Generation and Properties of N7-Xanthinium Ylides: Reactions of N7-
Xanthinium Ylides with Diphenylocyclopropanone and Acetylenic Compounds.
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Xanthinium N7-ylides (1) generated from 7-substituted 9-methylxanthinium tosylates using Et3N in
MeCN reacted with diphenylocyclopropanone 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.
Dihydropyrrolopurine derivative, a primary 1,3-dipolar cycloaddition product, was detected by NMR
measurement of the products.

Ring Contraction of 2-Chlorocyclohexanone with Grignard Reagents.
Mikio Hori*, Tadashi Kataoka, Hiroshi Shimizu, Eiji Imai,
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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-halocyclophanones and that of their
halohydrins in reaction solvents.

Ylide-induced Ylide Formation: A Thermal Reaction and a Double Cyclo-
addition 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 tri-
ethylamine in dry acetonitrile to afford a red solution of the ylides which were too unstable to be iso-
lated. 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.