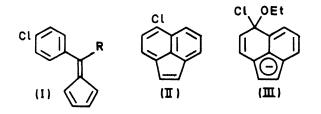
Nucleophilic Displacement of Chlorine from 5-Chloroacenaphthylene

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Summary 5-Chloroacenaphthylene is converted into 5ethoxyacenaphthylene by reaction with sodium ethoxide.

THE possibility that substituents in a benzene ring might be activated towards nucleophilic displacement by potential cyclopentadienide stabilisation does not appear to have



received attention. For example, it might be expected that the halogen atom in a 6-(p-chlorophenyl) fulvene (I) or in 5-chloroacenaphthylene (II) would be replaceable by a nucleophile under suitable experimental conditions.

It is now reported that compound (II) reacts slowly with sodium ethoxide in refluxing ethanol to give 5-ethoxyacenaphthylene as the major product (ca. 60%).† Minor products have not been identified. Under comparable reaction conditions α -chloronaphthalene gives no trace (<< 1%) of α -ethoxynaphthalene.

5-Ethoxyacenaphthylene, isolated as a yellow oil, was identified by n.m.r. and mass spectrometry. The mass spectrum showed the parent ion at m/e 196.0890 (calc. for $C_{14}H_{12}O^+$, m/e 196.0888). The location of the ethoxy-group was uniquely defined as C-5 by the presence of a high-field doublet at τ 3.42 (J 7.5 Hz) due to the proton on C-4, and of a low-field doublet of doublets (X part of ABX pattern) at τ 2.03 due to the hindered peri-proton on C-6.

The hypothesis of activation by potential cyclopentadienide stabilisation suggests the indenyl anion (III) as an intermediate in this substitution reaction.

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† 5-Chloroacenaphthylene, m.p. 68°,¹ was prepared by DDQ oxidation of 5-chloroacenaphthene.

¹G. P. Petrenko and E. N. Tellnyuk, J. Org. Chem. (U.S.S.R.), 1967, 3, 174.