A Powerful New Aldol Condensation Agent, Ba_3N_4[1]

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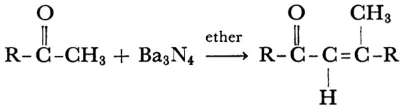
The thermal decomposition of many inorganic azides, especially those of heavy metals, proceeds explosively and results in the formation of the corresponding metal and nitrogen.[2] However, we have found that barium azide, $Ba(N_3)_2$, decomposes smoothly in organic solvents such as decalin or tetralin at the temperature of their respective boiling points to yield nitrogen and a fine black powder, barium pernitride, Ba_3N_4.[3,4]

Barium pernitride obtained was found to be exceedingly reactive with water and air. We now wish to report that this compound is also a highly active catalyst for an aldol condensation. Indeed, barium pernitride exhibits much greater reactivity than that of aluminum tri-*t*-butyl alcoholate, known as a powerful catalytic agent for this reaction.[5]

The typical results are described as follows. Barium azide (10 g.) and decalin or tetralin (50 ml.) were placed in a 100 ml. pyrex three-neck flask equipped with a Liebig reflux condenser. The air in the apparatus was replaced with dry nitrogen. The flask was heated slowly in an oil bath. The decomposition reaction started within 20 min. and after the solvents reached the boiling point, the mixture was refluxed for 30—40 min. to complete the reaction.

Upon cooling the system, the solvent was replaced with 50 ml. dried ether under a stream of dry nitrogen. Dried acetone (25 g.) was added dropwise into the suspension of Ba_3N_4 in ether with stirring at -15 to -20°C during 30 min. Mesityl oxide (14.2 g., b. p. 133°C/757 mmHg, 2, 4-dinitrophenylhydrazone m. p. 204°C) and diacetone alcohol (5.8 g., b. p. 160°C/757 mmHg, 2, 4-dinitrophenyl hydrazone m. p. 202°C) were obtained as the main products. When an excess of Ba_3N_4 was used, the dehydrate, mesityl oxide, was the only product formed (according to Eq. 1).

Ba_3N_4 (prepared from 12.2 g. $Ba(N_3)_2$) suspended in 60 ml. ether was reacted with 32 g. acetophenone at 30°C for 1 hr. Dypnone (25 g., b. p. 133°C/0.5 mmHg, 2, 4-dinitrophenylhydrazone m. p. 167°C, authentic compound m. p. 167°C[5]) was obtained.



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + Ba_3N_4 \xrightarrow{ether} R{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{H}{|}}{C}{=}\overset{\overset{CH_3}{|}}{C}{-}R} \qquad\qquad$$
$$+ N_2 + NH_3 + Ba(OH)_2 \qquad (1)$$

where $R=CH_3$ or C_6H_5.

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[1] Decomposition of Azides. II. Part I: Y. Okamoto and J. C. Goswami, *Inorg. Chem.*, **5**, 1281 (1966).

[2] For general discussion and references: a) F. P. Bowden and A. D. Yoffe, "Fast Reactions in Solids," Academic Press, Inc., New York, N. Y. (1958); b) P. Gray, *Quart. Revl (London)*, **1963**, 441.

[3] Y. Okamoto and J. C. Goswami, *Inorg. Chem.*, **5**, 1281 (1966).

[4] A possible constitution of Ba_3N_4 is the barium tetrazane salt, $3Ba^{+2}$ $(-\overset{|}{N}-\overset{|}{N}-\overset{|}{N}-\overset{|}{N}-)^{6-}$. Further investigation of the structure is being studied currently.

[5] W. Wayne and H. Adkins, *Org. Syn.*, **21**, 39 (1941).