〔Heterocycles, **23**, 2387 (1985)〕

Synthesis of 1, 2, 3, 4, 4a, 5, 10, 10a-Octahydro-7-hydroxy-2, 4a, 5-trimethyl-1, 5-ethanobenzo〔g〕quinoline; Bridged Benzomorphan with Antagonist Activity MIKIO HORI*, TADASHI KATAOKA, HIROSHI SHIMIZU, EIJI IMAI, NORIHIRO KAWAMURA

Title compound was synthesized from 3-methyl-11-(3-oxobutyl)-2,6-methano-3-benzazocine. N-Demethylation was succeeded with BrCN by protection of the ketone. Treatment of obtained 11-(3-oxobutyl)-2,6-methano-3-benzazocine with p-toluenesulfonic acid in benzene afforded tetracyclic benzomorphan derivative with enamine structure. Reduction of the enamine with H_2/Pd-C occurred stereoselectively to give title compound in 30.4%. The stereostructure of 2-methyl group was assigned as equatorial from the consideration that the reduction occurred from less hindered side. The title compound showed strong antagonist activity.

〔J. Med. Chem., **28**, 1656 (1985)〕

Novel Nonnarcotic Analgesics with and Improved Therapeutic Ratio. Structure-Activity Relationships of 8-(Methylthio)- and 8-(acylthio)-1, 2, 3, 4, 5, 6-hexahydro-2, 6-methano-3-benzazocines MIKIO HORI*, MASATOSHI BAN, EIJI IMAI, NORIYUKI IWATA, YOSHINARI SUZUKI, YUTAKA BABA, TOKIKO MORITA, HAJIME FUJIMURA, MASAKATSU NOZAKI, MASAYUKI NIWA

Three routes, diazotization, Grewe cyclization and Newman-Kwart rearrangement of benzazocines were investigated and the last method was selected. The thermal rearrangement, reductive cleavage and subsequent methylation or acylations gave the title compounds. Although analgesic activities of sulfur-containing benzazocines decreased compared to the corresponding hydroxy compounds, the N-methyl derivative (S-metazocine) showed potent analgesic activity.

〔J. Chem. Soc. Perkin Trans. I, **1985**, 2333〕

Generation of 〔1, 2, 4〕Triazolo〔1, 5-a〕pyrimidine N-Ylides and Their Ring Transformation Reactions. MIKIO HORI*, KIYOMI TANAKA, TADASHI KATAOKA, HIROSHI SHIMIZU, EIJI IMAI, KAZUHIKO KIMURA, YOSHINOBU HASHIMOTO

〔1,2,4〕Triazolo〔1,5-a〕pyrimidine (1) has been alkylated at the N(3)-position by treatment with alkyl halides in refluxing acetone. The ylides (3) were generated in situ from the iminium salts (2) and 1 eq. of triethylamine. Thermolysis of the ylides (3) in acetonitrile gave the 2-cyanamidopyrimidines. The N(3)-phenylacyliminium salt (2a) when treated with 2 eq. of triethylamine gave 2-(2-imino-5-phenyl-2,3-dihydrooxazol-3-yl)pyrimidine. The latter on hydrolysis gave the oxazolone, and on treatment with nucleophiles such as alcohols or amines under acidic conditions afforded the ring transposition products, imidazol-2-ylpyrimidines. The reaction mechanism for the novel thermolysis of the ylides is discussed.