Regiospecific Control of the Ene Reaction of *N*-Phenyl-1,2,4-triazoline-3,5-dione

By ARAVAMUDAN GOPALAN, RUDI MOERCK, and PHILIP MAGNUS*

(*Evans Chemistry Laboratory, The Ohio State University,* 140 *West* 18*th Avenue, Columbus, Ohio* 43210)

Summary *N*-Phenyl-1,2,4-triazoline-3,5-dione reacts with allylsilanes to give adducts of either type (A) or type (B) depending upon the substituents E (H or CN).

INTRODUCTION of amine functionality at a tertiary carbon is a difficult synthetic operation.[1] We sought to investigate the applicability of the ene reaction of allylsilanes† with the potent electrophile *N*-phenyl-1,2,4-triazoline-3,5-dione

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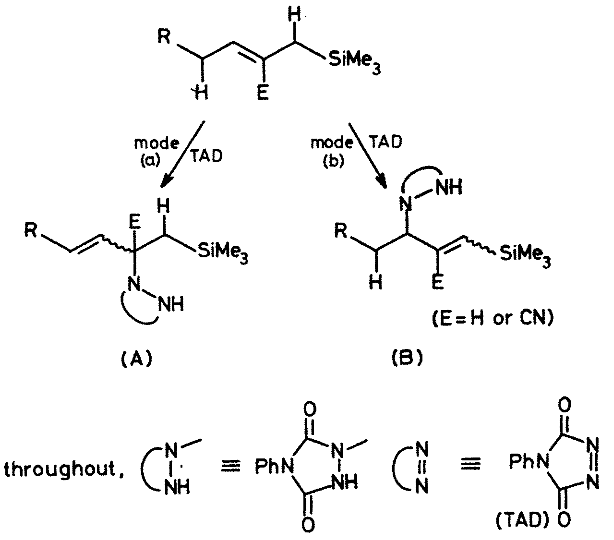
† The π-bond of an allylsilane is usually considered to be an electron-rich system because of the electropositive Si-atom. Prior to this study electron-deficient allylsilanes were unknown.

(TAD) to introduce nitrogen functionality at a highly substituted carbon atom. While TAD has been used extensively in organic synthesis,[2] and its reaction with allyltrimethylsilane and cyclic allylsilane documented,[3] no studies have described how substituents can affect the regiospecific outcome of ene reactions[4] between TAD and allylic systems capable of at least two modes of reaction (Scheme 1).

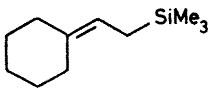


Scheme 1

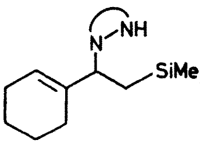
The allylsilane (**1**), prepared by the method of Seyferth,[5] was treated with TAD (room temperature, CH_2Cl_2) to give the adduct (**2**), 95%. No trace of any isomeric products could be detected. As a comparison ethylidenecyclohexane (**5**) reacted similarly giving only the ene product (**6**), 92%. The adamantylallylsilane (**3**), which can only react by mode (b), gave (**4**), 80%.

Diethyl cyanomethylphosphonate[6] was alkylated with iodomethyltrimethylsilane[7] (NaH, glyme) to give the reagent (**13**), 70%, b.p. 111—112 °C at 0·45 mmHg.[8] Treatment of (**13**) with sodium hydride in tetrahydrofuran followed by cyclohexanone gave (**7**), 57%; similarly cyclopentanone gave (**9**), 67%. When (**7**) and (**9**) were treated with TAD (room temperature, CH_2Cl_2) the adducts (**8**) and (**10**) were formed in near quantitative yield. Again no trace of any isomeric adducts could be detected. The compound (**11**) gave exclusively (**12**) when treated with TAD.

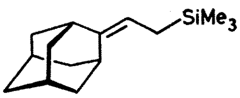
These results show that when E = H, pathway (a) is followed, and when E = CN, pathway (b) prevails. In a separate experiment benzyne was treated with (**1**) to give (**14**) (path a), albeit in low yield (*ca.* 20%).



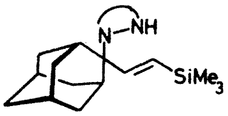
(1)



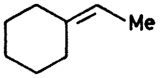
(2), m.p. 147-148 °C



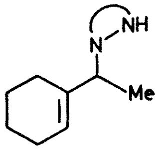
(3)



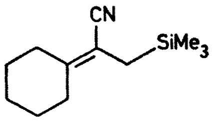
(4), m.p. 207-209 °C



(5)



(6)



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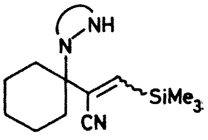

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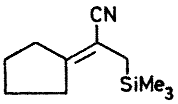
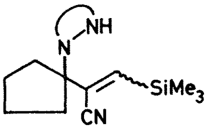
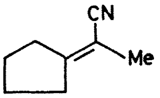


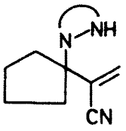
(9)



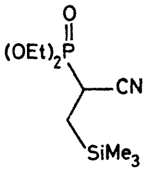
(10), m.p. 127-128 °C



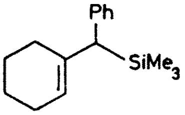
(11)



(12)

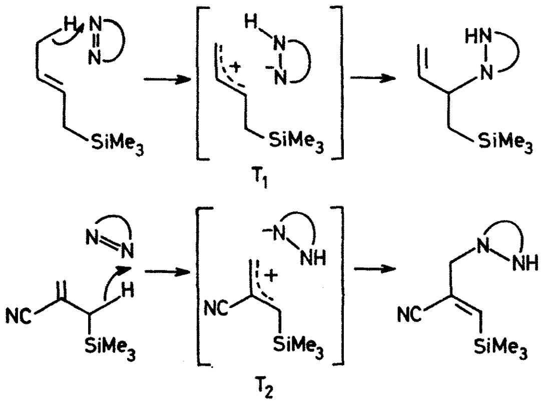


(13)



(14)

These regiochemical reversals can be rationalized by considering a polar transition state in which TAD removes a hydride ion from the substrate; the two transition states (Scheme 2) are T_1 and T_2. In T_1 there is a build-up of positive charge β- to the trimethylsilyl group, an energetically favourable situation,[9] leading to the observed products, (**2**) and (**6**). The alternative mode would cause a build-up of positive charge α- to the trimethylsilyl group. The cyano group completely overwhelms the trimethylsilyl group and the transition state T_2 involves the build-up of positive charge β- to the cyano group and α- to the trimethylsilyl group. Furthermore the double bond in mode (b) remains in conjugation with the cyano group. The alternative mode would produce a build-up of positive



Scheme 2

charge α- to the cyano group, forming an exceedingly high-energy intermediate. A concerted mechanism is of course feasible, but not so convenient to explain these results.

In summary, the electron-deficient αβ-unsaturated cyano compounds (**7**), (**9**), and (**11**) provide, because of electronic reasons, access to the adducts (**8**), (**10**), and (**12**), where a nitrogen functionality has been introduced at a hindered tertiary carbon atom.

All new compounds gave satisfactory spectral and analytical data in complete agreement with the proposed structures.

The N.S.F. is acknowledged for support of this work.

(*Received*, 6*th February* 1979; *Com.* 111.)

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[1] See L. Overman, *J. Amer. Chem. Soc.*, 1974, **96**, 597; L. E. Overman and M. Katımoto, *J. Org. Chem.*, 1978, **43**, 4564 and references therein.

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[8] For recent examples of alkylated phosphonates see M. F. Semmelhack, J. C. Tomesch, M. Czarny, and S. Boettger, *J. Org. Chem.*, 1978, **43**, 1259; W. A. Kleschick and C. H. Heathcock, *ibid.*, 1978, **43** 1256.

[9] For the most recent and comprehensive review of silicon chemistry see: W. E. Colvin, *Chem. Soc. Rev.*, 1978, **7**, 15.