Asian Journal of Chemistry Vol. 5, No. 4 (1993), 1137–1139

NOTES

A Simple and Convenient Synthesis of Alkyl Succinanilates

RAMAN K. VERMA
Organic Research Laboratories
M M Modi College, Patiala-147 001, India

Fairly good yields of substituted alkyl succinanilates are obtained when alcoholic solution of corresponding acid is treated with $HClO_4$.

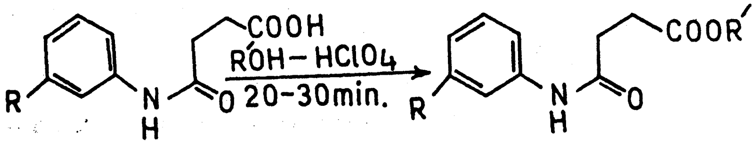
Generation of heterocyclics from suitably substituted anilic esters is well documented[1,2]. Oxidative photocyclization reactions of anilides and their analogous have also been shown to be of value in the synthesis of heterocyclics[3,4]. The author was interested in the photochemistry of anilic acid and their derivatives. The competing photodecarboxylation during photolysis of anilic acids will probably be affecting the yields of the photoproducts, hence the need of a dependable method for esterification of anilic acids.

Many useful methods for esterification have been developed and reviewed by Haslam[5]. Because of structural constraints, the conventional direct esterification methods either failed to esterify anilic acids[6] or do not give acceptable yields of anilic esters. Some of the recently developed methods[7,8] involve longer reaction time, vigorous conditions, undergo side reactions, are expensive in some cases and also poor yields of the ester obtained in many cases.

Use of alkyl phosphoric esters[10], a reagent of high synthetic potential for effecting esterification of succinailic acids, the only report available, has some disadvantages such as the reagent being hygroscopic in nature and its instability at higher temperature followed by 4 hrs of stirring during esterification.

In the present experiment, a mixing affair process using perchloric acid which at room temperature give farly good yields of succinanilic esters in less than half an hour, the shortest possible time to date, as an extension of previous work where $SOCl_2$ was used for effecting esterification in general[11] and of maleanilic[12] and succinanilic acid[13] in particular.

Dropwise addition of 70% perchloric acid to an alcoholic solution or suspension of succinanilic acid I, with stirring, followed by quenching of the reaction mixture in ice cold water after about 30 min. of stirring gave excellent yields of esters II. Solid esters filtered and recrystallized whereas liquid esters extracted with ether and purified by distillation.



I II

R = H, CH_3, OCH_3, Cl, NO_2 R′ = C_2H_5, n-C_3H_7, n-C_4H_9

This method shorten the reaction time from 4 hrs. to an uniformly short period of 20–30 min. only, involving neither refluxing nor specialised reagents and is emerging out as a mixing affair process successful for the preparation of higher succinanilates in addition to the previously reported methyl succinanilates only[11] (Table-1). The yields of the esters ranges from 60–80% irrespective of the substitution. At this stage mechanistic speculations are premature and must await the results of studies currently on hand in this laboratory.

TABLE 1
CHARACTERIZATION DATA OF SUCCINANILIC ESTERS*** (II)

Compd	R	R′	Mol formula*	mp (bp)** °C
IIa	H	C_2H_5	$C_{12}H_{15}NO_3$	65
IIb	CH_3	C_2H_5	$C_{13}H_{17}NO_3$	60
IIc	OCH_3	C_2H_5	$C_{13}H_{17}NO_4$	64
IId	Cl	C_2H_5	$C_{12}H_{14}NO_3Cl$	80
IIe	NO_2	C_2H_5	$C_{12}H_{14}N_2O_5$	82
IIf	H	n-C_3H_7	$C_{13}H_{17}NO_3$	62
IIg	CH_3	n-C_3H_7	$C_{14}H_{19}NO_3$	(-)
IIh	OCH_3	n-C_3H_7	$C_{14}H_{19}NO_4$	70
IIi	Cl	n-C_3H_7	$C_{13}H_{16}NO_3Cl$	82
IIj	NO_2	n-C_3H_7	$C_{13}H_{16}N_2O_5$	64
IIk	H	n-C_4H_9	$C_{14}H_{19}NO_3$	(-)
IIl	CH_3	n-C_4H_9	$C_{15}H_{21}NO_3$	(-)
IIm	OCH_3	n-C_4H_9	$C_{15}H_{21}NO_4$	(-)
IIn	Cl	n-C_4H_9	$C_{14}H_{18}NO_3Cl$	(-)
IIo	NO_2	n-C_4H_9	$C_{14}H_{18}N_2O_5$	(-)

*Satisfactory microanalyses were obtained: C ± 0.23; H ± 0.09; N ± 0.31% of theoretical values.

**Boiling points in case of liquid esters IIg, IIk–o could not be determined as these decompose on heating.

***(a) PMR spectra of all these esters showed signals characteristics of the ester alkyl group.

(b) IR spectra of all these esters displayed NH band at *ca* 3300 cm^{-1}, ester carbonyl at *ca* 1730 cm^{-1} and amide I and II bands at *ca* 1670 and 1625 cm^{-1} respectively.

Preparation of Alkyl Succinanilates

Perchloric acid (5–6 ml; 70%) was added dropwise to a stirred solution or suspension of succinanilic acid (1gm) in alcohol (15–20 ml) at room temperature, stirring continued for 20–25 minutes. The reaction mixture poured in water containing ice with constant stirring in instalments (4–5 ml each). The solid esters separated were filtered, washed 2–3 times with water, dried and recrystallised from alcohol.

The liquid esters were extracted with ether, ether extract washed successively with water, sodium bicarbonate solution, 1% HCl and water, dried (anhyd. Na_2SO_4), filtered, ether evaporated or distilled under reduced pressure leaving behind the liquid ester. The ester purified by distillation under reduced pressure.

ACKNOWLEDGEMENT

Financial assistance from UGC New Delhi for the research project of the author is gratefully acknowledged.

REFERENCES

1. P. Balasubramaniyan, M.V. Patel, S.B. Wagh and V. Balsubramaniyan, *Curr. Sci. (India)*, **51**, 279 (1982).
2. S.B. Wagh, P. Balasubramaniyan and V. Balasubramaniyan, *Indian J Chem.*, **21B**, 577 (1982).
3. S.L. Castle, J.K. Luo, H. Kudo and R.N. Castle, *J. Heterocyclic Chem.*, **25**, 1363 (1988).
4. J.K. Luo and R.N. Castle, *J Heterocyclic Chem.*, **27**, 1031 (1991).
5. E. Haslam, *Tetrahedron*, **36**, 2409, (1980).
6. Raman K. Verma and B. Kumar, *Indian J. Chem.*, **30B**, 822 (1991).
7. E. Mohacsi, *synth. Commun.*, **12**, 453 (1982).
8. A. Armstrong, I. Brackenridge, R.F.W. Jackson and J.M. Kirk, *Tetrahedron Letters*, **29**, 2483 (1988).
9. T.U. Qazi, *Curr. Sci. (India)*, **58**, 629 (1989).
10. V. Balasubramaniyan, G. Bhatia and S.B. Wagh, *Tetrahedron*, **39**, 1475 (1983).
11. B. Kumar and Raman K. Verma, *Synth. Commun.*, **14**, 1359 (1984).
12. B. Kumar, Raman K. Verma, and H. Singh, *Indian J. Chem.*, **25B**, 692 (1986).
13. Raman K. Verma, *J. Indian Chem. Soc.* (in Press).

(*Received*: 5 September 1992; *Accepted*: 27 February 1993) AJC–585