tert-BUTYLDIAZENE OXIDE AS A LEAVING GROUP

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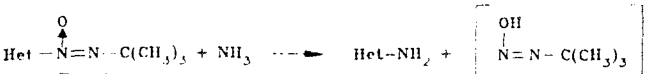
Diazene oxides can be prepared from almost any nitrogen-containing functional group, but the reverse reactions are limited primarily to oxidation and reduction reactions. The synthetic potential of diazene oxides containing substituents has been largely unexplored [1, 2].

We have found that the tert-butyldiazene oxide group in activated positions of pyridine (Ia-c) and quinoxaline (Id) readily undergoes nucleophilic substitution upon reaction with amines. For example, reaction with ammonia results in the formation of heterocyclic amines IIa-d and tert-butyldiazotate III, which is unstable:



$$\text{Het}-\overset{\overset{O}{\uparrow}}{N}=N-C(CH_3)_3 + NH_3 \longrightarrow \text{Het}-NH_2 + \left[\overset{\overset{OH}{|}}{N}=N-C(CH_3)_3\right]$$

Ia-d IIa-d III

I, II a Het = 3-nitro-4-pyridyl, b Het = 3-nitro-2-pyridyl, c Het = 3,5-dichloro-2-pyridyl, d Het = 3-chloro-2-quinoxalinyl

The diazene oxide group has thus shown itself to be more active than a halogen in the same position.

Compound Ia-d (0.01 mole) was dissolved in 25 ml ethanolic ammonia solution (2 moles/liter). After reaction was complete, the solution was evaporated and the known amino compounds IIa-d were crystallized from ethanol.

Compound IIa. T_{reac} 25°C, t_{reac} 5 min, yield 90%. **Compound IIb.** T_{reac} 25°C, t_{reac} 10 min, yield 92%. **Compound IIc.** T_{reac} 100°C, t_{reac} 5 h, yield 70%. **Compound IId.** T_{reac} 100°C, t_{reac} 3 h, yield 80%.

LITERATURE CITED

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2. C. F. Korte (ed.), *Methodicum Chimicum*, Vol. 6, Academic Press, New York–Stuttgart (1975).

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