to the strains caused by quenching, as the quenched foils did not behave differently from the furnace-cooled ones. As every foil was first immersed in 2 N H_2SO_4 for 3 to 4 min. (until it regained its shine) before it was used as a catalyst, the probability that the oxide film on its surface might be responsible for the increase in activity, is small. Incidentally it is worth noting that silver catalyst, too, exhibited similar increase in activity[3] when hydrogen peroxide decomposition and ethanol oxidation (and not formic acid dehydrogenation) were the probe reactions. This observation may be of significance to the understanding of the mechanism of metal catalysed reactions.

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ELECTRONIC SPECTRAL AND THERMAL STUDIES OF Ce(III), Pr(III) AND Nd(III) PICRAMATES

SOME inner transition metal picramates, *viz.*, lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, dysprosium and holmium picramates, were prepared recently by us and their stoichiometry established by elemental analysis, amperometric, conductometric and potentiometric studies[1,2]. We also suggested $-H_2N \rightarrow Ln$ coordination (Ln — rare earth ion) in metal picramates on the basis of i.r. spectral studies. The present communication reports the electronic spectral and thermal studies of cerium, praseodymium and neodymium picramates. The nature of the complexes has also been studied by measurements of electrical conductance.

The conductance and electronic spectra of the complexes were made as reported in the earlier communication[3].

The low molar conductivity of the complexes in dimethylformamide showed that these complexes are non-electrolytes. The spectral data of praseodymium and neodymium picramates in ethanol are summarised in Table I, and for comparison, data for aqueous salt solutions are also given.

The spectral behaviour of lanthanides is fundamentally different from that of d-block elements. The basic reasons for the differences lies in the fact that the electrons responsible for magnetic spectral properties of lanthanide ions of $4f$ electron and $4f$ orbitals are effectively shielded from interaction with external forces by the overlapping of $5s^2$ and $5p^6$ shells. The bands may be assigned to the transitions in which an f electron is excited to an outer d, s or p orbital[4] and the spectra have been assigned to $4f$-$5d$ transitions[5]. The electronic spectra of the cerium picramate show five bands appearing at 21735 (vw), 23250 (vw), 31755, 44455 and 47660 cm^{-1}. The first three bands may be due to Laporte-allowed $4f \rightarrow 5d$ transitions.

It is evident from Table I that the shifts in the spectra of praseodymium and neodymium picramates are towards lower wave numbers relative to the aquo ions. There are small differences in frequencies or molar absorption except that the hypersensitivity transition $^4I_{9/2} - {}^4G_{5/2}$ in the neodymium picramate which increases in intensity from $\epsilon = 6.25$ in the salt to $\epsilon = 17.50$ in the com-

TABLE I

Electronic spectra of praseodymium and neodymium nitrate and their corresponding complexes

	Transition	Ln$(NO_3)_3$ in water (cm^{-1})	ϵ salt	[Ln (C_6H_2) $(NO_2)_3$ $(NH_2O)_3 \cdot 2H_2O]$ in ethanol (cm^{-1})	ϵ complex	$\dfrac{\epsilon \text{ complex}}{\epsilon \text{ salt}}$
Pr	$^3H_4 \rightarrow {}^1D_2$	17,000	1·90	16,860 (0·0083)*	2·60	1·36
	$\rightarrow {}^3P_0$	20,750	3·00	20,700 (0·0024)*	3·55	1·18
	$\rightarrow {}^3P_1$	21,320	4·20	21,140 (0·0085)*	11·76	2·80
	$\rightarrow {}^3P_2$	22,470	9·95	22,430 (0·0017)*	10·89	2·09
Nd	$^4I_9 \rightarrow {}^4F_{5/2}, {}^2H_{9/2}$	12,500	6·42	12,450 (0·0040)*	11·90	1·85
	$\rightarrow {}^4F_{7/2}, {}^4S_{3/2}$	13,400	5·85	13,310 (0·0067)*	9·20	1·57
	$\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	17,300	6·25	17,150 (0·0087)*	17·50	2·80
	$\rightarrow {}^4G_{7/2}$	19,000	3·36	18,910 (0·0047)*	6·26	1·86
	$\rightarrow {}^4G_{9/2}$	19,500	1·65	19,400 (0·0051)*	3·66	2·21

* Values in parentheses show the nephelauxetic effect $(1-\beta)$.

plex. Thus it is clear that $4f$ orbitals do not participate much in bonding; if they did, vibronic coupling would lead to marked changes in intensity, position, and sharpness of the f-f transitions. Four bands have been observed in the electronic spectra of praseodymium picramate which are due to transition from the ground level $^3H_4$ to the excited J levels of $4f^2$ configuration respectively. The red shift or nephelauxetic effect which is regarded as a measure of the covalency of the coordination bond was calculated for the rare earth complexes by Jørgensen *et al.*[5-7], using the relation

$$1-\beta = (\bar{\nu} \text{ aquo} - \bar{\nu} \text{ complex})/\bar{\nu} \text{ aquo}$$

(where $\bar{\nu}$ is the wave number of absorption band of rare earth ion) and assuming that each J level of a $4f^n$ configuration is linearly dependent on the radial integrals. On the basis of this assumption, $\Delta\bar{\nu}/\bar{\nu}$ aquo of all bands of the same rare earth complex should be similar. However, our earlier observations[3] as well as the present results (Table I) indicate that the $\Delta \bar{\nu}/\bar{\nu}$ aquo values for different J levels of a rare earth complex differ from each other considerably.

Thermal Study.—Thermorgravimetric analysis of the samples was done by the method described by Agrawal *et al.*[8]. In the case of Ce picramate one water molecule is lost around 90° C and the second water molecule around 128° C. On the other hand, in the case of Pr and Nd picramates both the water molecules are lost around 130° C. Ce, Pr and Nd picramates decompose into the stable oxides (Ln_2O_3) at 450°, 650° and 700° C respectively; the increase in the thermal stability is perhaps due to a decrease in the O–Ln bond on account of lanthanide contraction.

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

IN our earlier publications[1] 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.

(a)   (b)   (c)   (d)
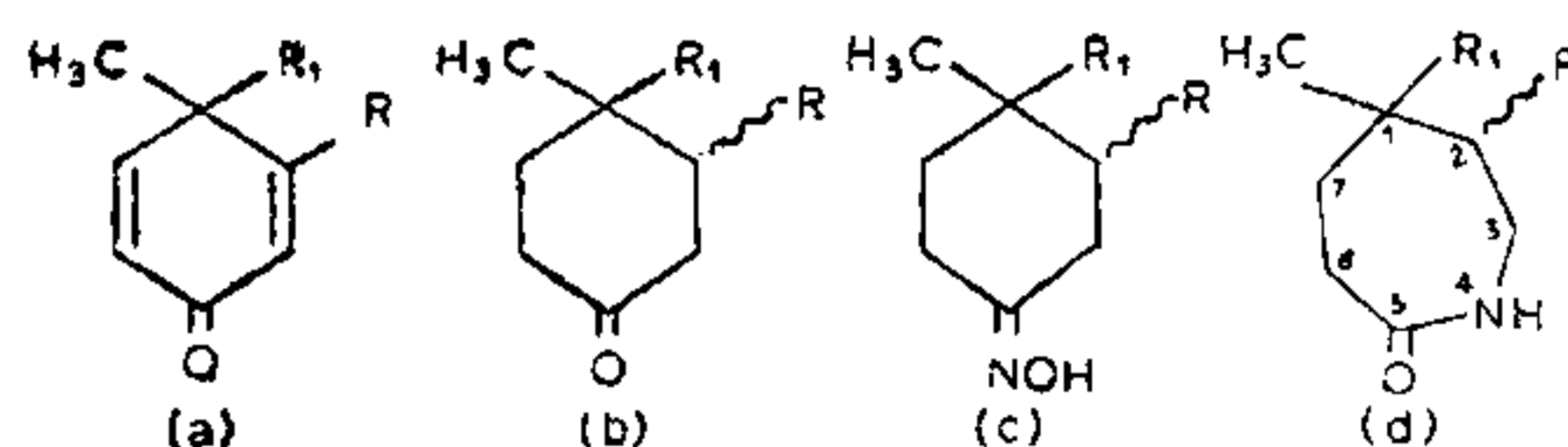
I. R = H, R_1 = $CHCl_2$:
   (*a*) m.p. 54°[2a] ;   (*b*) m.p. 47°[2b]
   (*c*) m.p. 132–34° :   (*d*) m.p. 152–54°.
II. R = H, R_1 = CCl_3 :
   (*a*) m.p. 104°[3a] ;   (*b*) m.p. 116°[3b] ;
   (*c*) m.p. 170–71° ;   (*d*) m.p. 160–61 .
III. R = CH_3 ; R_1 = $CHCl_2$:
   (*a*) m.p. 102°[2a] ;   (*b*) m.p. 87° ;
   (*c*) m.p. 157° ;   (*d*) m.p. 172–74 .

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 1·3 δ while a doublet around 0·9–1·1 δ for three protons was assigned to the methyl protons at C_5. The complex multiplet at 1·5–3·9 δ for seven protons corresponded to the six methylene and one methine proton at C_5. The singlet for one proton at 5·65 δ was