Tetrahedron Letters No. 24, pp 2079 - 2082, 1976. Pergamon Press. Printed in Great Britain.

OXIDATIVE DECARBOXYLATION OF DIHYDROAROMATIC ACIDS WITH LEAD TETRAACETATE: A SYNTHESIS OF OLIVETOL DIMETHYL ETHER AND OF ROSEFURAN

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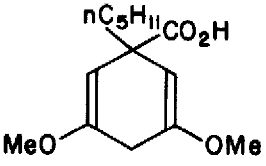
(Received in UK 12 April 1976; accepted for publication 3 May 1976)

1-Substituted 1,4-dihydrobenzoic acids are readily available by a two-stage[1] or a one-stage reduction-alkylation[2] process from benzoic acids. They have been briefly shown to be decarboxylated with lead tetraacetate to the substituted benzene in good yields.[1] Apart from one further example[3] the usefulness of the reaction in synthesis has been ignored.[4]

In connection with recent work[5] we have reinvestigated some synthetic aspects of the reaction using milder conditions than those previously used and illustrate it here with examples of the simple syntheses of some natural products as well as some useful synthetic intermediates.

Direct reaction[2] of the carbanion generated from Li-NH_3 reduction of 3,5-dimethoxybenzoic acid with 1-bromopentane gave (1) in almost quantitative yield,[6] identified by conversion into (2)[8] m.p. 174-177°. Reaction of crude (1) with a suspension of lead tetraacetate (1.2 equivalents) in a little benzene, in the presence of a catalytic proportion of cupric acetate[9] resulted in immediate evolution of carbon dioxide. After 5 minutes, the resulting crude olivetol dimethyl ether (3) (80%) was isolated and distilled. It was identified by comparison (i.r., g.l.c.) with an authentic specimen kindly provided by Dr. J.R. Cannon.

Since this ether is readily demethylated to the phenol,[10] the method constitutes a short and potentially versatile synthesis of 5-alkylresorcinols, probably superior to existing ones.[10] The route constitutes (potentially) a general procedure for introducing a variety of groups *meta-* to OMe in a benzene ring.



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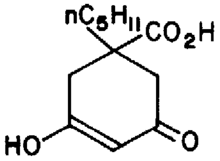

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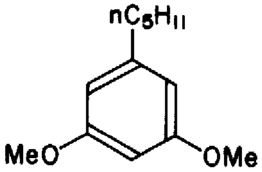

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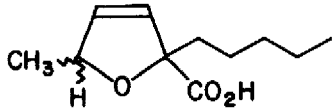

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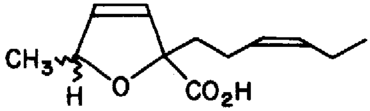

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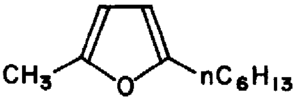

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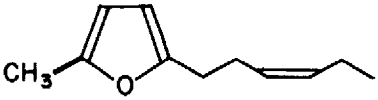

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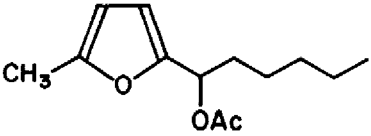

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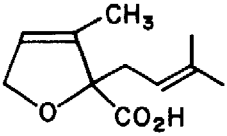

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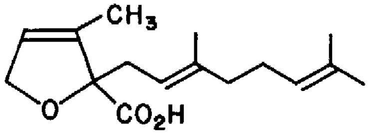

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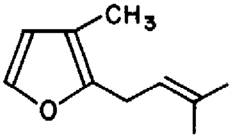

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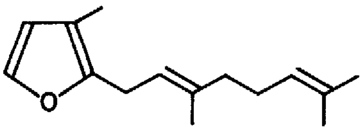

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Reduction and alkylation[5] of 5-methyl-2-furoic acid in NH_3 at -78° using 1-bromohexane or 1-bromo-*cis*-3-hexene[11] gave the acids (4) or (5) as mixtures of stereoisomers (85% and 65% yields respectively). Oxidative decarboxylation, as above but at 35°, gave (6) or (7) in about 80% yields. The usefulness of these compounds in the synthesis of dihydrojasmone or *cis*-jasmone has been demonstrated.[12] The identity of the products was confirmed for (6) by comparison (i.r., p.m.r., g.l.c.) with an authentic specimen,[13] and for (7) by published[11] spectral data. A minor product is probably (8), which becomes a major one under the original[1] oxidation conditions in acetic acid. Its formation is not unexpected.[14]

3-Methyl-2-furoic acid[15] was similarly alkylated using either 1-bromo-3-methyl-2-butene or geranyl bromide to give (9)(75% yield, cyclohexylamine salt, m.p. 161-164°) or (10)(60% yield, cyclohexylamine salt, m.p. 140-146°). Oxidation at 35° gave the rather unstable compounds, rosefuran (11, 70% crude yield) or the sesquirosefuran (12, 65%). These were identified by comparisons of the NMR spectra of purified specimens with those published.[16,17] Their previous syntheses[16,18] use the same starting-materials but the sequence is less simple and efficient. The reductive-alkylation oxidative-decarboxylation procedure constitutes a general method for the position-specific alkylation of furans[19,20] which should be especially useful in the synthesis of 2,3- or 2,4-dialkyl substituted furans.[16,21]

Other applications are being examined.

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