

New method for benzoyloxylation of aromatic hydrocarbons

M. Hogale

Department of Chemistry, Shivaji University, Kolhapur 416 004, India

A new method for the benzoyloxylation of aromatic hydrocarbons has been proposed by using benzoyl peroxide and cupric chloride supported on alumina. The yield of the products has been increased by about ten per cent over that in a procedure using benzoyl peroxide and a mixture of cupric and cuprous chloride.

BENZOATE esters can be prepared by the reaction of phenols with benzoyl chloride in presence of sodium hydroxide. This requires tedious reaction work-up¹. The copper(II) halide supported on alumina is used for halogenation in nonpolar solvents under mild conditions^{2,3} as alumina is most effective in activating copper chloride. Activated alumina has also electron acceptor properties and the formation of radical cation of an aromatic hydrocarbon adsorbed on alumina has been observed by ESR spectroscopy⁴. Therefore, it is worthwhile using alumina as support to facilitate the generation of radical cation of the aromatic hydrocarbon.

The advantages of this procedure are mild reaction condition and good yield. Dibenzoyl peroxide with Cu^{2+} can generate benzoyloxy radical, which can add to an aromatic ring leading to acyl benzoate⁵. Many workers have used copper salt ($\text{Cu}^{2+} + \text{Cu}^+$) to generate cuprous ion effectively⁶ and to increase the rate of the reaction. The aromatic benzoyloxylation induced by oxygen has been reported, with good yield of the product.

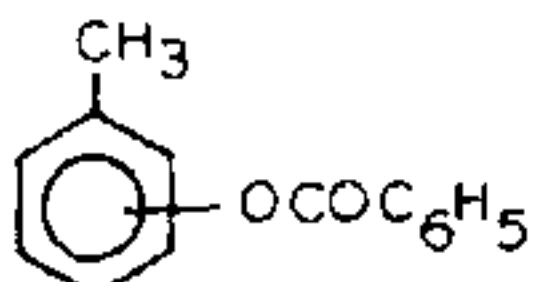
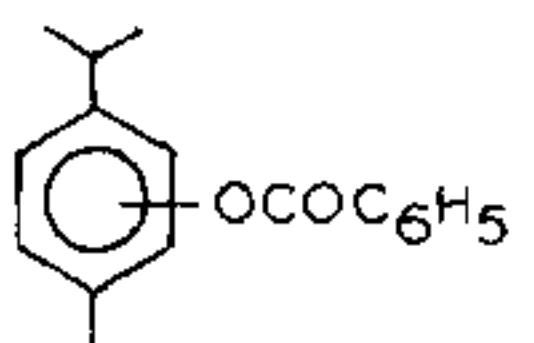
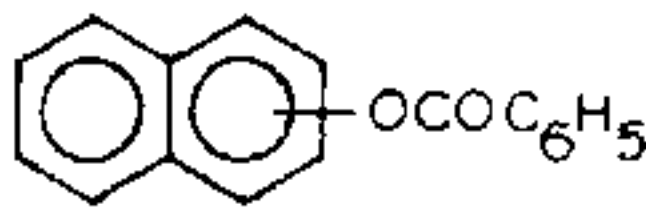
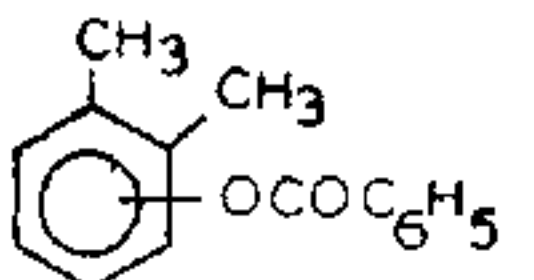
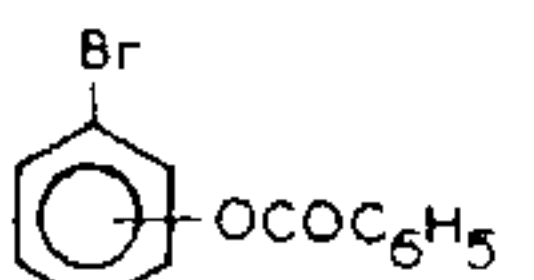
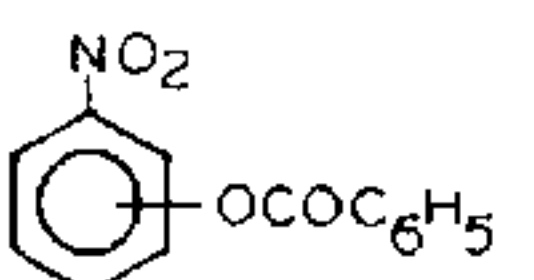
Here we report the benzoyloxylation of aromatic hydrocarbon by benzoyl peroxide using copper chloride supported on alumina as an efficient method for the preparation of benzoyloxy derivatives with better yield than in the procedure using $\text{CuCl}_2/\text{CuCl}$ mixture as catalyst in the system.

All chemicals used were of Analar grade and used without further purification. Neutral alumina was from ICN Biomedicals (Woelm N-super-I). Carbon tetrachloride was dried with calcium chloride and distilled. All ^1H NMR spectra were recorded on a Perkin Elmer R-32, 90 MHz spectrometer. The product mixtures were analysed by gas-liquid chromatography on a Hitachi Model 163 flame ionization instrument equipped with a 36-30 Chromosorb column.

To a solution of copper(II) chloride dihydrate (15 g) in distilled water (45 ml) neutral alumina (30 g, Woelm N-super-I) was added at room temperature. The water was evaporated using a rotary evaporator. The resulting alumina-supported reagent was dried under vacuum at 100°C for 20 h.

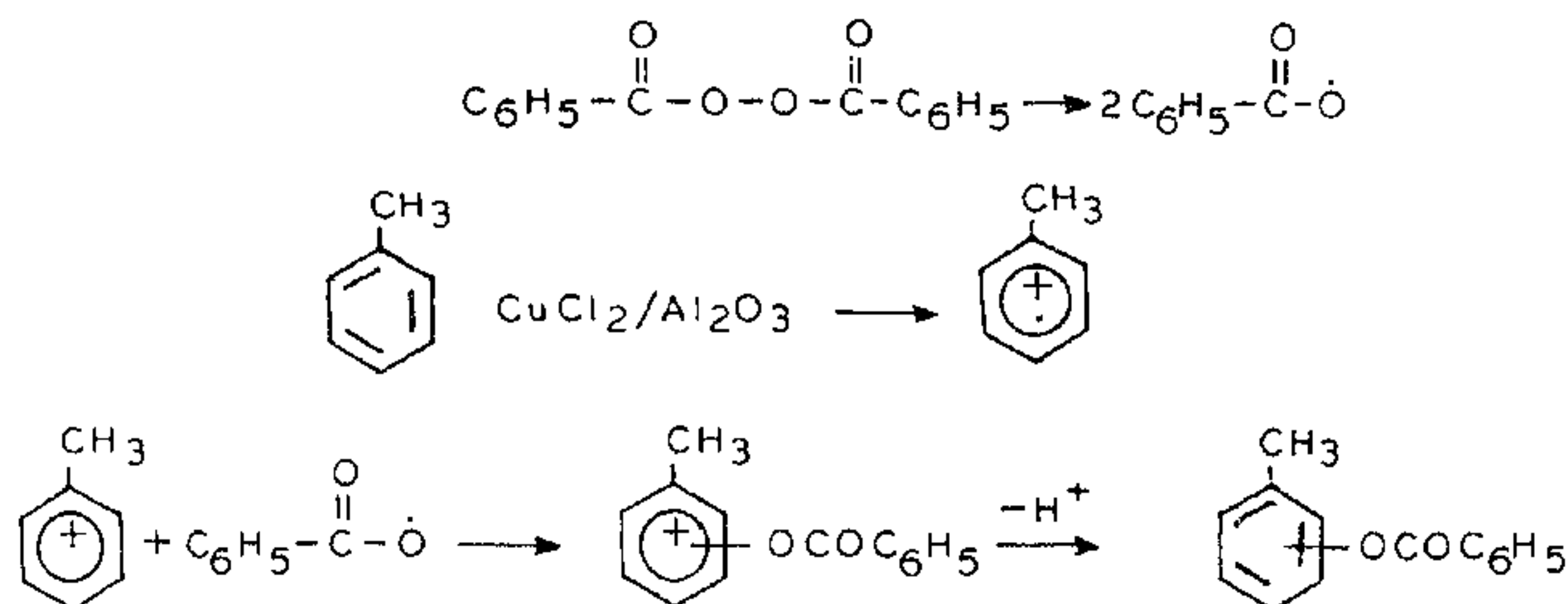
The following forms a typical experimental procedure for benzoyloxylation of aromatic hydrocarbon: Above reagent

Table 1. Physical data of benzoate esters of aromatic hydrocarbon.

Compound	Benzoate derivative	Total yield (%) of the products	Yield (%) of substituted benzoyloxy derivatives		
Toluene		55	2-50	3-35	4-15
p-Cymene		45	2-42	3-58	—
Naphthalene		60	1-60	2-40	—
o-Xylene		60	3-30	4-78	—
Bromobenzene		54	2-55	3-10	4-35
Nitrobenzene		52	2-13	3-75	4-72

(0.49 mol) and toluene (0.1 mol) in 50 ml acetonitrile in three necked flasks were warmed on water bath at 65°C . Benzoyl peroxide (0.02 mol) dissolved in 50 ml of acetonitrile was added through a dropping funnel at once and the mixture was stirred for 24 h. When all the peroxide disappeared, the reaction mixture was filtered and poured into ice-cold water (200 g) containing 100 ml of conc. hydrochloric acid. The separated organic layer was washed with saturated sodium carbonate (2 x 200 ml) followed by water (200 ml). The organic layer concentrated on a rotary evaporator was cooled and analysed by gas chromatography (Table 1). The products were characterized by NMR and IR spectroscopy, and gas chromatography. Dibenzoyl peroxide with Cu^{2+} adsorbed on alumina can generate benzoyloxy radical. Alumina acts as an electron acceptor to the aromatic hydrocarbon forming a radical cation. The CuCl_2 adsorbed on alumina can generate benzoyloxy radical, which can attack an aromatic radical cation to form a cationic complex, which loses a proton to yield aryl benzoate. The mechanism suggested for the reaction is shown in Scheme 1.

Both species, Cu^+ and Al_2O_3 , being electron acceptors, generate the radical cation of aromatic hydrocarbon more effectively than Cu^{+2} alone, which gets rapidly attacked



Scheme 1

by benzoyloxy radical; hence the proportion of the product formed is increased. The reaction being carried out at lower temperature, the rate of the decomposition of the benzoyloxy radical is comparatively slower. It undergoes competing reactions such as the radical recombination and chain reaction, forming little benzoic acid, carbon dioxide, biaryl, etc.^{9,10}

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Palynological dating of a coal seam in Ayyanapalem area, Khammam District, Andhra Pradesh, India

M. Rama Rao, G. Lakshminarayana and
C. G. K. Ramanujam

Geological Survey of India, Southern Region, Hyderabad 500 001, India
*Department of Botany, PG College of Sciences, Osmania University, Hyderabad 500 007, India

A palynological study of five subsurface samples of a coal seam near Ayyanapalem, Chintalapudi sub-basin of Godavari valley, Andhra Pradesh, was carried out. Twenty-five genera, including monosaccate, striate and nonstriate bisaccate, and trilete sporomorphs were identified; striate bisaccates predominate. Based on occurrence of *Rhizomaspora*, *Microbaculispora*, *Indotriletes*, *Crucisaccites* and *Corisaccites*, the coal seam is inferred to be similar in age to the Barakar Formation of the Lower Gondwana.

DURING a test drilling (GAG-1) (17°22'50"N, 80°40'E) for coal by the Geological Survey of India near Ayyanapalem, Chintalapudi sub-basin of Godavari valley, Khammam District, Andhra Pradesh, a 30-m thick coal seam (coal + carbonaceous shale) has been encountered at a depth of 27 m (Figure 1). This is a significant find as it opens up a favourable horizon for the exploration of coal in this area. Recent field work has established a succession of Talchir, Barakar and Kamthi formations of Lower Gondwana in this area¹.

A palynological study of five samples covering the entire coal seam has been undertaken with the purpose of assessing and evaluating the stratigraphic position of the coal-bearing formation. Twenty-five genera comprising monosaccate, striate and nonstriate bisaccate, monolete and trilete groups could be identified (Figure 2). The more significant

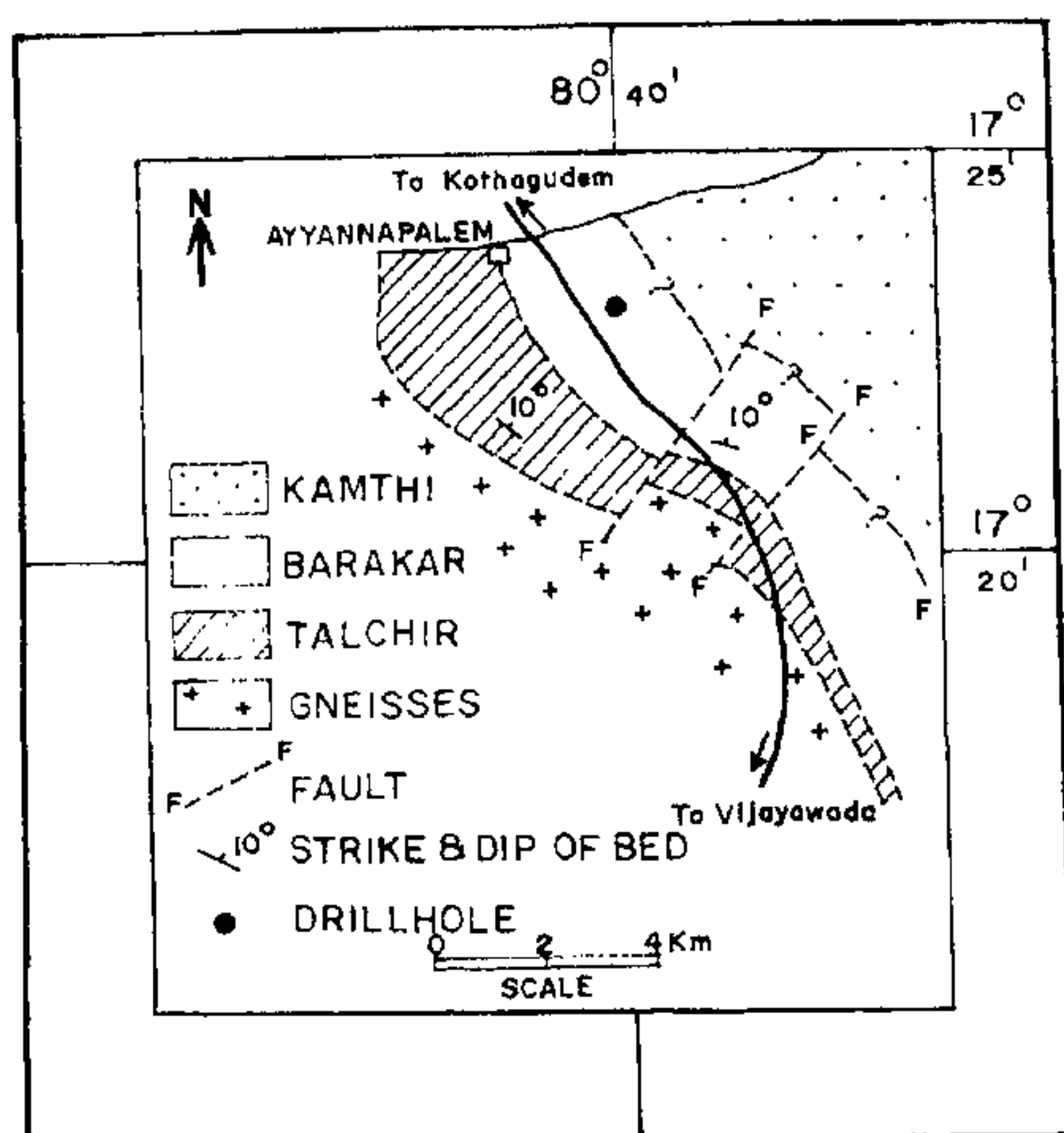


Figure 1. Geological map of Ayyanapalem area, Khammam District, Andhra Pradesh.