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Generation of Carbethoxynitrene by α Elimination and Its Reactions with Olefins under Two-Phase Conditions

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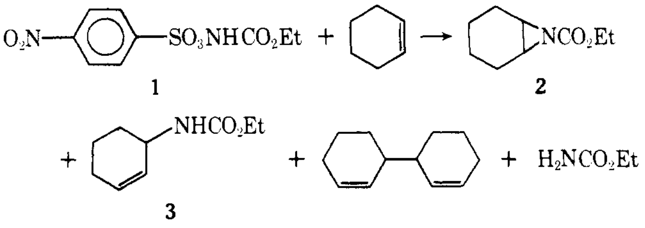
The base decomposition of ethyl *p*-nitrobenzenesulfonoxycarbamate (1) in organic–aqueous two-phase systems in the presence of cyclohexene and quaternary ammonium or phosphonium halides afforded 7-carbethoxy-7-azabicyclo[4.1.0]heptane (2), ethyl 3-cyclohexenylcarbamate (3), 3,3′-bicyclohexenyl, and ethyl carbamate. The reactivity of 1 and the product selectivity (addition/insertion ratio) are quite analogous to those reported for homogeneous reactions of 1 with cyclohexene, indicating the generation of a common intermediate of carbethoxynitrene by α elimination of 1. The reactions of 1 with *cis*- and *trans*-4-methyl-2-pentenes were also studied, and the results were interpreted in view of the electronic state of the nitrene.

The reactions between substances located separately in an organic phase and an aqueous phase are frequently accelerated by catalytic amounts of quaternary ammonium or phosphonium salts.[1] These systems are of particular advantage for the reactions which proceed via unstable intermediates such as carbanions,[2] ylides,[3] and carbenes[4] since most of these reactions have been considered to require aprotic solvents and strictly anhydrous conditions. Two-phase reactions by phase-transfer catalysts enable us to carry out these organic reactions using aqueous inorganic base solutions and are considered to be of great practical value.

The present study is concerned with the application of the two-phase reaction technique to the generation of carbethoxynitrene by α elimination and its reactions with olefins. Both the reactivity and selectivity of the nitrene generated in these systems will be examined in view of the effects of the aqueous phase and quaternary salts on the electronic state of the nitrene.

Results and Discussion

It has been reported by Lwowski and his co-workers that the treatment of ethyl *p*-nitrobenzenesulfonoxycarbamate (1) with triethylamine gives rise to carbethoxynitrene which is postulated to be of the singlet state.[5] We carried out this reaction in two-phase systems which consist of aqueous sodium bicarbonate solutions and dichloromethane solutions of olefins in the presence of a catalytic amount of quaternary ammonium or phosphonium halides. In the case of cyclohexene, both a presumed addition product of carbethoxynitrene to the C=C double bond, 7-carbethoxy-7-azabicyclo[4.1.0]heptane (2), and an insertion product into the C–H bond, ethyl 3-cyclohexenylcarbamate (3), were obtained together with small amounts of 3,3′-bicyclohexenyl and ethyl carbamate.



All of these compounds are common products obtained from the photodecomposition of ethyl azidoformate and from the homogeneous α elimination of 1 by triethylamine in the presence of cyclohexene.[5a,b] This indicates the formation of a common intermediate, carbethoxynitrene, also in the present two-phase system, although nitrenes have been con-

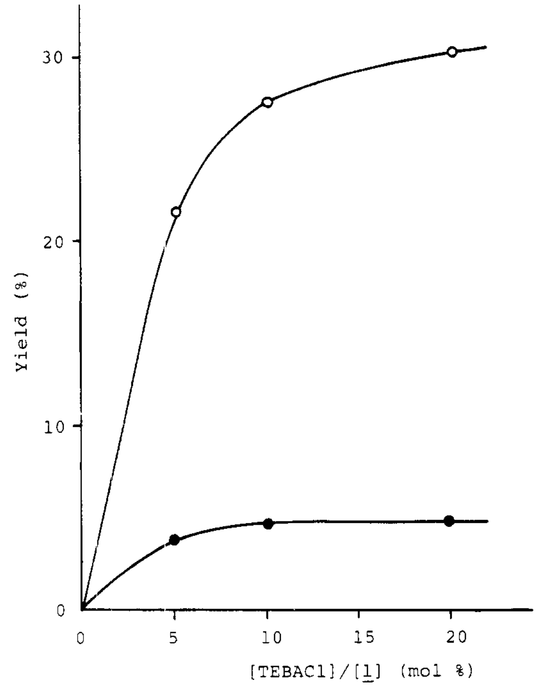


Figure 1. Yields of 7-carbethoxy-7-azabicyclo[4.1.0]heptane (**2**) (○) and ethyl 3-cyclohexenylcarbamate (**3**) (●) vs. the concentration of triethylbenzylammonium chloride (TEBACl): ethyl *p*-nitrobenzenesulfonoxycarbamate (**1**), 0.01 mol; cyclohexene, 0.02 mol; CH_2Cl_2, 40 mL; $NaHCO_3$, 0.03 mol; H_2O, 30 mL; room temperature for 2 h.

Table I. Reaction of Ethyl *p*-Nitrobenzenesulfonoxycarbamate (1) with Cyclohexene[a]

Catalyst	Yield, % 2	3	2:3
$(C_2H_5)_4NBr$	12.6	3.1	4.1
$(n\text{-}C_4H_9)_4NBr$	22.1	5.7	3.9
$(n\text{-}C_4H_9)_4PBr$	23.4	6.6	3.5
$(n\text{-}C_4H_9)_4NI$	5.9	10.3	0.57
$n\text{-}C_8H_{17}N(C_2H_5)_3Br$	19.7	4.7	4.2
$n\text{-}C_{12}H_{25}N(C_2H_5)_3Br$	19.0	4.1	4.6
$n\text{-}C_{16}H_{33}N(C_2H_5)_3Br$	22.7	4.6	4.9
$n\text{-}C_{16}H_{33}P(n\text{-}C_4H_9)_3Br$	14.6	4.6	3.2
$n\text{-}C_{16}H_{33}N(CH_3)_3Br$	22.5	4.7	4.8
$(C_6H_5CH_2)N(C_2H_5)_3Cl$	27.7	4.8	5.8
$(C_6H_5CH_2)N(C_2H_5)_3Br$	26.3	4.7	5.6
$(C_6H_5CH_2)N(C_2H_5)_3I$	6.3	5.8	1.1

[a] **1**, 0.01 mol; cyclohexene, 0.02 mol; catalyst, 1.0 mmol; CH_2Cl_2, 40 mL; $NaHCO_3$, 0.03 mol; H_2O, 30 mL; room temperature for 2 h.

sidered to be sensitive to water and easily hydrolyzed under aqueous conditions.

The effect of the concentration of triethylbenzylammonium chloride (TEBACl) on the yields of **2** and **3** is shown in Figure 1. No reaction occurred without a catalyst in this system. It should be noted that the ratio of **2** to **3** is 5–6 and almost independent of the catalyst concentration. The ratio is close to that reported for the homogeneous reaction of **1** with cyclohexene,[5a,b] and this also supports the intermediacy of carbethoxynitrene.

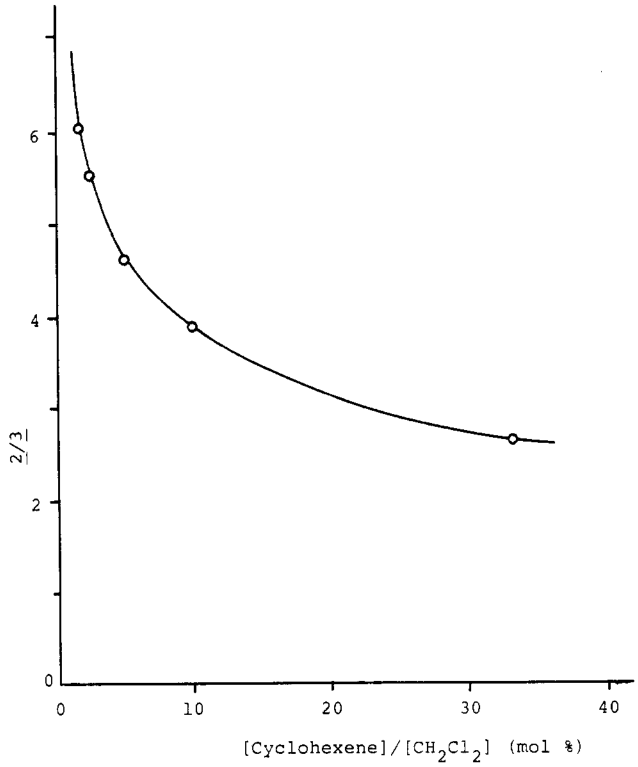


Figure 2. Effect of cyclohexene concentration on the addition/insertion product ratio: **1**, 0.01 mol; TEBACl, 1.0 mmol; total volume of organic phase, 40 mL; $NaHCO_3$, 0.03 mol; H_2O, 30 mL; room temperature for 2 h.

As mentioned above, the carbethoxynitrene generated by α elimination is supposed to be a singlet nitrene. The ground state of the nitrene is triplet, and a part of the generated nitrene is expected to decay to the triplet state. On the other hand, the C–H insertion reaction at the asymmetric carbon atom of 3-methylhexane was found to proceed with complete retention of configuration, suggesting that only the singlet nitrene participates in the insertion reaction.[6] As shown in Figure 2, a decrease in the concentration of cyclohexene in the present system leads to an increase in the ratio of the addition product to the insertion product. This can be explained as the consequence of an increasing frequency of the triplet nitrene reaction due to the lower probability of the singlet nitrene to react with cyclohexene at lower concentrations of cyclohexene.

Table I shows the variation of catalytic ability of several quaternary ammonium and phosphonium halides. There is a tendency that, among ammonium bromides used here, longer and more hydrophobic groups on nitrogen increase the catalytic ability. Therefore, it seems likely that extraction of hydroxide ion into organic phase and the subsequent formation of the anion of **1** is the major function of the catalysts. Alternatively, the anion of **1** may be formed at the interphase and then enter into the organic phase by the aid of the catalysts. Analogous results have been reported for other two-phase reactions such as the reaction of thiophenoxide ion with 1-bromooctane, where the catalytic ability depends primarily on the solubility of ammonium or phosphonium thiophenoxides in the organic phase.[7] Phosphonium salts gave a little lower ratio of **2** to **3**. The best catalyst among these is TEBACl, which is one of the recommended catalysts for the generation of dichlorocarbene by α elimination of chloroform under two-phase conditions.[4]

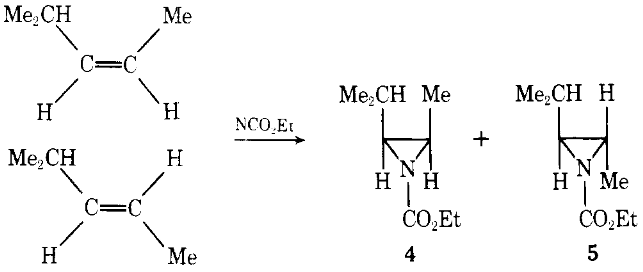
No significant differences were observed between ammonium chlorides and bromides, but ammonium iodides gave rather unusual results as shown in Table I; the yield of the addition product decreased, while that of the insertion product increased. It might be assumed that iodide ion enters into the organic phase easier than others and consumes the triplet nitrene by unknown processes or that it interferes with the decay of the singlet nitrene to the triplet state.

The results of the reactions of **1** with *cis*- and *trans*-4-methyl-2-pentenes under two-phase conditions are summarized in Table II. From *cis*-4-methyl-2-pentene, both the

Table II. Addition of Carbethoxynitrene to *cis*- and *trans*-4-Methyl-2-pentenes under Two-Phase Conditions[a]

	From cis olefin		From trans olefin	
Catalyst	% yield of aziridine	% fraction of trans product	% yield of aziridine	% fraction of cis product
$(n\text{-}C_4H_9)_4NBr$	19.8	41.9	17.8	14.8
$(n\text{-}C_4H_9)_4NI$	6.3	15.3	5.3	11.8
$PhCH_2N(C_2H_5)_3Cl$	26.7	38.2	24.9	17.3
$PhCH_2N(C_2H_5)_3Cl$[b]	28.5	14.4	16.4	14.1
$PhCH_2N(C_2H_5)_3Br$	34.3	35.3	28.3	19.4
$PhCH_2N(C_2H_5)_3I$	11.3	10.0	4.7	6.4

[a] **1**, 0.01 mol; olefin, 0.02 mol; catalyst, 1.0 mmol; CH_2Cl_2, 40 mL; $NaHCO_3$, 0.03 mol; H_2O, 30 mL; room temperature for 2 h. [b] **1**, 0.01 mol; olefin, 0.0706 mol; catalyst, 1.0 mmol; CH_2Cl_2, 0.636 mol; $NaHCO_3$, 0.03 mol; H_2O, 30 mL; room temperature for 2 h.



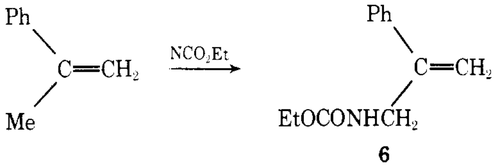
4 **5**

stereospecific addition product, *cis*-1-carbethoxy-2-isopropyl-3-methylaziridine (**4**), and the nonstereospecific addition product, *trans*-1-carbethoxy-2-isopropyl-3-methylaziridine (**5**), were obtained with small amounts of ethyl carbamate. In carbene reactions, the stereospecific addition is generally interpreted as indicating the reaction of a singlet carbene, while nonstereospecific addition indicates the participation of a triplet carbene.[8] The former is considered to add to olefins in one step, while the latter forms a diradical followed by spin inversion and ring closure by radical coupling. An analogous relationship between the electronic state and the stereochemistry has been postulated for carbethoxynitrene.[5c,9]

As shown in Table II, the stereospecificity of the addition of carbethoxynitrene to *cis*- and *trans*-4-methyl-2-pentenes depends on the structure of the ammonium halides. Ammonium iodides especially gave lower yields of the addition product and higher fractions of the stereospecific addition product. This indicates again that, in the case of quaternary ammonium iodide catalysts, the reaction via singlet nitrene predominates over that of triplet nitrene.

The decrease in the olefin concentration gave the anticipated result of an increase in the percent fraction of nonstereospecific addition products as seen in Table II, indicating that both the singlet and triplet nitrenes participate in the addition reaction.

Carbethoxynitrene generated in the present system also reacts with α-methylstyrene and cyclohexane to give 3-carbethoxyamino-2-phenyl-1-propene (**6**) and ethyl cyclohexylcarbamate (**7**), respectively. The yields of these products are comparable to those reported for the same reactions in homogeneous systems.[5b,c]



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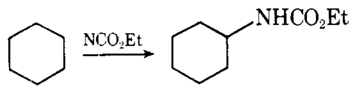

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Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Hitachi 215 spectrometer, and NMR spectra were taken at 60 MHz on a Hitachi R-20A spectrometer. Chemical shifts are reported in δ (ppm) from an internal standard of tetramethylsilane. GLC analyses were performed on a Hitachi 063 gas chromatograph. The yields of the products were determined based on calibration curves drawn using authentic samples. Elemental analyses were performed on a Perkin-Elmer 240 analyzer.

Quaternary ammonium and phosphonium halides used as phase-transfer catalysts were the products of Tokyo Kasei Kogyo Co. and were recrystallized three times from ethanol–ether or dichloromethane–ether. The purity of the salts was confirmed by melting point measurements. Olefins were distilled before use. Ethyl *p*-nitrobenzenesulfonoxycarbamate (**1**) was prepared and purified according to the method described by Lwowski,[5b] mp 117–118.5 °C (lit.[5b] mp 116.4–116.8 °C).

Anal. Calcd for $C_9H_{10}N_2O_7S$: C, 37.24; H, 3.47; N, 9.65. Found: C, 37.41; H, 3.48; N, 9.87.

Authentic samples of the reaction products of **1** with cyclohexene, *cis*- and *trans*-4-methyl-2-pentenes, α-methylstyrene, and cyclohexane were prepared by the methods described in the literature: ethyl 3-cyclohexenylcarbamate (**3**),[10] 3,3′-bicyclohexenyl,[10] *cis*- and *trans*-1-carbethoxy-2-isopropyl-3-methylaziridines (**4** and **5**),[5c] 3-carbethoxyamino-2-phenyl-1-propene (**6**),[5c] and ethyl cyclohexylcarbamate (**7**).[10] 7-Carbethoxy-7-azabicyclo[4.1.0]heptane (**2**) was isolated from the reaction products of **1** with cyclohexene and purified by distillation: bp 53–54 °C (0.5 mmHg); IR 1725 (carbonyl), 1281 and 1231 (C–O) cm^{-1}; NMR ($CDCl_3$) δ 1.26 (t, 3, CH_3, $J = 7$ Hz), 1.1–1.5 (m, 4, H-3 and H-4), ca. 1.86 (m, 4, H-2 and H-5), 2.53 (m, 2, CH), 4.04 (q, 2, OCH_2, $J = 7$ Hz); MS *m/e* 169.1 (M^+).

Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.93; N, 8.28. Found: C, 64.74; H, 9.11; N, 8.04.

Reactions of Ethyl *p*-Nitrobenzenesulfonoxycarbamate (1) with Cyclohexene. A solution of $NaHCO_3$ (0.03 mol) in H_2O (30 mL) was added to a solution of **1** (0.01 mol), cyclohexene (0.02 mol), and a phase-transfer catalyst (1.0 mmol) in dichloromethane (40 mL). The reaction mixture was stirred with a mechanical stirrer at a rate of more than 500 rpm for 2 h at room temperature. After the reaction, the mixture was diluted with 500 mL of water and extracted with dichloromethane. The organic layer was separated, washed with water, and dried over calcium chloride. The low boiling point components were distilled off under reduced pressure, and the residue was analyzed by gas chromatography using a 1 m, 10% SE-30 on 80–100 mesh Chromosorb column at 150 °C with tetralin as an internal standard. In several experiments **2** was isolated by distillation.

Reactions of Ethyl *p*-Nitrobenzenesulfonoxycarbamate (1) with *cis*- and *trans*-4-Methyl-2-pentenes. The reactions were carried out by similar methods to those described for the reaction of **1** with cyclohexene. The products were analyzed by GLC using a 2 m, 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on 80–100 mesh Shimalite column at 150 °C with mesitylene as an internal standard.

Reactions of Ethyl *p*-Nitrobenzenesulfonoxycarbamate (1) with α-Methylstyrene and with Cyclohexane. The same procedure as described above was employed for these reactions, and the main products, 3-carbethoxyamino-2-phenyl-1-propene (**6**) (11%) and ethyl cyclohexylcarbamate (**7**) (13%), respectively, were identified and determined by GLC using authentic samples. A 1 m, 10% SE-30 on 80–100 mesh Chromosorb column was used at 200 and 150 °C for **6** and **7**, respectively.

Registry No.—**1**, 2955-74-0; **2**, 1541-27-1; **3**, 1541-28-2; **4**, 16307-56-5; **5**, 16307-57-6; **6**, 16307-60-1; **7**, 1541-19-1; cyclohexene, 110-83-8; α-methylstyrene, 300-57-2; cyclohexane, 110-82-7; *cis*-4-methyl-2-pentene, 691-38-3; *trans*-4-methyl-2-pentene, 674-76-0.

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Reactions of Ketene Acetals, Ketene Thioacetals, and Ketene Aminals with Dialkyl Azodicarboxylate Esters

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Ketene acetals react with azodicarboxylate esters to give 5,6-dihydrooxadiazines. However, these compounds are not very stable and undergo thermal ring opening to give hydrazinylketene acetals. No 1,2-diazetidines could be detected in the reactions. If the starting ketene acetal bears no substitutent, the azodicarboxylate ester can react with the hydrazinylketene acetal product to give 2:1 adducts, which have been shown to be either 5-hydrazinyl-5,6-dihydrooxadiazines or dihydrazinylketene acetals. When ketene acetals with allyic hydrogens are used, such as dimethylketene dimethyl acetal, only ene reaction products are formed. When ketene thioacetals reacted with azodicarboxylate esters, the presence of 5,6-dihydrooxadiazines could not be demonstrated. Only ring-opening products, hydrazinylketene thioacetals, could be isolated. In the reactions of ketene aminals with azodicarboxylate esters a low yield of a 5,6-dihydrooxadiazine was isolated in one case; the main products were hydrolysis products of 1:1 adducts. All of the products of these reactions are very moisture sensitive, the acetal linkages undergoing facile hydrolysis to the corresponding open-chain esters.

The thermal addition of ketene acetals to anhydrides,[1] diazonium salts,[2] ketenes,[3–8] acrylate esters,[9] cyanoethylenes,[10,7] acetylenic esters,[10,11] azides,[12–14] isocyanates,[15–20] α,β-unsaturated aldehydes and ketones,[21–25] and nitroso compounds[6,7] has been reported. Ketene thioacetals undergo thermal addition to ketenes,[8] cyanoethylenes,[26] anhydrides,[26] and acetylenic esters.[27] Ketene aminals have been reported to add thermally to ketenes,[28,29] acrylate esters,[30] cyanoethylenes,[10,31–34] isocyanates,[35,36] and cyclopropenones.[37,38] Among these reports there are examples of 2 + 2, 2 + 4, and 1,3-dipolar cycloadditions, formation of substituted ketene acetals, ketene thioacetals, and ketene aminals, as well as adduct formation arising from electron transfer. All of these reactions are interrelated in that all represent the reaction of an electron-rich olefin with an unsaturated electron-poor acceptor.

The reactions of ketene acetals, ketene aminals, and ketene thioacetals with azodicarboxylate esters appear not to have been examined except for the example of Carey and Neergaard[39] indicating that an azodicarboxylate ester undergoes substitution in a ketene thioacetal. However, several related reactions have been examined, including the reaction of azodicarboxylate esters with tetramethoxyethylene,[7] tetramethoxyallene,[6] vinyl ethers,[40–49] vinyl thioethers,[41,45,46] vinyl acetates,[41,47] and enamines.[41,42,46,50]

Ketene acetals, ketene thioacetals, and ketene aminals were all found to react with dimethyl and diethyl azodicarboxylates at room temperature. The reactions were exothermic. The products of these reactions were sensitive to moisture and in some cases only hydrolysis products could be isolated.

When unsubstituted ketene acetals reacted with dimethyl and diethyl azodicarboxylates, both 1:1 and 2:1 adducts were formed. When ketene dimethyl acetal reacted with dimethyl azodicarboxylate, three products, **3a**, **4a**, and **6a**, were isolated in a ratio of 25:3.3:1. The structure of **3a** was proven by independent synthesis by hydrogenation of the carbomethoxyhydrazone of methyl glyoxylate, followed by acylation of the product with methyl chloroformate. The elemental analysis of **4a** was also consistent with the structure **5a** and the diazetidine **7**. However, the NMR of **4a** showed two singlets for the gem methoxy groups at 3.45 and 3.57 ppm, eliminating the symmetrical structure **5a**. The IR of **4a** showed three carbonyl stretching frequencies at 1760, 1750, and 1720 cm^{-1} and a band at 1683 cm^{-1}, characteristic of the C=N stretch in 5,6-dihydrooxadiazenes,[47] eliminating structure **7**.

On standing at room temperature, **4a** is quantitatively transformed into **6a**. This transformation can be monitored by NMR. After heating for 1 h at 40 °C in deuteriochloroform, only **6a** remained. This reaction appears to involve ring opening of the 5,6-dihydrooxadiazine **4a**, presumably through a 1,4-dipolar intermediate to form **5a**, which is very moisture sensitive and hydrolyzes to **6a**. Similarly, the major product, **3a**, most likely arises by hydrolysis of **2a** obtained from ring opening of **1a**.

The reaction of ketene dimethyl acetal with diethyl azodicarboxylate gave the 1:1 adduct **3b** and the 2:1 adducts **5b** and **6b** in a ratio of 1.5:1:1 as estimated from the NMR spectrum of the reaction mixture. Only **3b** could be isolated and purified. Its structure was proven by independent synthesis as described above for **3a**. When this reaction was run in deuterated benzene in the NMR spectrometer, the first identifiable product was the 5,6-dihydrooxadiazine **4b**, as shown by the appearance of the peak at 3.82 ppm, characteristic of C-5 proton. This is followed by the appearance of the hydrazinylketene acetal **5b** as shown by the appearance of singlet at 3.12 ppm for the two methoxy groups. At the same time, the NH peak at 7.32 ppm begins to appear.

When ketene diethyl acetal was reacted with dimethyl and

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