α,β-Unsaturated Carboxylic Acid Derivatives. XI. Convenient Synthesis of *tert*-Butyl 2-Alkoxy- and Hydroxy-2-acetylamino-3-mono- or 3,3-dihaloalkanoates[1]

Chung-gi SHIN, Yoshiaki SATO, and Juji YOSHIMURA*

Laboratory of Organic Chemistry, Faculty of Technology, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221

**Laboratory of Chemistry for Natural Products, Faculty of Science, Tokyo Institute of Technology, Ōkayama, Meguro-ku, Tokyo 152*

(Received December 10, 1975)

It was found that the halogenation of *t*-butyl 2-acetylamino-3-bromo-2-alkenoate (**3**) by NBS or NCS gave *t*-butyl 2-acetylimino-3,3-dihaloalkanoate (**6** and **7**). The addition of water or several saturated, unsaturated and polyhydric alcohols to the carbon–nitrogen double bond of **6** or **7** was accomplished to give *t*-butyl 2-acetylamino-2-alkoxy- and hydroxy-3,3-dihaloalkanoate. Similarly, the treatment of *t*-butyl 2-bromoacetylamino-2-alkenoate in alcohol gave *t*-butyl 2-acetylamino-2-alkoxy-3-bromoalkanoate, *via* the addition of alcohol to the imino intermediate (**2**). The formation mechanism and the structural assignment are discussed.

Because of the possible synthetic utility of α-alkoxy and α-hydroxy-α-acylamino acids as an important skeleton moiety or starting material for the total synthesis of bicyclomycin,[2] 6-methoxypenicillins,[3] 7-methoxycephalosporins,[3] and ergotamine,[4] there have been several reports on the synthetic methods of the above α-acylamino acids,[5–9] but some limitations are present in the above methods.

On the other hand, the present authors have recently reported the facile synthesis of *tert* (*t*)-butyl 2-bromoacetylamino-2-alkenoate (**1**) by the reaction of *t*-butyl 2-acetylamino-2-alkenoate with *N*-bromosuccinimide (NBS),[10] and its bromine migration into *t*-butyl 3-bromo-2-acetylamino-2-alkenoate (**3**).

In this paper, we wish to report that a further reaction of **3** with NBS occurs to give *t*-butyl 2-acetylimino-3,3-dibromoalkanoate (**6**) as a stable intermediate in a quantitative yield, and that the subsequent addition of water or alcohols to the carbon-nitrogen double bond of **6** easily takes place to form *t*-butyl 2-acetylamino-2-alkoxy- or hydroxy-3,3-dibromoalkanoate (**8**). Furthermore, the latter reaction was extended to the direct reaction of **3** with *N*-chlorosuccinimide (NCS) in alcohol and that of **1** with alcohol to give *t*-butyl 2-acetylamino-2-alkoxy-3-bromo-3-chloroalkanoate (**9**) and *t*-butyl 2-acetylamino-2-alkoxy-3-bromoalkanoate (**10**), respectively.

Results and Discussion

Addition of Protic Solvent to the Carbon-nitrogen Double Bond. When the *E*- or *Z*-isomer of **3** separated[10] was treated individually with NBS in chloroform at room temperature for 20 min, an identical yellowish syrup was obtained in a quantitative yield. Since the expected *t*-butyl 2-(*N*-acetyl-*O*-alkylhydroxyamino)-3-bromo-2-alkenoate (**5**) could not be obtained by the reaction of the above syrup with sodium alkoxide in alcohol,[10] and from the following experimental facts, the structure of the syrup isolated was confirmed to be **6**. It was concluded that *t*-butyl 3-bromo-2-bromoacetylamino-2-alkenoate (**4**) formed initially as an unstable intermediate and the subsequent migration of bromine from **4** gave **6**.

It was found that the treatment of **6** (R=CH_3 and C_2H_5) with protic solvent, water or alcohols at temperatures below 60 °C for 2—24 h gave 8 in a *ca.* 60% yield by the addition reaction of water or alcohols to the carbon-nitrogen double bond of **6**. The saturated (methanol, ethanol and benzyl alcohols), unsaturated (allyl and propargyl alcohols) and polyhydric alcohols (ethylene glycol and glycerol) were applied in the above addition. However, it was found that no reaction of **6** with isopropyl alcohol occurred, due to the steric hindrance between the bulkyl bromine in the 3-position and the isopropyl group. Accordingly, the primary hydroxyl group of glycerol should preferentially be added to **6**, in the case of **8h**.

It was found that *t*-butyl 2-acetylamino-3,3-dibromo-2-ethoxybutanoate (**8c**; R=CH_3) was also obtained directly in a 69.3% yield by the reaction of *t*-butyl 2-acetylamino-3-bromo-2-butenoate (**3**; *E*+*Z*) with NBS in ethanol at room temperature for 6 h. To extend this reaction, when compound **3** was treated with NCS in alcohols (methanol and benzyl alcohols), the expected **9** was obtained in a *ca.* 70% yield.

Furthermore, in order to generalize the above reaction, the addition of alcohols (methanol and benzyl alcohols) to the intermediate **2** was attempted, by stirring **1** with alcohol at room temperature for 48 h to give the expected **10** in a *ca.* 30% yield. On the other hand, an independent preparation of **10** by the addition reaction of alcohol to the carbon-carbon double bond of **3** was unsuccessful.

All the new compounds were obtained in high purities as a pale yellow syrup (**6**) or colorless crystals (**8, 9,** and **10**).

Structure and Formation Mechanism. The structures of all the new products were analyzed spectroscopically and the elemental analysis was satisfactory. From the NMR spectra, the NH proton peak signals of **8, 9,** and **10** appeared in the δ=6.25—7.02 region as broad singlets, except for **8h** (R=CH_3, δ 8.02). On the other hand, the appearance of secondary amide absorption bands in the regions 3200—3380 (–NH) and 1600—1700 and 1490—1520 cm^{-1} (–NHCO) in the IR spectra of **8, 9,** and **10,** and the disappearance of the tertiary amide (>NCO) bands in the regions 1720—1725 and

TABLE 1. *t*-BUTYL 2-ACETYLAMINO-2-ALKOXY- AND 2-HYDROXY-3,3-DIBROMOALKANOATES (**8**)

	Compound R	Compound R′	Yield %	Mp °C	Formula	Found (Calcd), % C	H	N	IR spectrum, cm^{-1}, in KBr	NMR spectrum,[a] δ OH	NH
8a	CH_3	H	46.1	104[b]	$C_{10}H_{17}NO_4Br_2$	32.25 (32.03)	4.64 (4.57)	3.91 (3.73)	3400, 3340, 1735, 1660, 1510	5.88	6.83
8b	CH_3	CH_3	81.7	113—114[c]	$C_{11}H_{19}NO_4Br_2$	34.39 (33.96)	4.96 (4.92)	3.48 (3.60)	3350, 1730, 1690, 1490		6.32
8b	C_2H_5	CH_3	65.3	105—106[b]	$C_{12}H_{21}NO_4Br_2$	35.92 (35.76)	5.29 (5.25)	3.25 (3.47)	3370, 1740, 1700, 1490		6.44
8c	CH_3	C_2H_5	63.6	120—121[b]	$C_{12}H_{21}NO_4Br_2$	36.08 (35.76)	5.26 (5.25)	3.36 (3.47)	3370, 1740, 1695, 1490		6.38
8c	C_2H_5	C_2H_5	52.6	109—110[b]	$C_{13}H_{23}NO_4Br_2$	37.54 (37.43)	5.62 (5.56)	3.28 (3.36)	3340, 1730, 1695, 1515		6.48
8d	CH_3	$CH_2C_6H_5$	81.9	125—126[d]	$C_{17}H_{23}NO_4Br_2$	43.97 (43.89)	4.96 (4.98)	3.06 (3.01)	3320, 1730, 1680, 1490		6.32
8d	C_2H_5	$CH_2C_6H_5$	80.2	120—121[b]	$C_{18}H_{25}NO_4Br_2$	45.14 (45.12)	5.19 (5.26)	2.83 (2.92)	3330, 1735, 1680, 1500		6.44
8e	CH_3	$CH_2CH{=}CH_2$	48.5	96—97[b]	$C_{13}H_{21}NO_4Br_2$	37.77 (37.62)	5.08 (5.10)	3.35 (3.37)	3310, 1740, 1690, 1490, 1640		6.37
8e	C_2H_5	$CH_2CH{=}CH_2$	37.5	75—76[b]	$C_{14}H_{23}NO_4Br_2$	39.25 (39.19)	5.38 (5.40)	3.22 (3.26)	3320, 1740, 1690, 1500, 1650		6.44
8f	CH_3	$CH_2C{\equiv}CH$	38.9	137—138[b]	$C_{13}H_{19}NO_4Br_2$	37.95 (37.80)	4.61 (4.64)	3.40 (3.39)	3200, 1740, 1690, 1495,(2100)		6.36
8f	C_2H_5	$CH_2C{\equiv}CH$	37.8	121—122[b]	$C_{14}H_{21}NO_4Br_2$	39.50 (39.37)	4.87 (4.96)	3.23 (3.28)	3230, 1730, 1690, 1490,(2100)		6.44
8g	CH_3	CH_2CH_2OH	74.7	97—98[d]	$C_{12}H_{21}NO_5Br_2$	34.77 (34.39)	5.22 (5.05)	3.44 (3.34)	3360, 3320, 1740, 1670, 1510	2.73	6.45
8g	C_2H_5	CH_2CH_2OH	60.6	117—118[b]	$C_{13}H_{23}NO_5Br_2$	36.10 (36.05)	5.20 (5.35)	3.29 (3.23)	3360, 3240, 1750, 1660, 1520	2.27	6.63
8h	CH_3	CH_2CHCH_2OH OH	48.6	121—123[e]	$C_{13}H_{23}NO_6Br_2$	34.94 (34.77)	5.31 (5.16)	3.12 (3.13)	3380–3280, 1740, 1670, 1500	4.09	8.02[g]
8h	C_2H_5	CH_2CHCH_2OH OH	37.1	112—115[f]	$C_{14}H_{25}NO_6Br_2$	36.37 (36.31)	5.36 (5.44)	2.97 (3.02)	3400–3150, 1740, 1670	2.93 3.25	6.64

a) Measured in $CDCl_3$. b) Colorless needles from ethanol–water. c) Colorless prisms from di-*n*-butyl ether. d) Colorless needles from di-*n*-butyl ether. e) Colorless prisms from chloroform. f) Colorless needles from carbon tetrachloride. g) Measured in DMSO-d_6.

TABLE 2. *t*-BUTYL 2-ACETYLAMINO-2-ALKOXY-3-BROMO-3-CHLORO- AND 3-MONOBROMOALKANOATES (**9** AND **10**)

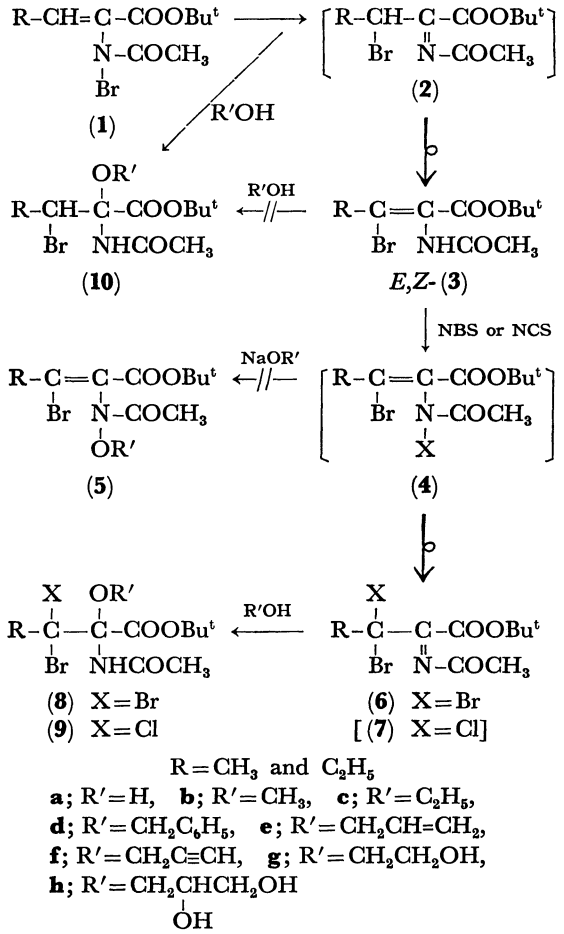
	Compound R	Compound R′	Yield %	Mp °C	Formula	Found (Calcd), % C	H	N	IR spectrum, cm^{-1} in KBr NH, COO, NHCO	NMR spectrum,[a] δ NH
9b	CH_3	CH_3	78.0	96—97[b]	$C_{11}H_{19}NO_4BrCl$	38.47 (38.34)	5.61 (5.56)	4.02 (4.06)	3350, 1740, 1690, 1500	6.35
9b	C_2H_5	CH_3	61.3	94—95[c]	$C_{12}H_{21}NO_4BrCl$	40.59 (40.19)	5.79 (5.90)	4.12 (3.91)	3380, 1745, 1700, 1490	6.38
9d	CH_3	$CH_2C_6H_5$	78.5	121—122[c]	$C_{17}H_{23}NO_4BrCl$	48.56 (48.53)	5.48 (5.51)	3.28 (3.33)	3330, 1740, 1695, 1510	6.25 6.33
9d	C_2H_5	$CH_2C_6H_5$	50.8	119—120[b]	$C_{18}H_{25}NO_4BrCl$	49.91 (49.73)	5.72 (5.80)	3.17 (3.22)	3350, 1740, 1690, 1500	6.38 6.50
10b	CH_3	CH_3	28.3	90—91[d]	$C_{11}H_{20}NO_4Br$	42.41 (42.59)	6.47 (6.50)	4.44 (4.52)	3320, 1730, 1695, 1510	6.46 6.98
10d	CH_3	$CH_2C_6H_5$	25.7	115—116[b]	$C_{17}H_{24}NO_4Br$	52.86 (52.86)	6.28 (6.26)	3.50 (3.63)	3350, 1730, 1690, 1520	6.42 7.02

a) Measured in $CDCl_3$. b) Colorless needles from ethanol–water. c) Colorless needles from di-*n*-butyl ether. d) Colorless needles from hexane.

1655—1660 cm^{-1} of **1** and **6** indicate the formation of **8**, **9**, and **10**.

The yields, physical constants, and spectral data of **8**, **9**, and **10** are summarized in Tables 1 and 2.

In recent reports,[8,9] it has been assumed that the formation of methyl 2-acetylamino-2-methoxyalkanoate derived from methyl 2-acetylamino-2-acetylthio- or 2-chloroacetylaminoalkanoate proceeded *via* the addition reaction of methanol to the unstable intermediate, methyl 2-acetyliminoalkanoate. Here, however, the above assumption was proven by isolation of the stable intermediate (**6**) and the subsequent addition of water or alcohols to **6**. Consequently, it was also confirmed that **9** and **10** were derived from the addition reaction of



R=CH_3 and C_2H_5

a; R'=H, **b**; R'=CH_3, **c**; R'=C_2H_5,
d; R'=$CH_2C_6H_5$, **e**; R'=$CH_2CH{=}CH_2$,
f; R'=$CH_2C{\equiv}CH$, **g**; R'=CH_2CH_2OH,
h; R'=CH_2CHCH_2OH (OH)

Scheme 1.

alcohols to the imino intermediates **7** and **2**, respectively.

Experimental

All the melting points are uncorrected. The IR spectra were recorded with a Hitachi EPI-G3 Spectrometer. The NMR spectra were measured with a JNM-PS-100 Spectrometer (Japan Electron Optics Laboratory Co., Ltd.), using tetramethylsilane as the internal standard.

Materials. Compounds **1** and **3** were prepared by methods previously reported.[10]

Preparation of **6**. Into a solution of **3** (0.0036 mol) in chloroform (10 ml) was added NBS (0.004 mol) portion by portion with stirring at room temperature. After stirring for 20 min, the reaction solution was concentrated to give a yellow syrup containing succinimide. After the addition of carbon tetrachloride (10 ml) to the residue, the succinimide which had thus separated out was filtered off, and the filtrate was evaporated under reduced pressure to give a pale yellow syrup in a quantitative yield. The syrup obtained was purified on a silica gel column using benzene as an eluent. *t*-Butyl 2-acetylimino-3,3-dibromobutanoate, IR (KBr disk): 1720 (-COO), 1655 (>NCO) cm^{-1}, NMR (δ): 2.30 ($COCH_3$). Found: C; 33.80, H; 4.20, N; 3.91%. Calcd for $C_{10}H_{15}NO_3Br_2$: C; 33.64, H; 4.23, N; 3.92%. *t*-Butyl 2-acetylimino-3,3-dibromopentanoate, IR (KBr disk): 1725 (-COO), 1660 (>NCO) cm^{-1}, NMR (δ): 2.29 ($COCH_3$). Found: C, 35.49; H, 4.81; N, 3.61%. Calcd for $C_{11}H_{17}NO_3Br_2$: C, 35.61; H, 4.62; N, 3.77%.

Preparation of **8a**. Into a solution of **6** (R=CH_3, 0.0036 mol) in dry *N,N*-dimethylformamide (10 ml) was added water (3 ml) drop by drop with stirring at room temperature. After stirring for 8 h, the reaction solution was poured into water (30 ml) and then the aqueous solution was extracted twice with benzene (20 ml). The benzene extracts were washed twice with water and then dried over anhydrous sodium sulfate. The benzene layer was evaporated under reduced pressure to give colorless crystals, which were identified as *t*-butyl 2-acetylamino-3,3-dibromo-2-hydroxybutanoate.

Preparation of **8b**. A solution of **6** (R=CH_3, 0.0036 mol) in methanol (10 ml) was stirred for 6 h, and was worked up similarly to give *t*-butyl 2-acetylamino-3,3-dibromo-2-methoxybutanoate.

In a similar manner, *t*-butyl 2-acetylamino-3,3-dibromo-2-methoxypentanoate was obtained from the reaction of **6** (R=C_2H_5) with methanol, after stirring for 24 h.

Preparation of **8c**. *Procedure A*: A solution of **6** (R=CH_3, 0.0036 mol) in ethanol (10 ml) was stirred for 10 h and worked up similarly to give *t*-butyl 2-acetylamino-3,3-dibromo-2-ethoxybutanoate.

In a similar manner, *t*-butyl 2-acetylamino-3,3-dibromo-2-ethoxypentanoate was obtained from the reaction of **6** (R=C_2H_5) with ethanol, after stirring at *ca.* 50 °C for 7 h and purification of the syrup obtained on a silica gel column using benzene–ethyl acetate (20: 1 V/V) as an eluent.

Procedure B: Into a solution of **3** (R=CH_3, 0.0036 mol) in ethanol (10 ml) was added NBS (0.004 mol) portion by portion with stirring at room temperature. After stirring for 6 h, the reaction solution was concentrated under reduced pressure to give a reddish syrup containing succinimide. The residue was dissolved in benzene (30 ml) and then the benzene solution was washed three times with water. The benzene layer was dried over anhydrous sodium sulfate and then evaporated under reduced pressure to give **8c** (R=CH_3). Yield: 69.3%.

Preparation of **8d**. After treating **6** (R=CH_3, 0.0036 mol) with benzyl alcohol (3 ml) with stirring at room temperature for 2 h, a similar work up gave a colorless syrup, which gradually crystallized when allowed to stand at room temperature. The colorless crystals were identified to be *t*-butyl 2-acetylamino-2-benzyloxy-3,3-dibromobutanoate.

In a similar manner, *t*-butyl 2-acetylamino-2-benzyloxy-3,3-dibromopentanoate was obtained from the reaction of **6** (R=C_2H_5) with benzyl alcohol, after stirring for 10 h.

Preparation of **8e**. After treating **6** (R=CH_3, 0.0036 mol) with allyl alcohol (5 ml) with stirring at *ca.* 60 °C for 10 h, a similar work up gave a yellow syrup. The syrup was subsequently purified on a silica gel column using benzene–ethyl acetate (15: 1 V/V) as the eluent to give colorless crystals of *t*-butyl 2-acetylamino-2-allyloxy-3,3-dibromobutanoate.

In a similar manner, *t*-butyl 2-acetylamino-2-allyloxy-3,3-dibromopentanoate was obtained from the reaction of **6** (R=C_2H_5) with allyl alcohol, after stirring for 20 h. The syrup obtained was purified on a silica gel column using benzene–ethyl acetate (20: 1 V/V) as an eluent to give colorless crystals.

Preparation of **8f**. After treating **6** (R=CH_3, 0.0036 mol) with propargyl alcohol (3 ml) with stirring at *ca* 50 °C for 10 h, a similar work up gave a brown syrup. The syrup was subsequently purified on a silica gel column using benzene–acetone (30: 1 V/V) to give colorless crystals of *t*-butyl 2-acetylamino-3,3-dibromo-2-(2-propynyloxy)butanoate.

In a similar manner, *t*-butyl 2-acetylamino-3,3-dibromo-2-(2-propynyloxy)pentanoate was obtained from the reaction of **6** (R=C_2H_5) with propargyl alcohol, after stirring at *ca.* 60 °C for 20 h. The syrup obtained was purified on a silica

gel column using benzene–ethyl acetate (30: 1 V/V) as the eluent to give colorless crystals.

Preparation of ***8g.*** After treating **6** ($R=CH_3$, 0.0036 mol) with ethylene glycol (5 ml) with stirring at room temperature for 5 h, a similar work up gave a pale yellow syrup, which gradually crystallized to give colorless crystals of *t*-butyl 2-acetylamino-3,3-dibromo-2-(2-hydroxyethoxy)butanoate.

In a similar manner, *t*-butyl 2-acetylamino-3,3-dibromo-2-(2-hydroxyethoxy)pentanoate was obtained from the reaction of **6** ($R=C_2H_5$) with ethylene glycol.

Preparation of ***8h.*** After treating **6** ($R=CH_3$, 0.0036 mol) with glycerol (5 ml) with stirring at *ca.* 60 °C for 4 h, water (30 ml) was added to the reaction mixture, and then the aqueous mixture was extracted three times with chloroform (60 ml). The chloroform extracts were washed with water twice and then dried over anhydrous sodium sulfate. Concentration of the chloroform solution gave a colorless syrup, which gradually crystallized to give colorless crystals of *t*-butyl 2-acetylamino-3,3-dibromo-2-(2,3-dihydroxypropoxy)-butanoate.

In a similar manner, *t*-butyl 2-acetylamino-3,3-dibromo-2-(2,3-dihydroxypropoxy)pentanoate was obtained from the reaction of **6** ($R=C_2H_5$) with glycerol. The syrup obtained was purified on a silica gel column using benzene–ethyl acetate (1: 5 V/V) as the eluent to give colorless crystals.

Preparation of ***9b.*** Into a solution of **3** ($R=CH_3$, 0.0036 mol) in methanol (10 ml) was added NCS (0.004 mol) portion by portion with stirring at room temperature. After stirring for 10 h, the reaction solution was concentrated under reduced pressure to give a colorless syrup containing succinimide. The residue was dissolved in benzene (30 ml) and then the benzene solution was washed three times with water. The benzene layer was dried over anhydrous sodium sulfate and then evaporated under reduced pressure to give colorless crystals, which were identified to be *t*-butyl 2-acetylamino-3-bromo-3-chloro-2-methoxybutanoate.

In a similar manner, *t*-butyl 2-acetylamino-3-bromo-3-chloro-2-methoxypentanoate was obtained from the reaction of **3** ($R=C_2H_5$) with NCS in the presence of methanol, after stirring for 5 h.

Preparation of ***9d.*** After treating a solution of **3** ($R=CH_3$, 0.0036 mol) in benzyl alcohol (3 ml) with NCS (0.004 mol), a similar work up gave a colorless syrup, which gradually crystallized. The crystals were identified to be *t*-butyl 2-acetylamino-2-benzyloxy-3-bromo-3-chlorobutanoate.

In a similar manner, *t*-butyl 2-acetylamino-2-benzyloxy-3-bromo-3-chloropentanoate was obtained from the reaction of **3** ($R=C_2H_5$) with NCS in the presence of benzyl alcohol, after stirring for 20 h.

Preparation of ***10.*** After allowing a solution of **1** ($R=CH_3$, 0.0036 mol) in methanol (10 ml) to stand at room temperature for 2 days, a similar work up gave colorless crystals of *t*-butyl 2-acetylamino-3-bromo-2-methoxybutanoate.

In a simlar manner, *t*-butyl 2-acetylamino-2-benzyloxy-3-bromobutanoate was obtained from the reaction of **1** ($R=CH_3$) with benzyl alcohol.

References

1) Part X: C. Shin, Y. Yonezawa, H. Sakamoto, and J. Yoshimura, *Bull. Chem. Soc. Jpn.*, **48**, 2891 (1975). This work was presented at the 31st and the 32nd Annual Meetings of Chemical Society of Japan, Sendai, October, 1974; Fukuoka, October, 1975.

2) T. Miyoshi, N. Miyairi, H. Aoki, M. Kohsaka, H. Sakai, and H. Kamiya, *J. Antibiotics*, **25**, 569 (1972).

3) a) R. Nagarajan, L. D. Boeck, M. Gorman, R. L. Hamill, C. E. Higgens, M. M. Hoehn, W. M. Stark, and J. G. Whitney, *J. Am. Chem. Soc.*, **93**, 2308 (1971); b) E. O. Stapley, M. Jackson, S. Hernandez, S. B. Zimmerman, S. A. Currie, S. Mochales, J. M. Mata, H. B. Woodruff, and D. Hendlin, *Antimicrob. Ag. Chemother.*, **2**, 122 (1972); c) T. W. Miller, R. T. Goegelman, R. G. Weston, I. Putter, and F. F. Wolf, *ibid.*, **2**, 132 (1972); d) A. K. Miller, E. Celozzi, B. A. Pelak, E. O. Stapley, and D. Hendlin, *ibid.*, **2**, 281 (1972).

4) a) A. Stoll, *Helv. Chim. Acta*, **28**, 1283 (1945); b) A. Hofmann, A. J. Frey, and H. Ott, *Experientia*, **17**, 206 (1961).

5) M. M. Chemiakine, E. S. Tchaman, L. I. Denisova, G. A. Ravdel, and W. J. Rodionow, *Bull. Soc. Chim. Fr.*, **26**, 530 (1959).

6) C. Gallina, M. Maneschi, and A. Romeo, *J. Chem. Soc., Parkin Trans. 1*, **1973**, 1134.

7) S. Nakatsuka, H. Tanino, and Y. Kishi, *J. Am. Chem. Soc.*, **97**, 5008 (1975).

8) H. Poisel and U. Schmidt, *Chem. Ber.*, **108**, 2547 (1975).

9) R. K. Olsen and A. J. Kolar, *Tetrahedron Lett.*, **1975**, 3597.

10) C. Shin, K. Nanjo, T. Nishino, Y. Sato, and J. Yoshimura, *Bull. Chem. Soc. Jpn.*, **48**, 2492 (1975).