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* Krishnamurti *et al.*² had reported the m.p. 144–46°. However this flavone, when made by their method, was found to have m.p. 178–79°.

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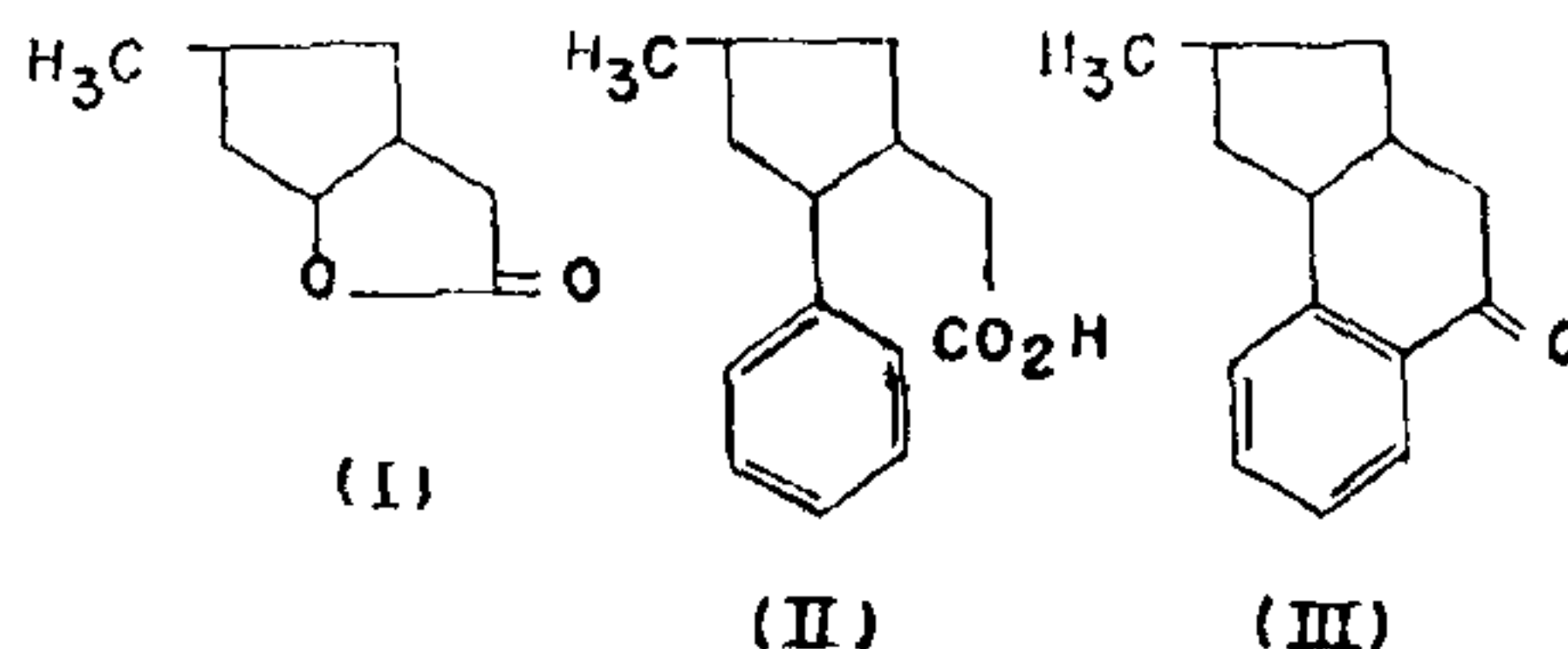
FRIEDEL-CRAFTS ALKYLATION OF AROMATIC HYDROCARBONS WITH SUBSTITUTED ALICYCLIC LACTONES

THE aluminium chloride-catalysed condensation of aromatic hydrocarbons with simple substituted alicyclic lactones like the lactone of 4-methyl-2-hydroxycyclohexaneacetic acid was found by Chatterjee and Bhattacharya¹ to afford a mixture of secondary alkylates consisting of 2-aryl and 3-aryl-4-methylcyclohexaneacetic acid to the exclusion of the tertiary alkylate, e.g., the 4-aryl isomer. The facile rearrangement in the cyclopentane system has also been observed by Chatterjee and coworkers² who studied the catalysed alkylation of aromatic hydrocarbons with the lactone of cyclopentanol-2-acetic acid. We now report the synthesis of lactone of 4-methyl-2-hydroxycyclopentaneacetic acid (I) and the Lewis acid catalysed alkylation of aromatics with it.

The lactone (I) was prepared from β -methyl adipic acid, m.p. 93° obtained from 4-methylcyclohexanol by oxidation with 50% nitric acid in the presence of V_2O_5 . The diethyl ester, b.p. 130–32°/14 mm, on Dieckmann cyclisation furnished 4-methyl-2-carbethoxycyclopentanone, b.p. 90–92°/1 mm., which on alkylation by ethyl chloroacetate in the presence of sodium ethoxide afforded ethyl 4-methyl-2-carbethoxy-2-acetate, b.p. 132–35°/0.5 mm. This on hydrolysis by 1:1 HCl yielded 4-methylcyclopentane-2-one-1-acetic acid, b.p. 155–60°/2 mm., semicarbazone, m.p. 210°, which on $NaBH_4$ reduction gave a stereoisomeric mixture of the desired lactone (I), b.p. 95–100°/1 mm, n_D^{20} 1.4650, containing a major amount of the trans variety³.

The Friedel-Crafts condensation of the lactone (I) with benzene in the presence of $AlCl_3$ gave as expected a secondary alkylate consisting of a stereoisomeric mixture of 4-methyl-2-phenylcyclopentane-

acetic acid (II), b.p. 155–57°/0.6 mm as the exclusive product, isolated through the ethyl ester, b.p. 140–41°/0.6 mm in 78% yield together with a small amount of 3-methylcyclopentaneacetic acid formed by hydride transfer and consequent reduction of the



lactone (I). The acid (II) on PPA cyclisation afforded 2-methyl-6-keto-6,7,8,9-tetrahydro-4,5-benzindane (III), b.p. 137–38°/1 mm. semicarbazone m.p. 206°. DNP derivative m.p. 209° as a stereoisomeric mixture. The structure of the ketone was confirmed by its reduction and dehydrogenation to 2-methyl-4,5-benzindane, picrate m.p. 91° TNB complex m.p. 103° as well as by its unequivocal synthesis starting from ethyl 4-methylcyclopentane-2-one-1-acetate and phenyl lithium followed by Paar reduction of the resulting lactone and cyclisation.

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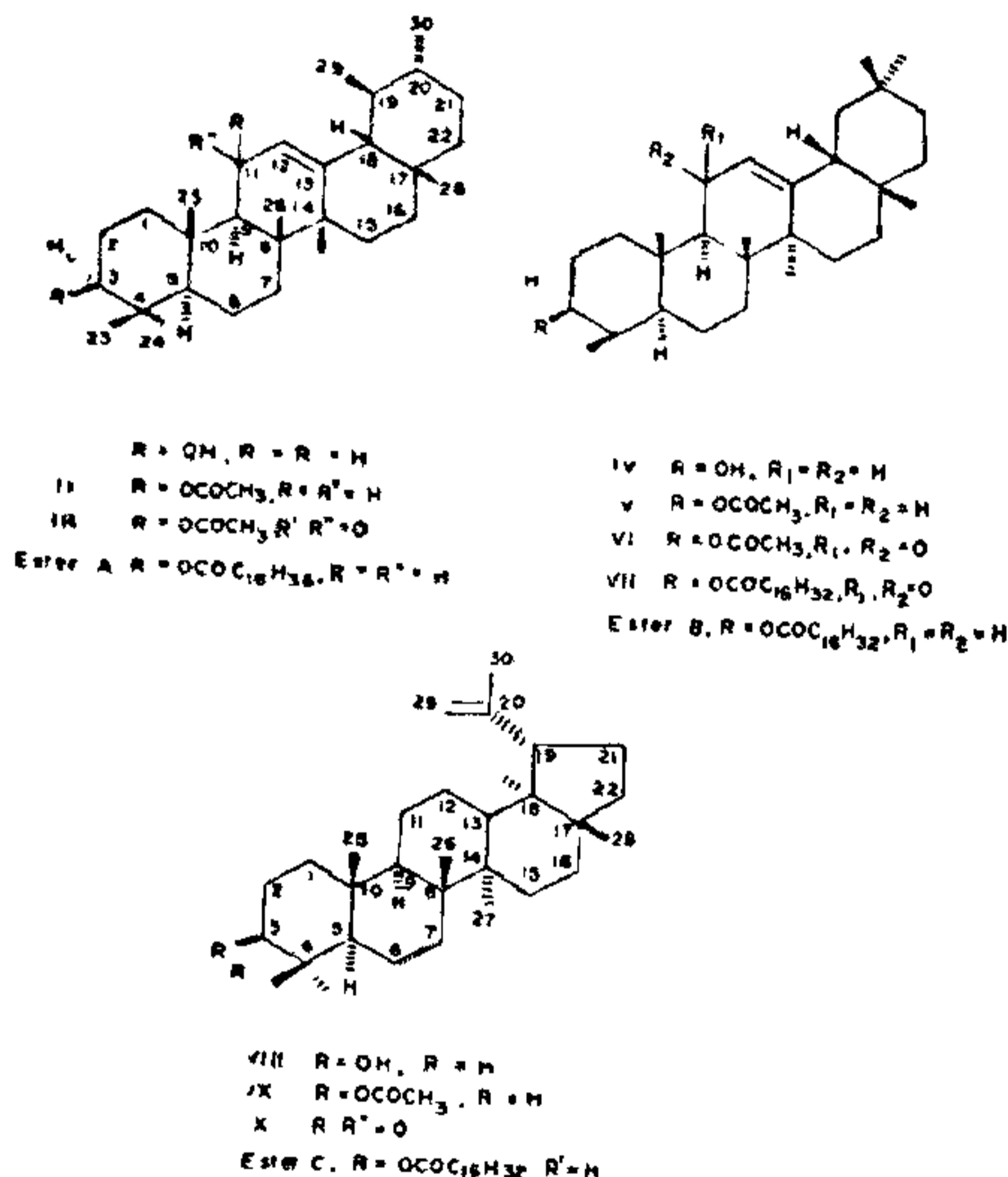
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ISOLATION OF α -AMYRIN STEARATE, β -AMYRIN AND LUPEOL PALMITATES FROM THE COSTUS LEAVES

THE isolation of taraxasterol and its acetate from the hexane extract of the leaves (and stalks) of the costus plant, *Saussurea Lappa* Clarke, has been reported.¹ By chromatography of the hexane extract over alumina and silver nitrate impregnated silicic acid, followed by crystallisation of some of the fractions, three low melting esters A, B, C have been isolated in the pure state. These have been identified as α -amyrin stearate, β -amyrin palmitate and lupeol palmitate respectively, by chemical reactions and comparison of physical constants and spectral data with those reported in literature.^{2,3,4} Ester A, $C_{38}H_{64}O_4$ m.p. 46–48° (EtOH + Me_2CO ; 1:4) (α)_D + 61° (benzene, c, 1.84). On saponification, yields stearic acid, $C_{18}H_{36}O_2$, M^r 284, m.p. 69° (EtOH) and α -amyrin (D), $C_{30}H_{50}O$, M^r 426, m.p. 181–183° (hexane + 10%

benzene), $(\alpha)_D + 83$ (CHCl_3 , c, 1). The latter is converted for characterisation into the acetate (II)¹, $\text{C}_{33}\text{H}_{54}\text{O}_2$, m.p. 218–220 (EtAc), $(\alpha)_D + 81$ (CHCl_3 , c, 1) and also to 11-keto acetate¹ (III), $\text{C}_{32}\text{H}_{50}\text{O}_3$, m.p. 274°–276° (EtAc), $(\alpha)_D + 97$ (CHCl_3 , c, 0.6) by sodiumdichromate¹ and acetic acid oxidation of (II).

Ester B, $\text{C}_{44}\text{H}_{80}\text{O}_2$, M⁺ 664 m.p. 76–78 ($\text{Me}_2\text{CO} - 10\%$ hexane), $(\alpha)_D + 57$ (benzene, c, 2.8) gives on saponification palmitic acid $\text{C}_{16}\text{H}_{32}\text{O}_2$, M⁺ 256, m.p. 62 (EtOH) and β -amyirin (IV) $\text{C}_{30}\text{H}_{50}\text{O}$, M⁺ 426, m.p. 193–194 (hexane + 10% benzene), $(\alpha)_D + 91$ (benzene; c, 2). The latter is converted for characterisation into the acetate (V), $\text{C}_{32}\text{H}_{52}\text{O}_2$, m.p. 236–238° (EtAc), $(\alpha)_D + 82$ (CHCl_3 , c, 1.5) and also to 11-keto acetate (VI), $\text{C}_{32}\text{H}_{50}\text{O}_3$, m.p. 264° (EtAc), $(\alpha)_D + 110$ (CHCl_3 , c, 0.9) by oxidation of (V) with sodium dichromate and acetic acid².



Oxidation of ester B with sodiumdichromate and acetic acid furnishes the 11-keto β -amyirin palmitate (VII), $\text{C}_{46}\text{H}_{78}\text{O}_3$, M⁺ 678, m.p. 148° (EtAc). It shows IR bands at 1736 ($>\text{C}=\text{O}$ of ester), 1660 ($>\text{C}=\text{O}$ conj. ketone) and 1613 cm^{-1} ($>\text{C}=\text{C}<$ conj); $\text{UV}\lambda_{\text{max}}$ $248\text{ m}\mu$, ϵ_{max} 12,500; NMR (CCl_4) signals at τ : 7.75 (1H, C_9 -proton adjacent to $\text{C}=\text{O}$ group); 5.53 (C_3 -proton) and at 4.5 (1H, olefinic proton at C_{12}).

Ester C, $\text{C}_{46}\text{H}_{80}\text{O}_2$, m.p. 77–78° (Me_2CO), $(\alpha)_D + 26$ ° (benzene, c, 2.8), on saponification gives palmitic acid and lupeol (VIII), $\text{C}_{30}\text{H}_{50}\text{O}$, M⁺ 426, m.p. 214–216° ($\text{MeOH} + \text{Me}_2\text{CO}$; 2:1), $(\alpha)_D + 28$ ° (CHCl_3 , c, 2.5). The latter is converted for characterisation into the acetate (IX) $\text{C}_{32}\text{H}_{52}\text{O}_2$, m.p. 215–217° (EtAc), $(\alpha)_D + 43$ ° (CHCl_3 , c, 1.2) and also to lupenone (X), $\text{C}_{30}\text{H}_{48}\text{O}$, M⁺ 424, m.p. 169–171° (Me_2CO), $(\alpha)_D + 57$ °

(CHCl_3 , c, 1.5); 2.4 DNP ($\text{C}_{36}\text{H}_{52}\text{N}_4\text{O}_3$, m.p. 212–214°), by oxidation with Jones' chromic acid reagent.

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ZINC (II) COMPLEXES WITH 2-ACETYL PYRIDINE

DIVALENT Zinc²⁺ has a completely filled $3d^{10}$ non-bonding shell and hence usually forms four-coordinated tetrahedral compounds utilising $4s4p^3$ hybrid orbitals for bonding. Several complexes of Zinc (II) with substituted pyridines have been reported^{1–4}. Similar complexes of Zinc (II) with 2-acetyl pyridine with different anions have been isolated and characterised now.

An ethanolic solution of the respective Zinc salts were treated with an ethanolic solution of 2-acetyl pyridine in 1:2 proportion. In all the cases the crystalline compounds separated after prolonged stirring. The compounds were filtered, washed with ethanol and dried *in vacuo*. The purity of the compounds was established by chemical analysis. The conductance measurements were made in acetone solution using a dip type cell. Infrared spectra were recorded using Unicam SP-200 Spectrophotometer on Nujol mulls. The relevant data are recorded in Table I.

All the complexes are diamagnetic as expected for a closed shell d^{10} configuration of the metal ion. The low conductance in acetone medium for the bromo and cyanato complexes are indicative of the non-electrolyte nature. The high conductance values for the perchlorato and thiocyanato complexes are indicative of 1:2 electrolytes. The I.R. spectrum in the region $5000\text{--}650\text{ cm}^{-1}$ were studied. A broad and strong band at $1020\text{--}1110\text{ cm}^{-1}$ for the perchlorate complex and a band at 2070 cm^{-1} for the thiocyanate complex confirmed the presence of ionic perchlorate^{5,6} and ionic thiocyanate⁷ respectively. The bands at 1380 cm^{-1} suggest⁸ a N-bonded cyanate group. So, the complexes reported in the present communication can be assigned the following formulae $[\text{Zn L}_2 \text{ Br}_2]$, $[\text{Zn L}_2 (\text{NCO})_2]$, $[\text{Zn L}_3 (\text{CNS})_2]$ and $[\text{Zn L}_3 (\text{ClO}_4)_2]$ (where L = 2-acetyl-pyridine). They can be presumed to be four co-ordinated, tetrahedral complexes similar to those reported earlier^{1,9,10}.