LETTERS TO THE EDITOR

MECHANISMS OF THE CLEAVAGE OF THE C–N BOND IN SUBSTITUTED AMINES

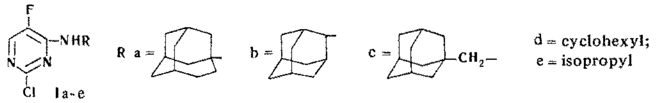
Ya. Yu. Polis

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 4, p. 571, 1970

UDC 547.853

We have observed cleavage of the C–N bond in the substituted aminopyrimidines I [R = $C(CH_3)_3$; $C(CH_3)_2CH_2C(CH_3)_3$; adamant-1-yl] when they were boiled with solutions of hydrohalic acids with the formation of aminopyrimidines and tertiary alkyl halides [1].

In order to study the mechanism of the cleavage of the C–N bond, compounds Ia-e with substituents forming carbonium ions of different stabilities have been synthesized



Compounds Ia-e were obtained from 2,4-dichloro-5-fluoropyrimidine and the corresponding amines in absolute ether at room temperature (Ia-c), in absolute ethanol at the boil (Id) or in absolute methanol at 100°C (Ie). A rapid and quantitative reaction took place in the case of Ia and b.

2-Chloro-5-fluoro-4-(homoadamant-3-ylamino)pyridimide (Ia), mp 133-134°C (absolute ethanol). 4-(Adamant-2-ylamino)-2-chloro-5-fluoropyrimidine (Ib), mp 178-179°C (absolute ethanol). 4-(Adamant-1-ylmethylamino)-2-chloro-5-fluoropyrimidine (Ic), mp 122-123°C (absolute ethanol). 2-Chloro-4-cyclohexylamino-5-fluoropyrimidine (Id), mp 78-78.5°C (petroleum ether). 2-Chloro-5-fluoro-4-isopropylaminopyrimidine (Ie), mp 60-61°C (ethanol - water).

The elementary analyses and the UV and IR spectra confirmed the structures of the compounds.

When Ia-e were boiled in solutions of hydrochloric acid, the C–N bond was cleaved only in the case of Ia, with the formation of 5-fluorocytosine and 3-chlorohomoadamantane [2]. The absence of cleavage of the C–N bond under these conditions in the case of Ib shows that the adamant-2-yl cation is considerably less stable than the adamant-1-yl cation. Compounds Ic-e were not decomposed, although they did not form hydrochlorides either, because of the instability of the primary and secondary carbonium ions.

Thus, the cleavage of the C–N bond in the substituted aminopyrimidines with acids takes place only where the formation of a stable tertiary aliphatic or alicyclic carbonium ion is possible.

REFERENCES

1. Ya. Yu. Polis, ZhOrKh, 5, 580, 1969.
2. H. Steller and P. Goebel, Chem. Ber., 96, 550, 1963.

29 September 1969

Institute of Organic Synthesis, AS Latvian SSR, Riga