

PREPARATION OF β , 2-FURYL ACRYLIC ACID

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DESPITE the relatively long history of furan compounds, dating from the discovery of furoic acid about 160 years ago, there is an astonishing paucity of information about them when compared to other heterocyclic types. A large portion of research in this field has centred round furfural, discovered¹ over a century back accidentally, or its numerous derivatives. The ready and spontaneous decomposition of many furan compounds and the ready formation of apparently intractable oils, resins, tars and chars may, perhaps, account for past sporadic investigations which culminated in a feeling on the part of some that reactions with labile furan types were extremely difficult and virtually impossible. Recent years have, however, witnessed many furan derivatives rising to prominence. They have come to play a part in industry² as plastics, synthetic resins, industrial solvents, etc., and in the group of synthetic drugs such as antiseptics,³ hypnotics or anaesthetics,⁴ sympathomimetics,⁵ mydriatics⁶ physiologically active compounds of the pyrazolone series,⁷ and as isoquinoline derivatives or analgesics.⁸

The preparation of β , 2-furyl acrylic acid in quantity has been of especial interest in connection with studies⁹ on the synthesis of possible analgesics. It may be well to recall, at this stage, that furylacrylic acid, although its pharmacology¹⁰ has been investigated without any definite findings, forms an important intermediate for the synthesis of a promising local anesthetic,¹¹ viz., 1-piperidino 2, 3-diol difuran acrylate. A scrutiny of the literature revealed that a few reports¹² had in the past appeared on the preparation of the acid. Out of these, the one entitled to serious consideration, from the point of view of a profitable preparative method, seems to be that of Johnson,¹³ who has developed a modification of the Perkin procedure. This communication is concerned with a method possessing certain advantages in respect of shortness of time, cost of the materials involved and grade purity of the finished product, over those already in existence for the large-scale productions of furyl acrylic acid.

The present procedure is essentially founded on the pyridine trace method¹⁴ as elaborated by Pandya and his collaborators. Various conditions were tried out in order to ascertain the factors influencing maximum yields and purity of the acid. The data obtained are presented in tabular form.

No.	Furfural	Malonic Acid	Pyridine	Piperidine	Period of heating at 100°	Yield and M.P. of acrylic acid	Remarks
1	24 g. (15 c.c. 1 mol.)	26 g. (1 mol.)	1 c.c. (0.05 mol.)	..	4 hrs.	..	Tarry product : not worked up.
2	24 g.	26 g.	3 c.c. (0.15 mol.)	..	4 hrs.	17.4 g., 138°	Tan coloured, yielding 12.5 g. pure acid.
3	24 g.	26 g.	6 c.c. (0.30 mol.)	..	2 hrs.	21.0 g., 139°	Slightly pale product
4	24 g.	26 g.	6 c.c.	..	4 hrs.	21.5 g., 139°	do.
5	24 g.	26 g.	6 c.c.	2 drops	4 hrs.	21.6 g., 139-40°	do.
6	24 g.	26 g.	12 c.c. (0.60 mol.)	..	2 hrs.	22.0 g., 141°	Almost white product
7	24 g.	26 g.	12 c.c.	..	4 hrs.	22.0 g., 141°	do.
8	24 g.	26 g.	20 c.c. (1 mol.)	..	1 hr.	19.5 g., 140-41°	do.
9	24 g.	26 g.	20 c.c.	..	2 hrs.	22.0 g., 141°	do.
10	24 g.	26 g.	20 c.c.	..	4 hrs.	22.0 g., 141°	do.
11	24 g.	26 g.	12 c.c. (0.60 mol.)	..	2 hrs.	21.9 g., 141°	do.
12	96 g. (60 c.c.)	104 g.	48 c.c.	..	2 hrs.	92.0 g., 141°	do.
13	96 g.	104 g.	48 c.c.	..	2 hrs.	91.0 g., 141°	do.
14	96 g.	104 g.	48 c.c.	..	2 hrs.	92.0 g., 141°	do.
15	192 g.	208 g.	96 c.c.	..	2 hrs.	184.0 g., 141°	do.

From the practical standpoint of convenience, economy and purity of the resulting product, choice was made of experiment No. 6 as meriting detailed study and investigation of the possibility of its development into a preparative method. This expectation has now been fully realised: allowing even for loss in recrystallisation, the average yield of furyl acrylic acid from numerous experiments (Nos. 12-15) works out to about 65 per cent. of the theoretical amount and compares favourably with 56 per cent. for a similar grade of acid obtainable by the method of Johnson.¹³

Experimental

The furfural used was an ordinary commercial variety, which was subjected to a single distillation and stored in a brown bottle, as also the malonic acid, marketed as "practical" quality by Messrs. Eastman Kodak Co.; the latter was, however, dried at 100° for 2 hours. The pyridine

required in these experiments was a commercial brand and was dried over solid potash.

The aldehyde (1 mol.), malonic acid (1 mol.) and the requisite amount of pyridine were brought together in a suitable vessel and the mixture heated on the boiling water-bath for the desired period. The reaction-mixture was diluted, a slight excess of dilute ammonium hydroxide added and the filtrate acidified with excess of hydrochloric acid. The separated product was filtered after cooling, washed and dried between filter-papers.

β , 2-Furyl acrylic acid.—In a 1 litre round-bottomed flask, fitted with a reflux condenser, were brought together furfural (192 g., 120 c.c., 2 mols.), malonic acid (208 g., 2 mols.) and pyridine (96 c.c., 1.2 mols.) and the mixture heated on the boiling water-bath for 2 hours, cooled and diluted with water (200 c.c.). Enough liquor ammonia was added in order to produce a clear solution, filtered through a fluted filter-paper and the paper washed with three 80 c.c. portions of water. The filtrate was treated, without external cooling, with an excess of dilute (1:1) hydrochloric acid. The mixture was cooled at the tap, allowed to stand at 0° for at least 1 hour, the separated acid filtered, washed on the filter with four lots (100 c.c. each) of ice water and dried between filter-papers.

Furyl acrylic acid, obtained as above, is crystalline (needles), nearly white and melts at 141°; yield 184 g., or 66–67 per cent.

The acid is of a high order of purity and can be utilised straightaway for further synthetic operations. If, however, a recrystallisation is desired, it is best effected from dilute alcohol with the addition of one-twentieth its weight of decolourising carbon. It is then obtained, on slow cooling with an approximate loss of 2 per cent., as slightly pale and several-inches-long needles, melting at 141°.

Summary

The factors influencing optimum yields and purity of furyl acrylic acid by the condensation of furfural and malonic acid in the presence of pyridine have been investigated.

A rapid and elegant preparative method for β , 2-furyl acrylic acid of a high degree of purity has been worked out.

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