

The method of synthesis used here is quicker, the conditions are mild, there was no significant substituent effect on the reaction, the yields are good to excellent, and by-products were not detected. The method appears to be of general applicability.

All the compounds synthesized have been tested for antifeedant activity following the 'non-choice test method'⁹ using six-hour-prestarved fourth instar larvae of *Spodoptera litura*. The results are given in table 1. The present study reveals that 2,8-di(2-thienyl)-4,6-dioxo-4H, 6H-benzo[1,2-b:5,4-b']dipyrans (IIIh) has the highest antifeedant activity.

Dichalcones (IIa-h): General procedure

A mixture of I (0.01 mol) and the appropriate aldehyde (0.02 mol) in ethanol (40 ml) was kept at room temperature for 12 h with aq. KOH (60%, 10 ml). The product, obtained on dilution and acidification with dil. HCl, was subjected to column chromatography over silica gel (200-mesh). Benzene-chloroform (8:2, v/v) eluates, on concentration, afforded II.

2,8-Disubstituted 4,6-dioxo-4H,6H-benzo[1,2-b:5,4-b'] dipyrans (IIIa-h): General procedure

Dichalcones (II) (0.01 mol) were suspended in dry dimethylsulphoxide (30 ml) and a crystal of iodine added. The mixture was refluxed for 10 min, cooled and diluted with cold water. The solid obtained was filtered, washed with 20% aq. Na₂S₂O₃, and recrystallized from alcohol.

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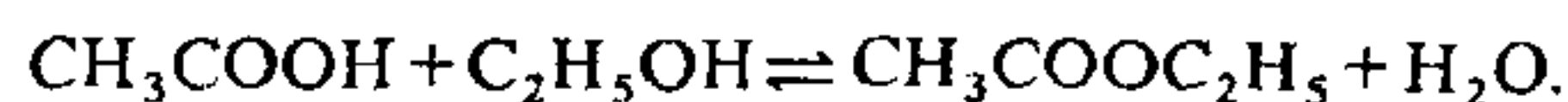
ESTERIFICATION WITH HYDROGEN FLUORIDE

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LIQUID hydrogen fluoride is a very useful reagent with high solvent power, particularly for oxygen-containing substances and also for aromatic compounds. It has been extensively used for its dehydrating and condensing properties. Compared to concentrated sulphuric acid, it is less likely to permit secondary reactions such as enolization, sulphonation, polymerization and tarry residues. Askam and Qazi^{1,2} reported cyclization in anhydrous fluoride with derivatives of diethyl phenylmalonate.

This communication reports the esterification reaction of various acids in the presence of anhydrous hydrogen fluoride. Fieser and Hershberg³ synthesized ethyl acetate in the presence of hydrogen fluoride, but the yield was only 17.5%. It was concluded that the poor yield obtained was due to the fact that the equilibrium in hydrogen fluoride solution favoured the left hand side of the equation below.



Traces of water formed during the reaction and their presence in hydrogen fluoride were stated to contribute to easy hydrolysis of CH₃COOC₂H₅.

The following general method was used for the preparation of the various esters. A mixture of acid and alcohol in 1:3 molar ratio was dissolved in 4 m anhydrous hydrogen fluoride by gentle swirling. A clear solution resulted, which was allowed to stand at room temperature for 6 h in a screw-capped polythene bottle. (Hydrogen fluoride reacts with glass containers.)

After 6 h the water vapour was allowed to escape. Hydrogen fluoride solvent (2 m) was added and the mixture shaken further for a few minutes and allowed to stand a further 20 h. The excess hydrogen fluoride was then evaporated in a polythene beaker.

Table 1 Features of esterification reaction in presence of hydrogen fluoride

Products	Time of reaction (h)	B.P.(°C)	Yield (%)
Ethyl acetate	26	76-77	82
Ethyl benzoate	26	213-214	95
Methyl benzoate	26	199-200	97
Propyl benzoate	38	110-112	98
Butyl benzoate	40	120-122 (10 mm Hg) (11 mm Hg)	92

The residue was neutralized with 30% sodium hydrogen carbonate solution. The reaction mixture was extracted thrice with diethyl ether and the combined extracts were dried over anhydrous magnesium sulphate for 4 h. On evaporation an oily product was obtained, which was fractionally distilled to give the ester in very high yield. The above method was used for the preparation of the esters listed table 1.

The products listed in table 1 were identified by comparing their b.p., IR spectra and refractive index with those of authentic specimens^{4,5}.

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LEPTOMERYX, AN OLIGOCENE ARTIODACTYL FROM THE LOWER MURREE OF SIAL SUI (KALAKOT TEHSIL), DISTRICT RAJAURI, JAMMU AND KASHMIR

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THE present note deals with the discovery and age implications of a traguloid artiodactyl *Leptomeryx*

recovered from the Lower Murree sediments occurring in the Kalakot tehsil of Rajauri district, Jammu and Kashmir, India. Geologically the Murree rocks occupy the peripheral part of the Kalakot, Metka and Mahogala inliers in the Rajauri district, forming a gradational contact with the underlying marine Subathu sediments. The Murree sequence comprises alternating maroon sandstone, clays, mottled clays, claystone, siltstone and grey sandstone, with a few intercalating pseudoconglomerates. The pseudoconglomerates are composed of maroon sandy matrix surrounding pedogenetic calcareous pebbles, mostly oval in shape and formed intraformationally.

The present specimen was collected from a 2-m-thick pseudoconglomerate bed in the Sial Sui I section, about 12 km north-west of Sair (figure 1a, b). Here, this richly fossiliferous horizon is sandwiched between maroon argillaceous sandstone units and occurs about 575 m above the Subathu-Murree contact at Jigni. Besides *Leptomeryx*, the horizon has also yielded a diverse faunal assemblage represented by rhinocerotoids, crocodiles and fishes. An adjacent small section (Sial Sui II), near Sial Sui post office, extending towards Paglot, also comprises a localized pseudoconglomerate bed (2 m thick), which has yielded the same Sial Sui I fauna and, in addition, rodents, (?)insectivore, pelecypods and charophytes. As the base of this section appears to be tectonically disturbed, the exact relationship of the section with the Sial Sui I section is difficult to state with certainty. However, on faunistic grounds, the two pseudoconglomerates from both these sections seem to be coeval.

While a great diversity of artiodactyls have been reported from the Fatehjang Zone and the Bugti Bone Beds (both in Pakistan)¹ the family Leptomerycidae is only represented by *Predremotherium* (?) *beatrice* and there is no known record of the genus *Leptomeryx* from the subcontinent. Recently² a few artiodactyls have been reported from the vicinity of the Kalakot tehsil. These are *Palaeochoerus* (Kalakot and Mahogala), *Microbunodon* (Kalakot) and *Gonotelmia* (Sial Sui). Although a number of leptomerycids are reported from the Upper Eocene to Upper Miocene sediments of Africa, Asia, Europe and North America³, the distribution of the genus *Leptomeryx* is confined only to the Oligocene of North America where it has attained the maximum grade of evolution, with some advanced forms becoming extinct in the Lower Miocene. A comparison of the Sial Sui *Leptomeryx* (probably a new species) with the North American species shows