overall yields to 68-84%.

Several methods[1] are available for the preparation of the coumarin ring system. However, all of these methods requires quite strong reaction conditions.

During studies[2] of the reaction of ynamines with (hetero)aromatic acyloins a facile lactone ring formation under mild conditions was observed. Now this method has been tested with some aromatic o-hydroxycarbonyl compounds (in the aliphatic series the reaction is unfavourable, because of the ready elimination of water). The commercially available 1-diethylaminopropyne (I) was used as the ynamine. The oveall reaction is as follows (Scheme 1).

Aldehydes reacted smoothly with neat I (in dry ether under argon and at room temperature), but ketones required a mild Lewis-acid catalyst (e.g. $MgBr_2$) to accelerate the reaction. After the proposed oxetene rearrangement[3] both (Z)- and (E)-isomers of the α-ethylenic amide (e.g. VI) were produced almost in the ratio 1:1. However, the unstable (Z)-isomer cyclized spontaneously to the coumarin ring system by expulsion of diethylamine. Also the (E)-isomer could be cyclized to coumarin in nearly quantitative yield by a mild acid medium. Thus the overall yield of coumarins were increased to 68-84%, if the syntheses were performed in two steps.



I II: VI:

III: $R^1=R^3=Me$

IV: $R^1=Me$, $R^3=OH$

V: $R^1=CH_2OMe$, $R^2=R^4=OMe$

		Overall Yield
VII:		84%
VIII:	$R^1=R^3=Me$	76%
IX:	$R^1=Me$, $R^3=OH$	74%
X:	$R^1=CH_2OMe$, $R^2=R^4=OMe$	68%

Every R = H, if not otherwise stated.[4]

Scheme 1.

It seems likely that the mild method described above for the preparation of coumarins can be extended to include other ynamines besides of I.

References and Footnotes

1. Elderfield R. C.,'Heterocyclic Compounds', John Wiley & Sons Inc., New York, 1951, p. 174.

2. Pennanen S. I., Heterocycles, To be published.

3. Ficini J., Tetrahedron, 1976, 32, 1449.

4. Satisfactory analytical data were obtained for all compounds prepared.

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