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Effect of Temperature and Solvent on the 1,3-Dipolar Cycloaddition of Diazodiphenylmethane with Several Dipolarophiles

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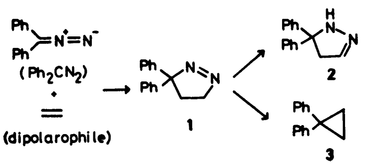
Synopsis. The title reaction is studied with a series of CN- or $COOCH_3$-substituted dipolarophiles. All the reactions obey the second-order rate law. The activation enthalpies and entropies are 44—52 kJ mol^{-1} and −(129—166) J K^{-1} mol^{-1}, respectively. The rate constants are insensitive to solvent. The reactivity and product of dimethyl maleate are anomalous.

In previous papers,[1,2] effects of temperature and solvent on the 1,4-cycloaddition reaction between tetracyanoethylene (TCNE) and styrenes have been investigated to shed light on the reaction mechanism. It is of considerable interest to compare the mechanism between 1,3-dipolar cycloaddition and 1,4-cycloaddition reactions. The cycloaddition reaction of diazodiphenylmethane (Ph_2CN_2) with some olefins has long been known,[3] and the first kinetic study of this reaction as a kind of 1,3-dipolar cycloaddition appeared two decades ago.[4] The reaction provides such adducts as 1-pyrazoline (**1**), 2-pyrazoline (**2**), and cyclopropane (**3**) depending on dipolarophiles used. The variety of these products is understood so far according to the following scheme:[5]



Scheme 1.

where **2** and **3** are formed from **1** by the H shift and the N_2 elimination, respectively. Until now there has been no thorough kinetic study where dipolarophiles are varied systematically so as to cover the product variety. It is worthwhile to examine the credibility of the Scheme 1 because some different scheme is proposed in a recent report on the 1,3-dipolar cycloaddition reaction of Ph_2CN_2 with TCNE in which the final product is of type **3**.[6]

Experimental

Materials. Ph_2CN_2 was obtained by the oxidation of benzophenone hydrazone with mercury(II) oxide (yellow).[3] Crude Ph_2CN_2 was recrystallized from petroleum ether in the form of needles, the melting point being 29 °C as reported;[3] crystals from methanol were of the form of flake with mp 22 °C. Dimethyl fumarate (DMF), dimethyl maleate (DMM), methyl acrylate (MA), fumaronitrile (FN), and acrylonitrile (AN) were supplied by Nakarai Chemicals, Ltd. and purified by the usual method. Maleonitrile (MN) was synthesized in a reported manner.[7] All solvents used were purified by the standard method.

Products. The adduct of each dipolarophile was identified by means of elemental analysis and by using the melting point, ^1H NMR, and IR data available in the literature: see Refs. 3, 8, and 9 for DMF, DMM, and MA and AN, respectively. FN and MN, which were studied here for the first time, gave 3,4-dicyano-5,5-diphenyl-2-pyrazoline, and unfortunately, the adduct could not be crystallized: NMR ($CDCl_3$) $\delta=$ 7.4, 7.2 (m 11H) and 4.81 (s 1H); IR (neat) 3300 (νNH) and 2220 cm^{-1} (νCN).

Kinetic Measurements. The disappearance of Ph_2CN_2 was followed around 525 nm by using a Hitachi Perkin-Elmer 139 UV visible spectrophotometer. Temperature was controlled to ±0.05 °C at 20, 25, 30, and 35 °C. Although Ph_2CN_2 is known to decompose (first-order reaction) at ambient temperature, the decomposition is so slow (1% in toluene at 25 °C for a period of 3.5 d) that it is negligible in the present work (each run finished within 6 h). All reactions studied obey the second-order rate law shown by

$$-\frac{d[Ph_2CN_2]}{dt} = k[Ph_2CN_2][\text{dipolhrophile}]$$

where [ ], t, and k denote the concentration, the time ,and the rate constant, respectively. The rate constants were determined from the second-order plots, *i.e.*, log $[Ph_2CN_2]/[\text{dipolarophile}]$ *vs.* t. Their uncertainty is about 1%.

Results and Discussion

In the temperature (T) range studied here, the values of $\ln(k/T)$ are linear against $1/T$. According to the Eyring equation[10] these linear relations lead to determination of the activation enthalpies ($\Delta H^{\neq}$) and entropies ($\Delta S^{\neq}$) listed in Table 1. In broad terms, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ differ little from one dipolarophile to another in spite of the product diversity; there exist some differences which will be discussed later in relation to the molecular structure of the dipolarophile. Thus, all reactions studied can be classified into the same kind of 1,3-dipolar cycloaddition from the kinetic point of view. The similarity of the transition state in these reactions strongly suggest that not only DMM but also other dipolarophiles once produce the adduct of type **1** just

TABLE 1. KINETIC PARAMETERS FOR 1,3-DIPOLAR CYCLOADDITION OF Ph_2CN_2 WITH VARIOUS DIPOLAROPHILES IN TOLUENE AT 25 °C

Dipolarophile[a)]	A[b)]	10^4k[c)]	$\Delta H^{\neq}$[d)]	$\Delta S^{\neq}$[e)]
X/=\X (DMM)	**1**	2.77	44±1	−166±1
X/=/X (DMF)	**2**	53.3	44±1	−141±1
=/X (MA)	**3**	19.8	44±3	−150±3
NC/=\CN (MN)	**2**	25.0	47±1	−136±2
NC/=/CN (FN)	**2**	9.97	51±1	−130±1
=/CN (AN)	**3**	9.72	52±2	−129±2

a) $X=COOCH_3$. b) Adduct of Ph_2CN_2; see Scheme 1. c) mol^{-1} dm^3 s^{-1}. d) kJ mol^{-1}. e) J K^{-1} mol^{-1}.

Table 2. Rate constants (k) for 1,3-dipolar cycloaddition reactions of Ph_2CN_2 with DMM, DMF, and MA in several solvents at 25 °C

Solvent	$10^4\ k/\mathrm{mol^{-1}\ dm^3\ s^{-1}}$		
	DMM	DMF	MA
PhMe	2.77	53.3	19.8
PhCl	2.57	62.3	21.5
$(ClCH_2)_2$	2.28	65.5	20.3
Me_2NCHO	3.36	96.3	31.0
MeCN	3.02	103.5	27.4

as illustrated by Scheme 1; when the adduct is of type **2** or **3**, type **1** exists only as an unstable intermediate. In the present work, low temperature (≈0 °C) experiments were carried out to find such an intermediate in the reaction mixture but not successful. Further consideration as to why the stability of type **1** depends so much on the substituents in the dipolarophile will be given later in this note.

These reactions seem to proceed by a concerted mechanism for the following reasons: 1) the values of $\Delta H^{\ast}$ and $\Delta S^{\ast}$ in Table 1 are in the ranges of the corresponding ones for some other 1,3-dipolar cycloadditions for which a concerted mechanism is concluded[11] and 2) the rate constants are insensitive to solvent polarity as seen in Table 2. The latter fact shows unlikelihood of a two-step machanism involving a zwitterionic intermediate; if the transition state has zwitterionic character to a significant extent, a rate factor of over 10^4 (*cf.* smaller than two in Table 2) would be expected in the range of solvent polarity covered in Table 2.[1,12]

Although differences in the kinetic parameters in Table 1 are relatively small, some of them are important. In the case of $COOCH_3$ substituted dipolarophiles, the *cis* form is less reactive than the *trans* form, while the former is more reactive than the latter in the case of CN-substituted ones. DMM is unique also with respect to the type of adduct. DMM is lower in reactivity than MN in spite of its lower $\Delta H^{\ast}$, the reactivity difference being controlled by the entropy term. The anomalous behavior of DMM would be ascribed to the steric hindrance between the bulky $COOCH_3$ groups. Since such a steric hindrance prevents conjugation due to coplanarity between the pyrazoline ring and $COOCH_3$ group in the adduct of DMM (type **1** and *cis* form[13]), the H shift does not occur, and thus, the *cis* form of type **1** (produced by DMM) which is thermodynamically less stable than the *trans* form (produced by DMF) is isolated. With heat or a catalyst,[8] the adduct can be isomerized to type **2** which is the same as the adduct of DMF. The above consideration is supported by the fact that MN and FN give the same adduct (type **2**); the steric hindrance by a CN group is negligible compared with that by a $COOCH_3$ group.

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13) It is widely accepted that the 1,3-dipolar cycloaddition is stereospecific. Although the product is described as the *trans* form without evidence in Ref. 8, the coupling constant $J_{3,4}$ is 7.5 Hz, which does not necessarily indicate the *trans* form.