

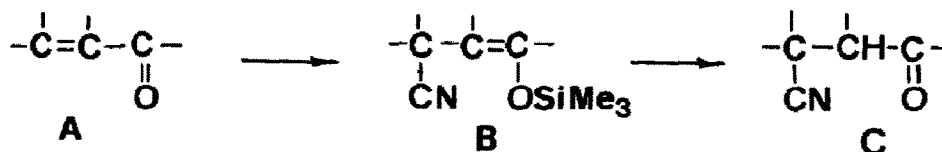
CONJUGATED ADDITION OF CYANOTRIMETHYLSILANE TO α,β -UNSATURATED KETONES

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Summary: Triethylaluminium-mediated reaction of cyanotrimethylsilane with 6-methylbicyclo[4.4.0]dec-1-en-3-one affords a mixture of diastereomeric 1,4-adducts. The reaction is kinetically controlled in toluene, whereas thermodynamically in refluxing THF. 4-Methyl-3-penten-2-one and carvone analogously give the respective 1,4-adducts and a conjugated dienone addords the 1,6-adduct in good yield.

Conjugated hydrocyanation of α,β -unsaturated carbonyl compounds with diethylaluminium cyanide has attracted considerable attention as a powerful tool in organic synthesis.¹ Selective 1,2-addition to enones has, however, been recorded with cyanotrimethylsilane.² This paper describes a novel conjugated addition of cyanotrimethylsilane to enones as well as a dienone by the action of triethylaluminium. The resulting cyanated siloxyalkenes B are useful intermediates in synthetic work³ and are easily transformed to β -cyano ketones C upon acidic hydrolysis.



To a solution of cyanotrimethylsilane (2.2 mmol, 0.28 ml) and triethylaluminium (2.0 mmol, 2.2 ml of 15% hexane solution) in 4 ml of THF was added 6-methylbicyclo[4.4.0]dec-1-en-3-one (I, 1 mmol, 0.16 g) at room temperature. The mixture was stirred at reflux for 20 h, cooled, worked up with aq. NH_4Cl , and extracted with benzene. The combined organic layers were washed (aq. NH_4Cl , sat. NaHCO_3 , brine), dried (MgSO_4), and concentrated affording 0.26 g (quant.) of a mixture of 1,4-adduct isomers (cis/trans = IIa/IIb = 95/5, thermodynamically controlled).^{4,5} When the reaction time was reduced to 3 h, the transformation was less sufficiently selective (IIa/IIb = 55/45, quant. yield). Moreover, the reaction seems to be kinetically controlled in toluene at room temperature, leading quantitatively to the 1,4-adducts (IIa/IIb = 31/69)⁶ after stirring for

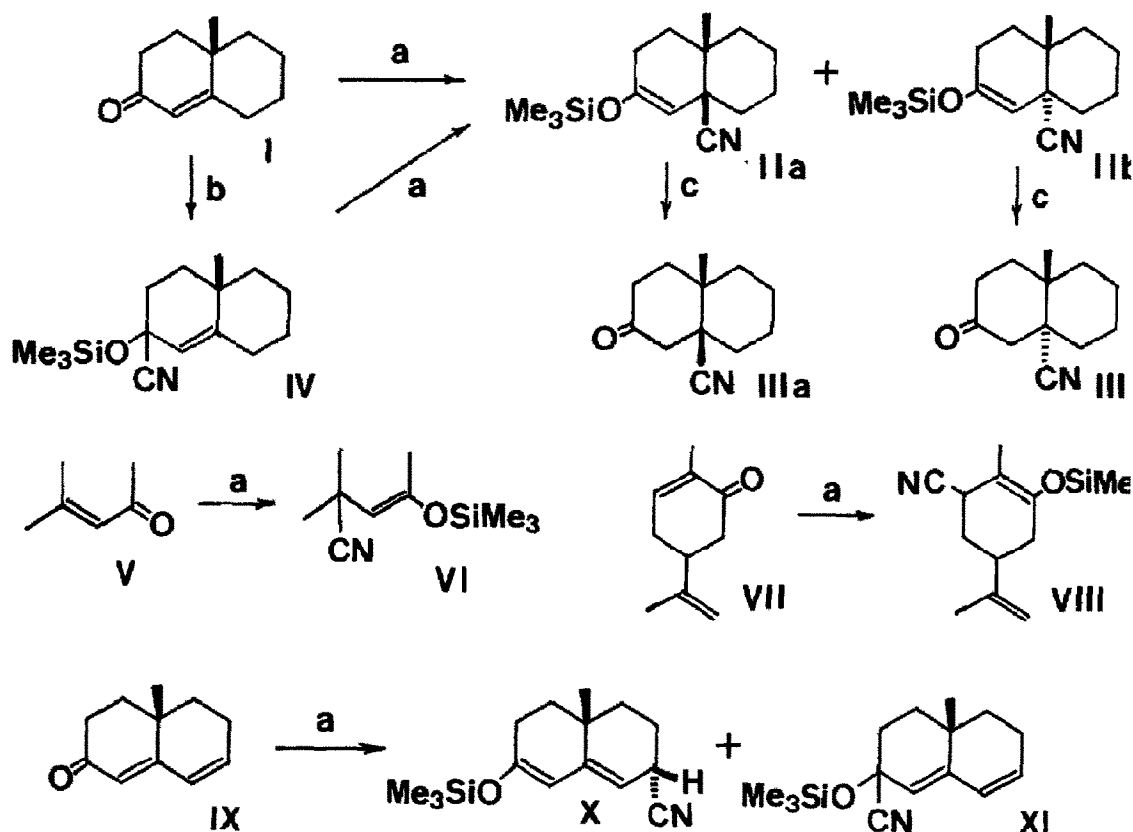
20 h. Hydrolysis of the 1,4-adducts, IIa and IIb, with dil. hydrochloric acid-THF gave β -cyano ketones, IIIa and IIIb, respectively, in quantitative yields.

When the reaction was carried out with 0.2 equiv. of triethylaluminium at room temperature for 3 h, a 1,2-adduct IV was obtained in 92% yield.⁷

Treatment of the 1,2-adduct (1 mmol) with triethylaluminium (2 mmol) and cyanotrimethylsilane (1.1 mmol) in 4 ml of THF in reflux for 3 h gave a mixture of 1,4-adducts (IIa/IIb = 67/33) in 95% yield. The reaction in toluene at room temperature overnight afforded a mixture (IIa/IIb = 46/54) in 96% yield.⁸

4-Methyl-3-penten-2-one (V, 2 mmol) was treated with cyanotrimethylsilane (4.4 mmol) and triethylaluminium (4 mmol, 4.4 ml of 15% hexane solution) in 8 ml of THF under reflux for 3 h affording the 1,4-adduct VI in 87% yield.³ The same reaction in THF at room temperature for 3 h gave the 1,2-adduct only.

Treatment of carvone (VII, 1 mmol) with cyanotrimethylsilane (2.2 mmol) and triethylaluminium (2 mmol) in refluxing 4 ml of THF for 6 h gave the adduct VIII in quantitative yield. The reaction in toluene overnight at room temperature afforded the same product VIII (quant. yield).^{3,9}



a: $\text{Me}_3\text{SiCN} + \text{Et}_3\text{Al}$ (2 equiv.)

b: $\text{Me}_3\text{SiCN} + \text{Et}_3\text{Al}$ (0.2 equiv.)

c: THF-dil. HCl

Application of this procedure to a conjugated dienone IX (1 mmol, treatment with 2.2 mmol of cyanotrimethylsilane and 2.0 mmol of triethylaluminium) afforded the expected 1,6-adduct X in 71% yield in refluxing THF for 20 h.¹⁰ On the other hand the reaction in toluene at room temperature for 20 h provided X in 35% yield and a substantial amount (12% yield) of the 1,2-adduct XI.

Catalytic action of diethylaluminium chloride or tripropylborane is illustrative of the applicability of other Lewis acids. Compound I was treated with cyanotrimethylsilane (2.2 equiv.) and diethylaluminium chloride (3.1 equiv.) in toluene at 0°C for 1 h affording a mixture of IIa and IIb (31/69) in quantitative yield and substitution of diethylaluminium chloride with tripropylborane gave the mixture in 72% yield after stirring at 0°C for 26 h.

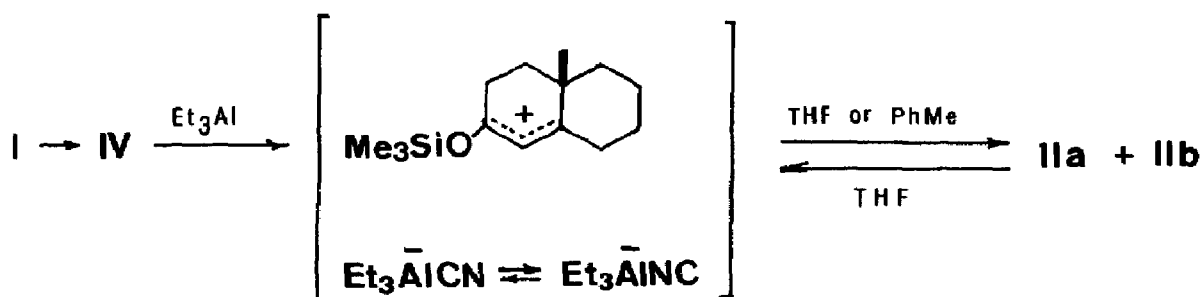
As can be seen from the above described results this reaction provides a convenient procedure of conjugated hydrocyanation. Synthetic applications of this procedure are under investigation.¹¹

REFERENCES AND NOTES

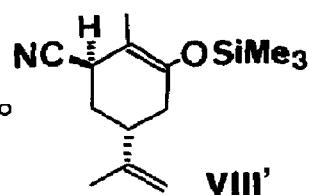
- (1) (a) W. Nagata, M. Yoshioka, and S. Hirai, J. Am. Chem. Soc., **94**, 4635 (1972); (b) W. Nagata, M. Yoshioka, and M. Murakami, ibid., **94**, 4644, 4654 (1972); (c) W. Nagata, M. Yoshioka, and T. Terasawa, ibid., **94**, 4672 (1972); (d) W. Nagata and M. Yoshioka, Org. React., **25**, 255 (1977).
- (2) (a) D. A. Evans, L. K. Truesdale, and G. L. Carroll, J. Chem. Soc. Chem. Commun., 55 (1973); (b) D. A. Evans, G. L. Carroll, and L. K. Truesdale, J. Org. Chem., **39**, 914 (1974); (c) D. A. Evans, J. M. Hoffman, and L. K. Truesdale, J. Am. Chem. Soc., **95**, 5822 (1973); (d) K. Deuchert, U. Hertenstein, and S. Hünig, Synthesis, 777 (1973).
- (3) Cyanated siloxyalkenes of type B have been prepared by the conjugated addition of diethylaluminium cyanide to enones followed by trapping of the resulting aluminium enolates with chlorotrimethylsilane: M. Samson and M. Vandewalle, Synth. Commun., **8**, 231 (1978).
- (4) Isolation of neither pure IIa nor IIb was successful yet. GLC (HVSG) could not separate the two components. The ratio of the products was determined by nmr as well as by glc of the hydrolyzed products IIIa and IIIb. The mixture of IIa and IIb shows: ir (neat) 2250, 1660, 1255, 1215, 878, 850, 759 cm^{-1} ; nmr (CCl_4) besides methylene protons (δ 1.1-2.5, m, 12H) and methyl protons of trimethylsilyl group (δ 0.21, s, 9H), angular methyl protons (δ 0.94, s, IIb; δ 1.18, s, IIa, the sum was equal to 3H), olefin proton (δ 4.50, broad s, IIb; δ 4.58, broad s, IIa, the total integration corresponded to 1H).
- (5) Thermodynamically controlled conjugated hydrocyanation with diethylaluminium cyanide gives a mixture of IIIa and IIIb in 87/13 ratio, reportedly (ref. 1c).
- (6) Kinetically controlled reaction with diethylaluminium cyanide provides a

mixture of IIIa and IIIb in 36/64 ratio. The ratio changes to 29/71 upon treatment with hydrogen cyanide-triethylaluminium in place of diethylaluminium cyanide (ref. 1c).

- (7) GLC and ^{13}C -nmr (*vide infra*) suggested the homogeneity of the 1,2-adduct whose stereochemistry was not determined yet. Lanthanoid-shifted nmr gave complicated charts which could not be analyzed. ^{13}C nmr (CDCl_3 , 20 MHz), shows 13 carbon atoms: δ ppm, 1.57, 22.03, 23.35, 28.07, 32.13, 33.77, 34.94, 36.11, 41.53, 68.72, 121.10, 121.56, 149.34.
- (8) The absence of the additional cyanotrimethylsilane in the isomerization of IV to II has yielded a complex mixture, although the role of the cyanosilane is not clear yet. Following assumptions explain the observed rearrangement.



- (9) GLC of the crude product showed one peak with small shoulder. The structure of the major product could be assigned as VIII' based on the proton signal ($\underline{\text{H}}\text{-C-CN}$, δ 3.1 ppm, $[J = 10 \text{ Hz}]$) which corresponds to the quasi-equatorial proton.



- (10) TLC (Kieselgel 60, benzene) indicated the homogeneity of the product. The structure X was determined by nmr analysis: a multiplet ($\underline{\text{H}}\text{-C-CN}$, δ 3.2 ppm, 1H) changed to a double doublet ($J = 4, 6 \text{ Hz}$) by double irradiation at a doublet ($\text{C}=\underline{\text{C}}\text{-CH-CN}$, δ 5.0 ppm, $J = 5 \text{ Hz}$, 1H). These observations suggest the stereochemistry of the proton geminal to cyano group should be equatorial.
- (11) The authors wish to thank Drs. T. Imagawa and R. Yamaguchi for ^{13}C nmr measurement as well as the Ministry of Education, Science and Culture, Japan, for Grant-in-Aid (303023, 403022).

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