

THE USE OF ANION-EXCHANGE RESIN (A-162) AS
A BROMINE CARRIER FOR THE BROMINATION OF 2-ACYLFURANS.

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ملخص

إستخدام المبادل الأنيوني (أ-١٦٢) كعامل للبروم فى برمنه
المركبات ٢-أسيل الفيوران

فى هذا البحث تم تحويل المبادل الأنيوني المتاح بالإسم التجارى
أ-١٦٢ من صورة الكلوريد إلى صورة البروميد وحيث تم استخدامه بعد
ذلك كعامل برمنه لمركبات ٢-أسيل الفيوران ، وتم الحصول على نتائج
وفيره لمشتقات أحادى البروم عند درجات الحرارة العاديه بدون ظهور
لأى نواتج جانبية. وقد تم فصل الراتنج فى نهاية التفاعل بعمليات
الترشيح البسيطة وتم إعادة إستخدامه مرة أخرى.

ABSTRACT

The anion-exchange resin A-162 commercially available in the chloride form was prepared in the perbromide form to be used as brominating agent for the bromination of 2-acylfurans. The monobromo derivatives were obtained in very high yield at normal temperature without the appearance of byproducts. The resin was separated at the end of the reaction by simple filtration and could be recycled for further runs.

INTRODUCTION

The utilization of cationic organic carriers for bromine in the form of perbromide have been explored to produce specific types of bromine-containing compounds. It was reported that the cations: Pyridinium⁽¹⁾, ammonium⁽²⁾, pyrrolidinium⁽³⁾ and phosphonium⁽⁴⁾ were used as bromine carriers. One of the most important aspects recently developed in the field of chemistry is the application of ion-exchange resin in organic synthesis. In recent years, Amberlyst A 26 was used as bromine carrier leading to performant bromination reactions at different temperatures with variable yields.

In this work, the resin A-162 commercially available in the chloride form was chosen and applied as bromine carrier to affect the monobromination of the selected synthesised 2-acylfurans.

EXPERIMENTAL

1) Apparatus:

a) Gas chromatograph model INTERSMAT IGC 120 DFL equipped with non-polar column of 10% ES 30 on chromosorb WAW (80 - 100 mesh) and of 1.8 m long and 1/8 inch diameter.

b) Rotary evaporator.

2) Preparation of starting 2-acylfurans:

The selected derivatives of these ketones were prepared by the direct condensation of furan and the corresponding carboxylic acids catalysed by the cation-exchange resin ES 467-H in the presence of trifluoroacetic anhydride, their m.ps. were in agreement with those reported in the literature.

3) Preparation of the resin in the perbromide form

The used anion-exchange resin A 162 has the following specifications:

Matrix : polystyrene

Functional group : Quaternary ammonium type 2 (see scheme 1)

Particle size : 0.3 - 1.2 mm

Ionic form : Chloride

Total capacity : 1.1 eq./lit

Specific gravity : 1.07 in chloride form.

Moisture retention capacity : 48 - 53%

Properties : macroporous

pH range : 0 - 14.

Maximum temperature : 750C in chloride form.

The applied sample of A-162 was treated by the following consecutive steps to prepare the perbromide form.

a) Preparation of the resin in hydroxide form:

The commercial resin (about 350 ml) was hydrated and introduced into a glass column, then washed with demineralised water followed by alcohol to remove all the impurities until the discolouration of the column effluent was achieved. The resin was again hydrated and treated with 1 N sodium hydroxide solution until the disappearance of the chloride ion in the effluent, and rinsed with demineralised water up to neutralization.

b) Preparation of the resin in bromide form:

The previously obtained resin was agitated in 1 N hydrogen bromide solution during 24 hours at ambient temperature, filtered, washed with water, acetone followed by ether and dried under vacuum for several hours. The obtained resin has: %Br = 22.27 and %N = 3.96.

c) *Preparation of the resin in perbromide form:*

The obtained resin was added to carbon tetrachloride (800 ml) contained in a reactor and mechanically agitated for 30 min. at room temperature. A solution of bromine (23 ml) in carbon tetrachloride (200 ml) was added dropwise over a period of 2 hours and agitated for further 12 hours. The resin was filtered, washed with CCl₄ followed by ether Soxhlet extraction and dried under vacuum for 24 hours. The obtained orange resin has:
%Br = 38.34 and %N = 3.10.

4) *Bromination of 2-acylfurans at 250C:*

A mixture of the ketone (40 moles), the obtained resin (25 g) and nitromethane as solvent (80 ml) was introduced into a reactor and mechanically agitated at normal temperature for the periods indicated in table 1. At the end of the reaction, the resin was filtered, washed with ether and dried for the reuse. The filtrate was subjected to evaporation in a rotary evaporator to remove the solvent and the product residue was distilled or recrystallized from petroleum ether.

RESULTS AND DISCUSSIONS

The preparation of anion-exchange resin A 162 in the perbromide form and its use for the monobromination of the selected 2-acylfurans was carried out according to the indicated steps in scheme 1.

The results shown in table 1 translate the remarkable reactivity of the resin via the synthesis of the monobromo-derivatives at normal temperature (250C) with the disappearance of byproducts especially the dibromo-derivatives. That was concluded from the gas chromatographic and NMR spectral data.

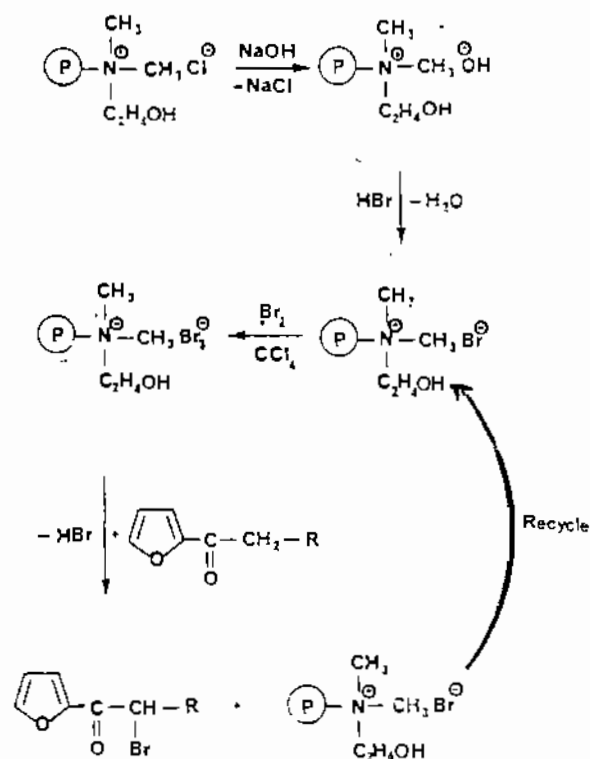
It is well known that furan ring is very sensitive to acidic species. In this case, it was noted that the liberated HBr did not affect the furan ring which could be attributed to the deactivation of furan ring by the attached carbonyl group or to the weak acidity of HBr in the organic solvent used. The separated resin after the end of the reaction could be reused for further runs which gives this process the economical property, for the synthesis in an industrial scale.

CONCLUSION

This study of the 2-acyl furans functionalization by the bromine fixed on an anion-exchange resin (A 162) has led to the production of the corresponding monobromo ketone in excellent conditions of yield and selectivity at normal temperature. The resin that remained without an appreciable change after the reaction could be reused for several times in further runs after being prepared again, in perpromide form.

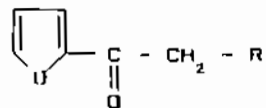
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SCHEME 1- BROMINATION OF 2- ACYLFURANS

Table 1: Bromination of 2-acylfurans :



No	R	Reaction time (hr)	Yield (%) (a)	m.p. (°C) or b.p. (°C/torr)	-CH- (b)	
					δ(ppm)	J(Hz)
1	H	3	84	104-105 /13	4.37	---
2	CH ₃	2.5	96	94-99 /14	5.18	6.4
3	C ₄ H ₉	2.5	95	137-139 /14	5.08	7.5
4	C ₁₄ H ₂₉	3	88	55.6	5.00	7.6
5	C ₆ H ₅	4	94	70.8	6.22	---
6	P.O.N.C ₆ H ₄	4	89	78.3	6.37	---

a) Calculated from the gas chromatography.

b) Proton Chemical displacement (ppm) and coupling constant (HZ) of -CH- group