A Novel Amination Dehydration of Nitromethane by Tris(dimethylamino)arsine

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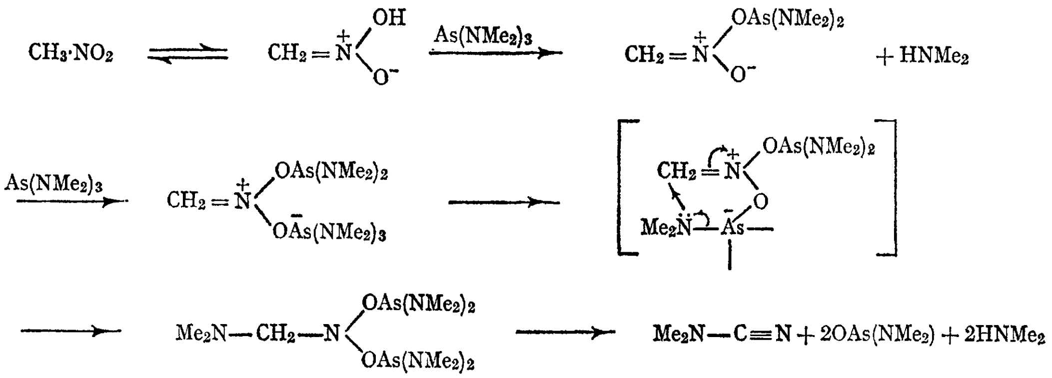
TRIS(DIMETHYLAMINO)ARSINE has been reported to interact with a number of dipolar molecules to give primarily exchange of substituents or insertion type reactions.[1] However, its reaction with nitromethane was found to be quite different giving rise to both amination and dehydration.



Tris(dimethylamino)arsine reacts with nitromethane exothermically evolving a large quantity of dimethylamine (identified by mass spectroscopy). A precipitate of arsenic trioxide (identified by *X*-ray diffraction) is formed, and an oil which was shown to be dimethylcyanamide (80% yield; b.p. 42°/6 mm.; n.m.r.: τ 7·97, 7% in benzene, tetramethylsilane internal standard; infrared spectrum identical with that of an authentic sample*).

A plausible mechanism for this transformation is described below.

$OAsNMe_2$ very likely has no discrete existence except as a unit in an –As–O–As–O– ring or chain molecule which can continue to react until the dimethylamino-groups are depleted.

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* An authentic sample of dimethylcyanamide was generously supplied by the American Cyanamide Co.

[1] H. J. Vetter and H. Nöth, *Z. anorg. Chem.*, 1964, **330**, 233.