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Nonstereospecificity in the [2 + 2] Cycloadditions of Tetracyanoethylene to Enol Ethers

Sir:

Concerted $[_{\pi}2_s + {}_{\pi}2_s]$ cycloadditions are forbidden by orbital symmetry.[1] This ban is bypassed by reactions occurring *via* biradicals[2] or zwitterions, as well as by the concerted process $[_{\pi}2_a + {}_{\pi}2_s]$.[1] Polycyanoolefin additions to electron-rich double bonds[3] are rated as a prototype of the mechanism with a zwitterionic intermediate,[4,5] though the evidence is still scant.

Proskow, *et al.*,[5] found the [2 + 2] cycloadditions of *cis*- and *trans*-1,2-bis(trifluoromethyl)-1,2-dicyanoethylene to ethyl vinyl ether highly stereospecific while those to *cis*- and *trans*-propenyl propyl ether were accompanied by loss of configuration at the dicyanoolefin component; allegedly, the stereochemistry of the propenyl ether bond was retained.[6] On reacting tetracyanoethylene (TCNE) with *cis*-anethole, Bartlett[7] observed a configuration loss which amounted to 10% in benzene and 49% in acetonitrile; *trans*-anethole reacted stereospecifically, and so did *cis*- and *trans*-3-ethylidene-1-methylcyclohexene.[7] The additions of fumaro- and maleonitrile to tetramethoxyethylene likewise proceed with retention, and stereospecificity was suggested as a criterion for distinguishing between the zwitterionic and the biradical paths.[8]

On treating *cis*-1-propenyl ethyl ether[9] (0.02 *M*) in benzene with 1.17 equiv of TCNE, adduct formation is quantitative in 8 hr; nmr analysis reveals 95% **3** and 5% **4**. Pure **3** and **4** were obtained by recrystallization of the products from the cis–trans isomeric enol ethers. Rotation of the assumed zwitterionic intermediate **1** starts to compete with the cyclization to give **3**. Though many zwitterion conformations are conceivable, discussing the steric course of cyclization requires only the cis and trans conformers **1** and **2**.

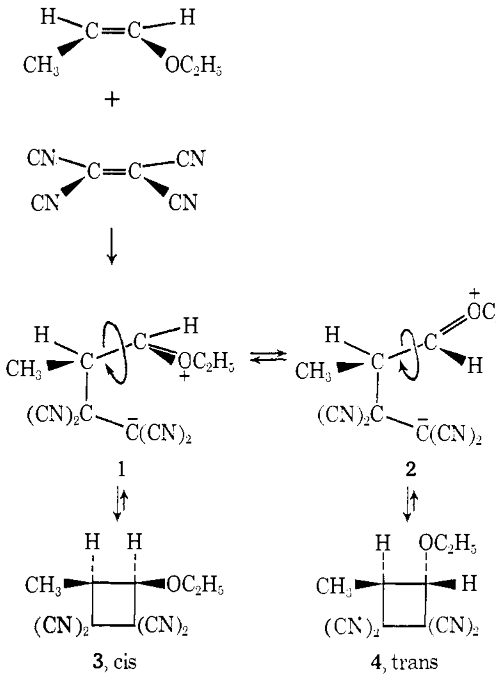


Table I. Steric Course of Cycloadditions of *cis*- and *trans*-Propenyl Alkyl Ethers (0.01–0.1 *M*) and TCNE (1.17 equiv) in Various Solvents at 20°; Percentages of Cis and Trans Adducts (±1%)

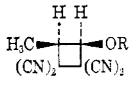
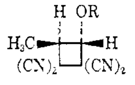
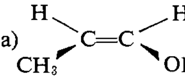
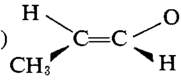
	 Cis adduct			 Trans adduct		
	R =					
Solvent	CH_3	C_2H_5	C_3H_7	CH_3	C_2H_5	C_3H_7
(a)  (cis) + $(CN)_2C=C(CN)_2$						
Benzene	95	95	96	5	5	4
Dichloromethane	94	95	95	6	5	5
Ethyl acetate	92	94	95	8	6	5
Acetone	91	92	91	9	8	9
Acetonitrile	84	85	86	16	15	14
(b)  (trans) + $(CN)_2C=C(CN)_2$						
Benzene	3	4	4	97	96	96
Dichloromethane	5	6	7	95	94	93
Ethyl acetate	9	10	9	91	90	91
Acetonitrile	20	23	19	80	77	81

Table I shows more results for *cis*- and *trans*-propenyl alkyl ethers. All the adducts were characterized by elemental analysis and configurationally elucidated by nmr. The nonstereospecific portion of the cycloaddition increases with solvent polarity. In acetonitrile 14–16% trans adducts were obtained from *cis*-propenyl ethers, and 19–23% cis adducts from *trans*-propenyl ethers (in contrast to the results with *trans*-anethole[7]). The ratio of retention to inversion of olefin configuration corresponds to the ratio of cyclization to rotation in the assumed zwitterionic intermediate.[10]

Are the cis:trans adduct ratios kinetically controlled?

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[1] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781, 847 (1969).

[2] L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86**, 622 (1964); P. D. Bartlett and L. K. Montgomery, *ibid.*, **86**, 628 (1964).

[3] J. K. Williams, D. W. Wiley, and B. C. McKusick, *ibid.*, **84**, 2210 (1962).

[4] T. L. Cairns and B. C. McKusick, *Angew. Chem.*, **73**, 520 (1961); R. Huisgen, R. Grashey, and L. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, p 786; D. Seebach, "Methoden der Organischen Chemie," Vol. IV/4, Georg Thieme, Stuttgart, 1971, p 287.

[5] S. Proskow, H. E. Simmons, and T. L. Cairns, *J. Amer. Chem. Soc.*, **88**, 5254 (1966).

[6] The model is very demanding because the cycloadduct possesses four chiral centers which make eight racemates conceivable. The structural assignment[5] is not unequivocal in our opinion.

[7] P. D. Bartlett, *Quart. Rev., Chem. Soc.*, **24**, 473 (1970).

[8] R. W. Hoffmann, U. Bressel, J. Gehlhaus, and H. Häuser, *Chem. Ber.*, 104, 873 (1971).

[9] The cis and trans isomers were separated by preparative vpc (Apiezon L on siliceous earth) and used with >99% purity. They are thermostable under the experimental conditions.

[10] R. Huisgen and G. Steiner, *J. Amer. Chem. Soc.*, **95**, 5055 (1973).

Not in benzene, but in acetonitrile the cyclobutane derivatives **3** and **4** slowly isomerize until an 18:82 equilibrium is reached. However, the cycloaddition of TCNE to *cis*-propenyl methyl ether (0.13 *M*) is 50,000 times faster than the subsequent cis → trans isomerization of the cycloadduct. This epimerization probably takes place *via* the same zwitterions which are passed in the formation of the cycloadducts.[11]

cis- and *trans*-1-butenyl ethyl ether display a similar solvent-dependent lack of stereospecificity in their TCNE cycloadditions. In going from benzene to acetonitrile, the nonstereospecific part rises from 2 to 18% for the *cis*- and from 2 to 16% for the *trans*-enol ether. TCNE combines with *cis*-1,2-diethoxyethylene in acetonitrile at 20° to give *cis*- and *trans*-1,2-diethoxy-3,3,4,4-tetracyanocyclobutane in an 89:11 ratio, while *trans*-1,2-diethoxyethylene produced the same cycloadducts in the ratio 17:83, respectively.

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(11) The cis–trans isomerization of the cycloadducts in acetonitrile takes place with concurrent polymerization. After 358 hr at 20°, only 70% of 1-methoxy-2-methyl-3,3,4,4-tetracyanocyclobutanes was reisolated from the brown solution.

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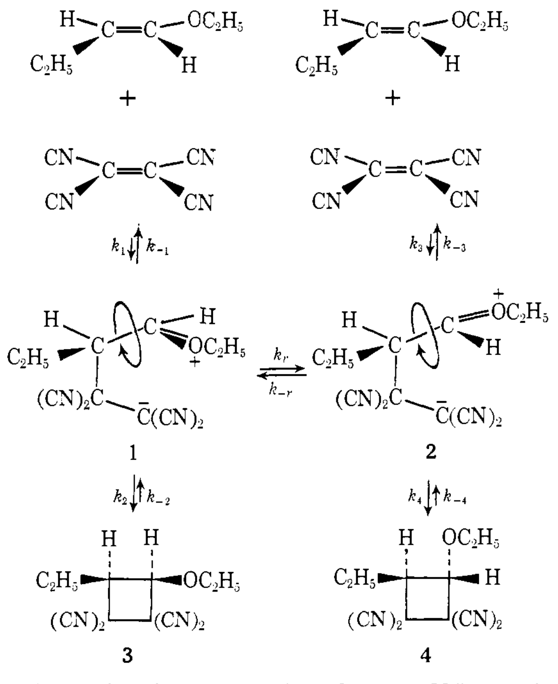
Reversibility of Zwitterion Formation in the [2 + 2] Cycloaddition of Tetracyanoethylene to Enol Ethers

Sir:

The lack of stereospecificity in the [2 + 2] cycloadditions of tetracyanoethylene (TCNE) to *cis*- and *trans*-1-alkenyl alkyl ethers was explained by a zwitterionic intermediate which can rotate.[1]



Is the zwitterion formation from TCNE and enol ethers reversible? On treating TCNE with 1.11 equiv of *cis*-1-butenyl ethyl ether in acetonitrile, the excess of the enol ether, *i.e.*, the unconsumed 0.11 equiv, turned out to be cis → trans isomerized to the extent of 18%. The cis:trans ratio of the cycloadducts also amounted to 82:18, by coincidence (Table I).[2] The simplest mechanism for cis–trans isomerization consists of zwitterion formation, rotation about the former double bond of the enol ether, and dissociation to the olefinic reactants. The trans content of the 1-butenyl ethyl ether is increased from 0 to 18% during the reaction which is over in a few seconds.

Table I. Cycloadditions of TCNE with *cis*- and *trans*-1-Butenyl Ethyl Ether (1.4 *M*) in Acetonitrile at 20°; Vpc Analysis of the Excess of Enol Ether with Toluene as Internal Standard; Nmr Analysis of the Cis–Trans Isomeric Cycloadducts

Equiv of enol ether based on TCNE	Consumed enol ether Calcd	Consumed enol ether Found	Unconsumed enol ether % cis	Unconsumed enol ether % trans	[2 + 2] cycloadduct % cis	[2 + 2] cycloadduct % trans
(a) Experiments with *cis*-1-Butenyl Ethyl Ether						
1.11	90	87	82	18	82	18
1.29	78	78	86	14	85	15
1.50	67	70	89	11	86	14
1.93	52	51	92	8	87	13
2.02	50	52	92	8	88	12
4.12	24	26	96	4	89	11
(b) Experiments with *trans*-1-Butenyl Ethyl Ether						
0.85					16	84
1.16	86	83	16	84	15	85
1.29	78	79	14	86	12	88
1.51	66	69	9	91	10	90
2.12	47	49	6	94	10	90
3.73	27	30	3	97	9	91

Thus, the intermediate zwitterions can undergo cyclization, configurational rotation (**1** ⇌ **2**), or reversal to reactants. Instead of integrating the unwieldy rate equation of adduct formation, which contains ten rate constants, we derived approximate rate ratios. The premise of excluding double conformational rotation is not unreasonable because rotation never amounts to more than 20% of the ring closure rate; therefore, double rotation from cis to trans and *vice versa* would not come to more than 4%. Without an excess of *cis*-1-butenyl ethyl ether, all the isomerized zwitterion **2** will end up as trans adduct **4**. Thus the limiting ratio of cis:trans cycloadduct will correspond to the rate ratio of ring closure to rotation, k_2/k_r for the cis zwitterion **1**.

On starting with 4.12 equiv of *cis*-1-butenyl ether, the trans content of the unconsumed enol ether drops to 4% (Table I). The chance for the isomerized material, the *trans*-1-butenyl ether, to enter into the reaction with TCNE a second time becomes small; 4% trans isomer in 3.12 equiv of excess enol ether means that 0.12 equiv of the trans zwitterion **2** suffered dissociation. The trans content of the cycloadduct formed in this experiment amounts to 0.11 equiv. Thus, the trans zwitterion **2** is partitioned into dissociation and cyclization in nearly a 1:1 ratio.

From the two series of experiments of Table I the rate ratios of Table II are deduced. Thus, cyclization is roughly five times faster than rotation for the oxonium zwitterions **1** and **2**. Both zwitterions undergo cyclization and dissociation to the unsaturated components with practically the same rate constants.

The comparison with the behavior of 1,4 biradicals

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(1) R. Huisgen and G. Steiner, *J. Amer. Chem. Soc.*, **95**, 5054 (1973).

(2) The 1-alkenyl alkyl ethers are configurationally stable under the reaction conditions, also in the presence of the cycloadduct.