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Reaction of 2,2,6-Trimethyl-1,3-dioxin-4-one with Imines[1]

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The reaction of 2,2,6-trimethyl-1,3-dioxin-4-one (diketene–acetone adduct) (1) with imines was investigated. Heating of the adduct **1** with *N*-(1-phenylethylidene)aniline (**6a**) gave 6-methyl-1,2-diphenyl-4(1*H*)-pyridone **7a**. Similar treatment of *N*-benzylideneaniline (**3a**) gave 3,4-dihydro-6-methyl-2,3-diphenyl-2*H*-1,3-oxazin-4-one (**4a**). *N*-Benzylidenealkylamines likewise reacted with the adduct **1** to give the corresponding 1,3-oxazine derivative **4**. Reaction of diketene with *N*-benzylidenealkylamines in the presence of triethylamine gave the corresponding 1,3-oxazine along with 3-acetyl-1-alkyl-4-phenylazetidin-2-one (**8**).

Keywords——diketene; diketene–acetone adduct; acetylketene; 2,2,6-trimethyl-1,3-dioxin-4-one; 1,3-oxazin-4-one derivative; azetidin-2-one derivative; imine; cycloaddition; thermal fragmentation; ring transformation

During the course of an investigation of potential uses of diketene, our interest was focused on the chemistry of the so-called diketene–acetone adduct (2,2,6-trimethyl-1,3-dioxin-4-one) (**1**), which can be easily prepared from diketene and acetone in the presence of an acidic catalyst.[2] Only a few reports are available on this adduct. Jäger and Wenzelburger reported that the adduct **1** reacted with isocyanates and cyanamides under heating to give 1,3-oxazine derivatives,[3] which had been also obtained by the use of diketene.[4] We observed that **1** is much more reactive than diketene itself towards amides, giving *N*-acetoacetyl compounds.[5] Such a high reactivity of **1** may be explained in terms of formation of an acetylketene intermediate (**2**) from **1** on heating, as suggested in the literature.[3]

Meanwhile, there are also many reports dealing with the reaction of diketene with compounds that possess a C=N double bond, revealing the diverse reactivity of diketene.[4] We previously observed that diketene reacts with Schiff bases (**3**) in an unusual manner to give 2-benzylideneacetoacetamides (**5**).[6] Later, Maujean and Chuche reported that the use of triethylamine as a catalyst changes the course of the reaction, giving 1,3-oxazine derivatives (**4**).[7]

In order to compare the reactivity of the adduct **1** with that of diketene itself in more detail, we investigated the reaction of **1** with imine derivatives.

When **1** was heated with ketone anils (**6a**—**6c**) at 130°C without any solvent, *N*-phenyl-4-pyridones (**7a**—**7c**) were obtained in 26—40% yields. As reported previously, the same products are formed from diketene and anils in acetic acid in the presence of *p*-toluenesulfonic acid in

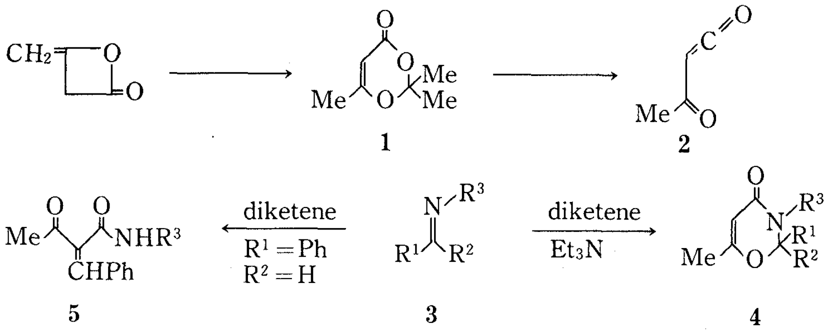

Chart 1

comparable yields.[8] In both cases, the products are presumably formed by *C*-acetoacetylation of the tautomeric enamine (**6′**) followed by cyclization.

In contrast, when the adduct **1** and *N*-benzylideneaniline (**3a**) were heated without a solvent, 3,4-dihydro-6-methyl-2,3-diphenyl-2*H*-1,3-oxazin-4-one (**4a**) was formed in 62% yield. Use of xylene as a solvent decreased the yield to 37%. The reaction did not take place at temperatures below 100°C even in the presence of triethylamine. Other imines, **3b**—**3k**, likewise reacted with **1** to afford the oxazines **4b**—**4k**. The results are summarized in Table II.

Yields of the oxazines **4** where R^2 is hydrogen and R^3 is an alkyl group are fairly dependent on the reaction conditions, especially on the reaction time and temperature. Namely, higher temperature and shorter reaction time favor the formation of the oxazine, and prolonged heating results in the formation of the corresponding acetoacetamide **5** as a by-product. This result indicates the conversion of the oxazine to the acetoacetamide during the reaction.

Interestingly, heating of *N*-benzylidene-*tert*-butylamine (**3i**) with **1** at 130°C for 10 min gave the azetidinone derivative (**8i**, 6%) along with the acetoacetamide (**5i**, 20%). When the reaction time was reduced to 5 min, the oxazine **4i** was obtained in 16% yield. The oxazine **4i**, on being heated at 135°C for 30 min, afforded the acetoacetamide **5i** and the azetidinone **8i**. In addition, heating of the oxazine **4i** with *N*-benzylidenebenzylamine (**3d**) resulted in exchange of the imine to give the oxazine **4d** in 54% yield. The oxazine **4h** (R^1=Ph, R^2=H, R^3=iso-Pr) was similarly converted to the oxazine **4a** on being heated with the imine **3a**. These exchange reactions strongly indicate that thermal fragmentation of oxazines **4h** and **4i** occurs to give acetylketene and imines.

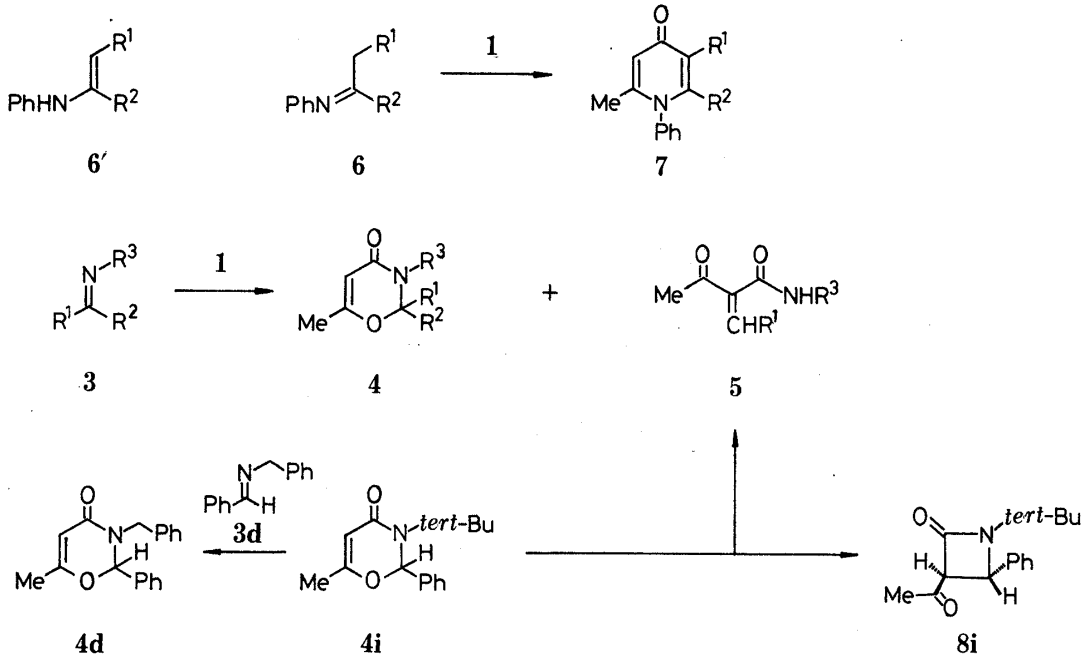

Chart 2

Reaction of diketene with the imine **3d** in the presence of triethylamine is reported to give only the oxazine **4d** in 56% yield.[7] When this reaction was reinvestigated in our hands, a small amount of the azetidinone **8d** (4%) was obtained along with the oxazine **4d** (39%). Similar treatment of diketene with **3g**, **3h**, and **3i** gave the azetidinones **8g** (5%), **8h** (19%), and **8i** (7%) along with the oxazines **4g** (43%), **4h** (12%), and **4i** (4%), respectively. The products **8** were assigned the *trans* structure on the basis of the coupling constant of the methine protons (J=2 Hz) in their proton nuclear magnetic resonance (^{1}H-NMR) spectra.

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TABLE I. Reaction of Adduct **1** with Ketone Anils **6**

Substituent			Reaction conditions				Product **7**		
	R^1	R^2	**1** (mmol)	**6** (mmol)	Temp. (°C)	Time (min)	Yield (%)	mp (°C) (lit.$^{a)}$ mp)	Recrystn. solvent
a	Ph	H	14	10	130—135	30	30	244—245	Benzene
			20	10	130—135	35	35	(238—239)	
b	Me	H	14	10	130—135	15	26	198 (195—197)	Ether
c	$(CH_2)_5$		10	10	125	20	27	295—295.5	Ethyl acetate–methanol
			20	10	128—130	15	40	(275—277 (dec.))	

a) Reference 8).

TABLE II. Reaction of Adduct **1** with Imines **3**

Substituent				Reaction conditions				Product					
				1	**3**				**4**			**5**	
	R^1	R^2	R^3	(mmol)	(mmol)	Temperature (°C)	Time (min)	Yield (%)	mp (°C) (lit. mp)	Recrystn. solvent$^{a)}$	Yield (%)	mp (°C) (lit. mp)	Recrystn. solvent$^{a)}$
a	Ph	H	Ph	6	5	120—121	20	62	94—94.5	A			
				6	5	Reflux in xylene	40	37	(90)$^{b)}$				
b	Ph	H	*p*-Meo-Ph	10	10	125	10	58	88—88.5	A			
c	H	H	Ph	6	5	120—121	20	71	67—68	A			
d	Ph	H	$PhCH_2$	10	10	128—130	10	65	77—79				
				10	10	130—131	60	5	(77)$^{b)}$	B	37	111—113	B
e	Ph	H	Me	10	10	130	10	50	61—62	A			
f	Ph	H	Et	10	10	130	5	61	38—39	A			
				10	10	130	30	62			25	88—89	B
g	Ph	H	Pr	10	10	131—132	10	87	Oil		16	80.5—83 (80.5—82.5)$^{c)}$	B
				10	10	125—130	20	27					
h	Ph	H	iso-Pr	10	10	132—133	10	41	100—102	A	7	78—80	B
				10	10	131—132	30	9			31		
i	Ph	H	*tert*-Bu	10	10	131—132	5	15	99—100	A	5	111—111.5	B
				10	10	131—132	10				20	(112—113)$^{d)}$	
j	Ph	H		14	10	130—135	10	62	125—126	A			
k	Ph	Ph	$PhCH_2$	12	10	125—130	30	68	162—164	A			

a) A, ether–hexane; B, ether.
b) Reference 7).
c) Reference 6*b*).
d) Reference 6*a*).

It is well known that treatment of acid chlorides with triethylamine gives ketenes, which add to imines to yield azetidinones. When acetoacetyl chloride was treated with the imine **3g** according to this method at —60°C, the oxazine **4g** (16%) and the azetidinone **8g** (14%) were formed.

Acetyl Meldrum's acid (**9**) plays a role as an acetylketene equivalent in some cases.[9] However, heating of **9** with the imine **3g** resulted in the formation of the oxazinedione derivative (**10**) (80%) along with a small amount of **4g**.

Lastly, generation of acetylketene from the adduct **1** was confirmed by an infrared (IR) spectroscopic study. When **1** was injected into a preheated gas cell (*ca.* 120°C), a weak absorption at 2150 cm^{-1} was observed. Diketene–diisopropylketone adduct (**11**) showed the same absorption more strongly. This characteristic absorption can be assigned to the C=C=O group.[10]

Possible mechanisms of the reaction of the imines **3** with the adduct **1**, diketene, and aceto-

TABLE III. Analytical and Spectral Data for **4**

Compd. No.	Formula	Analysis (%) Calcd (Found) C	H	N	IR (CHCl$_3$) cm^{-1} C=O	C=C	^{1}H-NMR (CDCl$_3$) δ C$_5$-H	C$_6$-Me
4b	$C_{18}H_{17}NO_3$	73.20 (72.95	5.80 5.74	4.74 4.51)	1664	1612	5.33	1.91
4c	$C_{11}H_{11}NO_2$	69.82 (69.79	5.86 5.73	7.40 7.46)	1665	1600	5.34	2.02
4e	$C_{12}H_{13}NO_2$	70.91 (71.21	6.45 6.38	6.89 6.83)	1665	1630	5.08	1.85
4f	$C_{13}H_{15}NO_2$	71.86 (72.14	6.96 7.15	6.45 6.32)	1661	1625	5.23	1.85
4g	$C_{14}H_{17}NO_2$	72.70 (72.77	7.41 7.32	6.06 6.24)	1659	1622	5.22	1.83
4h	$C_{14}H_{17}NO_2$	72.70 (72.75	7.41 7.57	6.06 6.00)	1656	1619	5.20	1.75
4i	$C_{15}H_{19}NO_2$	73.44 (73.13	7.81 7.95	5.71 5.52)	1661	1621	5.11	1.76
4j	$C_{17}H_{21}NO_2$	75.24 (75.04	7.80 7.99	5.16 4.91)	1659	1620	5.18	1.72
4k	$C_{24}H_{21}NO_2$	81.10 (81.09	5.96 5.96	3.94 3.83)	1672	1631	5.31	1.85

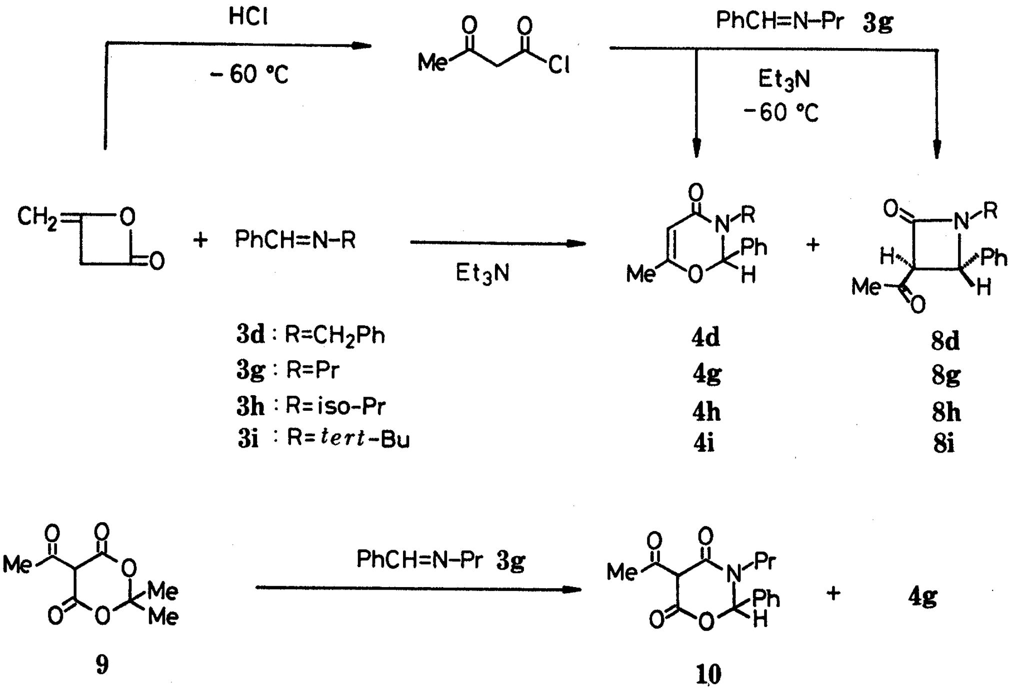

Chart 3

acetyl chloride are illustrated in Chart 4. Maujean *et al.* have proposed that the formation of oxazines **4** from diketene involves initial isomerization of diketene to acetylketene (**2**) by triethylamine catalysis.$^{7)}$ The results of our investigation strongly support this isomerization of diketene. The key intermediate **2** is also formed from **1** and from acetoacetyl chloride. 1,4-Cycloaddition of imines to **2** produces the oxazine **4**. As evidenced by the exchange reactions, the 1,4-addition is reversible at elevated temperature when R^2 is hydrogen and R^3 is an alkyl group. A concerted mechanism is favored for such a thermal and reversible reaction.

The competitive 1,2-cycloaddition of imines to **2** yields the corresponding azetidinone **8**. However, the 1,4-addition precedes the 1,2-addition at elevated temperature, resulting in the

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formation of the oxazine **4**. An exceptional formation of azetidinone **8i** under heating is observed in the reversible reaction of the highly thermolabile oxazine **4i**, which is isomerized to the thermally stable azetidinone **8i**.

Previously, the azetidinone **8** was presumed to be an intermediate to the acetoacetamide **5**.[6] However, isolated azetidinones are stable to prolonged heating and to bases such as triethylamine. Thus, we propose an alternative mechanism involving the zwitterionic intermediate **12**. The intermediate may be formed from diketene and the imine without a catalyst, and from the oxazine **4** under heating presumably *via* acetylketene. Addition of another molecule of the imine to **12** and subsequent elimination of the imine would give the product **5**.

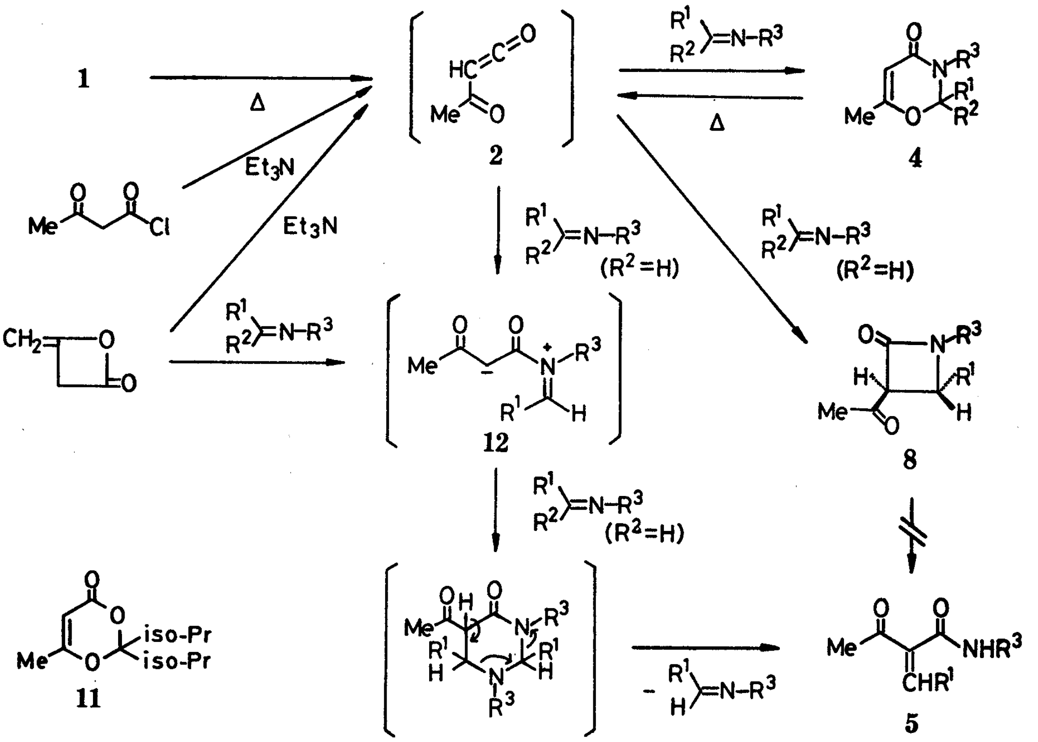

Chart 4

TABLE IV. Analytical and Spectral Data for **5**

Compd. No.	Formula	Analysis (%) Calcd (Found) C	H	N	IR (CHCl3) cm-1 C=O	NH	1H-NMR (CDCl3) δ
5d[a]	$C_{18}H_{17}NO_2$	77.39 (77.13	6.13 6.13	5.01 4.90)	1662	3420	2.10 (0.75H, s, Me), 2.31 (2.25H, s, Me) 4.52 (2H, d, CH2Ph, J=3 Hz) 5.86—6.35 (1H, br, NH) 7.21—7.70 (10.75H, m, Ph and =CH) 8.12 (0.25H, s, =CH)
5f	$C_{13}H_{15}NO_2$	71.86 (72.05	6.96 6.96	6.45 6.26)	1655	3430	1.12 (3H, t, J=7 Hz, CH2CH3) 2.40 (3H, s, Me) 3.39 (2H, quint., J=7 Hz, CH2CH3) 5.73—6.50 (1H, br, NH) 7.23—7.83 (6H, m, Ph and =CH)
5h	$C_{14}H_{17}NO_2$	72.70 (72.48	7.41 7.44	6.06 6.01)	1651	3460	1.15 (6H, d, J=7 Hz, CHMe2) 2.39 (3H, s, Me) 3.90—4.57 (1H, m, CHMe2) 5.53—6.10 (1H, br, NH) 7.16—7.77 (6H, m, Ph and =CH)

a) This compound was obtained as a mixture of geometric isomers.

TABLE V. Reaction of Diketene with Imines **3** to give Oxazines **4** and Azetidinones **8**

Substituent	**4** Yield (%)	**8** Yield (%)	Appearance mp (°C)	Formular	Analysis (%) Calcd (Found) C	H	N
d ($R^3=CH_2Ph$)	39	4	Oil	$C_{18}H_{17}NO_2$	77.39 (77.68	6.13 6.33	5.01 5.05)
g (R^3=Pr)	43	5	Oil	$C_{14}H_{17}NO_2$	72.70 (72.47	7.41 7.43	6.06 5.93)
h (R^3=iso-Pr)	12	19	Oil	$C_{14}H_{17}NO_2$	72.70 (72.61	7.41 7.37	6.06 6.07)
i (R^3=*tert*-Bu)	4	7	Prisms 90—92	$C_{15}H_{19}NO_2$	73.44 (73.44	7.81 7.74	5.71 5.65)

TABLE VI. Spectral Data for 2-Azetidinone Derivatives **8**

Compd. No.	IR ($CHCl_3$) cm^{-1} C=O	^1H-NMR($CDCl_3$)δ COMe	C_3-H	C_4-H	Ph	R
8d	1750, 1705	2.26 (3H, s)	4.03 (1H, d, *J*=2 Hz)	4.81 (1H, d, *J*=2 Hz)	6.87—7.51 (5H, m)	3.78, 4.73 (2H, ABq, *J*=15 Hz) 6.87—7.51 (5H, m)
8g	1755, 1715	2.30 (3H, s)	4.02 (1H, d, *J*=2 Hz)	4.96 (1H, d, *J*=2 Hz)	7.35 (5H, s)	0.88 (3H, t, *J*=7 Hz) 1.20—1.93 (2H, m) 2.58—3.16 (1H, m) 3.19—3.78 (1H, m)
8h	1750, 1715	2.28 (3H, s)	3.97 (1H, d, *J*=2 Hz)	4.98 (1H, d, *J*=2 Hz)	7.33 (5H, s)	1.04 (3H, d, *J*=7 Hz) 1.28 (3H, d, *J*=7 Hz) 3.72 (1H, q, *J*=7 Hz)
8i	1745, 1710	2.28 (3H, s)	3.90 (1H, d, *J*=2 Hz)	5.01 (1H, d, *J*=2 Hz)	7.26—7.46 (5H, m)	1.25 (9H, s)

In conclusion, acetylketene undergoes both 1,2- and 1,4-cycloaddition with imines, and the adduct **1** is a better precursor than diketene and acetoacetyl chloride for the preparation of the 1,4-cycloadduct.

Experimental

All melting points and boiling points are uncorrected. IR spectra were measured with JASCO A-102 and IR-S spectrometers. Mass spectra (MS) were taken with a Hitachi M-52G spectrometer. ^1H-NMR spectra were taken with a JEOL JNM-PMX 60 spectrometer. Chemical shifts are reported as ppm downfield from tetramethylsilane as an internal standard.

General Procedure for Reaction of Adduct 1 with Ketone Anils 6a,(11) 6b,(12) and 6c(13)——A mixture of **1** and **6** was heated under conditions shown in Table I. The reaction mixture was dissolved in chloroform and subjected to silica gel (50 g) column chromatography. After elution with a mixture of hexane–ethyl acetate (1 : 1, 200 ml), elution was continued with ethyl acetate to give the product **7**, which was purified by recrystallization. Yields and melting points are shown in Table I.

General Procedure for Reaction of Adduct 1 with Imines 3a,(14) 3b,(15) 3c,(16) 3d,(17) 3e,(18) 3f,(19) 3g,(20) 3h,(21) 3j,(23) and 3k(24)——A mixture of **1** and **3** was heated without any solvent. Products **4a**—**4c**, **4j**, and **4k** were crystallized from a mixture of ether–hexane (1 : 1). Crystals were collected by suction and recrystallized. Other products were purified by silica gel column chromatography using mixtures of hexane–ethyl acetate (3 : 1, 2 : 1, and then 1 : 1) as eluents. Reaction conditions, yields, recrystallization solvents and melting

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points are shown in Table II. Elemental analyses and spectral data for new compounds are shown in Table III and Table IV.

Reaction of Adduct 1 with *N*-Benzylidene-*tert*-butylamine (3i)——a) A mixture of **1** (1.42 g) and **3i**[22] (1.61 g) was heated at 130—132°C for 5 min. Hexane (*ca.* 10 ml) was added to the mixture. Precipitated crystals were collected by suction and washed with a mixture of hexane–ether (1 : 1, 3 ml). Recrystallizatoin from ether–hexane gave 3-*tert*-butyl-3,4-dihydro-6-methyl-2-phenyl-2*H*-1,3-oxazin-4-one (**4i**) as prisms of mp 99—100°C. Yield, 0.37 g. The hexane-soluble fraction was purified by silica gel column chromatography using a mixture of hexane–ethyl acetate (3 : 1) as an eluent to give 2-benzylidene-*N*-(*tert*-butyl)acetoacetamide (**4i**) as needles. Yield, 0.12 g.

b) A mixture of **1** (1.42 g) and **3i** (1.61 g) was heated at 130—132°C for 10 min. The reaction mixture was subjected to silica gel column chromatography. Elution with a mixture of hexane–ether (4: 1) gave 3-acetyl-1-*tert*-butyl-4-phenyl-2-azetidinone (**8i**) as prisms of mp 90—92°C (recrystallized from hexane–ether). Analytical and spectral data for compound **8i** are shown in Table V and Table VI. Subsequent elution with a mixture of hexane–ether (2: 3) gave **5i**. Yield, 0.73 g.

Conversion of 4i to 5i and 8i——Compound **4i** (0.25 g) was heated at 135°C for 30 min. The reaction mixture was subjected to silica gel column chromatography. Elution with a mixture of hexane–ether (4: 1) gave **8i**. Yield, 20 mg (8%). Subsequent elution with hexane–ether (2: 1) gave **5i**. Yield, 30 mg (12%).

Conversion of 4i to 4d——A mixture of **4i** (0.49 g, 2 mmol) and **3d** (0.39 g, 2 mmol) was heated at 135—136°C for 10 min. Purification by silica gel column chromatography using hexane–ether (2: 1) as an eluent gave **4d**. Yield, 0.30 g (54%).

Conversion of 4h to 4a——A mixture of **4h** (0.46 g, 2 mmol) and **3a** (0.36 g, 2 mmol) was heated at 135—136°C for 10 min. The reaction mixture was subjected to silica gel column chromatography. Elution with benzene–ether (20: 1) gave **4a** (0.06 g, 12%) and unreacted **4h** (0.21 g, 46%).

General Procedure for Reaction of Diketene with Imine 3 in the Presence of Triethylamine——A solution of **3** (10 mmol), diketene (0.84 g, 10 mmol), and triethylamine (200 mg, 2 mmol) in dry ether (10 ml) was stirred at room temperature for 1 d. After evaporation of the solvent *in vacuo*, the oily residue was subjected to silica gel column chromatography using hexane–ether (1: 1) as an eluent. The azetidinone **8** was first eluted. Subsequent elution with the same solvent gave the oxazine **4**. The yields of **4** and **8** are given in Table V. Analytical and spectral data for **8** are given in Table V and Table VI.

Reaction of Acetoacetyl Chloride with Imine 3g——Acetoacetyl chloride[25] was prepared from diketene (1.68 g, 20 mmol) and dissolved in dry ether (20 ml). This solution was added dropwise to a mixture of **3g** (2.94 g, 20 mmol), triethylamine (2.02 g, 20 mmol) and dry ether (20 ml) over a period of 10 min with stirring at −60°C. Stirring was continued for an additional 1 h at −60°C and then for 1 h at room temperature. Water was added to the reaction mixture and the mixture was extracted with ether. The organic layer was dried over magnesium sulfate and concentrated to give an oil. Purification by silica gel column chromatography using hexane–ether (1: 1) as an eluent gave **8g**, 0.83 g (18%) and **4g**, 0.6 g (13%).

5-Acetyl-3,4,5,6-tetrahydro-2-phenyl-3-propyl-1,3-oxazine-4,6-dione (**10**)——Compound **9** (mp 82—85°C) was prepared by the method described in the literature.[9a] A solution of **9** (0.47 g, 2.5 mmol) and **3g** (0.37 g, 2.5 mmol) in toluene (10 ml) was refluxed for 1 h. The reaction mixture was purified by silica gel column chromatography using hexane–ethyl acetate (4: 1) as an eluent to give **10** as colorless needles of mp 73—74°C (recrystallized from hexane). Yield, 0.55 g (80%). *Anal.* Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.71; H, 6.39; N, 4.90. IR ($CHCl_3$): 3600—3200 (br), 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.90 (3H, t, $J=7$ Hz, $CH_2CH_2C\underline{H}_3$), 1.20—1.90 (2H, m, $CH_2C\underline{H}_2CH_3$), 2.48 (3H, s, CH_3), 2.67—3.17 and 3.60—4.20 (each 1H, m, $C\underline{H}_2CH_2CH_3$), 6.15 (1H, s, C–H), 7.13—7.60 (5H, m, phenyl), 17.0 (1H, s, enol OH). MS *m/e*: 275 (M^+), 232 (M^+-CH_3CO). Subsequent elution with a mixture of hexane–ethyl acetate (2: 1) gave **4g**, 0.07 g (12%).

2,2-Diisopropyl-6-methyl-1,3-dioxin-4-one (**11**)——A mixture of diketene (8.4 g), diisopropyl ketone (17.1 g), and *p*-toluenesulfonic acid (0.1 g) was heated at 80°C for 4 h. Distillation of the reaction mixture gave **11** as an oil of bp 70°C (0.1 mmHg). Yield, 6.2 g (31%). *Anal.* Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.21; H, 9.54. IR ($CHCl_3$): 1710, 1640 cm^{-1}. ^{1}H-NMR (CCl_4) δ: 1.00 (12H, d, $J=6.5$ Hz), 1.93 (3H, s), 1.93—2.50 (1H, m), 4.86 (1H, s).

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