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Generation and Properties of N⁷-Xanthinium Ylides: Reactions of N⁷-Xanthinium Ylides with Diphenylcyclopropanone and Acetylenic Compounds.

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Xanthinium N⁷-ylides (1) generated from 7-substituted 9-methylxanthinium tosylates using Et₃N in MeCN reacted with diphenylcyclopropanone to give pyrone derivatives and isocaffeine in good yields. The reactions of N⁷-cyano-(1a) and N⁷-benzoylmethylides (1b) with dimethyl acetylenedicarboxylate or methyl propiolate (MP) afforded 5-pyrrol-1-yluracils in moderate yields. N⁷-Methoxycarbonylmethylide (1c) reacted with MP to give a pyrrolopteridine derivative together with a 5-pyrrol-1-yluracil derivative. Dihydropyrrolopyrimidine derivative, a primary 1,3-dipolar cycloaddition product, was detected by NMR measurement of the products.

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Ring Contraction of 2-Chlorocyclohexanone with Grignard Reagents.

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The reaction of 2-chlorocyclohexanone with phenylmagnesium bromide in refluxing benzene gave 2-phenylcyclohexanone. But the reaction in refluxing tetrahydrofuran (THF) unexpectedly afforded the ring-contracted product, cyclopentyl phenyl ketone, as the main product in moderate yield. The abnormal reaction was promoted in cyclic ethers such as THF. However, in the case of 2-bromocyclohexanone, the ring contraction did not occur. The reactivities of several 2-haloketones were examined. The migratory orientation was determined by the favorable conformation of 2-halocyclohexanones and that of their halohydrins in reaction solvents.

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Ylide-induced Ylide Formation: A Thermal Reaction and a Double Cycloaddition Reaction of [1,2,4]Triazolo[1,5-a]pyridinium Ylides.

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1-Alkyl[1,2,4]triazolo[1,5-a]pyridinium salts were synthesized by the reaction of [1,2,4]-triazolo[1,5-a]pyridine with alkyl halides in dry acetone under reflux. The iminium salts were treated with triethylamine in dry acetonitrile to afford a red solution of the ylides which were too unstable to be isolated. The thermal reaction of the ylides gave 2-cyanamidopyridines. The reaction of the ylides with methyl propiolate or dimethyl acetylenedicarboxylate resulted in the formation of pyrazolo[1,5-a]pyridine derivatives via a double cycloaddition reaction.