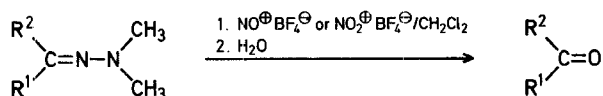
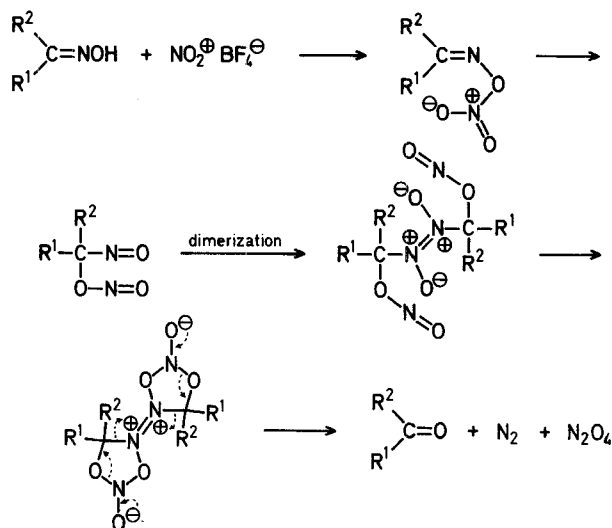


in recent years, we considered that oximes might undergo Beckmann rearrangement when subjected to these ionic reagents. The results of our ensuing investigation suggest that alternative modes of decomposition appear to dominate the reaction pathway which eventuates in the oxidative regeneration of the carbonyl compounds.

Cleavage of oximes to regenerate the parent carbonyl compounds has received much attention over the years. Hydrolytic cleavage or cleavage by exchange (hydrochloric acid/formaldehyde<sup>3</sup>, hydrochloric acid/levulinic acid<sup>4</sup>, H<sup>⊕</sup>/pyruvic acid<sup>5</sup>, sodium hydrogen sulfite<sup>6</sup>), oxidative cleavage [cerium(IV) ammonium nitrate<sup>7</sup>, lead(IV) acetate<sup>8</sup>, thallium(III) nitrate<sup>9</sup>, chromium(VI) oxide in the form of Jones and Collins reagents<sup>10</sup>, periodic acid<sup>10</sup>, ozone<sup>11</sup>, bis(triphenylphosphine)palladium/oxygen<sup>12</sup>, uranium(VI) fluoride<sup>13</sup>], and reductive cleavage [titanium(III) chloride<sup>14</sup>, chromium(II) acetate<sup>15</sup>, pentacarbonyliron<sup>16</sup>, Raney-nickel alloy in alkaline solution (nascent hydrogen)<sup>17</sup>, zinc/acetic acid<sup>18</sup>, aluminum triisopropoxide<sup>19</sup>] are employed. We consider that our procedure represents a useful addition to the array of deoxygenation methods as a mild and efficient cleavage method (Table 1).



The reaction of oximes with nitronium and nitrosonium ions is fast and exothermic, giving the corresponding carbonyl compounds on work-up. The involvement of nitroso intermediates during reaction with nitronium salts was indicated by the development of a blue-green color. This observation led us to propose the following mechanism.



**Table 1.** Cleavage of Oximes with Nitronium (A) and Nitrosonium (B) Tetrafluoroborate

Oxime of	Yield <sup>a</sup> [%] of Carbonyl Compound	
	(A)	(B)
Cyclohexanone	82	79
2-Methylcyclohexanone	84	80
4-Heptanone	75	72
Heptanal	55	53
Benzaldehyde	74	77
Acetophenone	80	64

<sup>a</sup> Isolated product, identified by comparison with authentic sample.

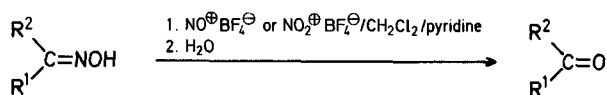
### Synthetic Methods and Reactions; XX<sup>1</sup>. Oxidative Cleavage of Oximes and Dimethylhydrazones with Nitronium and Nitrosonium Salts

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During the study of the synthetic utility of nitronium and nitrosonium salts<sup>2</sup> which have become readily accessible

The oxidative cleavage reactions have also been extended to dimethylhydrazones. As this class of compounds is gaining prominence in synthetic chemistry through their utility in controlled C—C bond-formation processes<sup>20</sup>, additional methods for the removal of the protective group would be useful. We considered that nitronium and nitrosonium salts should be capable of mediating hydrolysis of dimethylhydrazones either by electron transfer or by the nitrosative route. Accordingly, dimethylhydrazones were subjected to reaction with equimolar quantities of nitronium or nitrosonium tetrafluoroborate. An external base is not needed as acidic by-products are not produced (Table 2).



**Table 2.** Cleavage of Dimethylhydrazones with Nitronium (A) and Nitrosonium (B) Tetrafluoroborate

Dimethylhydrazone of	Yield <sup>a</sup> [%] of Carbonyl Compound	
	(A)	(B)
Cyclohexanone	75	73
2-Methylcyclohexanone	82	50
4- <i>t</i> -Butylcyclohexanone	59	70
Phenylacetone	66	53
2-Heptanone	86	80

<sup>a</sup> Isolated product, identified by comparison with authentic sample.

**Cleavage of Oximes with Nitronium- or Nitrosonium Tetrafluoroborate:** A solution of the oxime (10 mmol) in dry dichloromethane (5 ml) and pyridine (2 ml) is added dropwise to a stirred suspension of nitronium- or nitrosonium tetrafluoroborate (12 mmol) in dry dichloromethane (5 ml) under nitrogen. A vigorous reaction ensues, and gas evolution is observed. After 20 min at room temperature, the reaction is quenched with water, and the mixture extracted with dichloromethane (2 × 25 ml). Upon solvent removal, the dried organic extracts furnish an oil which is distilled (frothing!). The pure product is isolated by redistillation.

**Cleavage of Dimethylhydrazones with Nitronium- or Nitrosonium Tetrafluoroborate:**

A solution of the dimethylhydrazone (10 mmol) in dry dichloromethane (5 ml) is added dropwise to a stirred ice-cooled suspension of nitronium- or nitrosonium tetrafluoroborate (10 mmol) in dichloromethane (5 ml) under nitrogen. Stirring is continued for 1 h at 0°, the reaction is then quenched by the addition of water, and the mixture extracted with chloroform. The extract is dried and evaporated, the crude product is dissolved in benzene, and filtered through a short column of neutral alumina. Evaporation of the solvent gives the spectrally pure carbonyl compound.

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