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σ-π CONJUGATION IN TWO-STEP CYCLOADDITIONS (1,2)

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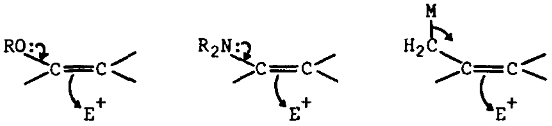
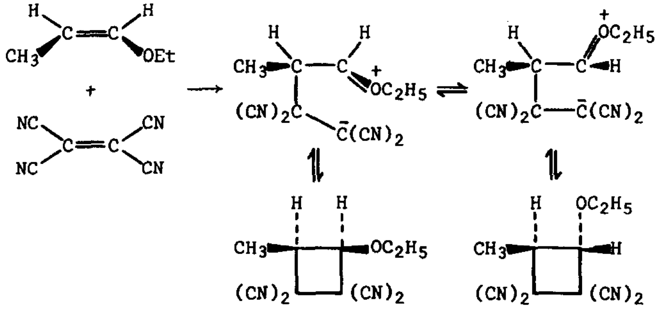
We wish to report a two-step cycloaddition of tetracyanoethylene to allyltrimethylsilane and other allyl derivatives of fourth group metals.

σ-π conjugation of carbon-metal bonds has been shown to be similar to n-π conjugation of lone-pair electrons in both its magnitude and geometrical effects (3). Quantitatively, the σ_p^+ values of R_3MCH_2 groups range from -0.3 to -1.3 (Si, Ge, Sn, Pb) (3a) compared to $\sigma_p^+ = -0.78$, -1.3 and -1.7 for MeO, $-NH_2$ and $-NMe_2$ respectively (4). These comparisons suggest that metalloalkyl olefins might take a place alongside enol ethers and enamines in increasing π-bond nucleophilicities in making carbon-carbon bonds (5).



As one test of this idea we chose to investigate the two-step cycloaddition of tetracyanoethylene, a reaction particularly well suited for the demonstration of resonance stabilized cationic intermediates (6-8) (reaction 1).

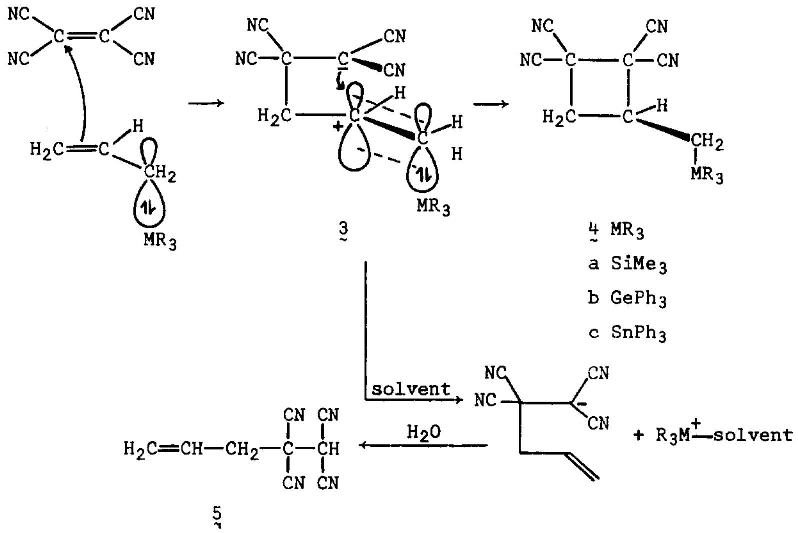


(1)

1 2

Because the rate of reaction 1 and the amount of epimerized product 2 increases with increasing solvent polarity, the indicated zwitter-ion mechanism was suggested (6,8)

Similarly, allyltriphenylstannane or allyltrimethylsilane reacted with TCNE more rapidly in more polar solvents to afford a mixture of two products which varied with solvent polarity. The reaction, along with an intermediate analogous to that in reaction 2, is shown below.



(2)

The products 4a and 5 from the allyltrimethylsilane were isolated in high yields from reaction with TCNE for one to three days at 50° in acetonitrile; purified and identified by spectra and analyses (9).

The percents of 5 in mixtures of 4a and 5 obtained in various solvents are compared with the percent epimerization in reaction 1 in Table 1 (10).

TABLE 1

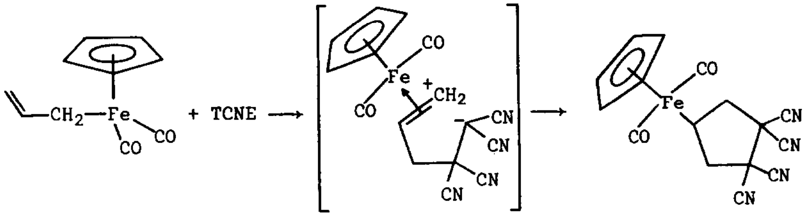
Percentage of Epimerized (trans) Product in the Reaction of Ethyl-1-Propenyl Ether and Open Chain Product from Reaction of Allyltrimethylsilane with Tetracyanoethylene.

Solvent	% Product 2 or 5	
	% 2, trans	% 5
CH_3CN	15	87
AcOEt	6	33
CH_2Cl_2	5	$<5^{a,b}$
C_6H_6	5	$<5^{a}$

- a. No 5 could be detected in the reaction mixture by nmr. The relative amounts of 4a and 5 were determined by nmr integration of reaction mixtures. In acetonitrile, these results were confirmed by isolation of the two products.
- b. Vinylferrocene afforded a quantitative yield of cycloaddition product in this solvent in 15 min. at room temperature (13).

In addition to the criteria of solvent effects upon rates and products, the rate dependence upon electron π donation by the metallomethyl group indicates the zwitter-ionic intermediate 3 (15). The rates of reaction are roughly: $\phi_3SnCH_2CH{=}CH_2 \cong$ (▷)$_2C{=}CH_2$ (17) > n-BuOCH$=$CH$_2$ (8b) $\cong$ FerCH$=$CH$_2$ > $Me_3SiCH_2CH{=}CH_2$ > ▷—CH=CH—◁ (17) in agreement with the σ^+ values of the groups Y in Y—CH$=$CH$_2$. Because simple olefins do not react with TCNE under our conditions and all the other reactions clearly proceed through zwitter-ionic intermediates, we conclude that all the products we observe are also derived from this kind of intermediate. Thus n-π conjugation by alkoxy groups, or σ-π conjugation by metalloalkyl groups or strained C—C bonds (17) leads to two-step zwitter-ionic addition to TCNE.

The results reported here can be contrasted to similar reactions of allyliron compounds studied by Giering and Rosenblum (18) in which rearranged products were obtained (19).



(3)

While their products are consistent with the bridged formulation, our cyclobutane products cannot be explained in this way. We therefore prefer to formulate all such reactions as analogous to eq. 2 in which the reactivity results from σ-π conjugation and the barrier to rearrangement as well as the secondary to primary cation equilibria depend upon the nature of the metal.

These results seem to confirm the idea that fourth-group metalloalkyl olefins behave like vinyl ethers towards electrophiles.

References

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2. Presented at the Pacific Coast Regional ACS Meeting, San Diego, Ca., November, 1973.
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9. Elemental analyses were consistent with the assigned structures. The proton nmr of **5**, mp 61-62°, was: ($CDCl_3$) 3.00 δ (2 H, d); 4.50 δ (1 H, s)*; 5.75 δ (3 H, m) while that of **4a** was: ($CDCl_3$) 0.10 δ (9 H, s); 1.25 δ (2 H, d); 3.30 δ (3 H, m). The decoupled ^{13}C magnetic resonance spectra of **4a** and **5** were recorded in CD_3COCD_3, and, expressed in ppm downfield from TMS, the singlet absorptions were: 30.6, 39.0, 39.4, 107.3, 110.2, 125.2, and 126.9 ppm for **5**; and 0.2, 22.5, 35.7, 40.9, 43.7, 46.2, 111.9, 113.4, and 113.8 ppm for **4a**. The 4.50 δ proton* in **5** exchanged rapidly with D_2O. The products from TCNE reactions with allyltriphenylstannane and allyltriphenylgermane have been identified by pmr with **5** and what are probably **4b** and **4c**. However, both allyltriphenylstannane and allyltrimethylstannane reactions also produced a blue-green material which has not been identified.
10. Because σ-π conjugation has the additional stereochemical feature (anti arrangement) implied in **3** and demonstrated elsewhere (11,12), the epimerization observed in reaction 1 would probably not occur, for it would violate this rather strong stereochemical requirement.
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15. Rate-limiting loss of R_3M^+ as R_3M^+-solvent etc. can be excluded by the observation of Cook, Eaborn, and Walton (16) that an $Me_3SiCD_2\text{-}\overset{+}{C}H_2$ lives long enough to rearrange even in protic solvents.
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19. The reaction of cyclopropylcarbinyltrimethylstannane with TCNE in acetonitrile gave only $CH_2{=}CHCH_2CH_2C(CN)_2CH(CN)_2$ (20) which also contrasts to the results of Rosenblum et al. (18).
20. G. Koermer, unpublished work.