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Synthesis of Trans – 3 - (4-Oxo-4*H*-1-Benzopyran-3) acrylic acid, Catalyzed by Basic Alumina under Microwave Irradiation

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Abstract:

Condensation of formyl chromones with malonic acid catalyzed and accelerated by using basic alumina, results bioactive trans-3-(4-oxo-4*H*-1-benzopyran-3)acrylic acids under the influence of microwave irradiation.

Introduction:

Reported applications of acrylic acid and its derivatives includes used as antibacterial[1], anti-histaminic[2], anti-allergic[3], anti-inflammatory[4] and hepotoprotective[5] activities.

The knoevenagel condensation of various aromatic aldehydes with malonic acid to give acrylic acid has been extensively studied using base catalyst like ammonia, primary and secondary amines, particularly piperidine, pyridine, pyridine with trace of piperidine and other secondary and tertiary amines[6-9]. It has been reported using acidic catalysts for the condensation like sulfuric acid[10-11]. However, both bases and acids as homogeneous catalyst are difficult to be recovered and easily pollute the environment.

Microwave has been increasingly used in organic synthesis[12]. Herein, we wish to report the efficient condensation, between various substituted formyl chromones and malonic acid using solid support, catalyst basic alumina under microwave irradiation.

Methodology:

General procedure:

4-Oxo-(4*H*)-1-benzopyran-3-Carbaldehydes 1a-I (10mmol) and malonic acid (10mmol) was mixed thoroughly in a25ml conical flask and then the reaction mixture was mulled with 5ml ethyl acetate and 3g basic alumina till all ethyl acetate was evaporated. The reaction mixture was exposed to microwave irradiation at an output

of600w for 4-5 minutes (See Table). The progress of reaction was checked by TLC. After completion of reaction as indicated by TLC the reaction mixture was cooled and extracted with ethyl acetate. The solvent was removed under vaccum and residual solid was recrystallized from proper solvent. Yellow colored crystals were obtained in 80-85%.

All the compounds obtained by above methods were compared with authentic samples in reported methods[8] for melting points and analytical data.

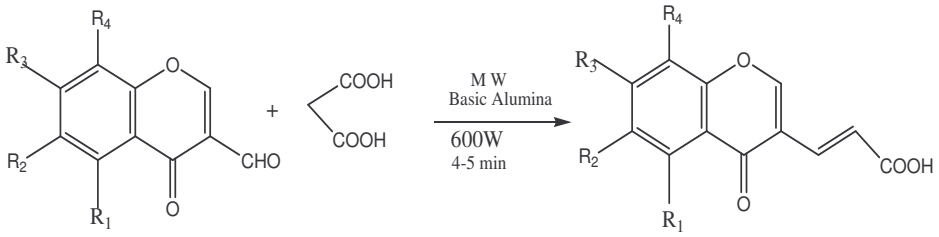
Experimental:

Melting points were measured in open capillaries in a paraffin bath and are uncorrected. All reactions were carried out in unmodified Domestic Microwave Oven Model 800T (2450MHz) manufactured by appliances and utilities Ltd., Bangalore, India.

The reactions were monitored by TLC [Silica Gel, light petroleum-ethyl acetate (8:2)] IR Spectra were recorded as Nujol mulls on FTIR instrument. ^{1}HNMR Spectra were recorded on Varian NMR Spectrophotometer (400MHz) Model Mercury plus $CDCl_3$ as a solvent and TMS as an internal standard.

Result and Discussion:

Reaction:



Table

Entry	R1	R2	R3	R4	MW (min)	MW % Yield	M. Pt. (^{0}C)
1a	H	H	H	H	5	80	250
1b	H	F	H	H	5	83	238
1c	H	Cl	H	H	5	80	278
1d	H	CH3	H	H	5	85	259
1e	H	Br	H	H	4	80	266
1f	H	Cl	H	CH3	4	85	260
1g	H	Cl	Cl	H	4	88	254
1h	H	Cl	H	Cl	4	88	258
1i	H	CH3	H	CH3	5	84	286

As shown in the scheme and table, the microwave technique represented a better procedure in terms of the higher yields, milder reaction condition, easier workup and short reaction time as compared to reported methods.

In conclusion, we have developed a practical condensation procedure for the synthesis of various bioactive acrylic acid derivatives using basic alumina as solid support and catalyst under microwave irradiation. The operational simplicity, use of inexpensive, non-corrosive and safety catalyst, high yields and non-pollution, solvent free reaction can make this procedure a useful and attractive to the currently available methods.

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