Pergamon

Tetrahedron Letters, Vol. 37, No. 36, pp. 6607-6610, 1996

0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)01411-6

Silicon as a Controlling Element for Regioselective Ene Reaction of Diethyl Azodicarboxylate with (Homo)Allylic Silanes. Applications to the Synthesis of Cyclic 1,2-Dinitrogen Compounds

Tarun K. Sarkar,* Binay K. Ghorai, Shyamal K. Das, Pulak Gangopadhyay and P.S.V.Subba Rao

Department of Chemistry, Indian Institute of Technology ,Kharagpur 721 302, India

Abstract : The reaction of diethyl azodicarboxylate with homoallylic silanes capable of two modes of reaction give ene adducts by preferential abstraction of allylic hydrogens nearer the silyl group. This regioselectivity has been exploited in the synthesis of some cyclic hydrazine derivatives.

Although the ene reaction has received considerable mechanistic and synthetic attention in the 50-plus years since its first systematic examination,[1] only a few studies concerning the regiochemistry of this transformation have been reported. These works reveal that a variety of structural and environmental factors such as hydrogen alignment,[2] rotational barriers,[3,4] secondary orbital interactions,[5] steric effects,[6-11] solvent effects,[12] and substituent field effects,[13] play important roles in dictating regiochemical outcome of this reaction.

Herein, we report the γ–effect[14] of a TMS substituent as a new structural factor which can influence the regiochemistry of ene reactions. Thus, we have found that the ene reaction of diethyl azodicarboxylate (DEAD) with homoallylic silanes is somewhat faster than with non-silylated systems and this enhanced reactivity is also reflected in the regiochemistry of hydrogen abstraction from homoallylic silanes with at least two reactive sites, like in the cases of γ-alkylated allylic silanes.[15,16] We have, furthermore, made use of this regiochemistry in the synthesis of some cyclic hydrazine derivatives.

From the classical mechanistic standpoint, it is generally agreed[17] that the concerted ene reaction involves a highly asynchronous transition state featuring a well-developed C,C bond prior to a relatively late proton transfer towards the incipient carbocation as shown in Figure 1(a) (X=electron withdrawing group). We reasoned that use of a homoallylic silane as the ene component in such a reaction with DEAD[18] as enophile could in principle stabilize the transition state *via* the percaudal interaction (the so-called γ-effect[14]) involving the backlobe of the carbon-silicon bonding orbital as shown in Figure 1(b), thereby allowing homoallylic silanes to act as activated ene donors in Alder ene reactions.[19,20]

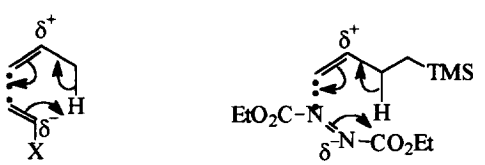
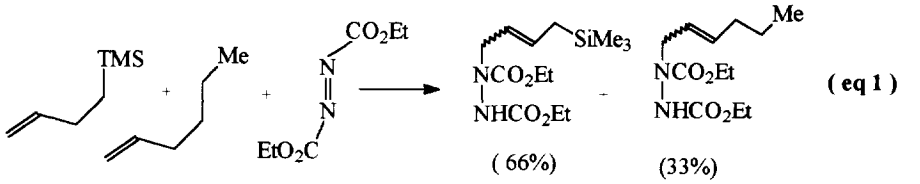


Figure-1 **(a)** **(b)**

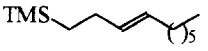
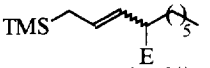
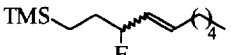
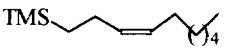
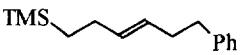
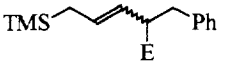
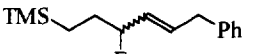
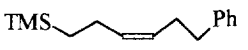
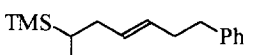
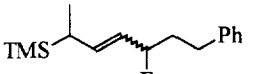
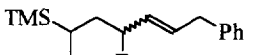
Accordingly, a competitive experiment was set up involving 4-trimethylsilyl-1-butene (10 mmol), 1-hexene (10 mmol) and DEAD (1 mmol) in benzene in a sealed tube at 90°C (eq. 1) : the homoallylsilane, in fact, was found to be twice as reactive as 1-hexene. It may be mentioned here that toward DEAD, allyltrimethylsilane having a π-homo orbital of higher energy is only 3.7 times more reactive than 1-hexene.[21]

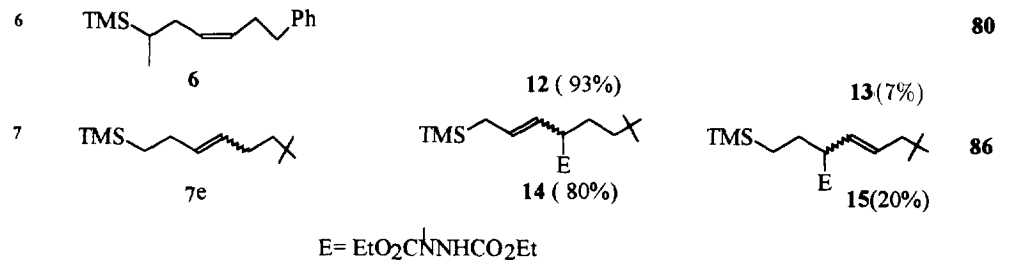


(eq 1)

Because a hydrogen β to silyl group is somewhat more easily removed than a hydrogen that is not, it is conceivable that with substituted homoallylic silanes, the ene reaction will be directed into the silicon-containing part of the alkenes. Thus, a series of homoallylic silanes **1-7** with variation in olefinic geometry and substitution pattern was exposed to DEAD in benzene at 90°C and the results are summarized in Table 1. These experiments show a general preference for hydrogen abstraction from the carbon which is nearer the silyl group and is most impressively demonstrated with **7** having a t-butyl group on one end and a TMS group on the other end of the alkene. Incidentally, the regiochemistry in these reactions is insensitive to the geometry of the homoallylic silanes.

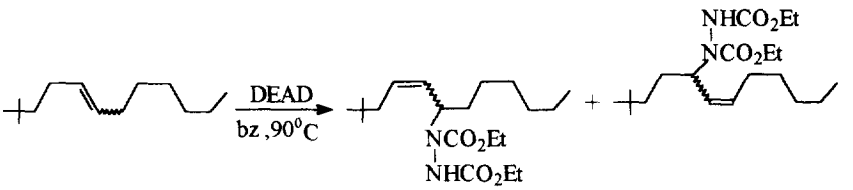
Table 1[e]. Regioselective Reactions of DEAD with Homoallylic Silanes

Entry	Substrates	Products[f]		Combined
		Allylic silanes [g]	bis-Homoallylic silanes [g]	Yield(%)[h]
1	 **1a**	 **8** (77%)	 **9** (23%)	77
2	 **2b**	**8** (77 %)	**9**(23%)	75
3	 **3**	 **10**(82%)	 **11**(18%)	83
4	 **4[c]**	**10** (85%)	**11**(15%)	87
5	 **5[d]**	 **12** (93%)	 **13**(7%)	84



[♀] All compounds were characterized by high-field ^{1}H NMR and GC-MS [a] *E/Z*=82/18; [b] *E/Z*=26/74; [c] *E/Z*=11/89; [d] *E/Z*=93/7; [e] *E/Z*=20/80; [f] product ratio was determined by high-field ^{1}H NMR and GC-MS; [g] predominantly *E*-isomer; [h] isolated yields of chromatographically pure products (homogeneous on TLC)

A single experiment was next carried out which indicated total lack of regioselectivity when the TMS substituent is absent (eq. 2).

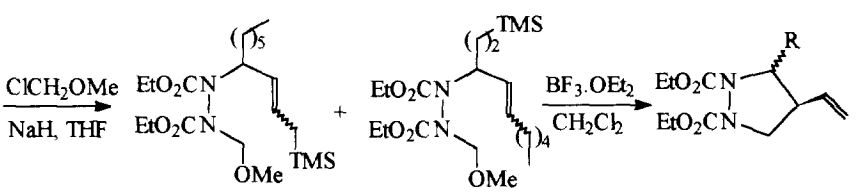


(eq.2)[22]

16(E/Z=22/78) **17**(53%) **18**(47%)

It thus appears that the development of the partial positive charge on the carbon γ to silicon may be more important than any unequal charge development in the hydrogen transfer part of the ene reaction. The interaction of silicon with a transient γ-positive charge in the transition state activates the alkenes and influences regiochemistry of hydrogen abstraction from substituted homoallylic silanes, although to a lesser extent when compared to similar reactions with allylsilanes as ene donors.[21]

Finally, the utility of acyclic hydrazides enriched in the isomer containing an allylsilane functionality was briefly examined for the synthesis of cyclic hydrazine derivatives, a class of compounds which are attractive objects of study both in their own right, and as analogues of bioactive mono-nitrogen compounds.[23] To this end, **8/9** was converted to the methoxy-methyl substituted hydrazides **19/20** and the latter on exposure to $BF_3.OEt_2$ gave **21** as a mixture of diastereomers,albeit in low overall yield,[23] after careful preparative layer chromatography of the crude product. Similarly, **21** {R=$(CH_2)_2$Ph} could be obtained from **10/11** (eq. 3.).[24]



(eq 3)[24]

Acknowledgement : This work was supported by CSIR, New Delhi [01(1368)/95-EMR-II].

References & Notes

1. Alder, K.; Pascher, F.; Schmitz, A. *Ber. Dtsch. Chem. Ges.* 1943, **76B**, 27.
2. Gollnick, K.; Schenck, G.O. In "*1,4-Cycloaddition Reactions. The Diels Alder Reaction in Heterocyclic Synthesis;*" Hamer, J., Ed.; Academic Press : New York,New York, 1967, **8**, pp. 255.
3. Houk, K.N.; Williams, J.C., Jr.; Mitchell, P.A.; Yamaguchi, K.J. *J. Amer. Chem. Soc.* 1981, **103**, 949.
4. Clennan, E.L.; Chen, X.; Koola, J.J. *J. Amer. Chem. Soc.* 1990, **112**, 5193.
5. Stephenson, L.M. *Tetrahedron Lett.* 1980, **21**, 1005.
6. Clennan, E.L.; Koola, J.J.; Oolman, K.A. *Tetrahedron Lett.* 1990, **31**, 6759.
7. Elemes, Y.; Stratakis, M.; Orfanopoulos, M. *Tetrahedron Lett.* 1989, 6903.
8. Orfanopoulos, M.; Stratakis, M.; Elemes, Y. *Tetrahedron Lett.* 1989, **30**, 4875.
9. Orfanopoulos, M.; Stratakis, M.; Elmes, Y. *J. Amer. Chem. Soc.* 1990, **112**, 6417.
10. Orfanopoulos, M.; Stratakis, M..; Elemes, Y.; Jensen, F. *J. Amer. Chem. Soc.* 1991, **113**, 3180.
11. Mikami, K; Loh, T.P.; Nakai, T. *J. Amer. Chem. Soc.* 1990, **112**, 6737.
12. Orfanopoulos, M.; Stratakis, M. *Tetrahedron Lett.* 1991, **32**, 7321.
13. Clennan, E.L.; Koola, J.J. *J. Amer. Chem. Soc.* 1993, **115**, 3802.
14. For a review see : Lambert, J.B. *Tetrahedron.*1990, **46**, 2677.
15. Dubac, J.; Laporterie, A.; Iloughmane, H.; Pillot, J.P.; Deleris, G.; Dunogues, J. *J. Organomet. Chem.* 1985, **281**, 149.
16. For a review on ene and retro-ene reactions in group 14 organometallic chemistry : Dubac, J.; Laporterie, A. *Chem. Rev.* 1987, **87**, 319.
17. Hoffmann, H.M.R. *Angew. Chem. Int. Ed. Engl.* 1969, **8**, 556.
18. Thaler, W.A. Franzus, B. *J. Org. Chem.* 1964, **29**, 2226.
19. Taber, D.F.*"Intramolecular Diels-Alder and Alder Ene Reactions"*, Springer-Verlag, Berlin, 1984, pp. 66.
20. In a number of related pericyclic reactions, either accelerating or retarding influence of the TMS substituent has been documented : (a) Magnus, P.; Cairns, P.M.; Moursoundis, J. *J. Amer. Chem. Soc.* 1987, **109**, 2469. (b) Fleming, I.; Goldhill, J.; Perry, D.A. *J. Chem. Soc. Perk I*, 1982, 1563.
21. Laporterie, A.; Dubac, J.; Lesbre, M. *J. Organomet. Chem.* 1975, **101**, 187.
22. Product ratio was determined by high-field ^{1}H-NMR and capillary GC.
23. (a) Rutjes, F.P.J.T.; Hiemstra, H.; Mooiweer, H.H.; Speckamp, W.N. *Tetrahedron Lett.* 1988, **29**, 6975. (b) Rutjes, F.P.J.T.; Teerhuis, M.; Hiemstra, H.; Speckamp, W.N. *Tetrahedron* 1993, **49**, 8605.
24. For some selected spectroscopic data : **21** (R=$(CH_2)_2$Ph), ^{1}H-NMR(200 MHz, $CDCl_3$) δ 7.31 - 7.17 (m, 5H), 5.80 - 5.50 (m,1H), 5.17 - 5.06 (m, 2H), 4.30 - 4.10 (overlapping q's, 4H), 4.06 - 3.90 (m, 1H), 3.13 - 3.03 (m, 2H), 2.80 - 2.60 (m, 3H), 1.90 -1.70 (m, 2H), 1.26 (overlapping t's, 6H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 157.35(s), 157.29(s), 141.69(s), 141.58(s), 136.49(d), 133.14(d), 128.46(d), 128.33(d), 128.14(d), 127.40(d), 125.87(d), 118.84(t), 117.06(t), 62.51(t), 62.39(t), 62.31(t), 62.24(t), 51.85(t), 50.38(t), 51.11(d), 47.07(d), 35.91(t), 32.64(t), 32.36(t), 29.76(t), 14.54(q), 14.47(q).

(*Received in UK* 26 *June* 1996; *accepted* 19 *July* 1996)