Heteroatom Chemistry
Volume 3, Number 5/6, 1992

The Reaction of Dipolarophiles with Arenealdoxime Dehydrodimer

Xudong Wei, Zhuangyu Zhang, Jiaming Li, and Hongwen Hu

Department of Chemistry, Nanjing University, Nanjing 210008, China

Received 30 June 1992

ABSTRACT

The reactions of dipolarophiles with arenealdoxime dehydrodimers **1** *have been studied. The reaction products depend upon the dipolarophile used. The reactions of* **1** *with styrene afford linear adducts. Active dipolarophiles, such as methyl acrylate and dimethyl acetylenedicarboxylate, lead to 1,3-cycloaddition products. The possible mechanisms for both cases are discussed.*

INTRODUCTION

The 1,3-dipolar reaction is considered to be the most useful method for the synthesis of five-membered heterocyclic ring systems containing one or more heteroatoms. Grundmann [1] has reported that arenealdoxime dehydrodimers react with a suitable dipolarophile, such as dimethyl maleate, norbornylene, acenaphthylene, or 1-dimethylamino-2-propyne, in refluxing chloroform or benzene to give a 1,3-cycloaddition product. However, in sharp contrast to the results with these dipolarophiles, we [2,3] found that styrene could react with benzaldoxime dehydrodimer or 3-chlorobenzaldoxime dehydrodimer in refluxing chloroform to give linear adducts as the products. It appears that different mechanisms may operate and the nature of the dipolarophile may play an important role in the determination of the addition type. As a part of our continuing studies, we decided to explore whether other substituted benzaldoxime dehydrodimers or dipolarophiles will undergo the same type of reaction. In this article, we wish to report the reactions of arenealdoxime dehydrodimers with styrene and other dipolarphiles and discuss the possible reaction mechanisms.

RESULTS AND DISCUSSION

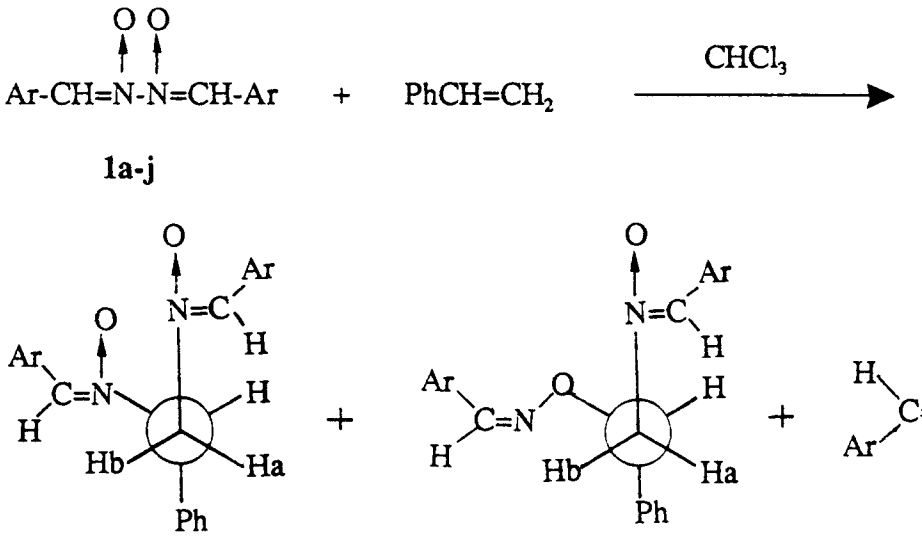
A variety of arenealdoxime dehydrodimers have been treated with styrene in refluxing chloroform (Equation 1). As summarized in Table 1, all reactions gave linear adducts, bisnitrones **2** and nitrone-oximinates **3–4**, as main products. For dehydrodimers **1a–b**, all three of the linear adducts could be obtained. However, in the cases of **1c–h** and **1i,j**, only two (**2c–h**, **3c–h**) and one linear adducts (**2i,j**), respectively, were obtained.

In our previous study [4], a free radical mechanism was proposed for the reaction of benzaldoxime dehydrodimer with styrene in refluxing chloroform based on an ESR study. The dehydrodimer is thought to decompose thermally to give two iminoxy radicals, which subsequently add to the electron-rich carbon–carbon double bond of styrene to yield linear adducts.

The structural and configurational assignments of the adducts are based on their physical data (Table 1) and on the comparison of these data to those of compounds **2a** and **3c**, the structures of which have been verified by X-ray crystallography [3]. For bisnitrone **2**, the ^{1}H NMR peak of Hb was found at lower field (ca. δ = 5.2) than that of Ha ca. δ = 4.4), due to the deshielding effect of the β-nitrone group. Compounds **3** and **4** are *syn-anti* isomers due to the restricted rotation around the C=N double bond in the oxime group. In the (*E*)-isomer **4**, since the methine proton (CH=N) is closer to the oxygen atom, it resonates at a lower field (ca. 0.7 ppm lower) than that of the (*Z*)-isomer **3** [5]. However, the chemical shifts of Ha (ca. δ = 4.2) and

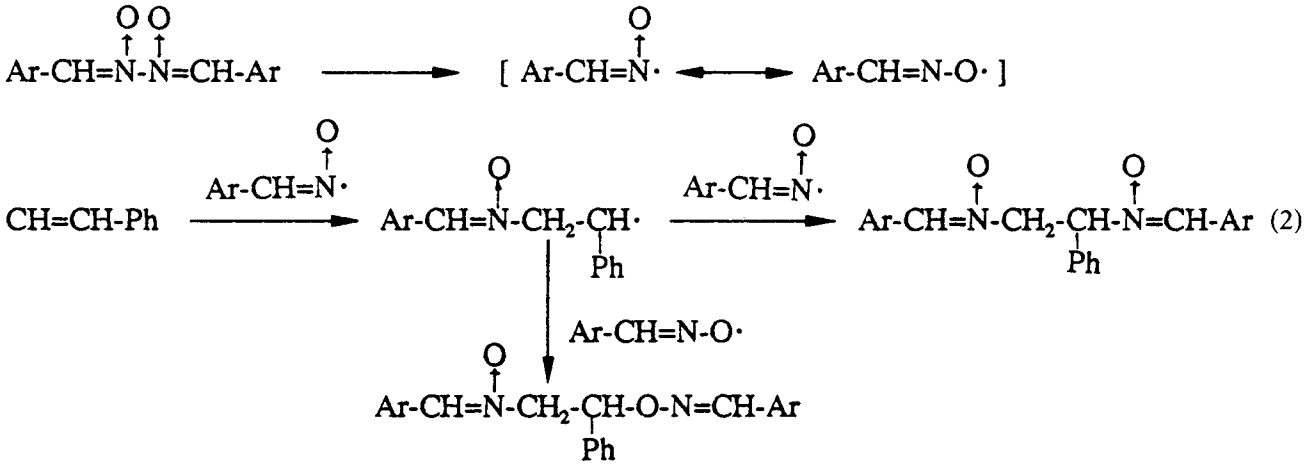
Dedicated to Prof. Huang Yao-Zeng on the occasion of his eightieth birthday.

1042-7163/92/$3.50 + .25



(1)

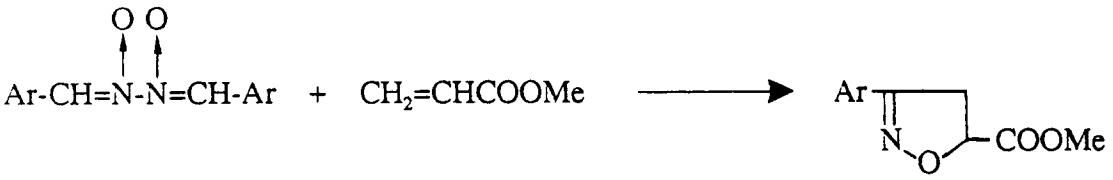
1-3	a	b	c	d	e	f	g	h	i	j
Ar:R-Ph, R=	H	4-Cl	3-Cl	2-Cl	3,4-Cl_2	3-Br	3-NO_2	4-NO_2	4-MeO	3,4-OCH_2O



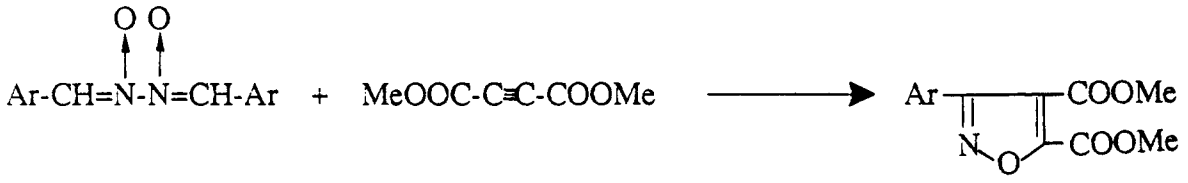
(2)

Hb (ca. δ = 4.4) are very close, demonstrating the much smaller deshielding effect of the oxime group than that of the nitrone group.

The behaviors of active dipolarophiles toward arenealdoxime dehydrodimers were also examined. Unlike styrene, no 1:1 adduct was obtained under the same reaction conditions. For example, in the case of methyl acrylate, the main product was the 1,3-cycloaddition product **5** (Equation 3). With a more active dipolarophile, the reaction of dimethyl acetylenedicarboxylate could proceed at room temperature to afford a 1,3-cycloaddition product **6b** (Equation 4). The results are summarized in Table 2. These results imply that the reaction mechanism must be different from that of styrene. It has been suggested in the literature [1] that dehydrodimers decompose thermally in refluxing chloroform or benzene, forming one equivalent each of nitrile oxide and aldoxime. If the nitrile oxide is trapped in situ by a suitable dipolarophile, the expected 1,3-cycloaddition product is obtained. In the absence of suitable reactants, such as olefins or acetylenes, it would add to undecomposed dehydrodimer to give a 1,2,4-oxadiazole and 1,2,4-oxadiazole-4-oxide or undergo dimerization to a furazan [1]. In attempts to obtain furazans, we



1a-b,g-j 5a-b,g-j (3)

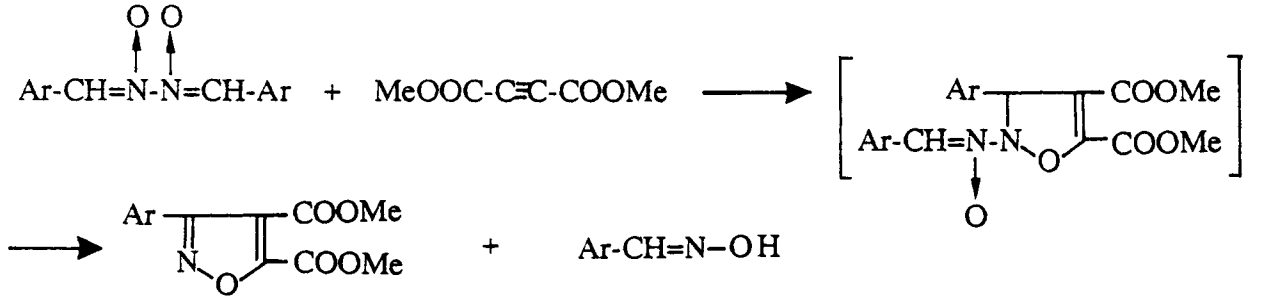


1b 6b (4)

1,5,6	a	b	g	h	i	j
Ar:R-Ph, R=	H	4-Cl	3-NO_2	4-NO_2	4-MeO	3,4-OCH_2O

have treated a variety of arenealdoxime dehydrodimers in refluxing chloroform; however, no furazans could be obtained. It is notable that, in our study, no furazans could be found in the reactions of **1** with active dipolarophiles. Based on these observations and the fact that a 1,3-cycloaddition of dimethyl acetylenedicarboxylate can occur at room temperature, the suggestion can be made that, although 1,3-cycloaddition products were obtained, nitrile oxide intermediates may not be involved in the above reactions. It is believed that the reaction proceeds by the addition of the nitrone group of the dehydrodimer to the dipolarophile, followed by elimination of an aldoxime to afford a 1,3-cycloaddition product. The possible mechanism is outlined in Equation 5.

Our previous study indicated that the ESR signals of iminoxy radicals could be detected only when chloroform solutions of arenealdoxime dehydrodimers were heated at a temperature over 40°C. Since the iminoxyls are electron-deficient (electrophilic) radicals, they can easily add to an electron-rich carbon–carbon double bond such as that in styrene. Generally, the moderately active dipolarophiles undergo reaction at higher temperatures, at which the dehydrodimers begin to decompose to iminoxy radicals and, therefore, free radical addition products are obtained. However, the active dipolarophiles, such as dimethyl acetylenedicarboxylate and methyl acrylate, react with dehydrodimers at lower temperatures and the addition of the nitrone group of the dehydrodimer to



(5)

TABLE 1 Physical Data of the Products of Addition of Arenealdoxime Dehydrodimers with Styrene

Product	Yield[a] (%)	mp (°C) (solvent) Molecular Formula[b]	IR (KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS)[c] δ, J (Hz)	MS m/z (%)
2a	30	189–190 (EtOH–$CHCL_3$) $C_{22}H_{20}N_2O_2$	1581, 1562, 1460, 1150, 1133, 805, 689	4.22 (dd, 1H, J_1 = 3.0, J_2 = 12.0, Ha) 5.32 (dd, 1H, J_1 = 10.0, J_2 = 12.0, Hb) 6.02 (dd, 1H, J_1 = 3, J_2 = 10, CH) 7.31–7.40 (m, 9H, ArH) 7.58 (s, 1H, CH=N) 7.63 (s, 1H, CH=N) 7.64–7.66 (m, 2H, ArH) 8.13–8.18 (m, 4H, ArH)	344 (M^+, 0.5)
2b	68	232–4 (EtOH–$CHCl_3$) $C_{22}H_{18}Cl_2N_2O_2$	1578, 1490, 1165, 1140, 1092, 850, 705	4.20 (dd, 1H, J_1 = 3.0, J_2 = 12.0, Ha) 5.27 (dd, 1H, J_1 = 10.0, J_2 = 12.0, Hb) 5.97 (dd, 1H, J_1 = 3.0, J_2 = 10.0, CH) 7.25–7.53 (m, 9H, ArH) 7.55 (s, 1H, CH=N) 7.60 (s, 1H, CH=N) 8.17 (d, 4H, J = 8.0, ArH) 8.19 (d, 1H, J = 8.0, ArH)	412 (M^+, 32)
2c	34	170–171 (EtOH–$CHCl_3$) $C_{22}H_{18}Cl_2N_2O_2$	1582, 1470, 1162, 1138, 812, 795, 812, 795, 700	4.21 (dd, 1H, J_1 = 3.0, J_2 = 12.5, Ha) 5.29 (dd, 1H, J_1 = 10.2, J_2 = 12.5, Ha) 5.99 (dd, 1H, J_1 = 3.0, J_2 = 10.2, CH) 7.23–7.43 (m, 7H, ArH) 7.54 (s, 1H, CH=N) 7.58 (s, 1H, CH=N) 7.61–7.63 (m, 2H, ArH) 7.79 (d, 1H, J = 7.8, ArH) 7.89 (d, 1H, J = 7.8, ArH) 8.38–8.41 (m, 2H, ArH)	412 (M^+, 13.5)
2d	48	161–163 (EtOH–$CHCl_3$) $C_{22}H_{18}Cl_2N_2O_2$	1575, 1468, 1170, 1145, 755, 700	4.10 (dd, 1H, J_1 = 3.0, J_2 = 12.0, Ha) 5.13 (dd, 1H, J_1 = 9.0, J_2 = 12.0, Hb) 5.75 (dd, 1H, J_1 = 3.0, J_2 = 9.0, CH) 7.00–7.45 (m, 11H, ArH) 7.66 (s, 1H, CH=N) 7.74 (s, 1H, CH=N) 8.75–9.05 (m, 2H, ArH)	413 (M^+ + 1, 15.9)[d]
2e	53	198–200 (EtOH–$CHCl_3$) $C_{22}H_{16}Cl_4N_2O_2$	1575, 1460, 1160, 1140, 890, 700	4.17 (dd, 1H, J_1 = 3.0, J_2 = 12.0, Ha) 5.25 (dd, 1H, J_1 = 10.0, J_2 = 12.0, Hb) 6.00 (dd, 1H, J_1 = 3.0, J_2 = 10.0, CH) 7.25–8.00 (m, 11H, ArH, 2 × CH=N) 8.05 (s, 1H, ArH) 8.53 (s, 1H, ArH)	483 (M^+ + 1, 0.5)[d]
2f	28	188–190 (EtOH–$CHCl_3$) $C_{22}H_{18}BrN_2O_2$	1575, 1450, 1155, 1140, 700, 680	4.21 (dd, 1H, J_1 = 3.0, J_2 = 12.0, Ha) 5.29 (dd, 1H, J_1 = 10.0, J_2 = 12.0, Hb) 6.15 (dd, 1H, J_1 = 3.0, J_2 = 10.0, CH) 7.00–8.10 (m, 13H, ArH, 2 × CH=N) 8.25–8.50 (m, 2H, ArH)	503 (M^+ + 1, 22.4)[d]
2g	25	206–209 (EtOH) $C_{22}H_{18}N_2O_6$	1580, 1565, 1520, 1160, 1145, 815, 735, 675	4.52 (dd, 1H, J_1 = 4.0, J_2 = 12.0, Ha) 5.20 (dd, 1H, J_1 = 10.0, J_2 = 12.0, Hb) 6.30 (dd, 1H, J_1 = 10.0, CH) 7.35–7.95 (m, 7H, ArH, 2 × CH=N) 8.15–8.66 (m, 6H, ArH) 9.47 (s, 2H, ArH)	435 (M^+ + 1, 5.9)[d]
2h	45	189–207[d]			
2i	34	200–202 (EtOH) $C_{24}H_{24}N_2O_4$	2830, 1600, 1505, 1175, 1150, 845, 700	3.79 (s, 6H, 2 × MeO) 4.18 (dd, 1H, J_1 = 3.0, J_2 = 12.0, Ha) 5.28 (dd, 1H, J_1 = 10.0, J_2 = 12.0, Hb) 5.96 (dd, 1H, J_1 = 3.0, J_2 = 10.0, CH) 6.82 (d, 2H, J = 9.0, ArH) 6.85 (d, 2H, J = 9.0, ArH) 7.35–7.41 (m, 3H, ArH)	405 (M^+ + 1, 61.9)[d]

TABLE 1 Continued

Product	Yield[a] (%)	mp (°C) (solvent) Molecular Formula[b]	IR (KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS)[c] δ, J (Hz)	MS m/z (%)
				7.51 (s, 1H, CH=N) 7.56 (s, 1H, CH=N) 7.63–7.65 (m, 2H, ArH) 8.13 (d, 2H, J = 9.0, ArH) 8.16 (d, 2H, J = 9.0, ArH)	
2j	39	192–193 (EtOH–$CHCl_3$) $C_{24}H_{20}N_2O_6$	1615, 1595, 1145, 1140, 700	4.28 (dd, 1H, J_1 = 3.0, J_2 = 12.0, Ha) 5.33 (dd, 1H, J_1 = 10.0, J_2 = 12.0, Hb) 6.03 (dd, 1H, J_1 = 3.0, J_2 = 10.0, CH) 6.05 (s, 4H, 2 × OCH_2O) 6.84 (d, 1H, J = 8.0, ArH) 6.87 (d, 1H, J = 8.0, ArH) 7.32–7.80 (m, 9H, ArH) 8.15 (s, 2H, 2 × CH=N)	433 (M^+ + 1, 23.2)[d]
3a	18	114–115 (EtOH) $C_{22}H_{20}N_2O_2$	1580, 1460, 1448, 1155, 945, 755, 709, 690	4.25 (dd, 1H, J_1 = 3.7, J_2 = 12.5, Ha) 4.44 (dd, 1H, J_1 = 9.5, J_2 = 12.5, Hb) 6.06 (dd, 1H, J_1 = 3.7, J_2 = 9.5, CH) 7.28–7.46 (m, 11H, ArH) 7.41 (s, 1H, CH=N) 7.42 (s, 1H, CH=N) 7.79–7.81 (m, 2H, ArH) 8.18–8.20 (m, 2H, ArH)	345 (M^+ + 1, 88.5)[d]
3b	9	144–146 (EtOH–$CHCl_3$) $C_{22}H_{18}Cl_2N_2O_2$	1585, 1485, 1155, 1090, 935, 910, 695	4.20 (dd, 1H, J_1 = 4.0, J_2 = 12.0, Ha) 4.51 (dd, 1H, J_2 = 8.0, J_2 = 12.0, Hb) 6.02 (dd, 1H, J_1 = 4.0, J_2 = 8.0, CH) 7.30–7.60 (m, 11H, ArH, 2 × CH=N) 7.80 (d, 2H, J = 8.0, ArH) 8.19 (d, 2H, J = 8.0, ArH)	412 (M^+, 1.2)
3c	15	113–115 (EtOH–$CHCl_3$) $C_{22}H_{18}Cl_2N_2O_2$	1580, 1470, 1455, 1160, 785, 770, 705	4.19 (dd, 1H, J_1 = 3.7, J_2 = 12.7, Ha) 4.45 (dd, 1H, J_1 = 9.2, J_2 = 12.7, Hb) 6.04 (dd, 1H, J_1 = 3.7, J_2 = 9.2, CH) 7.20–7.47 (m, 11H, ArH) 7.36 (s, 1H, CH=N) 7.99–8.01 (m, 2H, ArH) 8.06 (s, 1H, CH=N) 8.37 (m, 1H, ArH)	412 (M^+, 5.1)
3d	27	116–118 (EtOH) $C_{22}H_{18}Cl_2N_2O_2$	1565, 1460, 1165, 940, 760, 695	4.15 (dd, 1H, J_1 = 4.0, J_2 = 12.0, Ha) 4.45 (dd, 1H, J_1 = 8.0, J_2 = 12.0, Hb) 6.03 (dd, 1H, J_1 = 4.0, J_2 = 8.0, CH) 7.10–7.50 (m, 11H, ArH) 7.73 (s, 1H, CH=N) 7.85 (s, 1H, CH=N) 7.80–8.10 (m, 1H, ArH) 9.30–9.50 (m, 1H, ArH)	412 (M+, 24)
3e	18	119–121 (EtOH) $C_{22}H_{16}Cl_4N_2O_2$	1585, 1465, 1165, 1135, 937, 695	4.10 (dd, 1H, J_1 = 4.0, J_2 = 12.0, Ha) 4.42 (dd, 1H, J_1 = 8.0, J_2 = 12.0, Hb) 5.97 (dd, 1H, J_1 = 4.0, J_2 = 8.0, CH) 7.10–7.50 (m, 11H, ArH, 2 × CH=N) 7.95 (m, 1H, ArH) 8.40 (m, 1H, ArH)	482 (M^+, 0.4)
3f	39	111–113 (Me_2CO) $C_{22}H_{18}Br_2N_2O_2$	1575, 1450, 1155, 930, 680	4.18 (dd, 1H, J_1 = 4.0, J_2 = 12.0, Ha) 4.52 (dd, 1H, J_1 = 8.0, J_2 = 12.0, Hb) 6.10 (dd, 1H, J_1 = 4.0, J_2 = 8.0, CH) 7.05–7.78 (m, 12H, ArH, 2 × CH=N) 8.00–8.60 (m, 2H, ArH) 8.50 (m, 1H, ArH)	502 (M^+, 0.6)
3g	32	119–121 (Me_2CO) $C_{22}H_{18}N_4O_6$	1610, 1530, 1162, 735 670	4.23 (dd, 1H, J_1 = 4.0, J_2 = 12.0, Ha) 4.55 (dd, 1H, J_1 = 8.0, J_2 = 12.0, Hb) 6.06 (dd, 1H, J_1 = 4.0, J_2 = 8.0, CH)	434 (M^+, 1.2)

TABLE 1 Continued

Product	Yield[a] (%)	mp (°C) (solvent) Molecular Formula[b]	IR (KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS)[c] δ, J (Hz)	MS m/z (%)
				7.25–7.80 (m, 9H, ArH, 2 × CH=N) 8.00–8.30 (m, 4H, ArH) 8.52 (m, 1H, ArH) 9.10 (m, 1H, ArH)	
3h	30	157–159 (EtOH) $C_{22}H_{18}N_4O_6$	1592, 1515, 1160, 855 745, 690	4.25 (dd, 1H, J_1 = 4.0, J_2 = 12.0, Ha) 4.60 (dd, 1H, J_1 = 8.0, J_2 = 12.0, Hb) 6.08 (dd, 1H, J_1 = 4.0, J_2 = 8.0, CH) 7.33–7.75 (m, 7H, ArH, 2 × CH=N) 8.00–8.40 (m, 8H, ArH)	434 (M^+, 0.1)
4a	9	129–130 (EtOH) $C_{22}H_{20}N_2O_2$	1580, 1490, 1455, 1252, 1230, 1152, 760, 709 690	4.27 (dd, 1H, J_1 = 3.7, J_2 = 12.7, Ha) 4.47 (dd, 1H, J_1 = 9.2, J_2 = 12.7, Hb) 6.05 (dd, 1H, J_1 = 3.7, J_2 = 9.2, CH) 7.26–7.48 (m, 13H, ArH) 7.42 (s, 1H, CH=N) 8.12 (s, 1H, CH=N) 8.21–8.24 (m, 2H, ArH)	345 (M^+ + 1, 84.0)[d]
4b	17	138–140 (EtOH–$CHCl_3$) $C_{22}H_{18}Cl_2N_2O_2$	1585, 1485, 1155, 1090, 830, 700	4.12 (dd, 1H, J_1 = 4.0, J_2 = 12.0, Ha) 4.48 (dd, 1H, J_1 = 8.0, J_2 = 12.0, Hb) 6.02 (dd, 1H, J_1 = 4.0, J_2 = 8.0, CH) 7.30–7.60 (m, 12H, ArH, CH=N) 8.05 (s, 1H, CH=N) 8.10 (d, 2H, J = 8.0, ArH)	412 (M^+, 0.8)

[a]Yield of each isolated product **2–4** based on the dehydrodimer **1**.
[b]Satisfactory microanalyses obtained: C, ±0.3; H, ±0.2; N ± 0.3.
[c]Spectra of compounds **2b, 2i** were recorded on a Bruker-AM-500 spectrometer.
[d]FAB ionization.
[e]Very difficult to purify.

the dipolarophile occurs prior to the formation of free radicals, thus leading to 1,3-cycloaddition products.

EXPERIMENTAL

All reagents were of commercial quality obtained from freshly opened containers. Reagent quality solvents were used without further purification. Melting points were taken with a Yanaco micro melting point apparatus and are uncorrected. The IR spectra were obtained using a Shimazu IR 408 spectrometer. The ^1H NMR spectra were obtained using a JEOL 60SI spectrometer. Microanalyses were obtained using a Perkin-Elmer 240C element analyzer. Mass spectra were obtained using a VG-ZAB-HS spectrometer. Arenealdoxime dehydrodimers **1** were prepared by the procedure [4] described previously.

Reaction of Dehydrodimer **1** *with Styrene—General Procedure*

A mixture of the dehydrodimer (**1**, 5.0 mmol), styrene (3 mL), and chloroform (25 mL) was refluxed until it became homogeneous. After removal of the solvent, diethyl ether (10–15 mL) was added to the residue. The precipitate was isolated by suction filtration and recrystallized to give the bisnitrone **2**. The filtrate was concentrated, and the residue was chromatographed on silica gel using EtOAc-petroleum ether (60–90°C) (1:5) as eluent to give a small amount of **2** and compounds **3, 4**.

Reaction of Dehydrodimer **1** *with Methyl Acrylate—General Procedure*

A mixture of the dehydrodimer (**1a–b, g–j**, 5.0 mmol), methyl acrylate (3 mL), and chloroform (25 mL) was refluxed until it became homogeneous. The solvent was evaporated, and the residue was chromatographed with silica gel and eluted with EtOAc-petroleum ether (60–90°C) (1:6) to give the isoxazoline **5a–b, g–j.**

Reaction of the Dehydrodimer **1b** *with Dimethyl Acetylenedicarboxylate*

A mixture of 4-chlorobenzaldoxime dehydrodimer (**1b**, 1.0 g, 3.2 mmol), dimethyl acetylenedicarbox-

TABLE 2 Physical Data of 1,3-Dipolar Cycloaddition Products

Product	Yield[a] (%)	mp (°C) (Lit. mp) or Molecular Formula[b]	IR (KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, J (Hz)	MS[c] m/z (%)
5a	35	71–73 [5] (73–74)	1752, 1605, 1445, 890, 766, 696	3.55–3.70 (m, 2H, CH_2) 3.80 (s, 3H, CH_3) 5.15 (dd, 1H, J_1 = 8, J_2 = 10, CH) 7.25–7.70 (m, 5H, ArH)	
5b	30	69–70 $C_{11}H_{10}ClNO_3$	1757, 1600, 1495, 1430, 1030, 902, 838	3.61 (d, 2H, J = 9, CH_2) 3.80 (s, 3H, CH_3) 5.18 (dd, 1H, J_1 = 8, J_2 = 10, CH) 7.30 (d, 2H, J = 9, ArH) 7.61 (d, 2H, J = 9, ArH)	240 (M^+ + 1, 65.4)
5g	27	88–89 $C_{11}H_{10}N_2O_5$	1751, 1595, 1530, 1355, 739, 675	3.72 (d, 2H, J = 9, CH_2) 3.81 (s, 3H, CH_3O) 5.27 (dd, 1H, J_1 = 8, J_2 = 10, CH) 7.45–8.50 (m, 4H, ArH)	251 (M^+ + 1, 30.7)
5h	15	145–147 [6] (142–144)	1752, 1600, 1518, 890, 850, 690	3.70 (m, 2H, CH_2) 3.83 (s, 3H, CH_3) 5.25 (dd, 1H, J_1 = 4, J_2 = 10, CH) 7.85 (d, 2H, J = 8, ArH) 8.27 (d, 2H, J = 8, ArH)	
5i	30	66–68 $C_{12}H_{13}NO_3$	1755, 1610, 1511, 1352, 1025, 890, 839	3.67 (d, 2H, J = 9, CH_2) 3.84 (s, 3H, CH_3) 3.87 (s, 3H, CH_3O) 5.15 (dd, 1H, J_1 = 8, J_2 = 10, CH) 6.93 (d, 2H, J = 8, ArH) 7.65 (d, 2H, J = 8, ArH)	220 (M^+ + 1, 46.7)
5j	33	105–107 (109) [7]	1745, 1615, 1510, 1460, 940, 912, 812	3.65 (m, 2H, CH_2) 3.82 (s, 3H, CH_3) 5.18 (dd, 1H, J_1 = 8, J_2 = 9, CH) 6.00 (s, 2H, OCH_2O) 6.82–7.10 (m, 3H, ArH)	250 (M^+ + 1, 44.2)
6b	42	82–84 $C_{13}H_{10}ClNO_5$	1740, 1725, 1600, 1450, 1268, 830, 770	3.85 (s, 3H, CH_3O) 3.96 (s, 3H, CH_3O) 7.30–7.75 (m 4H, ArH)	296 (M^+ + 1, 87.1)

[a]Yield of each isolated product **5–6** based on the dehydrodimer **1**.
[b]Recrystallized from EtOH. Satisfactory microanalyses obtained: C, ±0.3; H, ±0.2; N ± 0.3.
[c]FAB ionization.

ylate (0.6 g, 4.2 mmol), and chloroform (25 mL) was stirred at room temperature for 7 days. The solvent was evaporated, and the residue was purified by chromatography over silica gel using EtOAc-petroleum ether (60–90°C) (1:5) as eluent to give **6b** (0.40 g, 42%) as a white solid.

ACKNOWLEDGMENTS

We wish to thank the State Education Commission of China and the Education Commission of Jiangsu Province for financial support.

REFERENCES

[1] C. Grundmann, G. F. Kite, *Synthesis,* 1973, 156.
[2] H.-W. Hu, X.-D. Wei, C. Li, H.-Z. Sun, Y.-M. Yao, Z.-Y. Zhou, K.-B. Yu, *Chin. J. Chem., 9,* 1991, 467.
[3] H.-W. Hu, X.-D. Wei, C. Li, H.-Z. Sun, Y.-M, Yao, Z.-Y. Zhou, K.-B. Yu, *Chin. J. Chem., 10,* 1992, 278.
[4] X.-D. Wei, H.-W. Hu, Y.-F. Hu, Y.-S. Jin, T.-Z. Jin, Y.-X. Xu, *Chin. J. Chem., 10,* 1992, 344.
[5] N. P. Kostyuckenco, A. F. Olienik, T. I. Vozyokova, K. Yu. Novitskii, Yu. N. Sheinker, *Khim. Geterotsikl. Soedin., 3,* 1974, 312.
[6] A. Quilico, G. S. D'Alcontres, P. Grünnanger, *Gazz. Chim. Ital., 80,* 1950, 479.
[7] R. D. Grant, J. T. Pinhey, E. Rizzardo, *Aust. J. Chem., 37,* 1984, 1217.
[8] K. E. Larsen, K. B. G. Torssell, *Tetrahedron, 40,* 1984, 2985.