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.

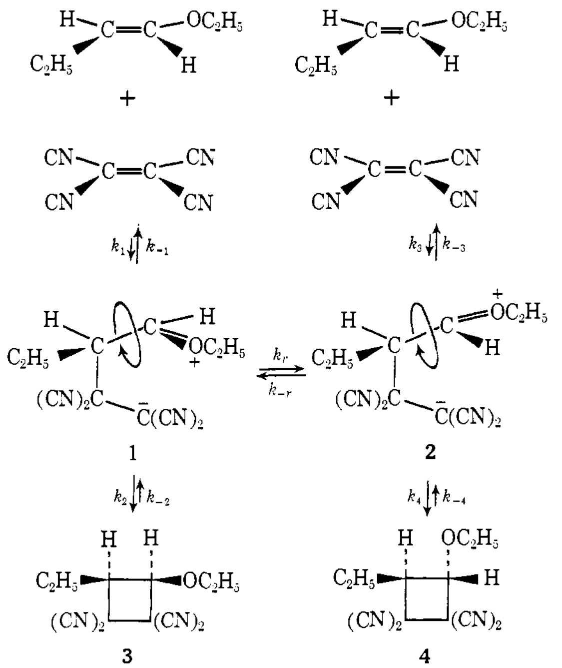
Rolf Huisgen,* Gerd Steiner
Institut für Organische Chemie der Universität
8 München 2, Germany

Received April 20, 1973

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	Found	Unconsumed enol ether % cis	% trans	[2 + 2] cycloadduct % cis	% 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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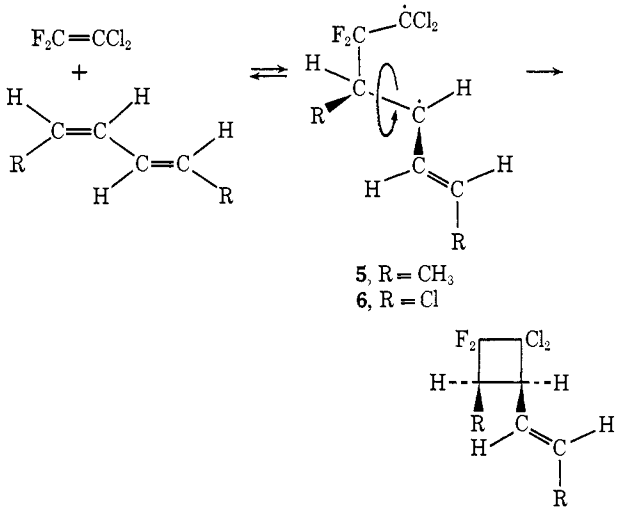
[1] R. Huisgen and G. Steiner, *J. Amer. Chem. Soc.*, **95**, 5054 (1973).

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

Table II. Ratios of Rate Constants Derived from the Data of Table I

	Ring closure/rotation	Ring closure/dissociation	Dissociation/rotation
Cis zwitterion **1**	$k_2/k_r = 4.6$	$k_2/k_{-1} = 1.1$	$k_{-1}/k_r = 4.2$
Trans zwitterion **2**	$k_4/k_{-r} = 5.3$	$k_4/k_{-3} = 0.88$	$k_{-3}/k_{-r} = 6.0$



5, R = CH_3
6, R = Cl

is revealing. For **5** at 80°, rotation about the marked double bond is ten times faster than cyclization.[3] The rotational equilibrium is nearly attained for **6** at 150°, while cyclization is 4.4 times faster than dissociation.[3] Thus, it is the rotation which is slowed down in the intermediates **1** and **2** of the TCNE cycloadditions due to the Coulomb attraction of the charged centers. Probably most of the zwitterions **1** and **2** are created in conformations with the smallest distance separating the charged centers.

The rate ratios of Table II refer to acetonitrile. In nonpolar solvents the rotation is suppressed even more by the higher Coulombic force which leads to larger ratios of cyclization *vs.* rotation, *e.g.* 50 for **1** and **2** in benzene.[1,4]

Further support for zwitterionic intermediates in TCNE cycloadditions to enol ethers comes from the dependence of rate on solvent polarity and on structure of the enol ether, as well as from the trapping reaction with alcohol.

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(3) P. D. Bartlett, C. J. Dempster, L. K. Montgomery, K. E. Schueller, and G. E. H. Wallbillich, *J. Amer. Chem. Soc.*, **91**, 405 (1969); P. D. Bartlett and G. E. H. Wallbillich, *ibid.*, **91**, 409 (1969).

(4) It may be emphasized that the ratio of ring closure to dissociation for the trans zwitterion **2** stems from experiments with *cis*-1-butenyl ether and *vice versa.* The smaller percentage of the material which isomerizes through rotation in *nonpolar* solvents does not allow the quantitative evaluation of the ratio of ring closure to dissociation here.

Rolf Huisgen,* Gerd Steiner
Institut für Organische Chemie der Universität
8 Munich 2, Germany

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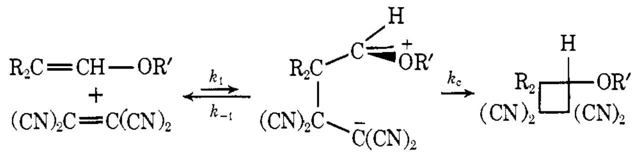
Tetracyanoethylene and Enol Ethers. Dependence of Cycloaddition Rate on Solvent Polarity

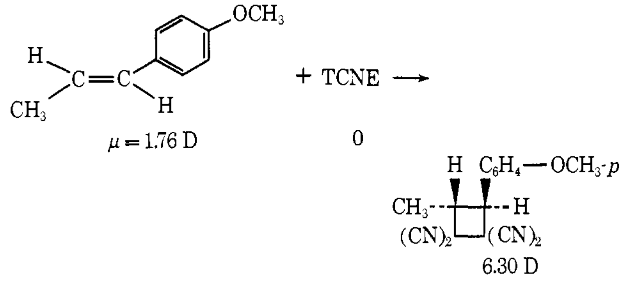
Sir:

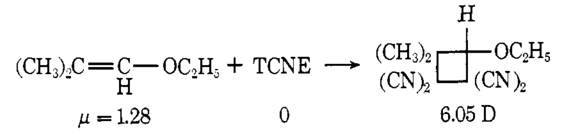
The kinetics of tetracyanoethylene (TCNE) cycloadditions to enol ethers (at least 10 equiv) have been measured photometrically by the color of the charge-transfer complex which is produced instantly. The overall k_2 values are the rate constants of zwitterion formation times the partition coefficient $k_c/(k_{-1} + k_c)$.[1]



The solvent influence on the cycloaddition rate constant (Figure 1) is of an unusual magnitude as evidenced by k(acetonitrile)/k(cyclohexane) = 29,000 for anethole,[2] 10,800 for 1-ethoxyisobutene, and 2600 for butyl vinyl ether, as well as k(acetonitrile)/k(CCl_4) = 17,000 for 2,3-dihydro-4*H*-pyrane. These ratios correspond to a $\Delta\Delta G^{\ddagger}$ of up to 5.5 kcal/mol for the increase of solvation energy during activation. This is a much higher solvent dependence than reported for the reaction of chlorotricyanoethylene with 4-methoxystyrene.[3]

The formation of the zwitterionic intermediate—its energy trough is surrounded by barriers of equal height (Figure 2)[1]—is assumed to be rate determining. In replacing a nonpolar by a polar solvent, the rate constant k_1 (and probably the overall constant k_2) profits from a decrease of activation energy by $\Delta E_2 - \Delta E_1$.





How can one distinguish between the zwitterionic mechanism and a hypothetical concerted cycloaddition with equal bond formation in the transition state? The dipole moments of reactants and adducts, measured in benzene, reveal a substantial increase of charge separation and suggest an acceleration by polar solvents.

Based on an electrostatic model of Kirkwood,[4] Laidler and Eyring[5] developed eq 1 for the solvent

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(1) See the preceding communication: R. Huisgen and G. Steiner, *J. Amer. Chem. Soc.*, **95**, 5055 (1973). A partition coefficient of 0.5 was found for TCNE + *cis*- and *trans*-1-butenyl ethyl ether in acetonitrile at 20°.

(2) Dr. D. W. Wiley, E. I. du Pont de Nemours Co., has measured k(acetonitrile)/k(cyclohexane) = 63,000 for the system TCNE + *p*-methoxystyrene (private communication).

(3) k(acetonitrile)/k(cyclohexane) = 200; J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Amer. Chem. Soc.*, **84**, 2216 (1962).

(4) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934). See also C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier, New York, N. Y., 1952.

(5) K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940); S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N. Y., 1944, p 419. See also E. S. Amis, "Solvent Effects on Reaction Rates and Mechanisms," Academic Press, New York, N. Y., 1966, p 59.