Reaction of the Group 15 Metalloid Amides with Diketene by 1,4-Addition Mode

Fumio ANDO,* Ryosuke MIO, and Jugo KOKETSU
Department of Industrial Chemistry, Chubu University, 1200 Matsumoto-cho, Kasugai, Aichi 487
(Received September 4, 1992)

(Dialkylamino)dimethylarsines, (dimethylamino)diphenylarsine, and (dialkylamino)dimethylstibines react with diketene to yield *N,N*-dialkyl-4-dimethylarsino-3-oxobutanamides, *N,N*-dimethyl-4-diphenylarsino-3-oxobutanamide, and *N,N*-dialkyl-4-dimethylstibino-3-oxobutanamides, respectively. These group 15 metalloid-substituted 3-oxobutanamides exist as keto-enol tautomers and the keto isomers are predominant in solution or in neat state. This reaction is the first example of 1,4-addition of heteroatom-nitrogen bond to diketene.

In a previous paper[1] we reported that the group 15 metalloid (As, Sb, or Bi) amides, alkoxides and alkanethiolates react with the C=C bond of ketene to yield the α-organometalloid-substituted acetamides, esters, and thioesters, respectively. Diketene has an exo C=C double bond and β-lactone ring in its 4-methylene-2-oxetanone skeleton, and numerous interesting reactions of diketene have been reported.[2] The most typical reaction of diketene is acylation of nucleophiles to afford acetoacetic acid derivatives. Thus, primary and secondary amines react with an equimolar diketene by a cleavage between the carbonyl carbon and vinyl oxygen bond to yield acetoacetamides, and the six-membered heterocyles, pyrones and pyridones, are also formed in a 1 : 2 molar reaction of primary amines in the presence of tertiary amine base. A few papers, however, have been reported on the reactions with organometallic amides. Diethylaluminium dimethylamide reacts with diketene by acyl carbon–oxygen cleavage followed by a rapid 1,3-hydrogen shift to yield the chelated aluminium β-keto enolate, Et_2Al–O–$C(CH_3)$=CH–CO–NMe_2.[3] Boron and tin amides also react with diketene to produce metal chelated β-keto enolates (Chart 1).[4]

Reaction of (dialkylamino)trimethylsilanes with diketene, however, gives a mixture of *N,N*-dialkyl-3-trimethylsiloxy-3-butenamides, R_3Si–O–$C(=CH_2)$–CH_2–CO–NR_2 and *N,N*-dialkyl-3-trimethylsiloxy-2-butenamides, R_3Si–O–$C(CH_3)$=CH–CO–NR_2.[5]

In this paper we describe insertion reactions of diketene across the As–N and Sb–N bonds of group 15 organometalloid amides in a different mode from those of the group 13 and 14 organometallic amides.

Results and Discussion

When (dimethylamino)dimethylarsine (**1a**) was treated with diketene in ether at 0 °C, a slow reaction took place to yield *N,N*-dimethyl-4-dimethylarsino-3-oxobutanamide (**2a**). (Diethylamino)dimethylarsine (**1b**) and (dimethylamino)diphenylarsine (**1c**) also reacted with diketene under similar reaction conditions to afford *N,N*-diethyl-4-dimethylarsino-3-oxobutanamide (**2b**) and *N,N*-dimethyl-4-diphenylarsino-3-oxobutanamide (**2c**), respectively. These 4-arsino-3-oxobutanamides (**2a**—**c**) are distillable colorless liquids and exist in equilibrium with the corresponding hydrogen-bonded enolic tautomers, *N,N*-dialkyl-4-dimethylarsino-3-hydroxy-2-butenamides (Chart 2).

These products were characterized by ^1H and ^{13}C NMR, IR, and mass spectra. The NMR specta of **2a**—**c** apparently consist of two structural types, keto–enol tautomers. For example, the ^1H NMR spectrum of **2a** (CCl_4) consists of nine resonances assignable as follows; δ=1.05 (s, enol $AsMe_2$), 1.07 (s, keto $AsMe_2$), 2.35 (s, enol $AsCH_2$), 2.73 (s, keto $AsCH_2$), 3.03 (s, NMe), 3.05 (s, NMe), 3.33 (s, keto $COCH_2CO$), 5.05 (s, =CH), and 15.21 (bs, =COH). The relative intensity of the peaks at δ=2.35 and 2.73 shows that 62% of the keto-form and 38% of the enol-form coexist in a 20% CCl_4 solution, and the keto-form is favored not only in CCl_4, $CDCl_3$, or acetone-d_6 solution but also in a neat liquid state. The concentration dependence of tautomeric equilibria of **2a** in CCl_4 was examined by ^1H NMR and the percentage of keto tautomer is listed in Table 1 along with the data for *N,N*-dimethylacetoacetamide. The keto-enol ratio of **2a** is almost independent in this concentration range, although in the case of the nonmetalloid acetoacetamide, an increase in concentration by a factor of 10 (from 10 to 100 wt%) leads to an increase of 1.4 times in keto percent. The keto percents of **2b** and **2c** in CCl_4 (ca. 20% solution at 25 °C) are

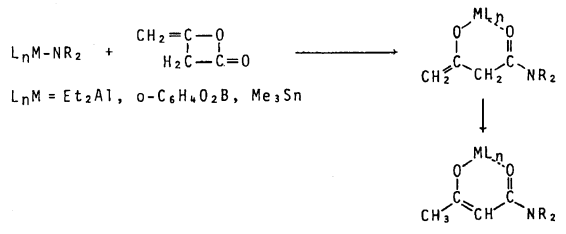


Chart 1.

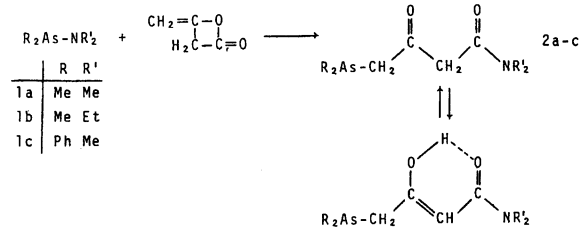


Chart 2.

Table 1. Percent Keto Tautomers for 3-Oxobutanamides in CCl_4 at 25 °C

wt%	keto%	
	$Me_2AsCH_2COCH_2CONMe_2$	$CH_3COCH_2CONMe_2$
10	63	53
20	62	61
40	65	67
80	62	75
100	69	75

67% and 86%, respectively.

The $^{13}C\{^1H\}$ NMR spectrum of **2a** ($CDCl_3$) consists of twelve resonances, as shown in Fig. 1: A (δ 9.61), B (δ 10.06), C (δ 33.24), D (δ 35.19), E (δ 37.79), F (δ 41.30), G (δ 49.74), H (δ 85.45), I (δ 166.48), J (δ 171.80), K (δ 176.83), and L (δ 201.67). On the basis of their chemical shifts and signal intensities, resonances A and B are assigned to enol Me_2As and keto Me_2As, respectively. Resonances D and E ($\Delta H=39.1$ Hz at 25 °C) are signals for two N-methyl groups (*Z*) and (*E*) to the carbonyl oxygen of the amide due to the restriction of rotation about the C–N bond by partial C–N double bond.[6] The signals coalesced to a broad doublet ($\Delta H=10.7$ Hz) at 80 °C showing the characteristic amide structure. Resonances C, F, G, and H are assigned to enol $AsCH_2$, keto $AsCH_2$, keto CH_2 adjacent to two carbonyl groups, and enolic =CH, respectively, as the corresponding resonance peaks of C, F, and G in the ^1H-coupled ^{13}C NMR spectrum of **2a** are all triplets but the resonance H splits into a doublet peak. Assignment of the other resonances is as follows; I (keto CON), J (enol CON), K (enolic =C–OH), and L (keto CO). The structures of **2a**—**c** were also confirmed by their IR spectra, each of which shows three strong absorption bands around 1700, 1650, and 1600 cm^- indicating the presence of ketonic C=O, amide C=O, and C=O conjugated C=C bonds, respectively.

Regioselective ring-opening reactions of β-propiolactone with arsenic amides and antimony amides were previously reported;[7] the former amides give the alkyl–oxygen bond cleavage product but the latter cause the acyl-oxygen fission of β-propiolactone. In the present work, however, the reaction of diketone with

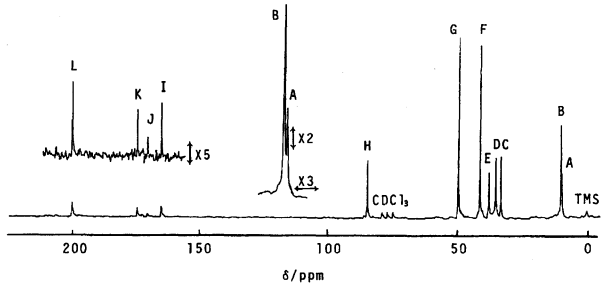


Fig. 1. $^{13}C\{^1H\}$ NMR spectrum of *N,N*-dimethyl-4-dimethylarsino-3-oxobutanamide.

antimony amides gave the same type reaction products with **2**. Thus, (dialkylamino)dimethylstibines (**3a**—**f**) reacted more smoothly with diketene to yield the corresponding *N,N*-dialkyl-4-dimethylstibino-3-oxobutanamides (**4a**—**f**), and which also exist with the enolic tautomers, *N,N*-dialkyl-4-dimethylstibino-3-hydroxy-2-butenamides (Table 2, Chart 3).

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **4a**—**f** and their assignments are very similar to those of the arsenic derivatives. These characteristic peaks in the NMR and IR spectra of **2a**—**c** and **4a**—**f** resemble those of *N,N*-dialkylacetoacetamides prepared by the reaction of diketene with dialkylamines. The compounds **2** and **4** are 1,4-adducts of the As–N and Sb–N bonds of **1** and **3** to diketene and are evidently of a different type from those of 1,2-adducts isolated from reactions of diketene with group 13 or 14 metal amides.[3—5]

The reactivity of the aminostibines **3** toward diketene are higher than of the aminoarsines **1**, but it is lower than of the corresponding secondary amines. Arsenic or animony chlorides, alkoxides and thiolates, however, did not react with diketene even by stirring the mixtures for 5 days at room temperature. These results suggest that the nucleophilic attack of the amino groups plays an important role in the reactions compared with the electrophilic attack by the pnictogen atoms. The formation of **2** and **4** can be shown as Scheme 1.

Initial nucleophilic attack of the nitrogen atom of the pnicogen amides **1** and **3** (Pn=As and Sb) to the carbonyl carbon of diketene causes an acyl carbon–oxygen bond cleavage to give enolate intermediates, and the following electrophilic attack of the pnicogen atom on the enolate carbon atom lead to the γ-organopnicogen-substituted 3-oxobutanamides **2** and **4**. As the HOMO coefficient calculated by HMO in the enolate intermediate is larger on the carbon (0.700) relative to oxygen

Table 2. Boiling Points and Yields of *N,N*-Dialkyl-4-dimethylstibino-3-oxobutanamides: $Me_2SbCH_2COCH_2CONR_2$

Compd	R	Bp/°C/Pa	Yield/%
4a	Me	108—110/1.3×10^{-2}	83
4b	Et	116—118/2.7×10^{-2}	79
4c	*n*-Pr	132—134/2.7×10^{-2}	74
4d	*i*-Pr	119—121/2.0×10^{-2}	78
4e	*n*-Bu	150—153/1.3×10^{-2}	73
4f	*s*-Bu	138—140/2.0×10^{-2}	72

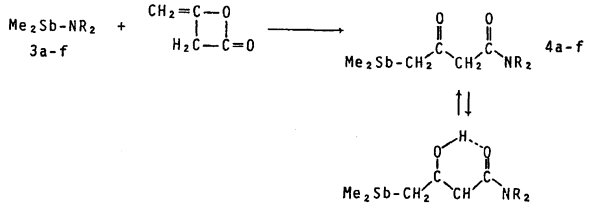
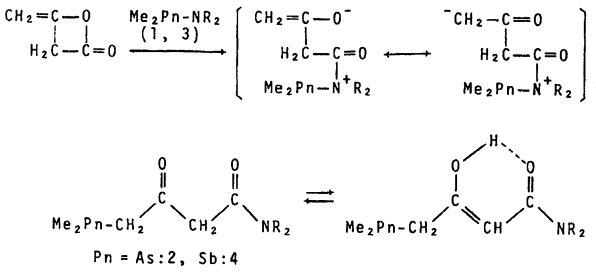


Chart 3.



Scheme 1.

(−0.405) and the charge density is higher on the oxygen (−0.93),[8] the heavier pnicogen atoms with soft acid character electrophilically attack at the soft carbon anion than the hard oxygen. The higher reactivity of the antimony amides **3** compared with the arsenic amides **1** would be attributed to the enhanced nucleophilicity of nitrogen atom caused by a weaker and polar antimony–nitrogen bond and the higher electrophilicity of antimony atom. This reaction mode of ring opening of diketene apparently differs from those of the group 13 or 14 amides which react by a concerted mechanism involving both nucleophilic attack by the nitrogen on the carbonyl carbon and electrophilic attack of the heteroatoms on the oxetane oxygen. The difference in the reaction modes between the group 15 amides and the group 13 or 14 amides may be mainly ascribed to the difference of Lewis acidity of heteroatom and of the affinity for oxygen or carbon. The present reaction is the first example of 1,4-addition of heteroatom–nitrogen bond to diketene with acyl–oxygen bond cleavage to yield acetoacetamide derivatives with organopnicogen substituents on γ-position.

Experimental

All reactions were performed under an atmosphere of nitrogen or argon. IR spectra were recorded on a Shimadzu IR 430 or a Perkin Elmer 1600 FT-IR spectrometer. ^{1}H NMR spectra were obtained with a JEOL C60 HL or a JEOL JNM FX 60 FT NMR spectrometer, and ^{13}C NMR spectra with a JEOL JNM FX 60 FT NMR instrument. Mass spectra were recorded on a Hitachi RMU-6L instrument.

Materials. (Dialkylamino)dimethylarsines, (dimethylamino)diphenylarsine, and (dialkylamino)dimethylstibines were prepared by transmetallation reaction of lithium salts of secondary amines with chlorodimethylarsine, chlorodiphenylarsine and chlorodimethylstibine, respectively.[9] Diketene was purified by distillation at reduced pressure (bp 75 °C/12.6 kPa).

Reaction of Aminoarsines with Diketene. Diketene (1.51 g, 18.0 mmol) was added with stirring at 0 °C to a solution of (dimethylamino)dimethylarsine (2.54 g, 17.0 mmol) in 10 ml of ether and the reaction mixture was warmed up to room temperature. After a further 30 min stirring at room temperature, the reaction mixture was concentrated under reduced pressure on a rotary evaporator. Distillation of the residue gave *N,N*-dimethyl-4-dimethylarsino-3-oxobutanamide (3.40 g, 86%): Bp 92—95 °C/13 Pa; IR(neat) 1694, 1644, and 1596 cm^{-1}; MS *m/z* 233 (M$^+$); Found: C, 41.53; H, 6.98; N, 6.17%. Calcd for $C_8H_{16}NO_2As$: C, 41.21; H, 6.91; N, 6.01%.

In a similar way, (diethylamino)dimethylarsine (2.39 g, 13.5 mmol) was allowed to react in ether at 0 °C with diketene (1.18 g, 14.0 mmol) to yield *N,N*-diethyl-4-dimethylarsino-3-oxobutanamide (2.01 g, 84%): Bp 101—104 °C/13 Pa; ^{1}H NMR (CCl_4) δ=1.05 (s, enol CH_3As), 1.07 (s, keto CH_3As), 1.10 (t, $NCCH_3$), 1.16 (t, $NCCH_3$), 2.30 (s, enol $AsCH_2$), 2.78 (s, keto $AsCH_2$), 3.31 (q, NCH_2), 3.35 (s, keto $COCH_2CO$), 3.40 (q, NCH_2), 4.99 (s, enol =CH), and 15.11 (br, enol OH); ^{13}C NMR δ=9.75 (enol CH_3As), 10.14 (keto CH_3As), 12.99 (NC*C*), 14.29 (NC*C*), 33.59 (enol $AsCH_2$), 40.15 (NCH_2), 41.45 (keto $AsCH_2$), 42.69 (NCH_2), 49.64 (keto CO*C*H$_2$CO), 85.90 (enol =CH), 165.81 (keto CON), 171.20 (enol CON), 176.14 (enol COH), and 201.94 (keto CO); IR (neat) 1695, 1642, and 1590 cm^{-1}; MS *m/z* 261 (M$^+$); Found: C, 46.41; H, 7.78; N, 5.62%. Calcd for $C_{10}H_{20}NO_2As$: C, 45.98; H, 7.72; N, 5.36%.

Reaction of (dimethylamino)diphenylarsine (3.07 g, 11.2 mmol) with diketene (1.08 g, 12.8 mmol) gave *N,N*-dimethyl-4-diphenylarsino-3-oxobutanamide (3.22 g, 82%): Bp 195—198 °C/2×10^{-2} Pa; ^{1}H NMR ($CDCl_3$) δ=2.76 (s, enol $AsCH_2$), 2.89 (s, keto $AsCH_2$), 3.25 (s, keto $COCH_2CO$), 3.36 (s, NCH_3), 3.39 (s, NCH_3), 4.79 (s, enol =CH), 7.38 (m, Ph), and 15.01 (br, enol OH); ^{13}C NMR ($CDCl_3$) δ=35.15 (NCH_3), 35.35 (enol $AsCH_2$), 37.55 (NCH_3), 42.36 (keto $AsCH_2$), 49.83 (keto CO*C*H$_2$CO), 86.81 (enol =CH), 128.52 (para), 128.52 (ortho), 132.87 (meta), 139.11 (ipso), 166.46 (keto CON) 171.75 (enol CON), 175.15 (enol COH), and 201.74 (keto CO); IR (neat) 1700, 1644, and 1600 cm^{-1}.

Reaction of Aminostibines with Diketene. Reactions of (dialkylamino)dimethylstibines (**3a—f**) with diketene were carried out in ether at −30 °C to afford the following *N,N*-dialkyl-4-dimethylstibino-3-oxobutanamides. Their yields and boiling points are listed in Table 2. The spectral and analytical data are as follows.

***N,N*-Dimethyl-4-dimethylstibino-3-oxobutanamide (4a):** IR (neat) 1720, 1642, and 1600 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.77 (s, CH_3Sb), 1.98 (s, enol $SbCH_2$), 2.20 (s, keto $SbCH_2$), 3.03 (s, NCH_3), 3.05 (s, NCH_3), 3.44 (s, keto $COCH_2CO$), 4.92 (s, enol =CH), and 15.05 (br, enol OH); ^{13}C NMR ($CDCl_3$) δ=−3.70 (CH_3Sb), 27.50 (enol $SbCH_2$), 30.14 (keto $SbCH_2$), 35.86 (NCH_3), 37.77 (NCH_3), 49.90 (keto CO*C*H$_2$CO), 86.94 (enol =CH), 168.40 (keto CON), 171.70 (enol CON), 176.59 (enol COH), and 204.20 (keto CO); Found: C, 34.75; H, 5.82; N, 5.12%. Calcd for $C_8H_{16}NO_2Sb$: C, 34.32; H, 5.76; N, 5.00%.

***N,N*-Diethyl-4-dimethylstibino-3-oxobutanamide (4b):** IR (neat) 1720, 1640, and 1592 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.73 (s, CH_3Sb), 1.14 (t, $NCCH_3$), 1.18 (t, $NCCH_3$), 1.94 (s, enol $SbCH_2$), 2.25 (s, keto $SbCH_2$), 3.25 (q, NCH_2), 3.50 (q, NCH_2), 3.50 (s, keto $COCH_2CO$), 5.05 (s, enol =CH), and 15.03 (br, enol OH); ^{13}C NMR ($CDCl_3$) δ=−3.70 (CH_3Sb), 12.99 (NC*C*), 14.23 (NC*C*), 27.61 (enol $SbCH_2$), 30.15 (keto $SbCH_2$), 40.22 (NCH_3), 42.75 (NCH_3), 49.71 (keto CO*C*H$_2$CO), 87.40 (enol =CH), 165.94 (keto CON), 171.33 (enol CON), 174.65 (enol COH), and 202.32 (keto CO); Found: C, 39.14; H, 6.61; N, 4.63%. Calcd for $C_{10}H_{20}NO_2Sb$: C, 38.99; H, 6.55; N, 4.55%.

***N,N*-Dipropyl-4-dimethylstibino-3-oxobutanamide (4c):** IR (neat) 1718, 1640, and 1592 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.75 (s, CH_3Sb), 0.90 (t, $NCCCH_3$), 1.51 (m,

$NCCH_2$), 1.94 (s, enol $SbCH_2$), 2.27 (s, keto $SbCH_2$), 3.25 (t, NCH_2), 3.51 (s, keto $COCH_2CO$), 5.08 (s, enol =CH), and 15.00 (br, enol OH); ^{13}C NMR ($CDCl_3$) δ=−3.64 (CH_3Sb), 11.50 ($NCCC$), 21.83 (NCC), 22.29 (NCC), 27.81 (enol $SbCH_2$), 30.99 (keto $SbCH_2$), 47.63 (NCH_3), 49.90 (keto $COCH_2CO$), 50.03 (NCH_3), 87.13 (enol =CH), 167.96 (keto CON), 171.29 (enol CON), 176.87 (enol COH), and 201.78 (keto CO).

***N, N*-Diisopropyl-4-dimethylstibino-3-oxobutanamide (4d):** IR (neat) 1720, 1640, and 1586 cm^{-1}; ^1H NMR (CCl_4) δ=0.81 (s, CH_3Sb), 1.21 (d, $NCCH_3$), 1.43 (d, $NCCH_3$), 1.97 (s, enol $SbCH_2$), 2.30 (s, keto $SbCH_2$), 3.63 (s, keto $COCH_2CO$), 3.64 (m, NCH), 5.08 (s, enol =CH), and 15.01 (br, enol OH); ^{13}C NMR ($CDCl_3$) δ=−3.72 (CH_3Sb), 20.53 (NCC), 20.57 (NCC), 27.50 (enol $SbCH_2$), 29.80 (keto $SbCH_2$), 46.00 (NCH), 49.60 (NCH), 52.24 (keto $COCH_2CO$), 88.90 (enol CH), 165.49 (keto CON), 168.25 (enol CON), 175.64 (enol COH), and 202.64 (keto CO).

***N,N*-Dibutyl-4-dimethylstibino-3-oxobutanamide (4e):** IR (neat) 1715, 1635, and 1585 cm^{-1}; ^1H NMR (CCl_4) δ=0.76 (s, CH_3Sb), 0.95 (t, $NCCCCH_3$), 1.20—1.70 (m, $NCCH_2CH_2$), 1.95 (s, enol $SbCH_2$), 2.28 (s, keto $SbCH_2$), 3.30 (m, NCH_2), 3.50 (s, keto $COCH_2CO$), 4.93 (s, enol =CH), and 15.11 (br, enol OH); ^{13}C NMR ($CDCl_3$) δ=−3.81 (CH_3Sb), 13.77 ($NCCCC$), 20.14 ($NCCC$), 27.61 (enol $SbCH_2$), 29.95 (NCC), 31.12 (NCC), 30.67 (keto $SbCH_2$), 45.61 (NCH_3), 48.28 (NCH_3), 49.83 (keto $COCH_2$), 87.00 (enol CH), 166.84 (keto CON), 168.75 (enol CON), 176.75 (enol COH), and 201.89 (keto CO); Found: C, 46.32; H, 7.86; N, 3.92%. Calcd for $C_{14}H_{28}NO_2Sb$: C, 46.18; H, 7.75; N, 3.85%.

***N, N*-Di-s-butyl-4-dimethylstibino-3-oxobutanamide (4f):** IR (neat) 1725, 1635, and 1590 cm^{-1}; ^1H NMR (CCl_4) δ=0.73 (s, CH_3Sb), 0.89 (d, $NCCH_3$), 0.93 (t, $NCCCH_3$), 1.60—2.10 (m, $NCCH_2$), 1.90 (s, enol $SbCH_2$), 2.24 (s, keto $SbCH_2$), 3.13 (m, NCH), 3.53 (s, keto $COCH_2CO$), 5.08 (s, enol =CH), and 15.12 (br, enol OH); ^{13}C NMR ($CDCl_3$) δ=−3.57 (CH_3Sb), 12.88 ($NCCC$), 19.95 ($NCCH_3$), 20.14 ($NCCH_3$), 26.44 ($NCCH_2$) 27.68 ($NCCH_2$), 27.68 (enol $SbCH_2$), 29.95 (keto $SbCH_2$), 49.90 (keto $COCH_2CO$), 52.95 (NCH), 55.88 (NCH), 87.33 (enol =CH), 166.92 (keto CON), 172.31 (enol CON), 174.39 (enol COH), and 201.74 (keto CO).

References

1) F. Ando, Y. Kohmura, and J. Koketsu, *Bull. Chem. Soc. Jpn.*, **60**, 1564 (1987).

2) a) R. J. Clemens, *Chem. Rev.*, **86**, 241 (1986); b) T. Kato, *Acc. Chem. Res.*, **7**, 265 (1974).

3) K. Urata, K. Itoh, and Y. Ishii, *J. Organomet. Chem.*, **63**, 11 (1973).

4) a) J. R. Horder and M. F. Lappert, *J. Chem. Soc. A*, **1969**, 173; b) J. R. Horder and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, **1967**, 485.

5) a) I. F. Lutsenko, Yu. I. Baukov, A. S. Kostyuk, N. I. Savelyeva, and V. K. Krysina, *J. Organomet. Chem.*, **17**, 241 (1969); b) L. I. Petrovskaya, E. I. Fedin, V. D. Sheludyakov, and V. P. Kozyukov, *Zh. Strukt. Khim.*, **8**, 51 (1967); *Chem. Abstr.*, **66**, 120633t (1967); c) V. D. Sheludyakov, V. P. Kozyukov, L. I. Petrovskaya, and V. F. Mivonov, *Khim. Geterotsikl. Soedin.*, **1967**, 185; *Chem. Abstr.*, **67**, 43858m (1967).

6) E. Breitmaier and W. Voelter, "Carbon-13 NMR Spectroscopy," 3rd ed, VCH, Weinheim (1987), pp. 226—232.

7) a) J. Koketsu and Y. Ishii, *J. Chem. Soc. C*, **1971**, 2; b) J. Koketsu, S. Kojima, and Y. Ishii, *J. Organomet. Chem.*, **38**, 67 (1972).

8) N. S. Isaacs, "Physical Organic Chemistry," Longman, Harlow (1987), pp. 248—249.

9) a) K. Moedritzer, *Chem. Ber.*, **92**, 2637 (1959); b) F. Kober, *Synthesis*, **1982**, 173; c) H. A. Meinema and J. G. Noltes, *Inorg. Nucl. Chem. Lett.*, **6**, 241 (1970).