

THE FRIEDEL CRAFT REACTIONS OF N-ALKENOIC ACIDS WITH BENZENE

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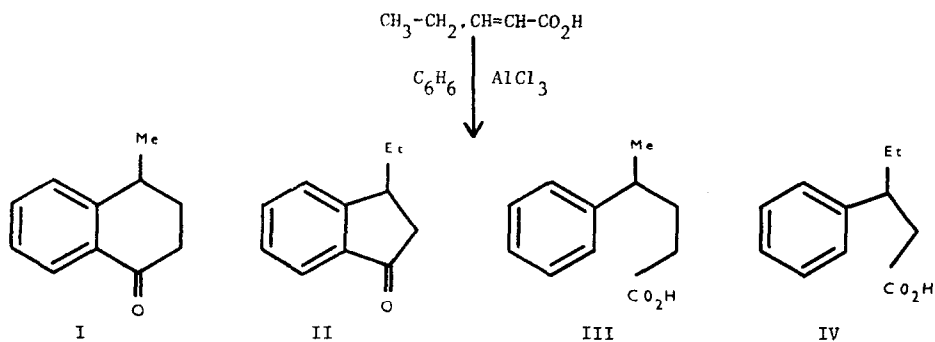
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Recent work on the Friedel Crafts reaction of ethyl pent-4-enoate and diethyl allylmalonate with anisole (1) and the reaction of the related  $\gamma$ -valerolactone with benzene (2) prompts us to record our results on the reactions between the three n-pentenoic acids and benzene in the presence of aluminium trichloride: In similar reactions Colonge and Grimaud (3) reported that phenylation of ethyl pent-4-enoate gave (eventually) 4-phenylpentanoic acid (S-benzylisothiuronium salt m.p. 161<sup>o</sup>) and Nenitzescu and Glatz (4a) reported that phenylation of pent-2-enoic gave only 4-phenylpentanoic acid (S-benzylisothiuronium salt m.p. 138<sup>o</sup>).

The results we have obtained from the reactions of each of the n-pentenoic acids with benzene in the presence of aluminium chloride under the conditions used by Nenitzescu and Glatz (4a) are tabulated below. The products from the pent-3- and the pent-4-enoic acid reactions were separated by extraction with alkali and shown to be homogeneous by g.l.c. Their structures were deduced from their n.m.r. and i.r. spectra. The neutral and acidic fractions from the pent-2-enoic acid reaction were isolated as above and then further resolved by preparative scale g.l.c. The compounds II and IV were identified by comparison with authentic specimens.



The melting points of the 2,4-dinitrophenylhydrazone derived from the ketones I and II agreed with those previously reported (5) and (6) respectively. In our hands the S-benzylisothiuronium salt derived from 4-phenylpentanoic acid has m.p. 147-148° which differs from both of the previously reported values (see above); the m.p. of the corresponding derivative of 3-phenylpentanoic acid is 158-159°.

Reaction of Pentenoic Acids with Benzene/ $\text{AlCl}_3$

Acid	Product					
	Neutral Product			Acidic Product		
	Yield	% Composition		Yield	% Composition	
		I	II		III	IV
Pent-2-enoic	34	76	24	13	79	21
Pent-3-enoic	35	100	0	43	100	0
Pent-4-enoic	41	100	0	19	100	0

Our results on the phenylation of pent-2-enoic acid contrast with those of Nenitzescu and Glatz. These workers assumed that their material was pure 4-phenylpentanoic acid and used it to prepare "authentic" 8-phenylnonanoic acid (8-phenylpelargonic acid), which was used to establish the fact that when treated with benzene in the presence of aluminium chloride "---- non-2-enoic acid yields only 8-phenylpelargonic acid ----" (4b). In view of our results this finding is questionable and our own preliminary investigation of the phenylation of non-2-enoic acid with benzene in the presence of aluminium chloride indicates that at least six phenylnonanoic acids and two cyclic ketones are obtained in this reaction.

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