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Bratislava, Czechoslovakia, 23—28 August 1987

Edited by

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## SYNTHESES OF HETEROCYCLES BY REACTIONS OF ISOELECTRONIC 1,3-DIPOLES WITH ETHYLENIC OR ACETYLENIC DIPOLAROPHILES

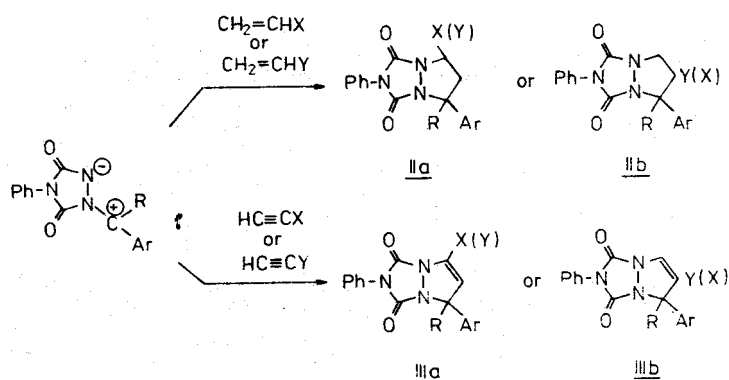
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Leningrad State University, Leningrad, USSR

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Organic 1,3-dipoles have already become traditional synthones in syntheses of five-membered heterocycles /1/. According to both main principles of the VMO theory and experimental data /2/, the rules of cycloadditions of 1,3-dipoles of different classes are not common.

As shown in our work, stable azomethinimines derived from triazolindiones /3/ can successfully be used for the preparation of the bicyclic nitrogen-containing systems according to the following scheme.

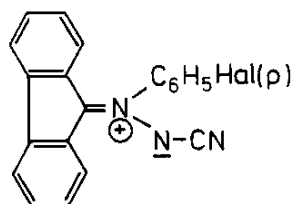


X = OR, CH<sub>2</sub>OR, (R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>)

Y = CO<sub>2</sub>R, CN

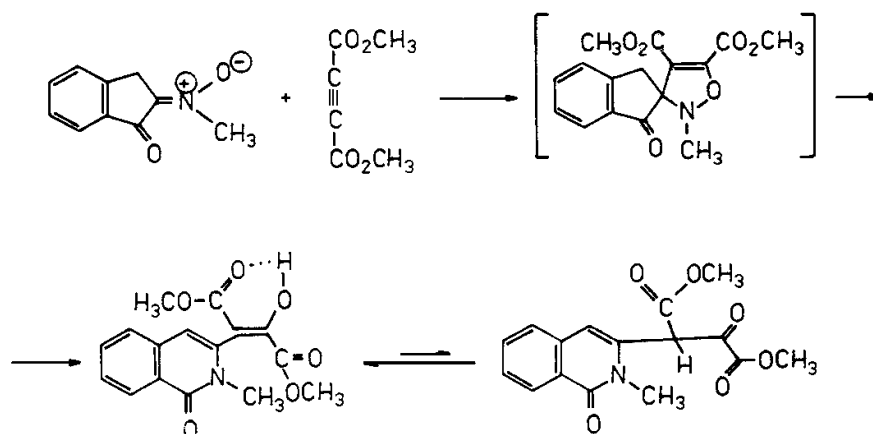
On the basis of kinetic investigation and the present data we may conclude, that the activity of azomethinimines in this process increases with the addition of electron-attracting groups to the carbon atom of 1,3-dipole. Reactivity of dipolarophiles depends to a large extent on electronic properties of terminal groups. Unsaturated compounds with electron-rich substituents at the double and triple bonds have the highest reactivity among ethylenic and acetylenic dipolarophiles.

Thus, selectivity of reactions with the mentioned azomethinimines is higher, than that of the azomethinimines of the other types (e.g. higher than dipoles obtained by Huisgen from diaryldiazo compounds and substituted azo compounds of the common formula /1, 4/):



It has been possible to influence the direction of the dipolar cycloaddition by varying the nature of substituents. Thus, we can obtain either 5- or 6-substituted cycloadducts (IIa/IIb, IIIa/IIIb).

In the case of five-membered cyclo- $\alpha$ -ketonitrones (iso-



electronic analogues of azomethanimines), cycloadditions are highly effective only with acetylenic dipolarophiles. Reactions with olefins are usually reversible and it is not possible to obtain isolable cycloadducts. With certain structural features the cycloaddition is accompanied by 1,5-sigmatropic shift of proton. This shift increases the aromatic character of the adduct and facilitates enlargement of the initial ring /5/.

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