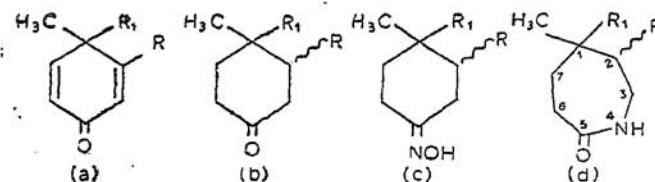


ϵ -CAPROLACTAMS FROM 4-ALKYL-,
4-DIHalo- AND 4-TRIHALO- ALKYL-2,
5-CYCLOHEXADIENONES

IN our earlier publications¹ we have reported some of the interesting reactions of 4-alkyl-, 4-dihalo- and 4-trihalo-alkyl-2, 5-cyclohexadienones. We report here the preparation of three caprolactam derivatives from these dienones. The latter were prepared from *p*-alkyl phenols by reaction with chloroform or carbon tetrachloride as described in literature and were catalytically reduced in alcohol solution with 5% Pd/charcoal to yield the corresponding cyclohexanone derivatives. The oximes of the latter, prepared as usual, when subjected to a Beckmann rearrangement in the presence of conc. sulphuric acid or PCl_5 afforded the lactams as colourless crystalline solids from benzene-pet. ether in yields ranging from 30–50% as in the case of III *d*. The rearrangement of the oxime II *c* takes place only with PCl_5 . Sulphuric acid however gives a tarry mass.



I. $\text{R} = \text{H}$, $\text{R}_1 = \text{CHCl}_2$:

(a) m.p. 54°2^a ;	(b) m.p. 47°2^b
(c) m.p. $132\text{--}34^{\circ}$;	(d) m.p. $152\text{--}54^{\circ}$.

II. $\text{R} = \text{H}$, $\text{R}_1 = \text{CCl}_3$:

(a) m.p. 104°3^a ;	(b) m.p. 116°3^b ;
(c) m.p. $170\text{--}71^{\circ}$;	(d) m.p. $160\text{--}61^{\circ}$.

III. $\text{R} = \text{CH}_3$; $\text{R}_1 = \text{CHCl}_2$:

(a) m.p. 102°2^a ;	(b) m.p. 87° ;
(c) m.p. 157° ;	(d) m.p. $172\text{--}74^{\circ}$.

In the case of the oximes there is the possibility of syn- and anti-isomers being formed but in all cases only one product could be isolated. Similarly, in the case of compounds III *b*–III *d*, the possibility of *cis-trans* isomers also exists but here again only one compound could be obtained. From the spectral data collected by us it is not possible to assign any definite configuration to the methyl group in these compounds.

The i.r. spectrum (KBr) of a typical caprolactam (I *d*) showed bands at 3200 , 1660 and 1300 cm^{-1} corresponding to an amide (secondary) grouping.

The n.m.r. spectrum (CDCl_3) of III *d* showed the methyl protons at C_1 as a singlet at $1\text{.3 } \delta$ while a doublet around $0\text{.9}\text{--}1\text{.1 } \delta$ for three protons was assigned to the methyl protons at $\text{C}_{2\alpha}$. The complex multiplet at $1\text{.5}\text{--}3\text{.9 } \delta$ for seven protons corresponded to the six methylene and one methine proton at $\text{C}_{2\beta}$. The singlet for one proton at $5\text{.65 } \delta$ was

attributed to the proton of the dichloromethyl group at C_1 . The NH proton was obtained as a broad singlet at 7.12δ .

All the compounds gave satisfactory analysis for C, H and N.

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