

Masahiro Fujiwara*, Akio Baba* and Haruo Matsuda

Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565, Japan

Received February 8, 1989

The cycloadditions of carbon dioxide, isocyanates and carbodiimides to oxetanes proceeded in the presence of catalytic amounts of tetraphenylstibonium iodide (**1**) under mild conditions, affording the corresponding six-membered heterocycles; 1,3-dioxan-2-ones, 1,3-oxazin-2-ones and 1,3-oxazin-2-imines in good yields, respectively. Moreover, the cycloaddition of 2-phenyloxetane proceeded *via* predominant ring-cleavage at substituted site.

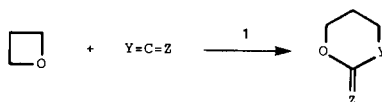
J. Heterocyclic Chem., **26**, 1659 (1989).

Various reactions of oxiranes including cycloaddition with heterocumulenes are well-known and applied to organic syntheses as a method introducing two carbon units

[1]. Oxetanes, similar small cyclic ethers to oxiranes, are considered important substrates as three carbon units. Their synthetic use, however, is extensively limited by

Table 1

Cycloaddition of Heterocumulenes to Oxetane [a]

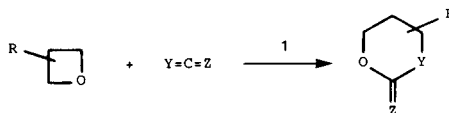


Compound No.	Y = C = Z	Solvent	Time (hours)	yield (%) [e]	bp (torr) (°C)
2 [b]	CO ₂	-	4	96	(mp 46-47)
3	C ₆ H ₅ -N=C=O	THF	4.5 (3.5 + 1) [d]	89	(mp 99)
4	<i>p</i> -CH ₃ C ₆ H ₄ -N=C=O	PhH	4 (3 + 1) [d]	80	(mp 127)
5	<i>p</i> -ClC ₆ H ₄ -N=C=O	THF	6 (5 + 1) [d]	41	(mp 88-89)
6	C ₄ H ₉ -N=C=O	PhH	12	86	81-82 (0.01 mm Hg)
7	(CH ₃) ₂ CH-N=C=O	PhH	15	66	74 (0.01 mm Hg)
8 [c]	CH ₃ -N=C=O	PhH	18	100	130 (2 mm Hg)
9	C ₆ H ₅ CH ₂ -N=C=O	PhH	19	58	(mp 35)
10	CH ₂ =CHCH ₂ -N=C=O	PhH	14	52	74 (0.01 mm Hg)
11	Cl(CH ₂) ₂ -N=C=O	PhH	21	40	64 (0.01 mm Hg)
12	<i>p</i> -CH ₃ C ₆ H ₄ SO ₂ -N=C=O	PhH	2 (1 + 1) [d]	77	(mp 111)
13	C ₆ H ₅ -N=C=N-C ₆ H ₅	PhH	10	99	(mp 106-107)
14	C ₆ H ₅ -N=C=N-C ₄ H ₉	PhH	18	92	66 (0.1 mm Hg)
15	C ₄ H ₉ -N=C=N-C ₄ H ₉	PhH	65	95	85 (0.01 mm Hg)

[a] Oxetane/Y=C=Z/1 = 10/5/0.5 mmole, solvent 5 ml, 40°. [b] Oxetane/1 = 20/0.4 mmole, 100°, CO₂ 50 Kg/cm². [c] Room temperature. [d] (Drop time + reaction). [e] Glic yield.

Table 2

Cycloaddition of Substituted Oxetanes.



Compound No.	R	Y = C = Z	Solvent	temperature (°C)	Time (hours)	yield (%)	bp (torr) (°C)
16 [a]	2-CH ₃	CO ₂	-	150	4	85	116-117 (2 mm Hg)
17 [a]	3-CH ₃	CO ₂	-	120	4	93	105-106 (2 mm Hg)
18 [a]	3,3-(CH ₃) ₂	CO ₂	-	150	4	19	(mp 110-111)
19 [a]	2-C ₆ H ₅	CO ₂	-	100	4	96	(mp 56-57)
20 [b]	2-CH ₃	C ₆ H ₅ -N=C=O	THF	60	23 (3 + 20) [c]	27 [d]	(mp 78-79)
21 [b]	2-C ₆ H ₅	C ₆ H ₅ -N=C=O	THF	80	3 (1 + 2) [c]	87 [e]	[g]
22 [b]	2-C ₆ H ₅	C ₄ H ₉ -N=C=O	PhH	80	40	92 [f]	[h]

[a] Oxetane/1 = 20/0.4 mmole, CO₂ 50 Kg/cm². [b] Oxetane/Y=C=Z/1 = 10/5/0.5 mmole, solvent 5 ml. [c] (Drop time + reaction time). [d] Only the 6-methyl derivative was yielded. [e] A mixture of the 4-phenyl isomer 21a and the 6-phenyl isomer 21b was obtained and ratio was determined by glc (21a:21b = 90:10). [f] A mixture of the 4-phenyl isomer 22a and the 6-phenyl isomer 22b was obtained and ratio was determined by ¹³C nmr (22a:22b = 76:24). [g] The mp of 21a and 21b were 143-144° and 196-197°, respectively. [h] The bp of the mixture was 99° (0.01 mm Hg).

their low reactivity [2], although some recent reports referred to the ring cleavage of oxetanes with carbon nucleophiles in the presence of boron trifluoride etherate [3]. On the other hand, six-membered heterocyclic compounds such as 1,3-oxazin-2-ones and 1,3-diazin-2-ones are important substrates. For example, 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone is employed as a coordinative solvent [4], and 1,3-oxazin-2-one derivatives are thought to be "masked" 1,3-amino alcohols and used as precursors of natural products such as L-*N*-benzoylristosamine [5]. The cycloaddition of heterocumulenes to oxetanes might be one of the simplest methods for preparing six-membered heterocycles without the formation of co-products, but this type of cycloaddition has been scarcely investigated perhaps by lack of effective catalysts [6]. On the other hand, on studying synthetic use of organoantimony compounds [7], we found that tetraphenylstibonium iodide (**1**) was a unique and effective catalyst for the cycloaddition of heterocumulenes to oxiranes where α -cleavage of monosubstituted oxiranes took place selectively [7c,e]. Moreover, our current papers briefly referred that **1** has high catalytic activity to the cycloaddition of carbon dioxide [7a] or ketenes [7f] to oxetanes. We now comprehensively report on the cycloaddition of carbon dioxide, isocyanates and carbodiimides to oxetanes in the presence of catalytic amounts of **1** under very mild conditions.

As shown in Table 1, oxetane reacted with various hetero-

ocumulenes to give the corresponding six-membered heterocycles in moderate to excellent yields. In the case of aryl isocyanates, dropwise addition of them was indispensable and THF was the best solvent. When aryl isocyanates were added at one portion or other solvents such as benzene and dichloromethane were employed, yields of 1,3-oxazin-2-ones drastically decreased and large amounts of the corresponding isocyanate trimers were obtained. Although the dropwise addition of alkyl isocyanates was not needed because of their lower trimerization property, longer reaction times were required. As the reaction proceeded under mild and neutral conditions, a variety of isocyanates such as allyl, 2-chloroethyl and tosyl isocyanates could be applicable. On the other hand, carbodiimides gave the corresponding 1,3-oxazin-2-imines quantitatively because carbodiimides have poor ability of trimerization. In the reaction of phenyl-*n*-butylcarbodiimide, the adduct was not 3-*n*-butyl-1,3-oxazin-2-(*N*-phenyl)imine, but 3-phenyl-1,3-oxazin-2-(*N*-*n*-butyl)imine.

Next, we investigated the reaction of substituted oxetanes. The results are summarized in Table 2. Monosubstituted oxetanes such as 2-phenyl and 3-methyloxetane readily reacted with carbon dioxide to furnish the corresponding monosubstituted six-membered cyclic carbonates in high yields. However, the disubstituted carbonate from 3,3-dimethyloxetane was obtained only in 19% yield. This might be due to steric hindrance of 3,3-dimethyl-

Table 3
Analytical Data of Products

No.	IR (cm ⁻¹)	Molecular formula	Analysis		
			Calcd./Found C	H	N
2	1765 (C = O)	C ₄ H ₆ O ₃	[a]		
3	1680 (C = O)	C ₁₀ H ₁₁ NO ₂	67.76 67.56	6.26 6.27	7.91 7.93
4	1685 (C = O)	C ₁₁ H ₁₃ NO ₂	69.09 69.05	6.85 6.90	7.22 7.22
5	1670 (C = O)	C ₁₀ H ₁₀ ClNO ₂	56.75 56.77	4.76 4.80	6.62 6.49
6	1680 (C = O)	C ₈ H ₁₃ NO ₂	61.12 60.85	9.62 9.60	8.91 8.84
7	1660 (C = O)	C ₇ H ₁₃ NO ₂	58.72 58.32	9.15 9.06	9.78 9.85
8	1680 (C = O)	C ₅ H ₉ NO ₂	52.16 51.90	7.88 7.87	12.17 12.00
9	1690 (C = O)	C ₁₁ H ₁₃ NO ₂	69.11 68.93	6.81 6.83	7.33 7.34
10	1680 (C = O)	C ₇ H ₁₁ NO ₂	59.56 59.62	7.85 7.90	9.92 10.04
11	1680 (C = O)	C ₆ H ₁₀ ClNO ₂	-	-	-
12	1710 (C = O)	C ₁₁ H ₁₃ NO ₄ S	51.75 51.76	5.13 5.02	5.49 5.40
13	1640 (C = N)	C ₁₆ H ₁₆ N ₂ O	76.16 76.02	6.39 6.38	11.10 11.16
14	1650 (C = N)	C ₁₄ H ₂₀ N ₂ O	72.38 72.11	8.68 8.67	12.06 12.01
15	1640 (C = N)	C ₁₂ H ₂₄ N ₂ O	67.44 67.88	11.43 11.39	13.01 13.19
16	1750 (C = O)	C ₃ H ₈ O ₃	[b]		
17	1755 (C = O)	C ₃ H ₈ O ₃	[b]		
18	1765 (C = O)	C ₆ H ₁₀ O ₃	[a]		
19	1735 (C = O)	C ₁₀ H ₁₀ O ₃	67.41 67.39	5.66 5.60	- -
20	1685 (C = O)	C ₁₁ H ₁₃ NO ₂	69.30 68.97	6.85 6.70	7.32 7.45
21a	1680 (C = O)	C ₁₆ H ₁₅ NO ₂	75.87 75.64	5.97 5.86	5.53 5.83
21b	1680 (C = O)	C ₁₆ H ₁₅ NO ₂	75.87 75.68	5.97 5.88	5.53 5.51
22 [c]	1685 (C = O)	C ₁₄ H ₁₉ NO ₂	72.07 71.79	8.21 8.33	6.00 6.01

[a] Ref 11. [b] Ref 16. [c] Mixture of 22a and 22b.

oxetane. On the other hand, regiochemistry of ring cleavage was a significant problem in the cycloaddition of

2-substituted oxetanes with isocyanates. Ring fission at unsubstituted site occurred selectively in the case of 2-methyloxetane. However, 4-phenyl-1,3-oxazin-2-ones were formed predominantly through ring opening at substituted site in the reaction of 2-phenyloxetane, as well as in the case of reported cycloaddition of ketenes to the oxetanes [7f]. Meanwhile, organotin iodide-Lewis base complexes gave 6-phenyl-1,3-oxazin-2-ones predominantly in the similar reaction [6b,c]. In comparison with these cases, **1** had opposite and higher regioselectivity. We have already revealed that **1** has inherent ability to give 3,4-disubstituted oxazolidines in the analogous cycloaddition of oxiranes, where ring fission of oxiranes also took place at the substituted site [7c,e]. According to these results, the predominant formation of **21a** and **22a** was understandable. This selectivity seems to be responsible for not only the stabilization of benzyl cation by conjugation of phenyl group, but also the specific character of **1**.

In conclusion, it was ascertained that **1** was an excellent catalyst for the cycloaddition of carbon dioxide, isocyanates and carbodiimides to oxetanes, and a variety of the corresponding six-membered heterocycles were prepared in good yields under mild conditions. Further mechanistic details of this cycloaddition are under investigation.

EXPERIMENTAL

Melting points were determined on a Yanaco Micromelting point apparatus and are uncorrected. The ir spectra were measured with a Hitachi 260-3 instrument for potassium bromide pellets or KRS-5 cells. The ¹H nmr and ¹³C nmr spectra were obtained on a Hitachi R-90H instrument operating at 90 MHz. Mass spectra were obtained on a Hitachi RUM-6 spectrometer operating at 70 eV. Analytical glc was performed on a Shimadzu GC-8A chromatograph with FID (OV-1, FFAP, OV-17). Elemental analyses were performed by the section on elemental analysis in our department.

Oxetane [8], 2-methyloxetane [9], 3-methyloxetane [10], 3,3-dimethyloxetane [11] and 2-phenyloxetane [12] were prepared according to described methods. All isocyanates were commercial ones and used without further purification. Diphenylcarbodiimide [13], phenyl-*n*-butylcarbodiimide [14], di-*n*-butylcarbodiimide [14] and tetraphenylstibonium iodide [15] were synthesized by described procedures.

General Procedure for Preparation of 1,3-Dioxan-2-ones.

A mixture of an oxetane (20 mmoles) and **1** (0.22 g, 0.4 mmoles) was placed in a 30 ml stainless steel autoclave. Then it was heated under carbon dioxide-pressure (50 Kg/cm²) at described temperature in Tables 1 and 2. After the reaction, unreacted oxetane was removed under reduced pressure. The residue was subjected to silica gel column chromatography (eluted by chloroform) and purification was achieved by recrystallization or distillation.

General Procedure for Preparation of 1,3-Oxazin-2-ones and 1,3-Oxazin-2-imines.

To a mixture of an oxetane (10 mmoles) and **1** (0.28 g, 0.5 mmole) in an appropriate solvent mentioned in Table 1 or 2 (5

Table 4

NMR Data of Products

No.	¹ H NMR δ (ppm) (deuteriochloroform)	¹³ C NMR δ (ppm) (deuteriochloroform)
2	2.05-2.35 (m, 2H), 4.49 (t, 4H, J = 6.0 Hz)	20.63 (t), 67.40 (t, 2C), 147.65 (s)
3	2.10-2.40 (m, 2H), 3.70 (t, 2H, J = 5.0 Hz), 4.40 (t, 2H, J = 5.0 Hz), 7.20-7.60 (m, 5H)	22.49 (t), 48.71 (t), 66.94 (t), 125.69 (d), 126.55 (d), 128.99 (d), 142.89 (s), 152.59 (s)
4	2.00-2.40 (m, 2H), 2.35 (s, 3H), 3.70 (t, 2H, J = 5.0 Hz), 4.40 (t, 2H, J = 5.0 Hz), 7.10-7.50 (m, 4H)	20.84 (q), 22.41 (t), 48.78 (t), 66.83 (t), 125.64 (d), 129.65 (d), 136.45 (d), 140.41 (s), 152.79 (s)
5	2.10-2.40 (m, 2H), 3.70 (t, 2H, J = 5.0 Hz), 4.45 (t, 2H, J = 5.0 Hz), 7.20-7.40 (m, 4H)	22.36 (t), 48.58 (t), 67.03 (t), 127.06 (d), 129.16 (d), 132.04 (d), 141.49 (d), 152.50 (s)
6	0.80-1.90 (m, 7H), 1.90-2.30 (m, 2H), 3.20-3.60 (m, 4H), 4.25 (t, 2H, J = 5.0 Hz)	13.49 (q), 19.56 (t), 22.00 (t), 28.83 (t), 44.74 (t), 48.86 (t), 66.09 (t), 153.10 (s)
7	1.15 (d, 6H, J = 6.5 Hz), 1.85-2.20 (m, 2H), 3.22 (t, 2H, J = 6.0 Hz), 4.22 (t, 2H, J = 5.5 Hz), 4.35-4.75 (m, 1H)	19.16 (q), 22.33 (t), 38.28 (t), 47.36 (d), 65.84 (t), 152.92 (s)
8	1.80-2.25 (m, 2H), 3.03 (s, 3H), 3.33 (t, 2H, J = 6.0 Hz), 4.26 (t, 2H, J = 5.0 Hz)	21.57 (t), 35.84 (q), 46.30 (t), 65.81 (t), 153.07 (s)
9	1.80-2.20 (m, 2H), 3.21 (t, 2H, J = 5.5 Hz), 4.25 (t, 2H, J = 6.0 Hz), 4.55 (s, 2H), 7.28 (m, 5H)	22.30 (t), 44.44 (t), 52.64 (t), 66.54 (t), 127.55 (d), 127.95 (d), 128.59 (d), 136.67 (s), 153.87 (s)
10	1.80-2.30 (m, 2H), 3.28 (t, 2H, J = 6.0 Hz), 3.95 (t, 2H, J = 6.0 Hz), 4.27 (t, 2H, J = 5.0 Hz), 5.00-5.55 (m, 2H), 5.55-6.20 (m, 1H)	22.00 (t), 44.19 (t), 51.33 (t), 66.30 (t), 117.25 (t), 132.04 (d), 153.20 (s)
11	1.85-2.30 (m, 2H), 3.20-3.90 (m, 6H), 4.37 (t, 2H, J = 8.0 Hz)	30.29 (t), 41.91 (t, 2C), 45.02 (t), 61.79 (t), 157.98 (s),
12	1.90-2.30 (m, 2H), 2.44 (s, 3H), 3.97 (t, 2H, J = 6.0 Hz), 4.28 (t, 2H, J = 5.0 Hz), 7.20-7.50 (m, 2H), 7.70-8.10 (m, 2H)	21.45 (q), 22.18 (t), 44.99 (t), 67.46 (t), 128.35 (d), 129.17 (d), 135.05 (s), 144.78 (s), 148.50 (s)
13	2.00-2.40 (m, 2H), 3.70 (t, 2H, J = 5.0 Hz), 4.30 (t, 2H, J = 5.0 Hz), 6.80-7.70 (m, 10H)	23.52 (t), 47.21 (t), 65.78 (t), 121.52 (d), 123.28 (d), 125.27 (d, 2C), 128.22 (d), 128.80 (d), 144.78 (s), 148.07 (s), 149.29 (s)
14	0.96 (q, 3H, J = 6.0 Hz), 1.10-1.60 (m, 4H), 1.95-2.40 (m, 2H), 3.20 (t, 2H, J = 6.8 Hz), 3.65 (t, 2H, J = 5.0 Hz), 4.27 (t, 2H, J = 5.0 Hz), 7.00-7.80 (m, 5H)	14.10 (q), 20.78 (t), 23.98 (t), 33.58 (t), 45.14 (t), 45.99 (t), 64.90 (t), 123.47 (d, 3C), 128.32 (d), 145.30 (s), 149.84 (s)
15	0.60-1.00 (m, 6H), 1.10-1.80 (m, 8H), 1.80-2.25 (m, 2H), 2.90-3.50 (m, 6H), 4.10 (t, 2H, J = 5.0 Hz)	14.07 (q, 2C), 20.14 (t), 20.75 (t), 23.49 (t), 28.89 (t), 34.41 (t), 44.68 (t), 44.93 (t), 49.22 (t), 64.87 (t), 150.27 (s)
16	1.44 (d, 3H, J = 6.6 Hz), 1.70-2.28 (m, 2H), 4.30-4.48 (m, 3H)	20.79 (q), 28.33 (t), 66.83 (t), 75.64 (d), 148.87 (s)
17	1.08 (d, 3H, J = 6.6 Hz), 2.16-2.64 (m, 1H), 4.12 (dd, 2H, J = 11.3 and 9.0 Hz), 4.30-4.60 (m, 2H)	11.59 (q), 25.93 (d), 73.04 (t, 2C), 148.34 (s)
18	1.13 (s, 6H), 4.10 (s, 4H)	20.66 (q), 28.10 (s), 77.12 (t)
19	2.12-2.45 (m, 2H), 4.42-4.56 (m, 2H), 5.52 (dd, 1H, J = 9.0 and 4.8 Hz), 7.13-7.62 (m, 5H)	29.17 (t), 66.82 (t), 80.00 (d), 125.49 (d), 128.69 (d), 137.71 (s), 148.57 (s)
20	1.50 (d, 3H, J = 5.0 Hz), 2.00-2.30 (m, 2H), 3.50-3.90 (m, 2H), 4.40-4.80 (m, 1H), 7.20-7.80 (m, 5H)	20.79 (q), 28.98 (t), 47.82 (t), 73.94 (d), 125.72 (d), 126.50 (d), 128.97 (d), 142.82 (s), 152.82 (s)
21a	1.90-2.85 (m, 2H), 4.25-4.60 (m, 2H), 5.10 (t, 1H, J = 5.0 Hz), 7.20-7.60 (m, 10H)	30.76 (t), 62.19 (d), 63.68 (t), 126.52 (d), 126.68 (d), 126.74 (d), 127.93 (d), 128.75 (d), 128.71 (d), 139.94 (s), 142.07 (s), 153.11 (s)
21b	2.18-2.43 (m, 2H), 3.26-3.94 (m, 2H), 5.40 (dd, 1H, J = 7.7 and 5.0 Hz), 6.88-7.67 (m, 10H)	29.90 (t), 47.86 (t), 78.69 (d), 125.61 (d), 125.79 (d), 126.77 (d), 128.35 (d), 128.60 (d), 129.15 (d), 138.87 (s), 142.81 (s), 152.59 (s)
22a	0.65-1.85 (m, 7H), 2.10-2.85 (m, 2H), 3.10-3.95 (m, 2H), 3.95-4.33 (m, 2H), 4.63 (t, 1H, J = 5.0 Hz), 7.00-7.60 (m, 5H)	13.46 (q), 19.62 (t), 28.98 (t), 30.41 (t), 47.43 (t), 57.82 (d), 62.40 (t), 125.91 (d), 127.46 (d), 128.41 (d), 139.93 (s), 153.35 (s)
22b	0.65-1.85 (m, 7H), 2.10-2.85 (m, 2H), 3.10-3.35 (m, 4H), 5.05-5.45 (m, 1H), 7.00-7.60 (m, 5H)	13.46 (q), 19.62 (t), 28.98 (t), 30.41 (t), 31.45 (t), 48.74 (t), 77.55 (d), 125.91 (d), 127.46 (d), 128.41 (d), 139.93 (s), 153.35 (s)

ml) was added an isocyanate or a carbodiimide (5 mmoles) under a nitrogen atmosphere and the resulting mixture was stirred under the conditions mentioned in Table 1 or 2. Isolation of products was performed in a similar manner to preparation of 1,3-dioxan-2-ones.

Acknowledgement.

This study was financially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

REFERENCES AND NOTES

- [1a] For review, see: C. H. Behrens and K. B. Sharpless, *Aldrichimica Acta*, **16**, 67 (1983); [b] A. S. Rao, S. K. Paknikar and J. G. Kirtane, *Tetrahedron*, **39**, 2323 (1983); [c] J. G. Smith, *Synthesis*, 629 (1984); [d] H. Ulrich, "Cycloaddition Reaction of Heterocumulenes", Academic Press, New York, 1967; [e] S. Ozaki, *Chem. Rev.*, **72**, 457 (1972).
- [2] J. G. Pritchard and F. A. Long, *J. Am. Chem. Soc.*, **80**, 4162 (1958).
- [3a] S. A. Carr and W. P. Weber, *J. Org. Chem.*, **50**, 2782 (1985); [b] M. Yamaguchi, Y. Nobayashi and I. Hirao, *Tetrahedron*, **40**, 4261 (1984); [c] M. Segi, M. Takebe, S. Masuda and T. Nakajima, *Bull. Chem. Soc. Japan*, **55**, 167 (1982).
- [4a] T. Mukhopadhyay and D. Seebach, *Helv. Chim. Acta*, **65**, 385 (1982); [b] D. Seebach, R. Henning and T. Mukhopadhyay, *Chem. Ber.*, **115**, 1705 (1982).
- [5a] M. Sakatani and Y. Ohfuné, *Tetrahedron Letters*, **28**, 3987 (1987); [b] M. Hiramata, T. Shigamoto and S. Ito, *J. Org. Chem.*, **52**, 3342 (1987).
- [6a] S. H. Metzger, Jr., U. S. Patent 3,479,351; *Chem. Abstr.*, **72**, 21699m (1970); [b] A. Baba, I. Shibata, M. Fujiwara and H. Matsuda, *Tetrahedron Letters*, **26**, 5167 (1985); [c] I. Shibata, T. Imoto, A. Baba and H. Matsuda, *J. Heterocyclic Chem.*, **24**, 361 (1987); [d] A. Baba, H. Kashiwagi and H. Matsuda, *Organometallics*, **6**, 137 (1987).
- [7a] A. Baba, H. Kashiwagi and H. Matsuda, *Tetrahedron Letters*, **26**, 1323 (1985); [b] R. Nomura, A. Ninagawa and H. Matsuda, *J. Org. Chem.*, **45**, 3735 (1980); [c] A. Baba, M. Fujiwara and H. Matsuda, *Tetrahedron Letters*, **27**, 77 (1986); [d] M. Fujiwara, A. Baba, Y. Tomohisa and H. Matsuda, *Chem. Letters*, 1963 (1986); [e] M. Fujiwara, A. Baba and H. Matsuda, *J. Heterocyclic Chem.*, **25**, 1351 (1988); [f] M. Fujiwara, M. Imada, A. Baba and H. Matsuda, *J. Org. Chem.*, **53**, 5974 (1988).
- [8] E. J. Horning, *Org. Synth.*, Coll Vol **3**, John Wiley and Sons, Inc., London, 1955, p 835.
- [9] F. Sondheimer and R. B. Woodward, *J. Am. Chem. Soc.*, **75**, 5438 (1953).
- [10] S. Searles, Jr., K. A. Pollart, and E. F. Lutz, *J. Am. Chem. Soc.*, **79**, 948 (1957).
- [11] S. Searles, D. G. Hummel, S. Nukina and P. E. Throckmorton, *J. Am. Chem. Soc.*, **82**, 2928 (1960).
- [12] K. Okuma, Y. Tanaka, S. Kaji and H. Ohta, *J. Org. Chem.*, **48**, 5133 (1983).
- [13] J. J. Monagle, *J. Org. Chem.*, **27**, 3851 (1962).
- [14] C. Palomo and R. Mestres, *Synthesis*, 373 (1981).
- [15a] J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1195 (1940); [b] G. O. Doak, G. G. Long and L. D. Freedman, *J. Organomet. Chem.*, **12**, 443 (1962).
- [16] K. Pihlaja and K. Passi, *Acta Chem. Scand.*, **B37**, 289 (1983).