

Short Communications

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ELECTROLYSIS OF UNDEC-10-ENOIC ACID

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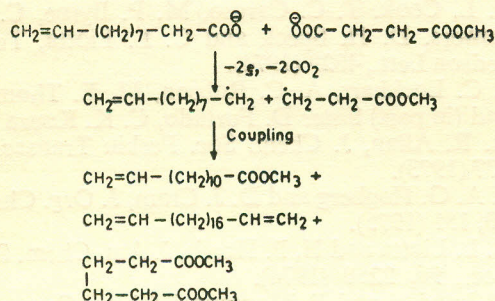
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It has been shown by Scott¹ that in the electrolysis of ω -unsaturated acids if the electrolyte is allowed to become alkaline, migration of the double bond to penultimate position gives rise to a mixture of dienes.

In the present work two carbon-chain extensions on undec-10-enoic acid to give tridec-12-enoic acid (51.8%) has been successfully employed, by using neutral conditions during the electrolysis. This indicates that normal Kolbe coupling of ω -unsaturated acids can be achieved, if the conditions are kept neutral during the electrolysis.

Undec-10-enoic acid was electrolysed, in a cell based on the design by Dinh-Nguyen² consisting of a circular platinum anode and a mercury cathode which maintains the electrolyte neutral during the electrolysis, in the presence of methyl hydrogen succinate.



The electrolysis product was separated into an acidic and a neutral fraction. The neutral fraction which was probably eicosa-1,19-diene, was not examined further.

The acidic fraction was extracted with petroleum ether (b.p. 60-80°). The petroleum insoluble portion gave adipic acid. The petroleum soluble portion was esterified by the action of diazomethane. This on GLC analysis (20 Carbowax, M20, 200°) showed one peak (99.5% of total curve). Purification by preparative scale GLC (20% Carbowax, M20, 200°) gave methyl tridecenoate. The IR spectrum of the purified liquid had absorption at 915 and 99.5 cm^{-1} ($-\text{CH}=\text{CH}_2$), 1640 cm^{-1} ($-\text{C}=\text{C}$) and 1740 cm^{-1} ($\text{C}=\text{O}$, ester). NMR (CCl_4): τ 4.9-5.2 (3H, m, $\text{CH}_2-\text{CH}-$), 6.40 (3H, s, $-\text{OOCCH}_3$) and 7.8 8.8 (20 H, complex, $-(\text{CH}_2)_{10}-$). A portion of the purified ester on hydrolysis gave tridec-12-enoic acid, m.p. 37-38° (lit.³ m.p. 38-39°). The yield of

tridec-12-enoic acid from the above electrolysis was 51.8% of theory.

Acknowledgement. The above work was carried out at the Department of Chemistry, Queen Mary College, University of London. The facilities extended by Professor B. C. L. Weedon in this respect are gratefully acknowledged.

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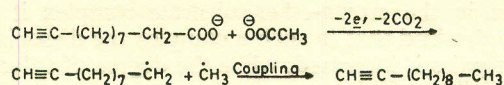
CROSS-KOLBE COUPLING REACTION WITH UNDEC-10-YNOIC ACID

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Further to our report¹ on the electrolysis of undec-10-enoic acid we wish to report that Cross-Kolbe coupling reaction can be successfully applied to terminal acetylenic carboxylic acids under neutral conditions.



Undec-10-ynoic acid (supplied by the courtesy of Professor Sir Ewart Jones of Oxford University, U.K.) in the presence of sodium acetate (1:10 molar ratio) was electrolysed in a cell based on the design by Dinh-Nguyen.² The electrolysis product was purified by preparative scale GLC (20% Ucon polar, 150°, aerograph model A-90-P3). The IR spectrum of the purified liquid showed a very strong absorption at 2100 cm^{-1} ($-\text{C}\equiv\text{C}-\text{H}$). NMR (CCl_4): τ 7.7-8.0 m. 2 H, m, $\text{HC}\equiv\text{C}-\text{CH}_2-$, 8.28 (1H, t, J 2 c/s, $\text{HC}\equiv\text{C}-\text{CH}_2-$), 8.35 8.95 (14H, methylene envelope and 8.95 9.35 (3H, complex, $-\text{CH}_2-\text{CH}_3$). These spectral data confirmed the structure of the product as undec-1-yne. The yield of undec-1-yne from the above experiment was shown to be 36% of the theory by absolute GLC analysis.

The low yield of the coupled product is presumably due to the attack of the terminal triple bond by acetoxy or methyl radicals formed during electrolysis.

Acknowledgement. The above work was carried out at the Department of Chemistry, Queen Mary College, University of London. The facilities extended by Professor B. C. L. Weedon in this respect are gratefully acknowledged.

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NITRATION AND THEORETICAL TREATMENT OF AROMATIC REACTIVITY

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The difficulties facing the MO theoretical treatment of aromatic reactivity which arises from the occurrence of a limiting rate in nitration have been discussed by Moodie and his coworkers.¹⁻² Recently, Clark and Fairweather³ correlated the cation localisation energies with the logarithms of the partial rate factors for the nitration of toluene and xylenes in acetic acid and obtained a linear relationship. However, their method of calculation of a theoretical model may be questioned by noting that in their treatment no assumption have been made to account for the additivity in the effects of the substituent.

The present authors replotted the logarithms of partial rate factors for nitration of different aromatic hydrocarbons in 12.5 - 15 mole.-1 aqueous nitric acid against the relative cation localisation energies and obtained a smooth curve. The same correlation for the other electrophilic substitutions such as chlorination gave a linear plot. This could be explained by the nature of halogenation which, in contrast to nitration are additive to a high degree.

The nonlinearity between the partial rate factors for nitration and localisation energies may be attributed to the nonlinear relationship Fig. 1 between the change in potential energy of the transition state for substitution at a particular position and the change in potential energy of the corresponding Wheland intermediate (Table 1). This indicates that with continued substitution the transition state for nitration gradually comes to resemble the reactant rather than the intermediate.

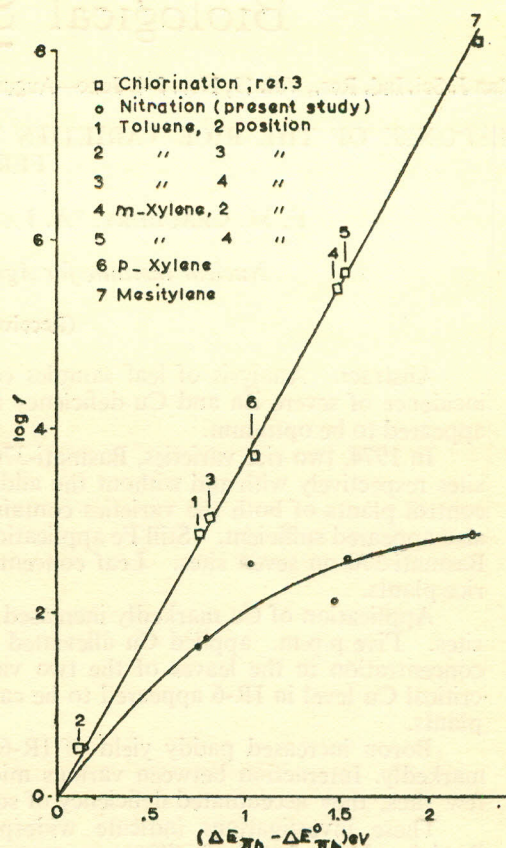


Fig. 1. The relation between partial rate factor and localization energies.

TABLE 1. PARTIAL RATE FACTORS AND CATION LOCALIZATION ENERGIES OF METHYL-SUBSTITUTED BENZENES.

| Compound | Position | Cation localization energy* | Partial rate factor |
|----------------------|----------|-----------------------------|---------------------|
| Benzene | — | 0.0 | 1 |
| Toluene | 2 | -0.783 | 41.8 |
| | 3 | -0.119 | 3.6 |
| | 4 | -0.815 | 52.9 |
| <i>m</i> -Xylene | 2 | -1.502 | 138.8 |
| | 4 | -1.556 | 425.7 |
| | 5 | -0.236 | — |
| <i>p</i> -Xylene | — | -1.028 | 300.0 |
| Mesitylene Ref. 3 | — | -2.233 | 760.0 |

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