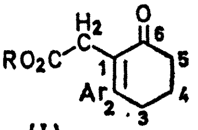
# Novel Aromatisation Reaction of Cyclohexenone Derivatives with Sodium Hydride and Dimethylformamide

By D. NASIPURI,* AMITAVA BHATTACHARYYA, and B. G. HAZRA

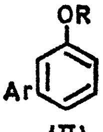
(*Department of Chemistry, Indian Institute of Technology, Kharagpur-2, India*)

*Summary* 2-Aryl-6-oxocyclohex-1-enylacetic esters are found to undergo dehydrogenation to phenols with concomitant loss of acetate side chain on exposure to sodium hydride and dimethylformamide at 100°.

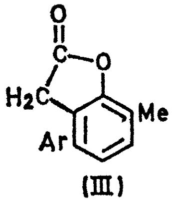
SODIUM hydride in dimethylformamide (DMF) has been widely used for generation of carbanions from active methylene compounds prior to their alkylation.[1] The system possesses certain advantages over other metal–solvent combinations[2] and no abnormal side-reaction has yet been reported. We wanted to use the method for the introduction of angular methyl at C(1) in some cyclohexenone derivatives [*e.g.*, (I; Ar = $\beta$-naphthyl)],[3,4] to obtain products easily convertible into hydroaromatic steroids.[5] The feasibility of such reaction depends on the initial formation of a carbanionic centre at C(3) and is already well precedented.[6] However, treatment of the ester or the acid (I; R = **Me or** H, Ar = $\beta$-naphthyl) with NaH–DMF–MeI under **the usual** conditions[2] afforded a phenolic ether (>70%), m.p. 90°, identified as 3$\beta$-naphthylanisole (II; R = Me, Ar = $\beta$-naphthyl). Subsequently, it was found that the esters (I; R = Me, Ar = Ph, *p*-MeOC$_6$H$_4$, and $\alpha$-C$_{10}$H$_7$) on treatment with NaH (3 mol) in DMF evolved hydrogen (1 mol) at room temperature and on heating at 100° for 30—40 min afforded 3-arylphenols (II; R = H, Ar = Ph, *p*-MeOC$_6$H$_4$, and $\alpha$-C$_{10}$H$_7$) as major products. Apparently, sodium hydride abstracted a proton from C(5) instead of C(3), the resulting enolate ion (IV) being stabilised by extended conjugation with the aromatic ring. The rest of the process may be envisaged as the Scheme.



(I)

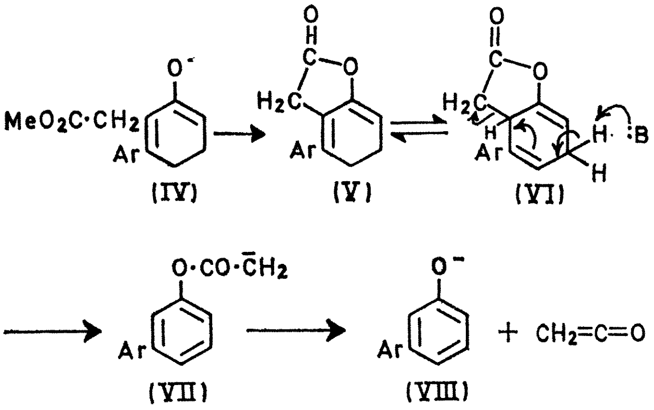


(II)



(III)

The following points may be noted in connection with this mechanism (Ar = $\beta$-naphthyly throughout). (i) The NaH–DMF–MeI treatment of the acid (I; R = H) afforded, in addition to the ether (II), minor products two of which were identified, one as the dimethylated acid [(I; R = H), Me$_2$ at C(5)], m.p. 212° (*ca.* 8%) and the other as the lactone (III), m.p. 135—138° (*ca.* 5%). The structure of the former was confirmed by spectral data (i.r. and n.m.r.)† and that of the latter by synthesis.[7] This proves that the anion formation did occur at C(5). (ii) The lactone (V) was actually isolated, although in trace amount, and its structure established by spectral data. (iii) Replacement of acetate by propionate side chain completely stopped the formation of the phenol. Apparently, a good leaving group like acetate is essential for the transformation. The acid (I; R = H) on similar treatment with sodium hydride in dimethylformamide yielded the phenol (II; R = H), m.p. 115° in poor yield (*ca.* 25%), but 3$\beta$-naphthylcyclohex-2-enone did not react at all. (iv) The isomerisation of the lactones (V) to (VI) may be attributable to a conformational factor, the $\gamma$-lactone ring in the former being considerably strained by two exocyclic double bonds. (v) No trace of the acetate (II; R = Ac) corresponding to the anion (VII) could be detected on t.l.c. of the product. The anion (VII) thus seems to be a transient intermediate probably losing the acetate moiety as ketene. We found that $\beta$-naphthylacetate under identical condition was quantitatively cleaved into $\beta$-naphthol.



SCHEME

Decomposition of DMF in presence of NaH is well-known[8]

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† Satisfactory elemental analyses and n.m.r. spectra have been obtained for all compounds described in this communication. N.m.r. spectra were taken by Dr. D. N. Roy, Shade Tree Research Laboratory, University of Toronto.

and occurs usually with the formation of sodiodimethylamine, carbon monoxide, and hydrogen. We observed, however, that when a suspension of sodium hydride in DMF was heated at 100° for 1 h, no appreciable gas evolution took place even after addition of water. On distillation of the acidified mixture, formaldehyde was found in the distillate. It appears therefore that under the present conditions, the decomposition took place according to equation (1). The

$$\mathrm{Me_2N{\cdot}CHO + NaH \rightarrow}$$
$$\mathrm{Me_2N{\cdot}CH_2O^-Na^+ \rightleftharpoons Me_2N^-Na^+ + CH_2O} \qquad (1)$$

effective base in the above transformation may thus be sodiomethylamine which is similar to *N*-lithioethylenediamine, a reagent often used for aromatisation of hydroaromatic rings.[9] We are currently investigating the use of other metal–solvent systems for angular methylation of the compounds (I).

The authors thank Dr. U. R. Ghatak of the Indian Association for Cultivation of Science, Calcutta, for helpful discussion, and C.S.I.R., New Delhi, for a grant.

(*Received, March* 25th, 1971; *Com.* 402.)

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