

1,4-dibromonaphthalene as indicated by the infrared spectrum. The crude product was suspended in diethyl ether and the mixture filtered. The insoluble portion was washed with ether, and the combined filtrates were evaporated. The insoluble fraction weighed 8.61 g. From the ether filtrate there was recovered 4.4 g. of solid which was identified as 1,4-dibromonaphthalene by means of its infrared spectrum. One recrystallization of the insoluble fraction from 1,2-dichloroethane gave 6.08 g. (52.5%) of dense, tan crystals, m.p. 196–198°. Further recrystallization from 1,2-dichloroethane raised the melting point of XVII to 202–203°.

Anal. Calcd. for $C_{16}H_8Br_2N_4O$: C, 44.68; H, 1.41; N, 13.03. Found: C, 45.06; H, 1.67; N, 13.02.

The ultraviolet spectrum in acetonitrile showed ($m\mu$ (log ϵ)) λ_{max} 320 (3.37), 259 (3.97), 267 (3.95), 278 sh (3.75), 298 sh (3.09), 3.08 (3.28), and 320 (3.25).

4,4,6,6-Tetracyano-3a,4,6,6a-tetrahydrofuran[2,3-c]-furan (XVIII). A suspension of 15 g. of TCNEO and 25 ml. of furan in 100 ml. of 1,2-dichloroethane was sealed in a stainless-steel-lined pressure vessel and heated for 16 hr. at 150° with shaking. The recovered reaction mixture was filtered to remove 11.9 g. of black polymeric solid. Evaporation of the residue left a dark solid which was sublimed to give 2.0 g. of reddish brown crystals which were recrystallized from 1,2-dichloroethane to give 1.10 g. of the furan adduct as colorless crystals, m.p. 161–162°. The melting point of the product was unchanged by further recrystallization and sublimation.

Anal. Calcd. for $C_{10}H_4N_4O_2$: C, 56.60; H, 1.90; N, 26.40. Found: C, 56.00; H, 1.95; N, 26.46.

The infrared spectrum showed absorption at 3.18 (unsaturated CH), 4.42 (C≡N), and 6.14 μ (C=C). There was also strong 9–10- μ absorption (ether).

4,4,6,6-Tetracyano-3a,4,6,6a-tetrahydrothieno[2,3-c]-furan (XIX). A suspension of 15 g. (0.104 mole) of

TCNEO in 26 g. (0.31 mole) of thiophene and 150 ml. of 1,2-dichloroethane was heated in a stainless-steel-lined pressure vessel for 16 hr. at 130°. The reaction mixture was filtered to remove a small amount of suspended black polymeric solid, and the filtrate was evaporated to leave a mass of black crystalline product. The product was dissolved in boiling benzene, treated with charcoal, and filtered. The filtrate deposited 11.8 g. of yellow needles, m.p. 158–162°. Further recrystallization from ethylene dichloride gave XIX with m.p. 159–160°, unchanged by further recrystallization. In spite of repeated recrystallizations followed by sublimation, the product retained a faint yellow color.

Anal. Calcd. for $C_{10}H_4N_4SO$: C, 52.62; H, 1.77; S, 14.05. Found: C, 53.42; H, 2.17; S, 14.40.

The infrared spectrum showed absorption (μ) at 3.25 (unsaturated CH), 3.33 and 3.37 (saturated CH), 4.44 (C≡N), 6.29 (C=C), and 8–10 (COC).

2-Chloro-4,4,6,6a-tetracyano-3a,4,6,6a-tetrahydrothieno[2,3-c]furan (XX). A suspension of 5.00 g. (0.0347 mole) of TCNEO in 11.9 g. (0.10 mole) of freshly distilled 2-chlorothiophene and 50 ml. of 1,2-dibromoethane was heated to reflux for 16 hr. The reaction mixture was cooled to room temperature, and the precipitate was collected by filtration to give 7.18 g. of dark solid which was recrystallized from 1,2-dichloroethane with charcoal to give 3.72 g. of nearly colorless crystals, m.p. 178–179°. Another 0.65 g. was obtained by concentration of the mother liquors. Further recrystallization from the same solvent raised the melting point of XX to 179–180°.

Anal. Calcd. for $C_{10}H_3ClN_4SO$: C, 45.72; H, 1.15; N, 21.33. Found: C, 45.09; H, 1.12; N, 21.25.

The infrared spectrum showed absorption (μ) at 3.23 (saturated CH), 3.33 (saturated CH), 4.41 and 4.44 (C≡N), 6.27 (C=C), and 9–10 (COC).

Tetracyanoethylene Oxide. III. Mechanism of the Addition to Olefins¹

William J. Linn

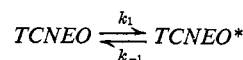
Contribution No. 1035 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware. Received December 11, 1964

The rate of addition of tetracyanoethylene oxide (TCNEO) to styrene and to trans-stilbene obeys the equation

$$\text{rate} = \frac{k_1 k_2 [\text{TCNEO}] [\text{olefin}]}{k_{-1} + k_2 [\text{olefin}]}$$

These rate constants are associated with the reaction sequence

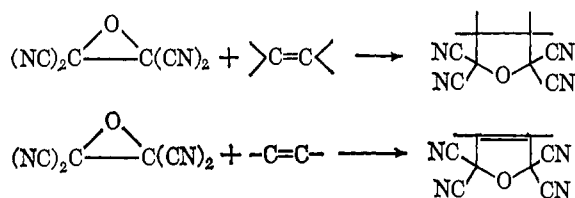
(1) This work was presented in part at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 20–22, 1964.



Over-all, the reaction is relatively insensitive to solvent and substituent changes. The best formulation of TCNEO* is a hybrid of biradical and zwitterionic species which adds to the olefin by a concerted or near-concerted cyclic process.

Introduction

Tetracyanoethylene oxide (TCNEO) readily adds to olefins, acetylenes, and certain aromatic systems to give derivatives of tetracyanotetrahydro- and -dihydrofurans. This thermal reaction is marked by an unorthodox

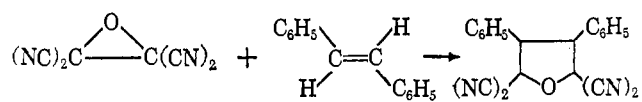


cleavage of the epoxide ring between the carbon-carbon bond. The limitations of the reaction and some generalized observations on the mechanism have been presented in the preceding paper in this series.²

A more detailed, although still incomplete, picture of the mechanism of the addition reaction has been obtained by a kinetic investigation of the reaction with styrene and substituted stilbenes.

Results

Kinetics of the Addition of TCNEO to Olefins. The addition of TCNEO to *trans*-stilbene in 1,2-dibromoethane at 125° gives a single adduct, *trans*-3,4-diphenyl-2,2,5,5-tetracyanotetrahydrofuran (I), in nearly quantitative yield.² Under these conditions, the re-



action *does not* display either simple first- or second-order kinetics but is in some intermediate range. It is possible to obtain reproducible, initially observed first-order rate constants ($k_{1 \text{ obsd}}$) by following the disappearance of TCNEO over the first 50% or more reaction. These observed rate constants are collected in Table I.

Table I. Observed Initial First-Order Rate Constants for the Formation of *trans*-3,4-Diphenyl-2,2,5,5-tetracyanotetrahydrofuran^a

[TCNEO] ₀ , mole/l.	[Stilbene] ₀ , mole/l.	$k_{1 \text{ obsd}} \times 10^4$, sec. ⁻¹
0.0050	0.0100	1.96
0.0074	0.0104	1.96
0.0102	0.0098	1.99
0.0100 ^b	0.0100	1.96
0.0103 ^c	0.0097	1.96
0.0151	0.0101	3.07
0.0202	0.0101	4.28
0.0251	0.0101	5.44
0.0289	0.0100	6.49
0.0250	0.0075	6.24
0.0053	0.0071	1.69
0.0050	0.0201	2.63
0.0100	0.0201	2.57
0.0100	0.0040	3.53
0.0101	0.0022	4.70
0.0207	0.0063	5.50
0.0193	0.0208	2.53
0.0195	0.0414	2.96

^a Solvent, 1,2-dibromoethane; temperature, 125.10 ± 0.05°.

^b An equimolar amount of the product was added to the reaction mixture to ensure that the product had no catalytic effect on the reaction. ^c This run was made by following the disappearance of *trans*-stilbene by ultraviolet spectroscopy.

(2) W. J. Linn and R. E. Benson, *J. Am. Chem. Soc.*, **87**, 3657 (1965).

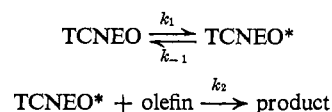
The first-order calculations are made for the appearance of product with time, assuming that the disappearance of *trans*-stilbene and the formation of product are equal to the disappearance of TCNEO, the quantity actually measured. That the first assumption is true was demonstrated by also following the disappearance of the ultraviolet absorption of *trans*-stilbene at 300 mμ. In a number of runs in which TCNEO was initially present in excess, the concentration of TCNEO remaining after 10 half-lives was checked and found to agree with the calculated value within 2–3%. This is reassurance that the second assumption is also true.

When either reagent is present in twofold or greater excess, the first-order plots are generally linear to better than 80% reaction.

It is seen from the data of Table I that when the initial concentration of stilbene is held constant and in excess of the initial TCNEO concentration, the observed k_1 is insensitive to changes in the TCNEO concentration. However, when the initial TCNEO exceeds the stilbene concentration, there is a rapid rise in $k_{1 \text{ obsd}}$ with increasing initial TCNEO concentration. On the other hand, the reaction rate is relatively insensitive to changes in the stilbene concentration when the initial TCNEO concentration is held constant.

The kinetics of the reaction are not consistent with a mechanism whereby TCNEO and the olefin undergo a bimolecular reaction in the rate-determining step, nor is the rate *solely* determined by a preliminary unimolecular activation of one of the reagents.

The data are consistent with a mechanism wherein TCNEO undergoes an equilibrium promotion to an activated species that in turn reacts with the olefin. The application of a steady-state approximation



to this formulation leads to the rate expression of eq. 1

$$\frac{dP}{dt} = \frac{k_1 k_2 T S}{k_{-1} + k_2 S} \quad (1)$$

where P = [product], T = [TCNEO], and S = [*trans*-stilbene]. During the early stages of any given run in which the initial TCNEO concentration exceeds that of the stilbene, the experimentally observed rate is given by eq. 2.

$$\frac{dP}{dt} = k_{1 \text{ obsd}} S \quad (2)$$

If the postulated rate equation is valid, (1) and (2) must be equal.

$$k_{1 \text{ obsd}} S = \frac{k_1 k_2 T S}{k_{-1} + k_2 S}$$

or

$$k_{1 \text{ obsd}} = \frac{k_1 k_2 T}{k_{-1} + k_2 S} \quad (3)$$

A similar expression may be developed for the situation in which the initial concentration of stilbene exceeds

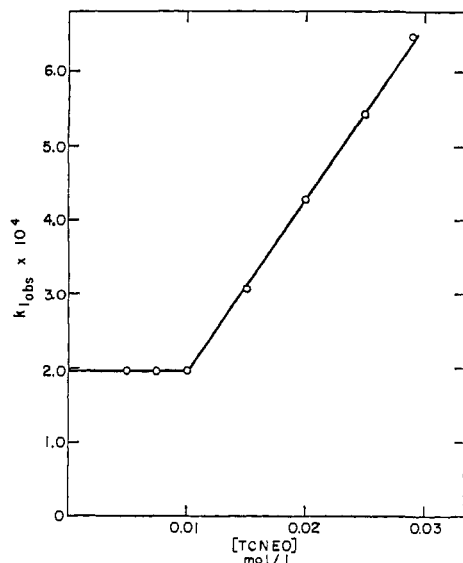


Figure 1. A plot of observed first-order rate constants against the initial concentration of TCNEO for individual runs in which the initial concentration of *trans*-stilbene is 0.01 *M*.

that of the TCNEO. In this case, the experimentally observed initial rate is given by

$$\frac{dP}{dt} = k_{1 \text{ obsd}} T \quad (4)$$

Equating (1) and (4) leads to the expression

$$k_{1 \text{ obsd}} = \frac{k_1 k_2 S}{k_{-1} + k_2 S} \quad (5)$$

According to eq. 3 (TCNEO in excess), a plot of $k_{1 \text{ obsd}}$ vs. initial T should be a straight line passing through the origin if the initial S is held constant, and from eq. 5 (stilbene in excess), $k_{1 \text{ obsd}}$ should be constant if the initial S is constant. These requirements are fulfilled as is seen in Figure 1.

Rearrangement of eq. 3 gives expression 6 from which a plot of $T/k_{1 \text{ obsd}}$ vs. the initial stilbene concentration should be linear with slope equal to $1/k_1$

$$\frac{T}{k_{1 \text{ obsd}}} = \frac{k_{-1}}{k_1 k_2} + \frac{S}{k_1} \quad (6)$$

and intercept $k_{-1}/k_1 k_2$. Figure 2 is a plot of this type of the data drawn from Table I, from which it is determined that $k_1 = 3.11 \times 10^{-4} \text{ sec.}^{-1}$.

A further check on the derived expressions may be had from the rearrangement of eq. 5 to 7. This equa-

$$\frac{1}{k_{1 \text{ obsd}}} = \frac{k_{-1}}{k_1 k_2 S} + \frac{1}{k_1} \quad (7)$$

tion, which pertains to the situation when the initial stilbene concentration is in excess of the TCNEO, predicts a linear plot of $1/k_{1 \text{ obsd}}$ against the reciprocal of the initial stilbene concentration. This plot is reproduced in Figure 3. Here again the fit is good, and k_1 by this method is $3.40 \times 10^{-4} \text{ sec.}^{-1}$, in good agreement with the previous value in view of the graphical method and approximations involved.

Another, and more rigorous, attack on this problem involves a kinetic investigation of the reaction of

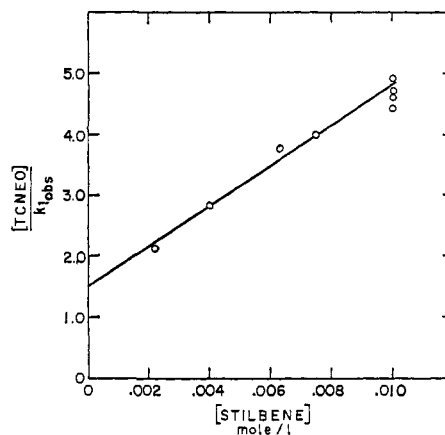


Figure 2. A plot of $\text{TCNEO}/k_{1 \text{ obsd}}$ vs. the initial concentration of stilbene for individual runs in which the TCNEO concentration is greater than that of the stilbene.

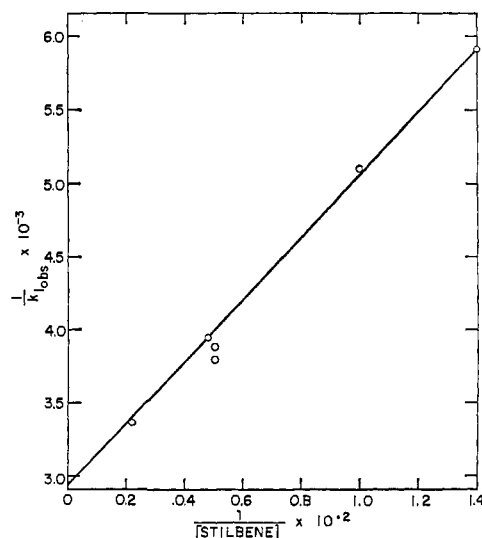


Figure 3. A plot of $1/k_{1 \text{ obsd}}$ vs. the reciprocal of the initial stilbene concentration for individual runs in which the stilbene concentration exceeds that of TCNEO.

TCNEO and styrene. A generalized form of the postulated rate eq. 1 may be written as (8). If the

$$\text{rate} = \frac{k_1 k_2 [\text{TCNEO}][\text{olefin}]}{k_{-1} + k_2 [\text{olefin}]} \quad (8)$$

product $k_2[\text{olefin}]$ is sufficiently large that k_{-1} may be neglected in the denominator, eq. 8 reduces to (9).

$$\text{rate} = k_1 [\text{TCNEO}] \quad (9)$$

Consequently, an increase in the concentration of a sufficiently reactive olefin should have little or no effect on $k_{1 \text{ obsd}}$ which should reach a constant value equal to the k_1 determined in the case of reaction with *trans*-stilbene. In other words, the *promotion of TCNEO to TCNEO* should become rate controlling*. This is found to be the case in the reaction of TCNEO and styrene. The observed first-order rate constants for this reaction are collected in Table II.

It is obvious that an increase in the olefin concentration has very little effect on $k_{1 \text{ obsd}}$. For example, a comparison of the second and fourth entries of part C of Table II shows that a 400% increase in styrene con-

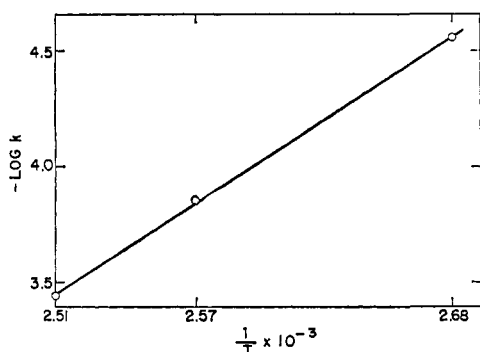


Figure 4. An Arrhenius plot for the reaction of TCNEO and styrene.

Table II. Observed First-Order Rate Constants for the Reaction of TCNEO and Styrene in 1,2-Dibromoethane

[TCNEO] ₀ , mole/l.	[Styrene] ₀ , mole/l.	k ₁ obsd, sec. ⁻¹
	A. 100.00°	
0.01001	0.01169	2.45 × 10 ⁻⁵
0.01008	0.1142	2.78 × 10 ⁻⁵
	B. 115.00°	
0.01021	0.01241	1.12 × 10 ⁻⁴
0.01140	0.04984	1.31 × 10 ⁻⁴
0.01033	0.1330	1.41 × 10 ⁻⁴
	C. 125.10°	
0.01005	0.01226	2.92 × 10 ⁻⁴
0.01018	0.05240	3.45 × 10 ⁻⁴
0.01017	0.1052	3.59 × 10 ⁻⁴
0.01007	0.2215	3.63 × 10 ⁻⁴
0.01007	0.3315	3.94 × 10 ⁻⁴
0.00513	0.01193	2.92 × 10 ⁻⁴

centration causes only a 5% increase in the rate constant. At 125.1°, the k₁ levels off around 3.6 × 10⁻⁴ sec.⁻¹, a value in good agreement with the k₁ found for the *trans*-stilbene reaction by a graphical and, therefore, more approximate treatment. The continued increase in k₁ obsd at styrene concentrations above 0.2 M is probably caused by a change in medium due to the large styrene concentration. The validity of this proposal is demonstrated by carrying out the reaction in xylene, whose molecular type is closer to that of styrene. High concentrations of the latter would not be expected to cause drastic changes in the over-all medium. The results of this study (Table III) fully justify the pre-

Table III. First-Order Rate Constants for the Reaction of TCNEO and Styrene in Other Solvents at 125.10°

Solvent	[TCNEO] ₀ , mole/l.	[Styrene] ₀ , mole/l.	k ₁ × 10 ⁻⁴ , sec. ⁻¹
Xylene ^a	0.00504	0.0502	3.02
Xylene	0.00505	0.2190	3.07
Xylene	0.00501	0.3004	3.18
C ₆ H ₅ NO ₂	0.01001	0.05212	1.44
C ₆ H ₅ NO ₂	0.01013	0.1020	1.54
C ₆ H ₅ NO ₂	0.00999	0.3002	1.80

^a Xylene refers to Merck reagent grade xylene which is presumably mainly the *meta* isomer.

diction that there should be negligible change of the rate constant with increasing styrene concentration.

The values of k₁ obsd determined at TCNEO concentrations of 0.01 M and styrene concentrations of 0.1 M must approach closely the true first-order rate constants for the promotion of TCNEO to TCNEO*. From these values, the energy of activation for this step is determined to be 30.2 kcal./mole and the entropy of activation 0.8 e.u. The Arrhenius plot is reproduced in Figure 4.

One more piece of kinetic evidence can be cited in support of the proposed two-step mechanism. If the reaction of TCNEO* with olefin were sufficiently slow to be rate determining, the reaction should be first order in each reactant. This is equivalent to imposing upon eq. 8 the condition that k₋₁ is large with respect to the product k₂[olefin], whereupon the equation is reduced to (10).

$$\text{rate} = \frac{k_1 k_2}{k_{-1}} [\text{TCNEO}][\text{olefin}] \quad (10)$$

Earlier experience² had shown that the presence of electron-withdrawing substituents on the olefin lowers the rate. Therefore, a second-order reaction should prevail with such an olefin. In support of this expectation, the reaction of TCNEO and 4-nitro-*trans*-stilbene exhibits good second-order kinetics within limits (see Table IV).

Table IV. Second-Order Rate Constants for the Reaction of TCNEO and 4-Nitro-*trans*-stilbene in 1,2-Dibromoethane at 125.10°

[TCNEO] ₀ , mole/l.	[4-Nitro- stilbene] ₀ , mole/l.	k ₂ × 10 ³ , l. mole ⁻¹ sec. ⁻¹
0.0050	0.0200	3.60
0.0100	0.0050	3.69
0.0050	0.0100	3.69
0.0050	0.0500	2.66

When the concentration of olefin becomes sufficiently high, it is no longer possible to neglect the k₂[olefin] term in the denominator of eq. 8, and consequently the second-order rate constant should begin to fall off as is actually observed.

All of the kinetic evidence presented so far seems to be consistent with the two-step formulation of the reaction. However, no information is available from these experiments as to the detailed nature of TCNEO* and the manner in which this species actually reacts with olefins. Deductions with respect to these features must be drawn from other experiments.

Solvent Effects on the Reaction. The effect of solvent on the rate of a reaction is generally regarded as a qualitative measure of the development of charge in the transition state. In the present work, a detailed study of this kind has not been made because of the difficulty of finding high-boiling solvents that are unreactive with TCNEO and do not interfere with the analytical method. A limited study, however, has given indications of effects that are probably significant. The bulk of the kinetic studies presented were carried out in 1,2-dibromoethane which has a dielectric constant of 4.78 at 25°. Rates that were obtained in

(3) N. A. Lange, "Handbook of Chemistry," 10th Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1961, pp. 1223-1225.

xylylene (dielectric constant around 2.3)³ have already been mentioned and do not differ appreciably from those in dibromoethane. A solvent with a high dielectric constant such as nitrobenzene (34.8 at 25°)⁸ should have a marked accelerating effect on a reaction which involves ionization. In fact, the reaction of TCNEO and styrene is *faster* in dibromoethane than in nitrobenzene, but only by a factor of about two (Table III).

Substituent Effects on Reaction Rate. Some substituted *trans*-stilbenes have been examined, and the initial observed first-order rates have been calculated as described above for *trans*-stilbene. The results are recorded in Table V. These observed first-order rate

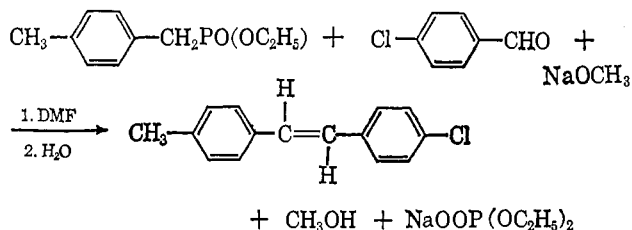
Table V. Observed First-Order Rate Constants for the Reaction of TCNEO and Substituted *trans*-Stilbenes in 1,2-Dibromoethane at 125.10°

Substituent	[TCNEO] ₀ , mole/l.	[olefin] ₀ , mole/l.	$k_1 \times 10^4$, sec. ⁻¹
4-OCH ₃	0.00506	0.01009	3.08
4-CH ₃	0.00500	0.01001	2.56
4-CH ₃	0.00505	0.00710	2.27
4-CH ₃	0.01006	0.01999	2.96
4-CH ₃	0.01004	0.04000	3.40
4-CH ₃	0.01002	0.00998	2.48
4-CH ₃	0.01998	0.01003	5.66
4-Cl-4'-CH ₃	0.00498	0.00999	1.78
4-Cl-4'-CH ₃	0.01997	0.01003	3.81
4-Cl	0.00501	0.00990	1.46
4-Cl	0.00955	0.00979	1.27
4-Cl	0.02010	0.00976	2.82
3-F	0.00500	0.01004	1.09
3-F	0.00999	0.00500	1.24
3-F	0.00509	0.03004	2.06

constants are not directly comparable, as they are actually combinations of first- and second-order rate constants related through the over-all expressions 3 and 5. By a comparison of runs made at the same initial concentrations, it is seen that the effect of structure on rate is in a definite direction but is very small.

A plot of eq. 7 using the data for 4-methyl-*trans*-stilbene from Table V gives a value for k_1 of 3.62×10^{-4} sec.⁻¹, in very good agreement with the k_1 obtained for both *trans*-stilbene and styrene. This lends further support to the validity of the postulated rate equation.

Two of the substituted *trans*-stilbenes of Table V, the 3-fluoro and 4-chloro-4'-methyl derivatives, are new. They were prepared in good yield by the condensation of the appropriate aldehyde and phosphonate ester using the method of Seus and Wilson.⁴



Stereochemistry of the Reaction. In the second step of the TCNEO-olefin reaction, it is necessary to dis-

rupt the π -system of the olefin and form two new bonds. This process could be either stepwise or synchronous. Some inference concerning this sequence may be made from the stereochemistry of the reaction.

The stereospecificity of the TCNEO-addition reaction has already been demonstrated² by the isolation of different adducts from the *cis* and *trans* isomers of 1,2-dichloroethylene, stilbene, and 2-butene.

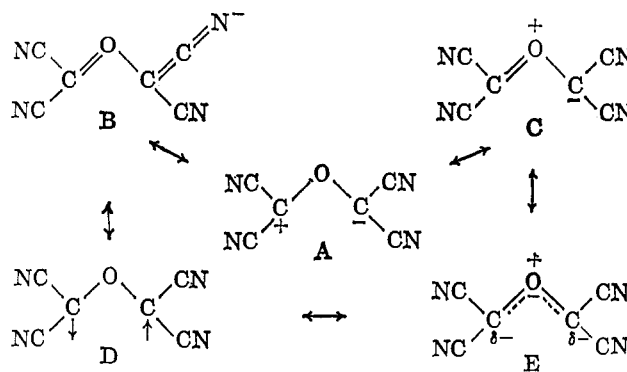
cis- and *trans*-1,2-dichloroethylene offer a convenient system for the determination of the relative rates of reaction with an isomeric pair. Each of the adducts has only a single characteristic proton resonance useful in an analysis of the reaction product. Such an analysis depends upon irreversibility of the reaction for validity. To test this, *cis*-3,4-dichloro-2,2,5,5-tetracyanotetrahydrofuran was heated in *trans*-1,2-dichloroethylene for 16 hr. at 130° with no detectable formation of *trans* adduct.

As another test of the reversibility of the addition reaction, 2,2,5,5-tetracyanotetrahydrofuran was heated in 1,2-dibromoethane in the presence of *trans*-stilbene. No gas was evolved in 20 hr., and none of the *trans*-stilbene adduct could be detected in the recovered solid product.

The competitive experiment gave a mixture of adducts whose composition was 84% *trans* and 16% *cis* or a relative rate ratio of *trans/cis* of approximately 5.

Discussion

The kinetic data provide rather convincing evidence that the addition of TCNEO to olefins takes place in two steps, the first of which is a thermal promotion of the epoxide to an activated species. The nature of TCNEO* is still a subject of speculation. Rupture of the carbon-carbon bond gives rise to a structure that may be pictorially represented by the resonance structures A-E. Many more such structures may be written involving delocalization of the charge by each of the four nitrile groups.



To view TCNEO* as a 1,3-dipolar ion is untenable, for whatever the structure, it is undoubtedly *symmetrical*. In fact, the evidence indicates that TCNEO* has very little ionic character at all. Solvent and substituent effects would be much more pronounced if ions were involved. All of the structures A through E (and others) contribute to the over-all structure of TCNEO* which is qualitatively best described as a zwitterion-biradical hybrid.

One cannot rule out completely the possibility that the intermediate is a true biradical, triplet species resulting from a homolytic cleavage of the carbon-carbon bond with a spin inversion. Such a process

(4) E. J. Seus and C. V. Wilson, *J. Org. Chem.*, **26**, 5243 (1961).

seems unlikely in view of the preserved stereochemistry of the olefin, but such evidence is not conclusive.

There still remains the question of the second step in which the intermediate TCNEO* reacts with olefins. This step is undoubtedly closely akin to the Diels-Alder reaction and 1,3-dipolar additions. Thus, the reaction is thermal in nature and relatively insensitive to solvent effects and structural changes. The stereochemical studies show that both new bonds are formed simultaneously or very nearly so. Another similarity with dipolar additions is the faster reaction rate with the *trans* isomer of a *cis-trans* pair⁵ which Huisgen has postulated as a criterion of a multicentered process. These are all characteristics of cyclic reactions which are "concerted" or "nearly concerted."

Experimental

Materials. Tetracyanoethylene oxide was purified by at least three recrystallizations from 1,2-dichloroethane followed by sublimation at 80° (0.1 mm.). The purified product melts at 177–178° (sealed capillary). *trans*-Stilbene (Eastman Kodak Scintillation Grade) was recrystallized from ethanol and sublimed. Substituted *trans*-stilbenes with the exception of 4-nitro-*trans*-stilbene were prepared by the method of Seus and Wilson⁴ as described below. They were recrystallized to constant melting point and dried under vacuum: 4-methyl-*trans*-stilbene,⁶ m.p. 121.5–122° from ethanol; 4-chloro-*trans*-stilbene,^{7,8} m.p. 130–130.5° from ethanol; and 4-methoxy-*trans*-stilbene,⁹ m.p. 137.5–138° from ethanol. 4-Nitro-*trans*-stilbene¹⁰ was recrystallized from 1-propanol to a melting point of 157–158° and dried. Styrene (Eastman Kodak) was distilled at reduced pressure and then redistilled immediately before use, b.p. 65° (51 mm.). 1,2-Dibromoethane was freshly distilled, and the center cut was stored in clean, dry bottles under nitrogen. Xylene (Merck, reagent grade) was distilled twice and the center cut, b.p. 138–140°, was collected in dried bottles and stored in a desiccator. Nitrobenzene was dried over P₂O₅ and had b.p. 95° (19 mm.).

Titration of TCNEO. Titration of TCNEO¹¹ was carried out in the presence of *trans*-stilbene and *trans*-3,4-diphenyl-2,2,5,5-tetracyanotetrahydrofuran. In neither case was more than 2.02 mequiv. of iodine liberated per millimole of TCNEO. It was also determined that styrene and 1,2-dibromoethane did not interfere with the titration of TCNEO by preparing weighed samples of the epoxide in 1,2-dibromoethane and styrene and titrating with a standardized thiosulfate solution after the addition of potassium iodide and acid.

Kinetic Analyses. The requisite amounts of TCNEO and olefin were weighed into a 100-ml. volumetric

flask and made up to volume with the solvent. When 1,2-dibromoethane was used as a solvent, the volumetric flask was not completely filled and was sealed under nitrogen and shaken on an automatic shaker until solution was achieved. The reaction mixture was then brought to volume with the proper amount of solvent. Pyrex test tubes were cleaned, dried, and constricted. They were filled with 5.0-ml. samples of the reaction mixture with a hypodermic syringe and sealed. Duplicate runs showed there was no difference in results if the tubes were flushed with nitrogen before sealing. The tubes were immersed in an oil-filled constant temperature bath maintained at the required temperature $\pm 0.1^\circ$. After the tubes were immersed, an auxiliary heater was used to return the bath to the desired temperature within 2–3 min. The tubes were removed at appropriate intervals, and the reaction was quenched by immersion in a bath of Dry Ice and acetone. The tubes were allowed to warm to room temperature, rinsed with acetone, tap water, and distilled water, and then broken under the surface of a solution of KI in 25 ml. of distilled water in a 1-l. heavy-walled Pyrex bottle. The proper amount of sulfuric acid was then added. For solutions having TCNEO concentration of 0.01 *M* or greater, 1.0 g. of KI and two drops of 10% H₂SO₄ solution were used. For solutions of less than 0.01 *M*, 0.5 g. of KI and 1 drop of 10% sulfuric acid were added. The reaction mixtures were then titrated to a starch end point with standard thiosulfate solution.

The run which was followed by ultraviolet spectroscopy was carried out in the same manner. Each 5.0-ml. sample was rinsed into a 25-ml. volumetric flask with spectroscopic grade cyclohexane which had been dried over sodium. The resulting solution was then given two tenfold dilutions with cyclohexane and the transmittance was measured with a Cary 10 recording spectrophotometer. The reference cell was filled with cyclohexane containing the same per cent 1,2-dibromoethane as the reaction mixture. An average of two determinations of the zero-time sample gave an extinction coefficient for *trans*-stilbene at 300 m μ of 2.87 $\times 10^4$.

Reaction of TCNEO and *trans*-Stilbene under Kinetic Run Conditions. A solution of 0.3707 g. (0.00257 mole) of TCNEO and 0.1803 g. (0.00100 mole) of *trans*-stilbene in 100 ml. of 1,2-dibromoethane was heated in an oil bath at 125.2° for 200 min. The reaction mixture was concentrated on a rotary evaporator and the residue transferred to a weighing dish in ethyl acetate solution. Most of the solvent was removed with a slow stream of nitrogen. The sample was finally dried in a vacuum desiccator at 0.1 mm. The weight of the residue was 0.4681 g. or 84.95% of the reactants charged. It is likely that some of the excess TCNEO was lost by volatilization. The residue was transferred to a sublimation apparatus and heated to 80–90° at 0.1 mm. The sublimate weighed 0.1340 g. and was shown to be recovered TCNEO by its infrared spectrum. This represents a 59.24% recovery of the excess TCNEO. The residue from the sublimation was a pale tan crystalline product weighing 0.3152 g. (97.19%). The melting point of the residue was 256–259°. The reported melting point of *trans*-3,4-diphenyl-2,2,5,5-tetracyanotetrahydrofuran is 258–259°.²

(5) R. Huisgen, H. J. Sturm, and H. Wagenhofer, *Z. Naturforsch.*, **17b**, 202 (1962).

(6) P. Pascal and L. Normand, *Bull. soc. chim. France*, [IV] **9**, 1060 (1911), report m.p. 120°.

(7) H. O. House, *J. Am. Chem. Soc.*, **77**, 3073 (1955), reports m.p. 128–129°.

(8) F. Bergmann, J. Weizman, and D. Schapiro, *J. Org. Chem.*, **9**, 408 (1944).

(9) A. Orekhoff and M. Tiffeneau, *Bull. soc. chim. France*, [IV] **37**, 1415 (1925), report m.p. 135–136°.

(10) H. Meerwein, E. Büchner, and K. V. Emster, *J. prakt. chem.*, **152**, 237 (1939), report m.p. 155°.

(11) W. J. Linn, O. W. Webster, and R. E. Benson, *J. Am. Chem. Soc.*, **87**, 3651 (1965).

The infrared spectrum of the residue was identical with the spectrum of an analytical sample of the *trans*-stilbene adduct.

Reaction of TCNEO and Styrene under Kinetic Run Conditions. A solution of 0.1450 g. of TCNEO and 0.13 ml. of styrene in 100 ml. of 1,2-dibromoethane was heated at 125.20° for 400 min. The solvent was removed by evaporation with a rotary evaporator and the residue washed into a weighing dish with ethyl acetate. The solvent was evaporated in a vacuum desiccator leaving a nearly colorless, crystalline residue weighing 0.1939 g. (78%). The melting point of the residue was 145–146°. The reported melting point of 3-phenyl-2,2,5,5-tetracyanotetrahydrofuran is 147–148°. The infrared spectrum of the product was identical with that of an analytical sample of the adduct of styrene and TCNEO.

Reaction of TCNEO and 4-Nitro-trans-stilbene under Kinetic Run Conditions. A solution of 0.1447 g. of TCNEO and 0.2250 g. of 4-nitro-*trans*-stilbene in 100 ml. of 1,2-dibromoethane was heated at 125.15° for 43 hr. Concentration of the reaction mixture with a rotary evaporator left a crystalline residue which was washed into a weighing dish with tetrahydrofuran. Most of the solvent was removed by evaporation, and the residue was dried in a vacuum desiccator to give 0.3623 g. (98.1%) of crystalline residue the infrared spectrum of which was identical with that of an authentic sample of 3-phenyl-4-*p*-nitrophenyl-2,2,5,5-tetracyanotetrahydrofuran. A small sample of the residue was sublimed at 170–200° at 0.1 mm. to give a sublimate with m.p. 222–225°. The authentic product melts at 223.5–224°.

3-Fluoro-trans-stilbene. To a suspension of 6.0 g. (0.11 mole) of sodium methoxide in 100 ml. of dimethylformamide there was added 22.8 g. (0.10 mole) of diethyl benzylphosphonate.¹² The resulting suspension was cooled to around 5°. A solution of 12.4 g. (0.10 mole) of freshly distilled *m*-fluorobenzaldehyde (Columbia Organic Chemicals Co.) in 50 ml. of dimethylformamide was added dropwise at such a rate that the temperature remained around 30°. When the addition was complete, the reaction mixture was stirred at room temperature for 1 hr. and then poured into ice-water. The colorless solid was collected by filtration and air-dried to give 15.5 g. of colorless solid, m.p. 72–74°. The melting point was raised to 74–75° by recrystallization from ethanol.

Anal. Calcd. for C₁₄H₁₁F: C, 84.82; H, 5.59; F, 9.58. Found: C, 84.46; H, 5.45; F, 9.30.

The infrared spectrum is characteristic of a *trans*-stilbene showing absorption at 10.38 μ (*trans* CH=CH). The ultraviolet spectrum (EtOH) is also characteristic, showing λ_{\max} 321 m μ sh (ϵ 16,800), 307 (27,400), 295 (27,200), 234 sh (12,000), and 227 (15,700).

trans-3-Phenyl-4 (m-fluorophenyl)-2,2,5,5-tetracyanotetrahydrofuran. A suspension of 2.18 g. (0.015 mole) of TCNEO in 35 ml. of 1,2-dibromoethane was heated to reflux, and a solution of 3.00 g. (0.015 mole) of *trans*-3-fluorostilbene in 15 ml. of 1,2-dibromoethane was added dropwise over a period of 3 hr. The reaction mixture was heated to reflux for an additional 16 hr.

(12) G. M. Kosalopoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 151.

and cooled. The crystals which separated were collected by filtration and air-dried to give 4.44 g. of crude product, m.p. 253–256°. Recrystallization from 1,2-dichloroethane gave 3.90 g. (76%) of colorless needles, m.p. 255–257°.

Anal. Calcd. for C₂₀H₁₁N₄FO: C, 70.17; H, 3.24; N, 16.37. Found: C, 70.03; H, 3.54; N, 16.56.

The infrared spectrum of this product is as expected with absorption at 4.44 μ (C \equiv N) and at 6.17, 6.25, and 6.68 μ (aromatic unsaturation).

trans-4-Chloro-4'-methylstilbene. To a suspension of 3.0 g. (0.055 mole) of sodium methoxide in 50 ml. of dimethylformamide there was added 12.1 g. (0.05 mole) of diethyl (4-methylbenzyl)phosphonate.¹² The suspension was cooled to 5°, and a solution of 7.0 g. (0.05 mole) of *p*-chlorobenzaldehyde in 25 ml. of dimethylformamide was added with stirring at such a rate that the temperature remained between 15 and 20°. A homogeneous solution did not form, but the suspension became more viscous. When the addition was complete, the ice bath was removed, and the reaction mixture was stirred for 30 min. and poured into ice-water. The precipitate was collected by filtration, washed with water, and air-dried to give 10.0 g. of colorless crystals, m.p. 201–205°. The crude product was recrystallized from 1,2-dichloroethane to give 8.40 g. (74%) of colorless plates, m.p. 203.5–204°.

Anal. Calcd. for C₁₅H₁₃Cl: C, 78.77; H, 5.73; Cl, 15.50. Found: C, 78.66; H, 5.76; Cl, 15.50.

The ultraviolet spectrum in ethanol showed λ_{\max} 315 m μ (ϵ 31,560), 303 (31,300), and 230 (14,390). The infrared absorption for *trans* CH=CH is at 10.35 μ .

trans-3-(p-Chlorophenyl)-4-p-tolyl-2,2,5,5-tetracyanotetrahydrofuran. A suspension of 4.56 g. (0.02 mole) of *trans*-4-chloro-4'-methylstilbene and 2.88 g. (0.02 mole) of TCNEO in 50 ml. of xylene was stirred and heated in an oil bath at 130° for 6 hr. The reaction mixture was cooled and filtered. The precipitate was washed with a little benzene to give 5.96 g. of tan solid which was recrystallized from *n*-butyl alcohol to give 5.01 g. (67.5%) of colorless crystals, m.p. 238–239°. The melting point was raised to 241–242° by further recrystallization from the same solvent.

Anal. Calcd. for C₂₁H₁₃ClN₄O: C, 67.65; H, 3.51; Cl, 9.51. Found: C, 67.65; H, 3.87; Cl, 9.42.

trans-3-Phenyl-4-(p-nitrophenyl)-2,2,5,5-tetracyanotetrahydrofuran. A mixture of 4.0 g. (0.028 mole) of TCNEO and 6.2 g. (0.028 mole) of *trans*-4-nitrostilbene in 50 ml. of 1,2-dibromoethane was heated to reflux for 14 hr. The reaction mixture was cooled, and the crystalline solid which separated was collected by filtration to give 7.00 g. of pale tan crystals. Concentration of the mother liquors caused the precipitation of another 2.16 g. of slightly darker solid. The two fractions were recrystallized from benzene to give 8.15 g. (80%) of product, m.p. 223–225°. Because of the large volume of benzene required, chlorobenzene was used for subsequent recrystallization, and the melting point of the analytical sample was 223.5–224°.

Anal. Calcd. for C₂₀H₁₁N₅O₃: C, 65.04; H, 3.00; N, 18.96. Found: C, 65.35; H, 3.20; N, 18.83.

trans-3-Phenyl-4-(p-methoxyphenyl)-2,2,5,5-tetracyanotetrahydrofuran. A suspension of 2.88 g. (0.02

mole) of TCNEO in 50 ml. of 1,2-dibromoethane was heated to reflux, and a solution of 4.20 g. (0.02 mole) of 4-methoxystilbene in 50 ml. of 1,2-dibromoethane was added dropwise over a period of 2.5 hr. The heating was continued for another 15 min., and the rather dark reaction mixture was concentrated on a rotary evaporator to leave a dark semisolid residue that was taken up in boiling ethanol, treated with charcoal, and filtered. The product separated when the filtrate was cooled and was collected by filtration to give 6.6 g. (69%) of colorless needles, m.p. 203–204.5°. Subsequent recrystallization from ethanol appeared to cause some degradation and the analytical sample, m.p. 202.5–203°, was recrystallized from a mixture of benzene and hexane.

Anal. Calcd. for $C_{21}H_{14}N_4O_2$: C, 71.18; H, 3.98; N, 15.81. Found: C, 70.76; H, 4.12; N, 15.99.

Competition Experiment with cis- and trans-1,2-Dichloroethylene. *cis*-1,2-Dichloroethylene (b.p. 59°)

and *trans*-1,2-dichloroethylene (b.p. 47.5–48°) were purified by distillation immediately before use. Into a 240-ml. Hastelloy-lined shaker tube there was placed 10.0 g. (0.069 mole) of TCNEO and 50 g. of a 50:50 mixture of the *cis* and *trans* olefins. The reaction vessel was heated at 130° and shaken for 16 hr. The pressure vessel was cooled, and the excess olefin was volatilized in a vacuum and collected in a cooled trap. Analysis of the composition of the recovered olefin by integration of the proton spectrum (*cis*, τ 3.57; *trans*, τ 3.65) gave 41% *trans* and 59% *cis*. The crude reaction product weighed 16.7 g. (100%) and was also analyzed by the proton spectrum determined in acetonitrile (*cis*, τ 4.23; *trans*, τ 4.44). The composition was 84% *trans* and 16% *cis*.

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Relative Nucleophilic Reactivities of Amino Groups and Mercaptide Ions in Addition Reactions with α,β -Unsaturated Compounds^{1,2}

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Factors were investigated which govern nucleophilic reactivities of functional groups in aminothiols, thiols, and other model compounds with α,β -unsaturated compounds such as acrylonitrile. Rates as a function of pH correlate with theoretical rate equations and indicate that mercaptide ions and nonprotonated amino groups participate in the rate-determining step. Possible reaction pathways of aminothiols are considered in terms of the two functional groups. A quantitative estimate of the influence of steric and polar parameters on rates of mercaptide ions was obtained from a Hammett-Taft-type, free-energy relation derived from observed linear Brønsted-type plots. The polar and steric reaction parameters of mercaptide ions are similar to those of amino groups. At comparable pK values and steric environments, sulfur anions are about 280 times more reactive than amino groups. This difference in reactivities is explained in terms of polarizabilities of nonbonded electrons on nitrogen and sulfur, charge distributions in ground and transition states, and solvation factors. A single, free-energy equation is developed that relates reactivities of mercaptide ions and amino groups to polar, steric, and nucleophilic parameters. Relative rates of these functional groups with several

vinyl compounds remain essentially constant. The predictions of kinetic data that α,β -unsaturated compounds should react preferentially with SH groups in aminothiols attached to primary carbon atoms, but not with those attached to tertiary, were confirmed by synthetic applications.

Amino acids, peptides, and related natural products frequently contain two or more functional groups which may react concurrently with α,β -unsaturated compounds. The relative rates of reaction of these groups with vinyl derivatives determine the pathways of reactions and the nature of products. Kinetic studies of reaction rates of α,β -unsaturated compounds, such as acrylonitrile, with amino and sulfhydryl groups of amino acids, aminothiol acids, thiol acids, and related model compounds were made to determine the factors governing the relative reactivities of these groups and to establish the influence of one group upon the reactivity of the other.

Previously² it was demonstrated that the rates of reaction of amino groups in amino acids and peptides with acrylonitrile were a function of amino acid anion concentration which is determined by the pK values of the amino groups and the pH of the medium. The rates of reaction were also shown to obey a Hammett-Taft free-energy relationship of the type

$$\log \frac{k_A(\text{any amino acid or peptide})}{k_A(\text{glycine})} = \rho\sigma^A + Es \quad (1)$$

(1) Presented at the Division of Organic Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 30–Sept. 4, 1964, Abstracts, p. 41S.

(2) Paper II of a series on reactions of amino acids, peptides, and proteins with α,β -unsaturated compounds. For paper I, see M. Friedman and J. S. Wall, *J. Am. Chem. Soc.*, **86**, 3775 (1964).

(3) A laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.