

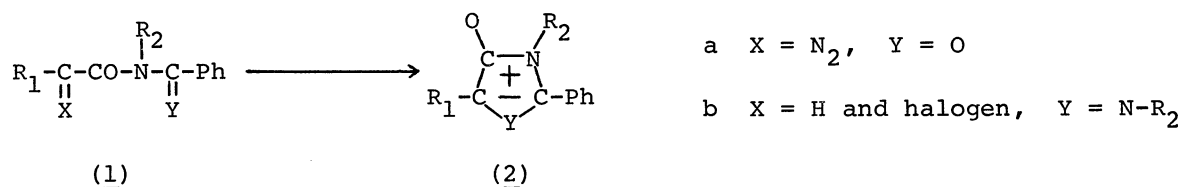
INTERMEDIATORY FORMATION OF MESOIONIC IMIDAZOLIUM-4-OXIDES IN THE
REACTION OF α -HALOACYL CHLORIDES WITH AMIDINES

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Reaction of α -haloacyl chlorides with benzamidines in the presence of triethylamine generated mesoionic imidazolium-4-oxides (2b) as intermediates which gave pyrroles on treatment with acetylenic compounds via 1,3-dipolar cycloaddition followed by extrusion of isocyanates.

We have reported the formation of mesoionic 1,3-oxazolium-4-oxide (2a) by intramolecular carbene-carbonyl reaction in the copper chelate-catalyzed decomposition of diazoimide (1a).¹ We now wish to describe analogous intramolecular cyclization of α -haloacylamidines (1b) to give imidazolium-4-oxides (2b) in the reaction of α -haloacyl chlorides with N,N'-disubstituted benzamidines (4), and describe that treatment of 2b with acetylenic dipolarophiles gives pyrroles via cycloaddition and elimination of isocyanates.



In a typical experiment, a mixed solution of two molar amount of N,N'-dimethylbenzamidine and one molar amount of triethylamine in benzene was added to a benzene solution of α -bromophenylacetyl chloride under vigorous stirring at room temperature. The yellow color developed indicates the formation of anhydro-1,3-dimethyl-2,5-diphenyl-4-hydroxyimidazolium hydroxide (2b). Dimethyl acetylenedicarboxylate (1.5 molar amount) was added to the solution and kept at 80°C until yellow color of mesoionic imidazoliumoxide disappeared. The reaction mixture was separated on column chromatography to give dimethyl 2,5-diphenyl-N-methylpyrrole-3,4-dicarboxylate (78%).

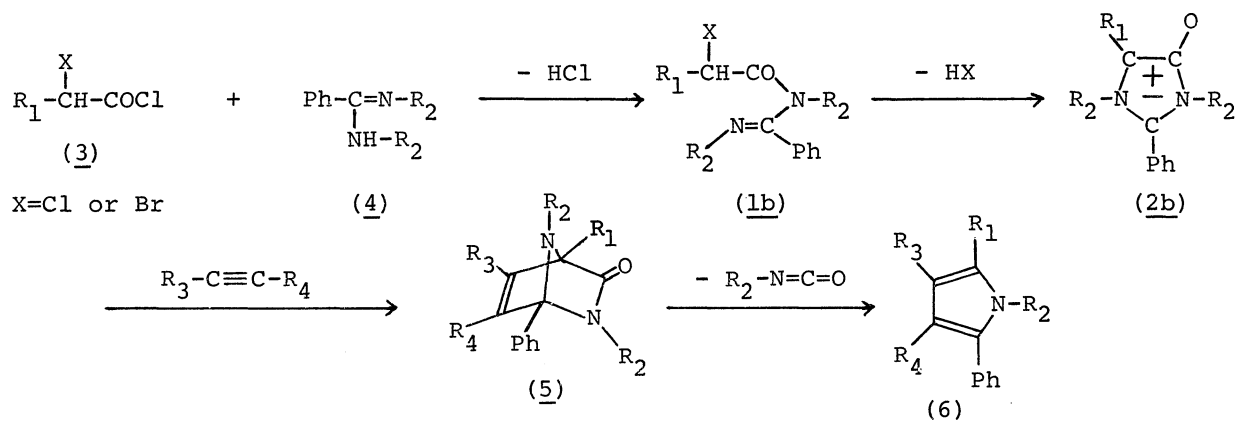


Table. Yields and Melting Points of Pyrroles (6)

run	R ₁	R ₂	R ₃	R ₄	yield (%)	mp (°C)
a	Ph	Me	COOMe	COOMe	78	147-148
b	Ph	Me	PhCO	PhCO	74	202-203
c	Ph	Me	H	COOMe	65	99-100
d	Ph	Me	Me	COOMe	38	190-193
e	Ph	Me	Ph	COOMe	42	167-168
f	Ph	Me	H	Ph	25	176-177
g	Ph	Ph	COOMe	COOMe	71	201-202
h	Me	Me	COOMe	COOMe	74	94-95
i	Me	Ph	COOMe	COOMe	54	157-158
j	H	Me	COOMe	COOMe	32	118-119
k	H	Ph	COOMe	COOMe	30	125
l	H	Ph	H	COOMe	57	109-110
m	p-NO ₂ C ₆ H ₄	Me	COOMe	COOMe	51	163-164

Combination of acid chlorides, amidines and acetylenes gave various pyrroles (6)² (see Table). The formation of (6) may reasonably be explained by the extrusion of isocyanate from the cycloadduct (5) of acetylene and mesoionic imidazolium-4-oxide (2b) which was formed by the reaction of acid chloride (3) and amidine (4) through 1b. Monocyclic imidazolium-4-oxide having no acyl group at 5-position was described to be unstable³ and only a few compounds of this type were synthesized.^{4,5} Attempts to isolate 2b in pure state in our reaction condition were also unsuccessful. Therefore, modification of reaction conditions is now in progress.

References

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- 2) All new compounds reported here gave satisfactory elemental analyses, and melting points of 6a, 6b, 6c, 6f and 6h were in good agreement with values in the literature.
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