Bull. Chem. Soc. Jpn., **55**, *1921—1925 (1982)*

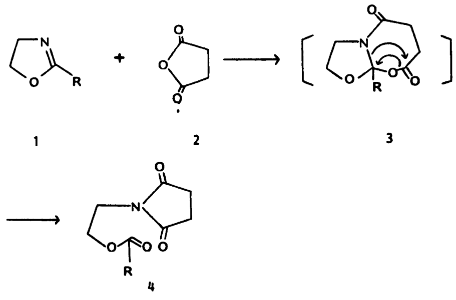
Addition Reaction of Carboxylic Anhydrides to the Carbon-Nitrogen Double Bond of Unsubstituted Cyclic Imidates

Shiro Kobayashi, Michihisa Isobe, and Takeo Saegusa*
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606

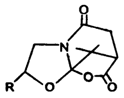
(Received December 18, 1981)

Acyclic and cyclic (SAn and GAn) carboxylic anhydrides were added at room temperature to the C=N bond of unsubstituted cyclic imidates of 2-oxazoline (OZO) and 5,6-dihydro-4*H*-1,3-oxazine (OZI) to give addition products quantitatively. In contrast to these findings, the reactions of acetyl halides with OZO and OZI yielded ring-opened products and the reactions of carboxylic anhydrides with 2-benzyl-2-oxazoline (BzOZO) afforded also the ring-opened products. The bicyclic addition product of OZO with SAn is equilibrated with a mixture of starting materials. The stereochemistry of addition products having a six-membered ring system is discussed.

Reactions of substituted 2-oxazolines with carboxylic anhydrides have been reported in several papers.[1–4] In these reactions amide and imide derivatives were formed. For example, the reaction of 2-substituted 2-oxazoline (**1**) with succinic anhydride (**2**, SAn) gave a succinimide product (**4**), probably through an intermediate (**3**) which is an addition product of **2** onto the reactive C=N bond[5] of **1** and isomerized to **4**.[3] In the specific combination of 2-isopropyl-2-oxazolines and maleic anhydride, products **5** have been obtained,



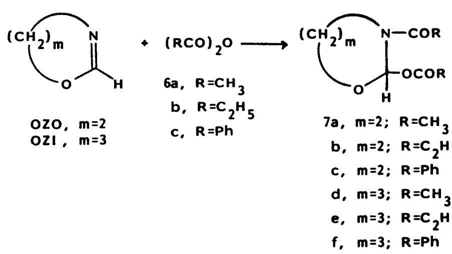
which has been claimed to correspond to the above intermediate **3**.[4]



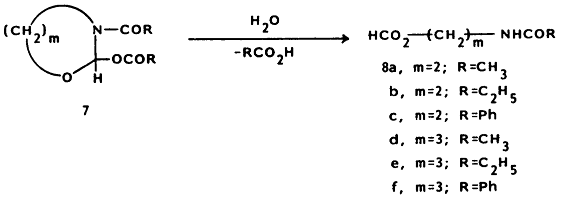
The present paper describes the addition reactions of carboxylic (acyclic and cyclic) anhydrides onto the C=N double bond of unsubstituted five- and six-membered cyclic imidates of 2-oxazoline (OZO) and 5,6-dihydro-4*H*-1,3-oxazine (OZI), respectively. Products exactly correspond to the intermediate **3** which has been assumed in the previous study.[3] It should be noted also that prior to the present work unsubstituted OZO and OZI had not been employed for the reaction with carboxylic anhydrides probably due to the difficulties of their preparation. In the polymerization chemistry, however, OZO and OZI have recently been used extensively as a monomer of cationic ring-opening polymerization to produce poly(*N*-formylaziridine) and poly(*N*-formylazetidine) respectively.[6]

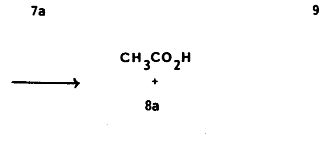
Results and Discussion

Reactions of OZO and OZI with Acyclic Carboxylic Anhydrides. In $CHCl_3$ or CH_2Cl_2, OZO and OZI reacted with acyclic carboxylic anhydrides (**6**) at room temperature to give addition products (**7**). In all combinations, products **7a**—**f** were produced quantitatively. The structure of **7** was determined by IR and NMR spectroscopy, elemental analysis, as well as hydrolysis experiments of **7**.



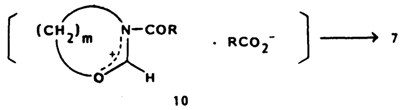
Products **7** were readily hydrolyzed with an equimolar amount of water to give quantitatively formate derivatives (**8**) with elimination of one molecule of carboxylic acid. Products **8** were purified by distillation *in vacuo* and the structure was determined by IR and NMR spectroscopy and by elemental analysis. The production of **8a**, for example, is explained by the following course of reaction from **7a** and water through an intermediate **9**:





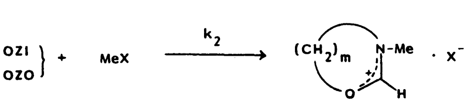
Results of hydrolysis experiments are taken to support the structure of the addition products **7**.

The addition reaction of **6** to the C=N bond of OZO or OZI proceeded much faster with OZI than with OZO, *i.e.*, the reactions of OZI with **6** finished within several minutes at room temperature whereas those of OZO with **6** took one day at the same temperature. This difference is due to the difference in nucleophilic reactivity of OZI and OZO in the formation of intermediate **10**, which is probably a rate-determining step.



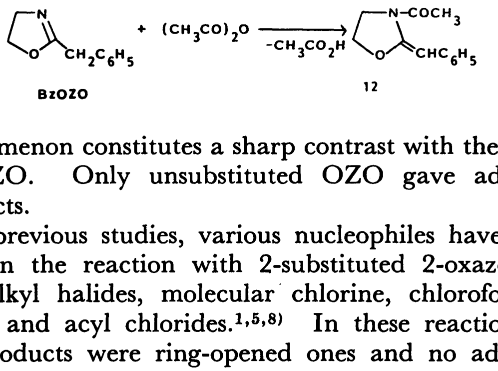
10

For example, our previous study has shown that the nucleophilic reaction of OZI with MeX (X=I and p-$CH_3C_6H_4SO_3$) producing *N*-methyl onium **11** proceeded about 12 times faster than that of OZO reflected by the second order rate constant (k_2).[7)]



11

In the reaction of 2-substituted 2-oxazoline, *e.g.*, 2-benzyl-2-oxazoline (BzOZO), with acetic anhydride, the addition product corresponding to **7** was not produced but a new product (**12**) was obtained with liberation of an equimolar amount of acetic acid. This phenomenon constitutes a sharp contrast with the result of OZO. Only unsubstituted OZO gave addition products.



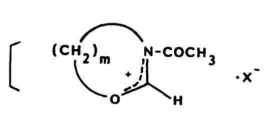
BzOZO 12

In previous studies, various nucleophiles have been used in the reaction with 2-substituted 2-oxazolines, *e.g.*, alkyl halides, molecular chlorine, chloroformate esters, and acyl chlorides.[1,5,8)] In these reactions all the products were ring-opened ones and no addition product at the C=N bond was formed. In order to examine the behavior of unsubstituted cyclic imidates, reactions of OZO and OZI with acetyl halides were carried out and found to give ring-opened products **13** but not an addition product corresponding to **7**. With

$$\left.\begin{matrix}\text{OZO}\\\text{OZI}\end{matrix}\right\} + \underset{(X=Cl,\ Br)}{CH_3COX} \longrightarrow X\!-\!(CH_2)_m\!-\!\underset{\displaystyle CHO}{NCOCH_3}$$

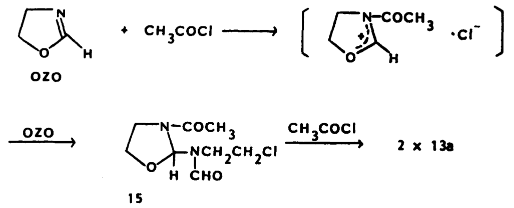
13a, m=2; X=Cl
b, m=2; X=Br
c, m=3; X=Cl
d, m=3; X=Br

an equimolar feed reactions of OZO–CH_3COCl, OZI–CH_3COCl, and OZI–CH_3COBr systems gave **13** quantitatively within a few minutes in CH_2Cl_2, which was confirmed by NMR of the reaction mixture. The reaction probably involves an onium intermediate **14**.



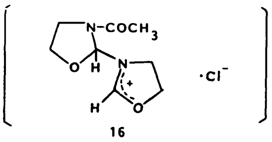
14

In the combination of OZO–CH_3COCl (1 : 1), on the other hand, it was found that the 2 : 1 reaction product (**15**) was first formed and then **15** was gradually converted to **13a** within one day at room temperature by reacting further with CH_3COCl. **15** was actually isolated from the OZO–CH_3COCl (2.5 : 1) reaction system. **15** was formed *via* the intermediate **16** derived from **14a** and OZO. The reaction mechanism of **15** with CH_3COCl has not been fully understood.



OZO

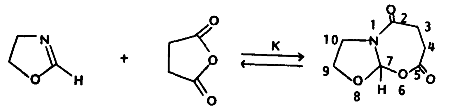
15



16

Thus, the reaction mode of acetyl halides with OZO and OZI is quite different from that of carboxylic anhydrides. The reaction mode of OZO and OZI toward acetyl halides, however, is analogous to that of 2-substituted 2-oxazolines toward acyl chlorides.[8)]

Reactions of OZO and OZI with Cyclic Carboxylic Anhydrides. It was found by NMR study that the reaction of OZO with succinic anhydride (SAn) produced a bicyclic adduct 6,8-dioxa-1-azabicyclo-[5.3.0]decane-2,5-dione (**17a**), a product corresponding to **7** in the case of cyclic carboxylic anhydrides, and that **17a** is present in solution in equilibrium with starting materials of OZO and SAn. It has been unsuccessful so far to isolate **17a** in pure form. The NMR spectrum of the reaction system shows a new peak at δ 7.1 ascribed to the specific methine proton of **17a** beside a signal at δ 6.8 due to the methine proton of OZO. When the temperature was varied the intensities of these two signals changed. This change was reversible with the temperature variation. Therefore, the equilibrium constant (K, $l \cdot mol^{-1}$) could be determined. Figure 1 shows the temperature dependency of K measured at −25, 35, 50, and 80 °C. From the observed plot of $\ln K$ *vs.* $1/T$, enthalpy (ΔH) and entropy (ΔS) values were calculated from the following equation:



OZO SAn 17a

$$-RT \ln K = \Delta H - T\Delta S$$

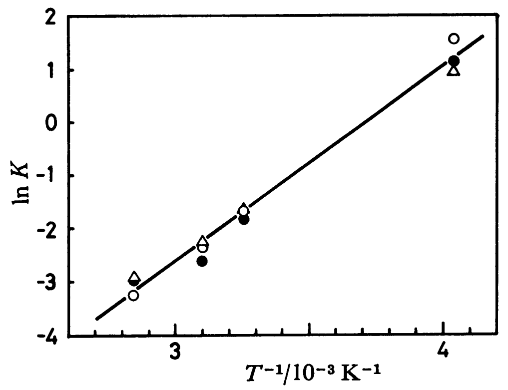
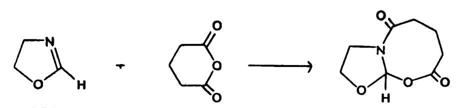


Fig. 1. Temperature dependency of the equilibrium constant K(l·mol^{-1}): the total amount of OZO+SAn =2.0 mmol in 0.4 ml of CD_3CN: OZO/SAn ratio; ○, 2.0; △, 1.0; ●, 0.5.

as $\Delta H = -30$ kJ mol^{-1} and $\Delta S = -110$ J K^{-1} mol^{-1}.

To support the structure of **17a**, the IR spectrum of the reaction mixture of OZO–SAn in CH_2Cl_2 showed a new band at 1730 cm^{-1} ascribable to the ester group and no band around 1580 cm^{-1} assignable to a carboxylate anion was observed.

The reaction of OZO with glutaric anhydride (GAn) yielded a bicyclic addition product, 7,9-dioxa-1-azabicyclo[6.3.0]undecane-2,6-dione (**17b**) quantitatively, which was obtained as a white solid. It is considered that the reaction equilibrium goes far to the right in this system. **17b** is insoluble in most organic solvents and hence NMR spectrum of the compound has not been obtained.



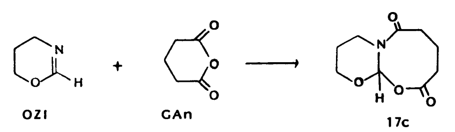
OZO GAn 17b

The hydrolysis of **17b** readily occured and gave a formic ester **18a**, which was taken to support the structure of **17b**.

$$\mathbf{17b} \xrightarrow{H_2O} HCO_2CH_2CH_2NHCOCH_2CH_2CH_2CO_2H$$

18a

The reaction of OZI with GAn was exothermic, which was completed in a few minutes at room temperature to give a white solid of 7,9-dioxa-1-azabicyclo[6.4.0]-dodecane-2,6-dione (**17c**). The reaction equilibrium lies far to the side of product in this system, too.



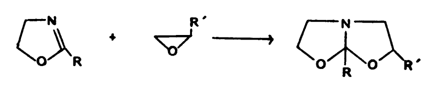
OZI GAn 17c

Similarly to **17b** the hydrolysis of **17c** gave **18b**, supporting the structure of **17c**.

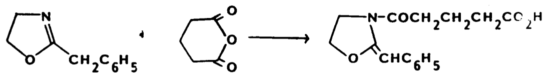
$$\mathbf{17c} \xrightarrow{H_2O} HCO_2CH_2CH_2CH_2NHCOCH_2CH_2CH_2CO_2H$$

18b

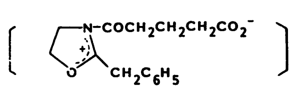
Formation of bicyclic addition products (**17**) is interestingly compared with that of bicyclic amide acetals (**19**) from 2-substituted 2-oxazolines and epoxides, where epoxides add to the C=N bond of the oxazolines.[9] In comparison with the results of unsubstituted cyclic imidates of OZO and OZI the reaction of BzOZO with GAn was examined. The reaction gave **20**, which is not a bicyclic addition product of GAn onto the C=N bond of BzOZO but corresponding to the product **12**. An intermediate **21** is probably involved.



19

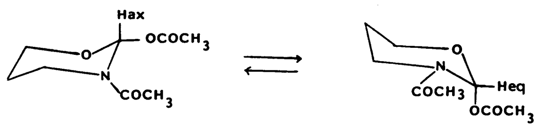


BzOZO GAn 20



21

Stereochemistry of Cyclic Addition Products Having Six-membered Ring. Addition products of five-membered ring system, *e.g.*, **7a** and **17a**, showed a single peak of the methine proton at δ 7.1 in the NMR spectra ($CDCl_3$ solvent). In contrast, the methine proton of addition products derived from six-membered OZI, *e.g.*, **7d** and **17c**, appeared as two peaks. The peak of the higher field at δ 7.1 and that of the lower field at δ 7.5 are ascribed respectively to the axial and equatorial methine proton of a six-membered chair form,[10] *e.g.*,



7d-ax 7d-eq

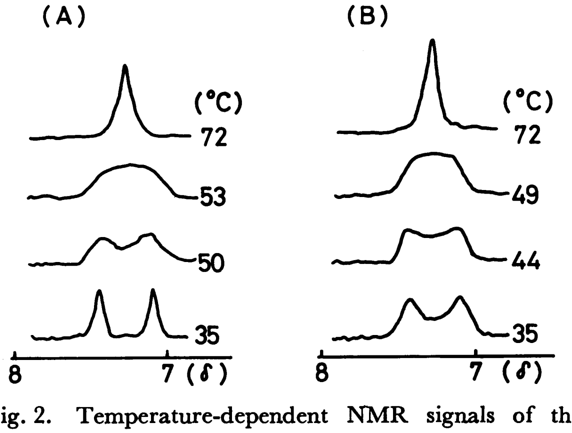


Fig. 2. Temperature-dependent NMR signals of the methine proton of **7d** (A) and **17c** (B) in CD_3CN.

With variation of temperature in CD_3CN, in which two methine signals at δ 7.1 and 7.5 appear as shown in Fig. 2, the coalescence time (T_c) was obtained as 53 °C for **7d** and 49 °C for **17c**, respectively. Then, the free-energy of activation ($\Delta F^{\neq}$) of the interconversion like **7d**-ax$\rightleftarrows$**7d**-eq was calculated to be 69.4 kJ mol^{-1} for **7d** and 68.6 kJ mol^{-1} for **17c**, respectively.[11] These $\Delta F^{\neq}$ values are somewhat higher than those obtained for cyclohexane derivatives.[11a]

Experimental

Materials. Solvents of CH_2Cl_2, $CHCl_3$, $CDCl_3$, CH_3CN CD_3CN, and DMSO-d_6 were purified by distillation under nitrogen. 2-Oxazoline (OZO),[6a] 5,6-dihydro-4*H*-1,3-oxazine (OZI),[6b] and 2-benzyl-2-oxazoline (BzOZO)[12] were obtained according to the reported procedures. Acetic and propionic anhydrides were dried over $CaCl_2$ and distilled. Benzoic anhydride was purified by recrystallization from diethyl ether. Succinic (SAn) and glutaric (GAn) anhydrides were recrystallized from $CHCl_3$ and $CHCl_3$–diethyl ether, respectively. Acetyl chloride and bromide were purified by distillation under nitrogen after drying over $CaCl_2$.

Measurements. NMR spectra were recorded at 60 MHz on a Hitachi R-20B spectrometer. IR spectra were taken on a Hitachi EPI G31 spectrophotometer.

Reaction of OZO and OZI with Acyclic Carboxylic Anhydrides (6). A typical run was as follows. A mixture of OZO and acetic anhydride (**6a**) (10 mmol each) in 4 ml of $CHCl_3$ was allowed to react at room temperature for 24 h under nitrogen. At this point it was confirmed by NMR of the mixture that the reaction was completed to yield addition product (**7a**) quantitively. The product **7a** was isolated by distillation *in vacuo* using Kugelrohl to give **7a** (1.63 g, 94% yield). Likewise, **7b** (91%), **7d** (92%), and **7e** (89%) were obtained. The quantitative production of **7c** and **7f** was confirmed by NMR of the reaction system carried out in $CDCl_3$ but the isolation of **7c** and **7f** has not been succeeded.

Data for the structural determination of products **7** are as follows. **7a**: bp 95—96 °C/0.13 Torr (1 Torr=133.322 Pa); IR (neat): 1730 and 1660 cm^{-1}; NMR ($CDCl_3$): δ 2.05 (s, 6H), 3.64 (t-like, 2H), 4.23 (t-like, 2H), and 7.08 (s, 1H). Found: C, 48.25; H, 6.37; N, 8.15%. Calcd for $C_7H_{11}NO_4$: C, 48.55; H, 6.40; N, 8.09%. **7b**: bp 110—112 °C/0.15 Torr; IR (neat): 1735 and 1665 cm^{-1}; NMR ($CDCl_3$): δ 1.15 (t, 6H), 2.33 (q, 4H), 3.65 (t-like, 2H), 4.21 (t-like, 2H), and 7.10 (s, 1H). Found: C, 53.89; H, 7.41; N, 6.97%. Calcd for $C_9H_{15}NO_4$: C, 53.72; H, 7.51; N, 6.96%. **7c**: NMR($CDCl_3$): δ 3.84 (2H), 4.25 (2H), and 7.1—8.1 (11H). **7d**: bp 83—84 °C/0.09 Torr; IR (neat): 1720 and 1660 cm^{-1}; NMR ($CDCl_3$): δ 1.73 (2H), 2.08 (6H), 3.0—4.5 (4H), and 7.1+7.5 (1H). Found: C, 51.09; H, 7.25; N, 7.47%. Calcd for $C_8H_{13}NO_4$: C, 51.33; H, 7.00; N, 7.48%. **7e**: bp 109—111 °C/0.15 Torr; IR (neat): 1730 and 1660 cm^{-1}; NMR ($CDCl_3$): δ 1.15 (t, 6H), 1.75 (2H), 2.36 (q, 4H), 3.5—4.5 (4H), and 7.1+7.5 (1H). Found: C, 55.74; H, 7.96; N, 6.33%. Calcd for $C_{10}H_{17}NO_4$: C, 55.80; H, 7.96; N, 6.51%. **7f**: NMR ($CDCl_3$): δ 1.4—2.5 (2H), 3.1—4.6 (4H), and 7.0—8.2 (11H).

Hydrolysis of Addition Products (7). A typical example of hydrolysis of **7a** was carried out as follows. To 3.24 mmol of **7a** 5.6 mmol of water was added and stirred at room temperature. The hydrolysis took place exothermically. After 10 min the vacuum distillation with Kugelrohl gave 3.90 g (92% yield) of **8a**. Furthermore, 1.90 g (97% yield) of acetic acid was obtained in the trap cooled in a Dry-Ice bath during the distillation. Analogous procedures for **7b**—**f** gave respectively **8b** (96%), **8c** (85%), **8d** (90%), **8e** (87%), and **8f** (80%).

The structure of these six hydrolysis products was determined based on the following data. **8a**: bp 83—85 °C/0.1 Torr; IR (neat): 3280, 3070, 1725, 1660, 1545, and 1180 cm^{-1}; NMR ($CDCl_3$): δ 2.00 (s, 3H), 3.45 (2H), 4.20 (t, 2H), 7.05 (br s, 1H), and 7.98 (s, 1H). Found: C, 46.01; H, 7.01; N, 10.70%. Calcd for $C_5H_9NO_3$: C, 45.80; H, 6.92; N, 10.68%. **8b**: bp 116—118 °C/0.3 Torr; IR (neat): 3280, 3070, 1720, 1650, 1540, and 1180 cm^{-1}; NMR ($CDCl_3$): δ 1.13 (t, 3H), 2.17 (q, 2H), 3.48 (2H), 4.18 (t, 2H), 6.9 (br s, 1H), and 7.95 (s, 1H). Found: C, 49.76; H, 7.85; N, 9.73. Calcd for $C_6H_{11}NO_3$: C, 49.65; H, 7.64; N, 9.65%. **8c**: bp 158—162 °C/0.25 Torr; IR (neat): 3300, 3070, 1725, 1650, 1540, and 1180 cm^{-1}; NMR ($CDCl_3$): δ 3.65 (2H), 4.27 (t, 2H), 6.58 (br s, 1H), 7.4 (5H), and 7.94 (s, 1H). Found: C, 62.50; H, 5.89; N, 7.24%. Calcd for $C_{10}H_{11}NO_3$: C, 62.17; H, 5.74; N, 7.25%. **8d**: bp 105—108 °C/0.25 Torr; IR (neat): 3280, 3070, 1720, 1650, 1550, and 1180 cm^{-1}; NMR ($CDCl_3$): δ 1.86 (2H), 1.96 (s, 3H), 3.25 (2H), 4.15 (t, 2H), 6.3 (br s, 1H), and 7.95 (s, 1H). Found: C, 49.46; H, 7.74; N, 9.79%. Calcd for $C_6H_{11}NO_3$: C, 49.65; H, 7.64; N, 9,65%. **8e**: bp 117—119 °C/0.3 Torr; IR (neat): 3280, 3070, 1720, 1650, 1550, and 1180 cm^{-1}; NMR ($CDCl_3$): δ 1.14 (t, 3H), 1.86 (2H), 2.18 (q, 2H), 3.28 (2H); 4.15 (t, 2H), 5.9 (br s, 1H) and 7.96 (s, 1H). Found: C, 53.04; H, 8.46; N, 8.89%. Calcd for $C_7H_{13}NO_3$: C, 52.82; H, 8.23; N, 8.80%. **8f**: bp 170—175 °C/0.25 Torr; IR (neat): 3300, 3060, 1720, 1640, 1540, and 1180 cm^{-1}; NMR ($CDCl_3$): δ 1.95 (2H), 3.45 (2H), 4.18 (t, 2H), 6.74 (1H), 7.4 (5H), and 7.94 (s, 1H). Found: C, 63.99; H, 6.26; N, 6.55%. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76%.

Reaction of BzOZO with Acetic Anhydride. BzOZO and acetic anhydride (**6a**) (10 mmol) each were allowed to react in 4 ml of CH_2Cl_2 at room temperature for 30 min. Evaporation of the solvent gave a white solid of **12** which was purified by recrystallization from a $CHCl_3$/diethyl ether mixed solvent (1.40 g, 96% yield); mp 128—129 °C; IR (KBr): 1675 and 1640 cm^{-1}; NMR ($CDCl_3$): δ 2.10 (s, 3H), 3.65 (t-like, 2H), 4.10 (t-like, 2H), 6.07 (s, 1H), and 7.1 (5H). Found: C, 70.72; H, 6.40; N, 6.86%. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89%.

Reactions of OZO and OZI with Acetyl Chloride or Bromide. In 0.5 ml of $CDCl_3$, OZO, or OZI (1 mmol) and acetyl chloride or bromide (1 mmol) were mixed. By NMR the reaction was found to finish within several minutes except for the OZO–acetyl chloride system which took one day for the completion of the reaction. The product (**13**) was isolated by using Kugelrohl and data for the structure determination are given as follows. **13a**: bp 81—83 °C/0.25 Torr; IR (neat): 1725 and 1670 cm^{-1}; NMR ($CDCl_3$): δ 2.42 (s, 3H), 3.58 (t, 2H), 4.01 (t, 2H), and 9.08 (s, 1H). Found: C, 40.30; H, 5.60; N, 9.48%. Calcd for $C_5H_8NO_2Cl$: C, 40.15; H, 5.39; N, 9.36%. **13b**: bp 96—98 °C/0.20 Torr; IR (neat): 1725 and 1670 cm^{-1}; NMR ($CDCl_3$): δ 2.43 (s, 3H), 3.40 (t, 2H), 4.03 (t, 2H), and 9.08 (s, 1H). Found: C, 30.82; H, 4.12; N, 7.06%. Calcd for $C_5H_8NO_2Br$: C, 30.95; H, 4.16; N, 7.22%. **13c**: bp 85—87 °C/0.30 Torr; IR (neat): 1725 and 1665 cm^{-1}; NMR ($CDCl_3$): δ 1.98 (m, 2H), 2.40 (s, 3H), 3.50 (t, 2H), 3.77 (t, 2H), and 9.09 (s, 1H). Found: C, 44.33; H, 6.28; N, 8.65%. Calcd for $C_6H_{10}NO_2Cl$: C, 44.05; H, 6.16; N, 8.56%. **13d**: bp 104—107 °C/0.25 Torr; IR (neat); 1725 and 1670 cm^{-1}; NMR ($CDCl_3$): δ 2.05 (m, 2H), 2.43 (s, 3H), 3.35 (t, 2H), 3.78 (t, 2H), and 9.12 (s, 1H). Found: C, 34.92; H, 4.85; N, 6.82%. Calcd for $C_6H_{10}NO_2Br$: C, 34.64; H, 4.84; N, 6.73%.

A mixture of OZO (10 mmol) and acetyl chloride (4 mmol) was allowed to react in 3.2 ml of $CHCl_3$ at room temperature for 24 h. The evaporation of $CHCl_3$ and unreacted OZO gave a 2 : 1 reaction product **15** (92% yield), which was further purified by silica-gel TLC (ethanol solvent). IR (neat): 1660, and 1100 cm^{-1}; NMR ($CDCl_3$): δ 2.95 (s, 3H), 3.5—4.4 (m, 8H), 6.18 (s, 1H), and 8.36 (s, 1H). Found: C, 43.38; H, 6.08; N, 12.65%. Calcd for $C_8H_{13}N_2O_3Cl$: C, 43.55; H, 5.94; N, 12.70%. An attempt to distill **15** with Kugelrohl *in vacuo* resulted in decomposition to give **13a**

Reaction of OZO with GAn. All operations were performed under nitrogen. In 4 ml of CH_3CN,OZO (10 mmol) and GAn (10 mmol) were mixed at 0 °C. A white solid precipitated after several minutes. Then, the solid product (**17b**) was separated using a sintered-glass filter and washed several times with CH_2Cl_2 (1.73 g, 93% yield): mp 87—88 °C; IR (KBr): 1735 and 1670 cm^{-1}. Found: C, 51.66; H, 6.01; N, 7.75%. Calcd for $C_8H_{11}NO_4$: C, 51.89; H, 5.99; N, 7.56%.

Reaction of OZI with GAn. All operations were carried out under nitrogen. A mixture of OZI (10 mmol) and GAn (10 mmol) was stirred at 0 °C in 4 ml of CH_2Cl_2. The reaction mixture immediately become viscous. After 30 minutes dry diethyl ether (5 ml) was added to the system, well shaken and kept at −25 °C for 2 h. Then, the system was separated into two layers. The lower layer was dissolved in 4 ml of CH_2Cl_2. This solution was added to a large amount of diethyl ether to separate a viscous liquid material. This reprecipitation procedure was repeated twice. The separated viscous liquid product (**17c**) became a white solid after drying *in vacuo* (1.75 g, 88% yield): mp 53—55 °C; IR (KBr): 1715, 1650, and 1090 cm^{-1}; NMR ($CDCl_3$): δ 1.4—2.7 (8H), 3.2—4.6 (4H), and 7.1+7.5 (1H). Found: C, 51.33; H, 7.04; N, 6.71%. Calcd for $C_9H_{13}NO_4(H_2O)_{0.6}$: C, 51.47; H, 6.82; N, 6.67%.

Hydrolysis of 17b and 17c. **17b** (or **17c**) (5 mmol) was reacted with 30 mmol of water. The hydrolysis finished immediately. The evaporation of excess water gave a viscous liquid. This liquid was dissolved in CH_3CN and poured into a large amount of diethyl ether to separate the liquid again. This procedure of purification was repeated three times to give an oily product **18a** (or **18b**) in almost quantitative yield. **18a**: IR (neat): 3280, 3070, 1720, 1640, 1550, and 1180 cm^{-1}; NMR (CD_3CN): δ 1.5—2.5 (m, 6H), 3.30 (q-like, 2H), 4.04 (t, 2H), 6.63 (br s, 1H), and 7.89 (s, 1H). Found: C, 47.35; H. 6.61; N, 7.01%. Calcd for $C_8H_{13}NO_5$: C, 47.29; H, 6.45; N, 6.89%. **18b**: IR (neat): 3280, 3070, 1725, 1640, 1560, and 1180 cm^{-1}; NMR (CD_3CN): δ 1.4—2.5 (m, 8H), 3.14 (q-like, 2H), 4.05 (t, 2H), 6.78 (br s, 1H), and 7.91 (s, 1H). Found: C, 48.96; H, 7.35; N, 6.47%. Calcd for $C_9H_{15}NO_5$: C, 49.76; H, 6.96; N, 6.45%.

Reaction of BzOZO with GAn. A mixture of BzOZO and GAn (5 mmol each) in CH_3CN (2 ml) was kept at room temperature for 20 h to give needle crystals **20**, which was separated and washed with CH_2Cl_2 (0.72 g, 52%): mp 63—64 °C (from DMSO); IR (KBr): 1690, 1630, and 1120 cm^{-1}; NMR (DMSO-d_6): δ 1.5—2.7 (m, 6H), 3.88 (t-like, 2H), 4.29 (t-like, 2H), 6.25 (s, 1H), and 6.7—7.4 (m, 5H). Found: C, 65.41; H, 6.31; N, 5.28%. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09%.

References

1) J. A. Frump, *Chem. Rev.*, **71**, 483 (1971).

2) P. F. Tryon, U. S. Patent, 2410318 (1946); *Chem. Abstr.*, **41**, 2076b (1947).

3) S. P. Rowland, U. S. Patent, 2547542, 2547494 (1951); *Chem. Abstr.*, **45**, 9567d (1951), **46**, 1050c (1952).

4) R. Nehring and W. Seeliger, *Justus Liebigs Ann. Chem.*, **82**, 448 (1970).

5) W. Seeliger, E. Aufderhaar, W. Diepers, R. Feinauer, R. Nehring, W. Thier, and H. Hellmann, *Angew. Chem.*, **78**, 913 (1966).

6) a) T. Saegusa, H. Ideda, and H. Fujii, *Polym. J.*, **3**, 35 (1972); b) T. Saegusa, Y. Nagura, and S. Kobayashi, *Macromolecules*, **6**, 495 (1973); c) T. Saegusa and S. Kobayashi, "International Review of Science, Physical Chemistry Series Two, Vol. 8, Macromolecular Science," Butterworth, London, (1975), Chap. 4; d) T. Saegusa and S. Kobayashi, "Encyclopedia of Polymer Science and Technology," John Wiley and Sons, Inc., New York (1976), Suppl. Vol. 1, pp. 220—237; e) S. Kobayashi, M. Isobe, and T. Saegusa, *Macromolecules*, in press.

7) T. Saegusa, S. Kobayashi, and Y. Nagura, *Macromolecules*, **7**, 265 (1974).

8) R. Nehring and W. Seeliger, *Justus Liebigs Ann. Chem.*, **709**, 113 (1967).

9) R. Feinaurer, *Synthesis*, **1971**, 16; R. Feinauer and W. Seeliger, *Justus Liebigs Ann. Chem.*, **698**, 174 (1966).

10) L. M. Jackman and S. Sternhell, "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon, Oxford (1969), p. 238.

11) L. M. Jackman and F. A. Cotton, "Dynamic Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York (1975), Chap. 14; L. W. Reeves, "Adv. Phys. Org. Chem.," Academic Press, New York (1965), Vol. 3, p. 187; M. Tabei, T. Tezuka, and M. Hirota, *Tetrahedron*, **27**, 301 (1971).

12) T. Kagiya, S. Narisawa, T. Maeda, and K. Fukui, *Kogyo Kagaku Zasshi*, **69**, 732 (1966); *Chem. Abstr.*, **65**, 15510d (1966).