REARRANGEMENTS OF INTERMEDIARY TRICYCLIC
7-AZABENZONORBORNENES, OBTAINED FROM DIELS-ALDER REACTION
OF PYRIDO[2,1-a]- AND 2,4-DIMETHYLPYRIMIDO[2,1-A]ISOINDOLES WITH
MALEIMIDE DIENOPHILES

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Our studies of isoindole derivatives with annelated heterocycle ring and nodal nitrogen I in
reaction with maleimides II have shown that the products depend on the nature of annelated
heterocycle A. Reaction of maleimides with pyrido[2,1-a]isoindole I (annelated heterocycle A =
pyridine) leads to 2:1 adducts IV, which are the products of new rearrangement of intermediary
Michael-Diels-Alder exo-adducts III [1,2], while reaction of maleimides II with 2,4-
dimethylpyrimido[2,1-a]isoindole I (A = 4,6-dimethylpyrimidine) leads to completely different
products, namely, to 4-amino-2-R-9-(1-R-2,5-dioxotetrahydro-1H-3-pyrrolyl)-2,3-dihydro-1H-
benzo[f]isoindole-1,3-diones V, which are the result of nitrogen bridge atom extrusion within the
intermediary Michael-Diels-Alder exo-adducts III [3,4] (Scheme 1).

Such a trigger effect of X-atom may be explained by push-pull effect between \( \pi \)-donor heterocycle
ring A and \( \pi \)-acceptor carbonyl group, which passes via \( \sigma \)-C-C bond thus cleaving it (Picture 1). This
effect will be suppressed in case of 2,4-dimethylpyrimido[2,1-a]isoindole I because of electronegative
pyridine-type nitrogen (atom X).

Scheme 1

References
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Picture 1