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A Regiospecific Ene Reaction between γ-Alkylated Allyltrimethylsilanes and TCNE

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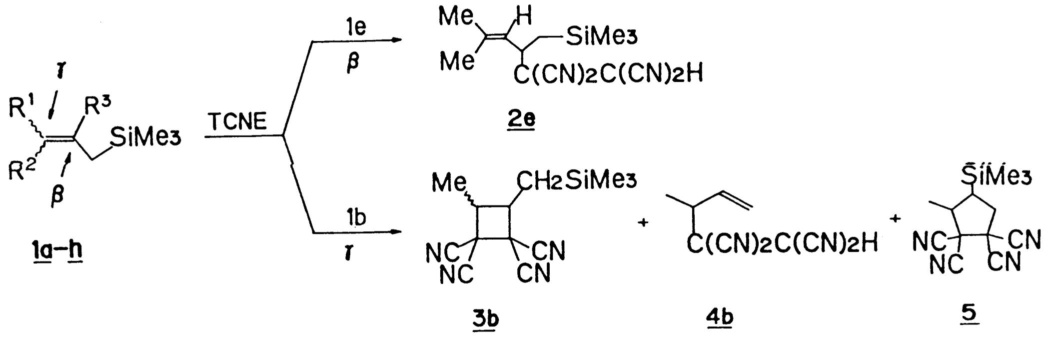
TCNE undergoes a regiospecific ene reaction with γ-alkyl (Et, Bu, i-Pr, and c-C_6H_{11}) substituted allyltrimethylsilanes via an addition to the allylic β-carbon and a hydrogen abstraction from the γ-alkyl group.

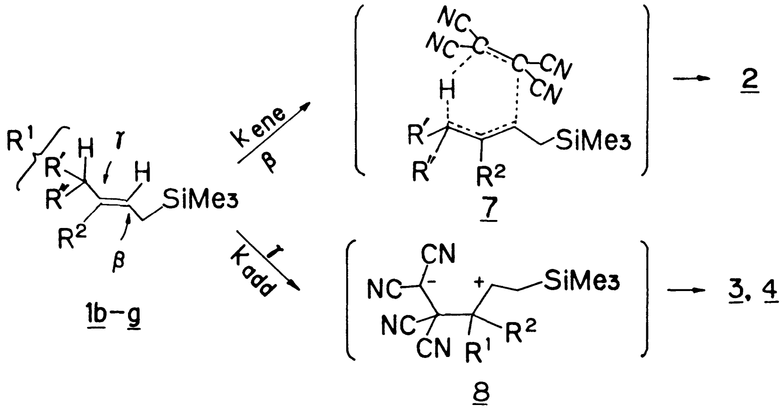
Tetracyanoethylene (TCNE) is a potential good enophile but surprisingly its ene reactions with simple alkenes have rarely been exemplified.[1] TCNE undergoes a [2+2] cycloaddition reaction with allyltrimethylsilane (**1a**).[2] Now we show an alternative process, an ene reaction, to occur predominantly when alkyl groups are present at the allylic γ-carbon.

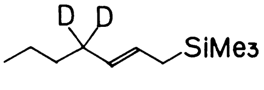


a) $R^1=R^2=R^3=H$, b) $R^1=Me$; $R^2=R^3=H$, c) $R^1=Et$; $R^2=R^3=H$, d) $R^1=Bu$; $R^2=R^3=H$,
e) $R^1=i\text{-}Pr$; $R^2=R^3=H$, f) $R^1=c\text{-}C_6H_{11}$; $R^2=R^3=H$, g) $R^1=R^2=Me$; $R^3=H$, h) $R^1=R^2=H$; $R^3=Me$

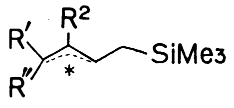
A purple solution of TCNE (0.10 mmol) and 1.1 equiv. trans-(4-methyl-2-pentenyl)trimethylsilane (**1e**) in dichloromethane (50 cm^3) became colorless on standing at 25 °C for a week under argon affording an ene product, 1,1,2,2-tetracyano-5-methyl-3-(trimethylsilylmethyl)-4-hexene (**2e**), in 92% isolated yield.[3] The reaction with cis-**1e** gave the same product as well, although the cis-isomer was much less reactive than the trans-isomer. A similar ene reaction also occurred cleanly with (3-cyclohexyl-2-propenyl)-trimethylsilane (**1f**). In contrast, 2-butenyl- and (2-methyl-2-propenyl)-

trimethylsilanes (**1b** and **1h**) did not yield ene products at all under similar reaction conditions; these β- and γ-methyl substituted allylsilanes exclusively gave [2+2]cycloadducts **3** together with a small amount of open products **4**, as does the parent allyltrimethylsilane.[2) A small amount of a cyclopentane derivative **5** was also obtained in the reaction with trans-**1b**. The [2+2] cycloaddition was practically stereospecific for trans-**1b** but not for cis-**1b** (74% d.e.) providing a stereochemical support for a stepwise mechanism involving a γ-addition of TCNE to form a zwitterion **8**.[2) On the other hand, both the ene and the cycloaddition reactions occurred competitively in the cases of 2-pentenyl- and 2-heptenyltrimethylsilanes (**1c** and **1d**). These results are listed in Table 1 which also includes the relative reactivity (k_{rel}) of the allylsilanes determined by competition experiments. The relative rates for the ene (k_{ene}) and the γ-addition (k_{add}) reactions were estimated from the k_{rel} and product ratios [**2**/(**3**+**4**)].





1d-4,4-d2



9 (radical)
10 (cation)

Several features are apparent. First, the relative rates for the γ-addition decreases with increasing steric size of the γ-alkyl groups in the order (H) < Me < Et < i-Pr, while the ease of the ene reaction increases in this order in dichloromethane solutions. It is also noteworthy that a γ,γ-dimethyl substrate **1g** underwent the ene reaction instead of the cycloaddition in contrast to the γ-methyl substrate **1b**. Second, the ene and the γ-addition reactions make different responses to the change in solvent polarity. Thus, in the case of **1c**, the ene reaction predominated in dichloromethane, while the γ-addition occurred preferentially in acetonitrile. A similar dramatic solvent effect was also seen in the reaction with **1g**. Apparently, a polar solvent facilitates the γ-addition.[4) **1e**, however, cleanly underwent the ene reaction in acetonitrile as well as in dichloromethane. The second-order rate constants for this ene reaction in these two solvents were determined spectrophotometrically under pseudo first-order reaction conditions as follows: $k_2 = 2.20 \times 10^{-4}$ and 3.84×10^{-5} $dm^3\ mol^{-1}\ s^{-1}$ in dichloromethane and in acetonitrile respectively at 25 °C. The solvent effect is relatively small, but obviously the rate of the ene reac-

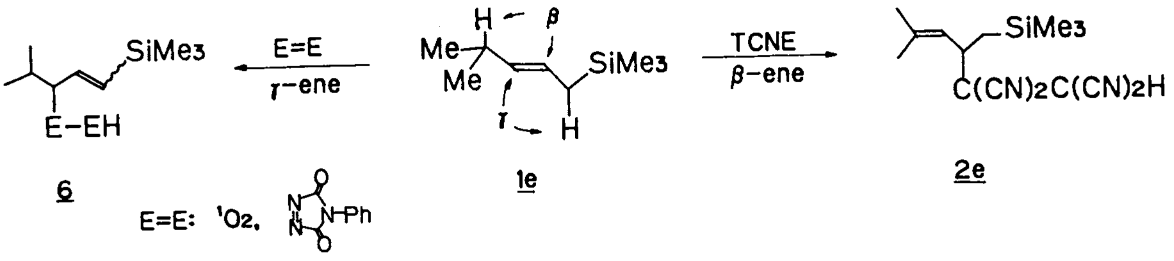
Table 1. Reaction of TCNE with 2-Alkenyltrimethylsilanes

Substrate	Conditions[a)]	Yield % [b)]	Ratios 2	3	4	Relative reactivity k_{rel}[c)]	k_{ene}	k_{add}
1a				>95	<5[d)]	1.0		1.0
trans-**1b**	A, 7 d	88[e)]	0	>98[f)]		0.49	v.slow	0.49
cis-**1b**	A, 26 d	91	0	81[g)]	19	0.10	v.slow	0.10
trans-**1c**	B, 30 d	95[h)]	82[f)]	18		0.41	0.07	0.34
trans-**1d**	C, 4 d	97[i)]	87[f)]	13				
trans-**1d**-4,4-d_2	C, 10 d	91[h)]	67	33				
trans-**1e**	B, 7 d	92	100			5.74	5.74	v.slow
cis-**1e**	B, 60 d	89[h)]	100			0.17	0.17	v.slow
trans-**1f**	B, 4 d	94	100					
1g	B, 210 d	85	>95		<5	0.047	0.045	<0.002
1h	B, 1 d	77	0	100		$>10^3$		$>10^3$
trans-**1c**	D, 3 d	88	11	7	82			
trans-**1e**	D, 7 d	75	100					
1h	D, 3 d	54[i)]	0		>95			

a) A; dichloromethane/45 °C, B; dichloromethane/25 °C, C; 1,2-dichloroethane/45 °C, D; acetonitrile/25 °C. b) Isolated yield. c) Determined by competition experiments in dichloromethane. d) Ref. 2. e) **5** (10%) was included. f) Exclusively trans. g) cis/trans=87/14. h) Yield was corrected for incomplete conversion. i) Yield of crude products.

tion decreases with increasing solvent polarity. Third, in the reaction between TCNE and trans-2-heptenyltrimethylsilane (**1d**), deuterium-substitution at C_4 resulted in a significant change in the chemoselectivity: **2**/**3**=87/13 from **1d**, while 67/33 from **1d**-4,4-d_2. Provided the deuterium-substitution at C_4 does not affect the rate of the γ-addition, the observed product ratios lead to the primary kinetic isotope effect of k_H/k_D=3.3 for the ene reaction indicative of a rate-determining cleavage of a C_4-H bond.

Noteworthy is the regiospecificity of the present ene reaction. Typical enophiles, 4-phenyl-1,2,4-triazoline-3,5-dione (PTD) and singlet oxygen ($^1O_2$), underwent ene reactions with trans-**1e** not via the β-attack but via the γ-attack and H-abstraction from a trimethylsilylmethyl group



affording the corresponding vinylsilanes **6** as a single product in both cases.$^{5)}$ In addition, the relative order in k_{ene} for the TCNE-ene reaction markedly differs from those observed in the PTD-ene and the $^1O_2$-ene reactions: trans-**1e**:trans-**1c**:**1g**:trans-**1b**=1.0:0.06: 0.008:<10^{-3} for the TCNE-ene, while 1.0:2.0:7.6:2.1 and 1.0:7.2:72:3.8 for the PTD- and the $^1O_2$-ene reactions, respectively.$^{5)}$ Although the effect of the γ-alkyls on the TCNE-ene reaction is parallel to the stability of the corresponding alkyl radicals, a simple stepwise mechanism via an allylic radical **9** is unlikely because of the regiospecific formation of the β-ene product **2**. An ionic mechanism involving an allylic cation **10** is also untenable because of the negative solvent effect as well as the complete preservation of a trimethylsilyl group during the ene reaction. The present TCNE-ene reaction would probably be associated with the low ionization potentials of allylsilanes$^{6)}$ since simple alkenes are almost inactive to TCNE under the conditions given in Table 1. These results are consistent with a concerted mechanism between the neutral substrates (**7**) or most likely between their ion radicals.

A puzzling question is why TCNE does not lead to an ene product at all via its γ-attack in contrast to PTD and $^1O_2$. Presumably, the γ-addition is highly ionic to form a zwitterion **8** of which anion end is too weakly basic to abstract a proton and prefers to cyclize or accept a silyl group instead of a proton.$^{7)}$

References

1) Ene reactions of TCNE with several 1,3-dienes have been reported: A. M. Lautzenheiser and P. W. LeQuesne, Tetrahedron Lett., 1969, 207; P. D. Bartlett, Q. Rev., Chem. Soc., 24, 473 (1970).

2) G. D. Hartman and T. G. Traylor, Tetrahedron Lett., 1975, 939.

3) All new compounds showed satisfactory spectral and analytical data. The following is representative. **2e**: mp 109-110 °C; IR (Nujol) 2255, 1250, 860, 840 cm^{-1}; NMR (CCl_4) δ=0.05 (9H, s), 0.96–1.14 (2H, m), 1.81 (6H, s), 3.23 (1H, t of d, J=5, and 10 Hz), 4.35 (1H, s, disappeared on addition of D_2O), 4.96 (1H, broad d, J=10 Hz); Anal. (C, 63.31; H, 7.15; N, 19.65%).

4) R. Huisgen, Acc. Chem. Res., 10, 117 (1977) and references cited therein.

5) N. Shimizu, F. Shibata, S. Imazu, and Y. Tsuno, Chem. Lett., 1987, 1071.

6) W. Weidner and A. Schweig, J. Organomet. Chem., 39, 261 (1972).

7) A controlled reaction of TCNE with **1g** in CD_3CN indicated the formation of an $SiMe_3$-transferred product which instantly reacted with water to give **4g**.

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