Kinetics of the 1,3-dipolar Cycloaddition of p-substituted 3-phenylsydnones with DMAD

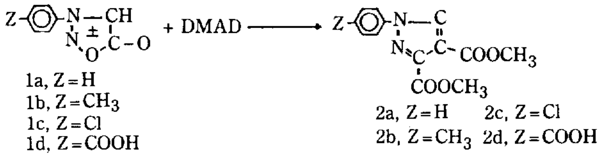
Byoung Hee Youn*, Hak Soo Lyu, Jee Hyun Han, Soon Jong Hahn, and Sun Hwan Kim

Department of Chemistry, Yonsei University, Seoul 120, *Received December 19, 1986*

The kinetics of the 1,3-dipolar cycloaddition of p-substituted 3-phenylsydnones la-d with DMAD have been investigated. The reaction rates over a temperature range 100-140°C were measured by UV spectrometry. The reactions found to be second-order overall, insensitive to the dielectric constants of the solvents, and characterized by a large entropy of activation. These findings are consistent with the rate-determining step involving the formation of cyclic transition state 1 and the reaction proposed to be concerted.

Introduction

1,3-dipolar addition reaction of sydnones with dipolarophiles affords a convenient and versatile route for the preparation of five-mimbered heterocycles, such as pyrazoles,[1,2] triazoles,[3] and pyrazolines.[4] 3-Phenylsydnone and other sydnone derivatives have been found by Huisgen and his co-workers to undergo 1,3-dipolar addition with olefins and acetylenes[5]. The intermediate of this reaction is thought to be the azomethine-imine, which has been known to behave as 1,3-dipole. Recently, it was reported that pyrazoledicarboxylic esters have been prepared by a new photo 1,3-dipolar addition of 3-phenylsydnone with dimethylacetylene dicarboxylate(DMAD), and studies have also reported[6] its molecular orbital treatments[7]. Most of mechanistic investigations of the 1,3-dipolar addition reaction of 1,3-dipole substrates with dipolarophiles have been reported, and the reactions wich generally known to be one-step cyclic concerted mechanism.[8] However, mechanistic study of 1,3-dipolar addition of 3-phenylsydnones with DMAD has not been studied. In this paper, we will suggest that the 1,3-dipolar addition mechanism of p-substituted 3-phenylsydnones with DMAD.



Results and Discussion

Since the UV absorbance of pyrazoledicarboxyic esters are maximum at between 280 and 290 nm, the rates of its formation were measured at this wavelength. Second-order rate constants for varing temperatures and solvents obtained by this method are summarized in Table 1. Activation parameters derived from the rate constants at 120.0°C are taulated in Table 2.

Table 1. Solvent Effect on the Reaction Rates in the Formation of Pyrazoledicarboxylic Esters

	dioxane	chlorobenzene	nitrobenzene
ε^{a}	2.21	5.60	34.8
		10^2k_2, $^{b}M^{-1}s^{-1}$	
temp^{c},	dioxane	chlorobenzene	nitrobenzene
	1a(1.0 10^{-2}) + DMAD(2.0 10^{-2})		
100.0	6.65 ± 0.09	6.53 ± 0.07	7.96 ± 0.09
110.0	8.98 ± 0.06	8.80 ± 0.09	10.8 ± 0.9
120.0	12.1 ± 0.08	11.9 ± 0.09	14.5 ± 0.8
130.0	16.3 ± 0.8	16.0 ± 0.9	19.6 ± 1.0
140.0	22.1 ± 0.8	21.7 ± 0.6	26.4 ± 0.9
	1b(1.0 × 10^{-2}) + DMAD(2.0 × 10^{-2})		
100.0	6.33 ± 0.08	6.86 ± 0.10	7.28 ± 0.10
110.0	8.46 ± 0.07	9.16 ± 0.09	9.72 ± 0.09
120.0	11.3 ± 0.08	12.2 ± 0.08	13.0 ± 0.10
130.0	15.1 ± 0.09	16.4 ± 0.09	17.4 ± 0.12
140.0	20.2 ± 0.07	21.9 ± 0.07	23.2 ± 0.09
	1c(1.0 × 10^{-1}) + DMAD(2.0 × 10^{-2})		
100.0	8.21 ± 0.07	8.80 ± 0.09	9.16 ± 0.08
110.0	11.2 ± 0.09	12.0 ± 0.08	12.5 ± 0.09
120.0	15.4 ± 0.08	16.5 ± 0.09	17.2 ± 0.10
130.0	21.0 ± 0.08	22.5 ± 0.1	23.5 ± 0.09
140.0	28.9 ± 0.1	31.0 ± 0.08	32.3 ± 0.07
	1d(1.0 × 10^{-2}) + DMAD(2.0 × 10^{-1})		
100.0	9.59 ± 0.09	9.31 ± 0.05	9.99 ± 0.10
110.0	13.3 ± 0.1	12.9 ± 0.12	13.8 ± 0.06
120.0	18.5 ± 0.08	17.9 ± 0.09	19.2 ± 0.08
130.0	25.6 ± 0.05	24.8 ± 0.12	26.6 ± 0.06
140.0	35.5 ± 0.06	34.4 ± 0.08	36.9 ± 0.07

[a] Dielectric constant. [b] Rate constants were obtained by least-squares methods with standard errors in individual measurements and uncorrected for solvent expension from room temperature. [c] Temperatures were maintained within ± 0.2°C.

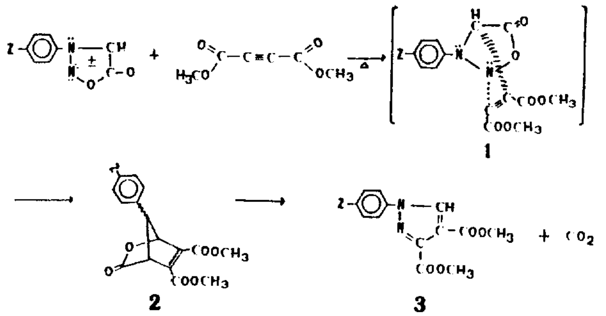
The results indicate that these are standard second-order reactions. Regardless of reaction medium and substituent group on the phenylring of sydnones, Table 1 show that the rates of reaction for p-substituted 3-phenylsydnones with DMAD are not significantly different. Though this small difference seems to be caused by substituent groups, it is not large enough to justify speculation on a different mechanism for the reaction. In addition, one is strucked by the similarity between the activation parameters and compounds having different substituents. The most fundamental kinetic assumption that can be drawn from the fact the reactions under investigation have such highly similar activation parameters is that the reaction mechanisms are almost certainly the same. Also noteworthy are the large negative values for the activation entropies under all the conditions used, bellow-25 eu in

Table 2. Activation Parameters for the Formation of Pyrazoledicarboxylic Esters in Various Solvents at 120.0°C

solvent	1a(1.0×10^{-2}) + DMAD(2.0×10^{-2})	1b(1.0×10^{-2}) + DMAD(2.0×10^{-2})	1c(1.0×10^{-2}) + DMAD(2.0×10^{-2})	1d(1.0×10^{-2}) + DMAD(2.0×10^{-2})
	ΔH^*, Kcal mol^{-1} ΔS^*, eu	ΔH^*, Kcal mol^{-1} ΔS^*, eu	ΔH^*, Kcal mol^{-1} ΔS^*, eu	ΔH^*, Kcal mol^{-1} ΔS^*, eu
dioxane	8.39 ± 0.3[a] -28.2 ± 1.0	8.09 ± 0.4 -29.0 ± 1.1	8.86 ± 0.5 -26.5 ± 1.3	9.16 ± 0.5 -25.4 ± 0.9
chlorobenzene	8.39 ± 0.2 -28.2 ± 0.9	8.08 ± 0.3 -28.9 ± 1.0	8.86 ± 0.4 -26.4 ± 1.1	9.16 ± 0.4 -25.4 ± 0.7
nitrobenzene	8.39 ± 0.3 27.9 ± 0.9	8.09 ± 0.2 -28.8 ± 1.2	8.86 ± 0.5 -26.3 ± 1.2	9.16 ± 0.5 -25.4 ± 0.7

[a] The errors were estimated from the extreme slopes of a ln k_2/T vs. $1/T$ plot.

reactions. These findings imply that the rate-determining step must highly restricted in freedom, and on the basis of many examples it is reasonable to assume that the transition state is most likely a charged transition state[9] or a cyclic form.[10,11] If these reactions under examination proceed through a charged transition state, then it is strongly to be expected that the reaction rates would show significant solvent effect and substituent group influence. However, the rate constants for each compound under examination do not differ significantly in spite of the use of solvents which differ appreciably in their dielectric constants, and it is not likely that the transition state involves a charge separation. The most plausible structure for the transition state in these reactions is a cyclic form 1, and this explains that the large negative entropy values and not only the solvents but the p-substituted compounds 1a-d are independent of the rate constants. This cyclic transition state 1 will lead to intermediate 2. Since it could not be isolated, it is not possible to prove existence of intermediate 2. Next, it can readily be assumed that the transition from 2 to 3 is faster than the decarboxylation of p-substituted 3-phenylsydnones with DMAD due to the instability of the cyclic intermediate 2. The rate determining step is most likly to be the formation of transition state 1, and this would be a concerted process. The mechanism proposed for this reaction is as shown in scheme.



Scheme

Experimental

Materials. All solvents employed for kinetic measurements were purified by methods given in the literature.[12,13] Dioxane(Shinyo chemical Co., reagent grade) was treated with sodium and distilled (101-101.3°C). Chlorobenzene (Wako chemical Co., reagent grade) was distilled in the presence of calcium chloride(131-131.5°C). Nitrobenzene (Wako chemical Co., reagent grade) was treated with calcium chloride and distilled in vacuum [80-81°C (10mm)]. Compounds Ia[14], Ib[15], Ic[16], and Id[17] were prepared by literature methods. Commercial dimethyl acetylenedicarboxylate (DMAD) was distilled prior to use.

Kinetics. Rate constants were determined from measurements of increase in absorbance at between 280 and 290 nm accompanying formation pyrazoledicarboxylic esters. One-milliliter portions of a solution containing 1.00×10^{-2}M of p-substituted 3-phenylsydnone and 2.00×10^{-2}M of DMAD in a specific solvent were pipetted into each of pyrex ampules. The solutions in the ampules were sealed. All the ampules were placed simultaneously in an oil bath at room temperature, and the room temperature of the oil bath was raised and maintained at a constant temperature (±0.2°C) by a micro thermoregulator (Shimadzu chemical Co., model 3015). Ampules were removed from the oil bath one at a time at appropriate time intervals and quenched in an ice-water mixture to stop further reaction. The first (zero-time) ampule in a given run was removed from the oil bath when the temperature reached the specified temperature. From 10 to 12 ampules were used for each kinetic run. After all the quenched ampules had been allowed to reach thermal equilibrium (-1h) at room temperature and were then opened, alliquots were diluted with the same solvents to 2×10^{-4}M. Absorbances were measured with a Shimadzu Model UV -240 double-beam spectrometer using a 1-cm quartz cell recorded by a Teflon stopper. The second-order rate constants were obtained from the slopes of plots of $\ln[2(A_\infty - A_t)/2(A_\infty - A_o)-(A_t - A_o)]$ vs. time derived from $k_2 = [1/_t(2a-b)]\ln[b(a-x)/a(b-2x)]$ for our situation of $b = 2a$.[18a] The values of the activation parameters were obtained by using the Arrhenius plot at five different temperatures and the Eyring equation.[18b]

Acknowledgement. This research was supported by a grant awarded by the ministry of Education, republic of Korea.

References

1. R. Huisgen, H. Gotthardt, and R. Grashey, *Angew. Chem.*, **74**, 30 (1962).
2. J. K. Stille, F. W. Harris, and M. A. Bedford, *J. Heiero-cyclic. Chem.*, **3**, 155 (1966).
3. A. Ya. lazaris, *Zh. Organ. Khim.*, **2**, 1322 (1966).
4. D. P. Ainsworth and H. Suchitzky, *J. Chem. Soc. (C)*, 315

(1967).
5. R. Huisgen, H. Gottardt, and R. Grashey, *Chem. Ber.*, **101**, 536 (1968).
6. H. Heimagartner, and H. Schmid, *Helv. Chem. Acta.*, **60**, 1087 (1977).
7. H. Gotthardt, and F. Reiter, *Chem. Ber.*, **112**, 1193 (1979).
8. H. Huisgen, *J. Org. Chem.*, **41**, 403 (1976).
9. A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2nd ed., Wiley, New York, 1961, chapter 7.
10. P. Scheiner, J. H. Schomaker, and G. P. Nowack, *J. Am. Chem. Soc.*, **87**, 306 (1965).
11. J. H. Hall, F. E. Behr, and R. l. Reed, *J. Am. Chem. soc.*, **94**, 4952 (1972).
12. J. A. Riddick and W. B. Bunger, "Organic Solvents", 3rd ed., Wiley-Interscience, New York, 1970.
13. D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals", Pergamon Press, London, 1966.
14. R. A. Eade and J. C. Earl, *J. Chem. Soc.*, 2307 (1948).
15. W. Baker, W. D. Ollis, and V. D. Poole, *J. Chem. Soc.*, 307 (1949).
16. P. M. Weintraub, *J. Chem. Soc.*, 760 (1970).
17. C. V. Greco, W. H. Nyberg, and C. C. Cheng, *J. Med. Pharm. Chem.*, **5**, 861 (1962).

Stereoselective Synthesis of (7Z, 11E)-7, 11-Hexadecadien-1-yl Acetate, Sex Pheromone of the Angoumois Grain Moth

Suk-Ku Kang*, Kyung-Ok Yoo, and Hong Sik Moon

Department of Chemistry, Sung Kyun Kwan University, Natural Science Campus, Suwon 170

Received February 16, 1987

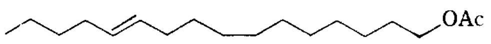
(7Z, 11E)-7, 11-Hexadecadien-1-yl acetate(**1**), the sex pheromone of the female Angoumois grain moth, *Sitotroga cerealella*, was synthesized via the acetylenic intermediate, (11E)-11-hexadecen-7-yn-ol THP ether(**2**). The acetylenic compound was prepared from 7-octyn-1-ol THP ether(**4**) and (3E)-1-bromo-3-octene(**3**). The (E)-homoallylic bromide **3** was synthesized by the Julia olefin synthesis of 1-cyclopropylpentan-1-ol(**6**).

Introduction

(7Z, 11E)-7, 11-Hexadecadien-1-yl acetate(**1**) (Figure 1) was identified as the sex pheromone of the Angoumois grain moth, *Sitotroga cerealella*, in 1974 by Vick *et al*[1]. This compound was also identified as a component of the sex pheromone of the female pink bollworm moth *Pectinophora gossypiella*(Saunders), a destructive pest of cotton by Hummel et al[2]. in 1973.

Serious economic losses of stored grains are caused by the Angoumois grain moth. In connection with our work on insect pheromones of agricultural importance, we became interested in the synthesis of this pheromone. Also, Institute of Agricultural Science in Suwon, Korea, needed a fair amount of the Angoumois grain moth pheromone to conduct biological activity tests in Korea.

In the literature, the compound **1** was synthesized via acetylenic intermediates[3-5] or Wittig olefination reactions[6-8]. Here we wish to describe a synthesis of (7Z, 11E)-7, 11-hexadecadien-1-yl acetate(**1**) employing the Julia olefin synthesis[9] to introduce the E-11 double bond.



1

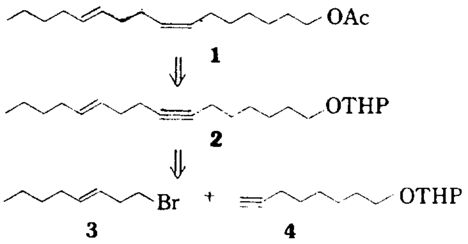
Figure 1

Results and Discussion

A simple retrosynthetic analysis (Scheme 1) reveals that (11E)-11-hexadecen-7-yn-1-ol tetrahydropyranyl ether(**2**) is the penultimate compound which in turn can be prepared from (3E)-1-bromo-3-octene(**3**) and 7-octyn-1-ol THP ether(**4**).

In the literature, (3E)-1-bromo-3-octene(**3**)[4] was prepared from 3-octyn-1-ol by reduction with Na in NH_3 and ether, fractional distillation, and bromination with PBr_3.

The hydrogen bromide promoted rearrangement of secondary cyclopropylmethanols for the preparation of (E)-homoallylic bromide is a useful synthetic reaction.[9]. Thus, cyclopropylcyanide(**4**) was reacted with n-butylmagnesium bromide to give 1-cyclopropylpentan-1-one(**5**)[10]. LAH reduction furnished 1-cyclopropylpentan-1-ol(**6**)[10].



Scheme 1