Heteroatom Chemistry
Volume 4, Number 4, 1993

Synthesis of Silyl, Germyl, and Phosphino-Substituted Acylketenes from Pivaloylethoxyacetylene

Nikolai V. Lukashev* Aleksei A. Fil'chikov, Marina A. Kazankova, and Irina P. Beletskaya

Chemical Department, Moscow (Lomonosov) University, 119899, Moscow Lenin Hills, Russia

Received 21 May 1992

ABSTRACT

The reaction of pivaloylethoxyacetylene with silicon halides, which has been found to occur as a 1,4-addition, leads to allenic ethers, which readily eliminate ethyl halides and are converted to previously unknown types of ketenes—stable element-substituted acylketenes. Germanium-substituted acylketenes are also formed; however, clear evidence of 1,4-addition of germanium halides was not obtained. In the reaction between Ph_2PCl *and pivaloylethoxyacetylene, phosphorus (III) substituted acylketenes initially formed underwent rapid [3 + 3] cyclodimerization.*

INTRODUCTION

Acylketenes have been attracting attention for a long time due to problems of their synthesis, stability [1–3], and utilization as the 4π-component in [4 + 2] cycloaddition reactions for building oxygen-containing heterocycles [1,4,5]. There are two main synthetic routes for the synthesis of acylketenes: Wolff's rearrangement of 2-diazo-1,3-diketones [4,5] and methods based on thermal and photochemical fragmentation [6,7]. However, an overwhelming majority of acylketenes are unstable. Several examples have been detected by low-temperature IR spectroscopy at 77 K or in an Ar matrix at ca. 12–18 K [3,8–10]. Steric hindrance reduces the reactivity of acylketenes; thus, isopropyl(isopropylcarbonyl)ketene was reported to be stable in solutions for 2–3 days at 20°C [5], and *tert*-butyl(*tert*-butylcarbonyl)ketene is stable under similar conditions for several months [11]. Recently, the synthesis of bis-pivaloylketene was reported. A solution of this ketene is stable below 0°C [12]. Electron acceptor substituents bound to the carbonyl group of acylketenes (for example, perfluoralkyl groups) also increase their stability [13].

Recently, one of us has elaborated a new synthetic route to element-substituted ketenes through the reaction of alkyl- or element-substituted alkoxyacetylenes with organohalides of IVb group elements [14]. In the preceding articles, we have reported the synthesis of phosphorus (III) [15] and phosphorus (IV) [16] substituted ketenes. The first phosphorus (IV) substituted acylketene $t\text{-}Bu_2P(S)AcC{=}C{=}O$ was also reported [17]. Further investigations have been extended to the synthesis of stable acylketenes through the reaction of acylalkoxyacetylenes with organohalides of silicon, germanium, and phosphorus. Pivaloylethoxyacetylene, which is the most stable among known acylalkoxyacetylenes [18], was chosen as the starting compound.

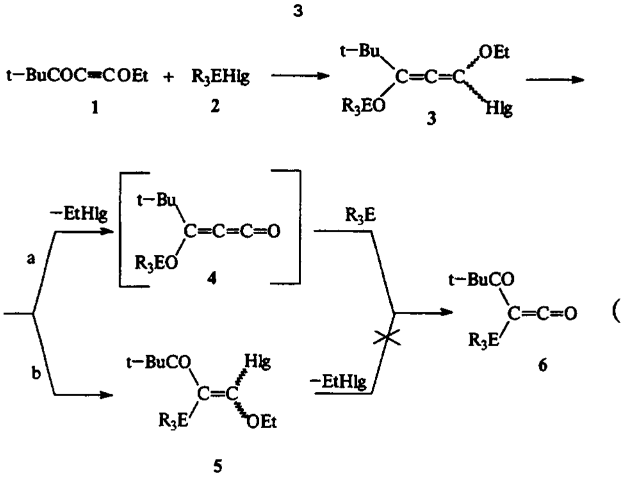
RESULTS AND DISCUSSION

We have obtained stable silyl and germyl substituted acylketenes in high yields by the reaction of the acetylene **1** in dichloromethane with trialkylsilyl and trialkylgermyl halides.

---

*To whom correspondence should be addressed.

1042-7163/93/$5.00 + .25



(1)

2,3,5: Hlg = I(a–d), Br(e,f); 2–6: E = Si(a,c,e), Ge(b,d,f); R = Me(a,b,e,f), i–Pr(c), Et(d).

The structures of ketenes **6a–d** (see Table 1) were established on the basis of IR (ν(C=C=O) 2100, ν(C=O) 1710–1720, and 1650 cm^{-1}) and ^{1}H and ^{13}C NMR data. The ^{13}C NMR spectrum displayed a low field shift of the β-carbon atom (δ 45 for **6b,d** and 24–28 for **6a,c**) in comparison with *bis*-element substituted ketenes [19] due to deshielding of the β-C atom by the electron withdrawing pivaloyl group.

The acetylene **1** reacts with silicon halides by 1,4-addition, with the formation of allenic ethers **3** followed by the elimination of the ethyl halide and the migration of the R$_3$Si group from oxygen to carbon (route a). The reaction of pivaloylethoxyacetylene with trimethyl- and triisopropyliodo silanes in dichloromethane affords allenes **3a–c**, Hlg=I after 10–15 minutes at 20°C (IR spectrum displays a band of stretching vibration ν(C=C=C) 1960 cm^{-1} in about 10–20 minutes). The iodoallenic ethers **3a,c** are rapidly converted to acylketenes **6a,c**. The reaction is complete within 1 hour for **6a** and 2 hours for **6c** (see Table 1). The reaction of acetylene **1** with trimethylbromosilane is complete within 10–12 hours at 20°C; intermediate allene **3e** is detected in the reaction mixture within 4–6 hours. The presence of the latter compound was shown by IR (ν(C=C=C) 1960 cm^{-1}) and ^{1}H NMR spectra (δH(CD$_2$Cl$_2$): 3.75 (2H, q, CH$_2$O), 1.5 (3H, t, Me in EtO), 1.11 (9H, s, Me in *t*-Bu), 0.05 (9H, s, Me$_3$Si). It should be noted that the considerable steric hindrance of the *i*-Pr$_3$Si group in the case of ketene **6c** does not lead to appreciable reduction of its thermodynamic stability, and isomerization with the formation of an O–Si bond to give siloxymethylenketene and pivaloyltriisopropylsiloxyacetylene does not occur.

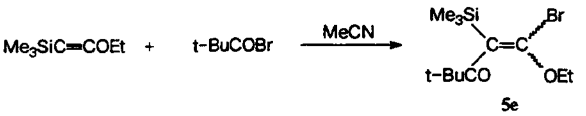
The reaction of the acetylene **1** with trialkylgermyliodide leads to **6b,d** (Table 1). However, we failed to detect intermediate iodoallenic ethers **3b,d** or vinyl ethers **5b,d** in these cases (IR monitoring). Obviously, the intermediates in the reactions with germanium halides are converted to product at a rate considerably greater than the rate of their formation.

Route b was investigated as a possible route to the ketenes **6**. It was found that Reaction 2 proceeds very slowly, even in acetonitrile, and affords vinyl ether **5e** within 3 weeks in 50% yield (IR and NMR tests; IR data ν(C=C) 1620, ν(C=O) 1680 cm^{-1}). Vinyl ether **5e** was not converted into **6a** by means of ethyl bromide elimination, either by storage for a month at 20°C or under refluxing in acetonitrile. Also, the rearrangement of **5e** into **3e** was not observed, and only decomposition of **5e** took place. It is evident that the vinyl ether **5e** cannot be the intermediate of ketene formation by route 1b.

TABLE 1 The Synthesis of Pivaloyl(trialkylsilyl)- and pivaloyl(trialkylgermyl)ketenes ***t*-BuC(O)(R$_3$E)C=C=O (6a–d)** and Their Spectral Data

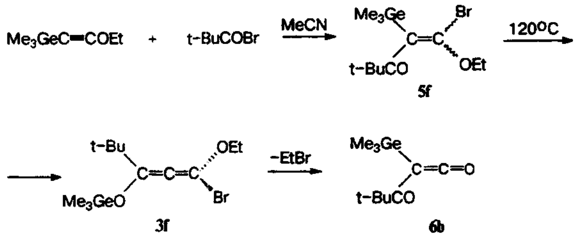
					^{1}H NMR (CDCl$_3$), δH			^{13}C NMR (CDCl$_3$), δC			
Compound	*Reagents*	*Reaction Time (in CH$_2$Cl$_2$)*	*Yield*[a] *(%)*	*bp, °C (torr)*	*t-BuC(O)*	*R$_3$E*	*C=O*	*C=C=O*	*t-BuC=O*	*R$_3$E*	*t-Bu*
6a[b]	1+Me$_3$SiI	1 hour	30	62(9)	1.2[c]	0.23	178.1[c]	28.32	201.94	−0.95	47.06, 27.25
6a	1+Me$_3$SiBr	12 hours	35								
6b[d]	1+Me$_3$GeI	3 days	55	70–73(12)	1.25	0.52	173.95	45.11	202.61	−0.47	46.51, 27.28
6c[e]	1+*i*-Pr$_3$SiI	2 hours	40	70(0.1)	1.0	0.8 (m)	177.86	24.44	203.27	18.67, 18.35	47.08, 27.22
6d[e]	1+Et$_3$GeI	2 weeks	50	58–60 (0.1)	(1.26)	1.0 (m)	173.47	44.95	203.13	5.36, 8.40	46.29, 27.30

[a] Yields before distillation are 80–90%. [b] Anal. found: C, 59.60; H 9.33. C$_{10}$H$_{18}$O$_2$Si requires C, 60.56; H, 9.15. [c] ^{1}H- and ^{13}C-NMR spectra were recorded in C$_6$D$_6$. [d] Anal. found: C, 48.27; H, 7.91. C$_{10}$H$_{18}$GeO$_2$ requires C, 49.08; H, 8.07. [e] Ketenes **6c** and **6d** were obtained after distillation together with 20% *i*-Pr$_3$SiI or 10% Et$_3$GeI correspondingly. The correct data of analysis are not available.



(2)

An additional confirmation of the route (1a) was obtained by the investigation of the reaction between trimethylgermaniumethoxyacetylene and pivaloyl bromide (Equation 3). The adduct **5f** was formed in 80–90% yield within 4–5 days in acetonitrile. The vinyl ether **5f** is partially rearranged into the bromoallenic ether **3f** (IR data: ν(C=C=C) 1950 cm^{-1}). The latter compound slowly eliminates EtBr with ketene **6b** formation. Obviously, traces of Me_3GeBr or other electrophiles might be a catalyst for the **5f** to **3f** rearrangement [20]. During distillation under vacuum (120°C, 10 torr), the vinyl ether **5f** is also partially transformed (20–30% conversion) to bromoallenic ether **3f**. The latter undergoes debromethylation very slowly (3–4 weeks at 20°C), followed by rapid 1,3-migration of the Me_3Ge group with the formation of the pivaloylketene **6b**. Distilled vinyl ether **5f** was stable at room temperature for half a year.

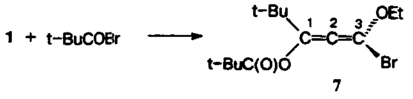


(3)

The vinyl ether **5f** is very slowly transformed into **3f** and it is improbable that it is an intermediate of the formation of the ketene (route 1b). It is reasonable to suggest that the absence of isomerization of **5e** to bromoallenic ether **3e** is due to the higher energy barrier for migration of the Me_3Si group than that of Me_3Ge from carbon to oxygen [20].

The reaction of pivaloylethoxyacetylene with pivaloyl bromide gave the allenic ester **7** *via* 1,4-addition.

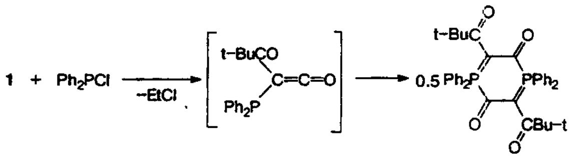
6



(4)

The allenic ester **7** is thermally stable. It does not eliminate ethyl bromide nor does it isomerize to the 1,2-addition product under heating or vacuum distillation. The structure of **7** was proved by IR and ^1H and ^{13}C NMR data. Several spectral features should be mentioned. The protons of the methylene group are diastereotopic with $^2J_{HH}$ 10 Hz, and the C^2 atom resonance (δ 171.7) was upfield in contrast with the carbon atom of the analogous allene (δC 212.6). The latter fact could be explained by enhanced shielding of the carbon atom due to the +M electron donating effect of oxygen atoms. The signals with δC 135.8 and 115.3 can be attributed to atoms C^1 and C^3 respectively, on the basis of the proton coupled ^{13}C NMR spectrum; the downfield signal is a complex multiplet, and the upfield signal is a triplet.

The reaction of the acetylene **1** with diphenylchlorophosphine gave the diphosphacyclohexadiendione **8** in 60% yield. Compound **8** could arise by [3 + 3] cyclodimerization of the phosphorus (III) substituted ketene.



(5)

Previously, we have observed the formation of analogous heterocycles in the reaction of phosphorus substituted alkoxyacetylenes with chlorophosphines [21].

In conclusion, it should be mentioned that pivaloylketenes are an unique type of a stable acylketene. We have failed to obtain sterically less hindered stable acylketenes by reaction of acetylethoxyacetylene with halides of IVb group elements. The formation of allenic ethers **3** and **7** is not surprising, taking into account conjugation of the triple bond with the carbonyl group in **1**, the high affinity of silicon and germanium to form bonds to oxygen, and the ability of Me_3SiI to add to a carbonyl group. The absence of ethyl bromide elimination from vinyl and allenic ethers **3** and **7**, respectively, is unexpected, because it is well known that such an elimination takes place in the case of bis-element substituted α-halogenvinylalkylethers and readily occurs in the presence of electron withdrawing substituents at the β-carbon atom [22].

Since R_3Ge groups readily undergo reversible O—C migrations in α-germyl substituted carbonyl compounds [20], we cannot rule out a possibility of reversible germanotropic rearrangement in the examples which we have investigated (for example, in Reaction 3). However, we failed to find clear evidence for such reversible processes.

EXPERIMENTAL

Proton NMR spectra were recorded with Tesla BS-465 and Varian VXR-300 spectrometers and ^{13}C and ^{31}P NMR spectra with Varian FT-80 and VXR-300 spectrometers. Chemical shifts in parts per million are quoted relative to tetramethilsilane (δH, δC) or 85% H_3PO_4 (δP). The IR spectra were obtained on an IKS-22 instrument. All the experimental procedures were carried out under argon using dry solvents.

Pivaloylethoxyacetylene (**1**)

A suspension of lithium ethoxyacetylide prepared from ethoxyacetylene (0.03 mol) in THF (70 ml) and 2N *n*-buthyllithium (0.03 mol) pentane solution was cooled to −50°C and added dropwise to a solution of pivaloyl chloride (0.036 mol) in THF (70 ml) at −78°C. An orange solution containing an insoluble white solid was formed. The reaction mixture was allowed to warm to room temperature and was stirred for 2 hours. The solvent and the excess of pivaloyl chloride were evaporated in vacuum, hexane (150 ml) was added to the residue, and the insoluble lithium chloride was centrifuged off. The remaining lithium chloride was frozen out by cooling for 12 hours at −20°C and centrifuged off again. The solvent was removed in vacuum to afford **1** in 80% yield with 90% spectral purity according to ^1H NMR data; bp 37–39°C at 0.1 torr, with decomp. IR: ν_{max} 2230 (C=C), 1660 cm^{-1} (C=O); δH (CD_2Cl_2): 4.3 (2H, q, CH_2O), 1.48 (3H, t, Me), 1.17 (9H, s, *t*-Bu); δC (CD_2Cl_2): 193.48 (1C, C=O), 103.37 (1C, $C_{sp}O$), 42.3 (1C, C_{sp}), 77.66 (1C, CH_2O), 14.74 (1C, Me), 26.69 (3C, *t*-Bu), 44.73 (1C, C in *t*-Bu).

1-Ethoxy-1-bromo-2-trimethylgermanium-4,4-dimethylpenta-1-en-3-one (**5f**)

Pivaloyl bromide was added dropwise to a solution of trimethylgermaniumethoxyacetylene in acetonitrile (5 ml). The reaction mixture was stored for 3 days at room temperature until **1** was no longer evident in the IR spectrum. The solvent was evaporated in vacuum to afford **5f** in 90% yield (PMR spectra monitoring). After distillation in vacuum, **5f** was obtained in mixture with ca. 20% isomeric **3f**, overall yield 70%, bp 86–90°C at 0.1 torr. For **5f** IR: ν_{max} 1620 (C=C), 1680 cm^{-1} (C=O); $\delta H(C_6D_6)$ 3.6 (2H, q, CH_2O), 1.0 (3H, t, Me), 1.2 (9H, s, *t*-Bu), 0.3 (9H, s, Me_3Ge); δC ($CDCl_3$), 211.46 (1C, C=O), 132.86 (1C, C=), 127.51 (1C, =COEt), 68.85 (1C, CH_2O), 14.06 (1C, Me), 44.32 (1C, *t*-Bu), 27.93 (3C, *t*-Bu), 0.2 (3C, Me_3Ge). Anal. found: C, 41.45; H, 6.63. $C_{12}H_{23}BrGeO_2$ requires C, 40.97; H, 6.59%.

Pivaloyltrialkylsilyl(germyl)ketenes (**6a–d**)

Trialkylsilyl(germanium)halide (0.01 mol) was added dropwise to a solution of the pivaloylethoxyacetylene in dichloromethane (5 ml). The IR 2230 cm^{-1} band due to the initial acetylene **1** was replaced by the 2100 cm^{-1} band of ketene. The solvent and ethyl halide were removed in vacuum, and the residue was distilled (see Table 1).

1-Ethoxy-1-bromo-3-pivaloyl-4,4-dimethylpentane-1,2-diene (**7**)

Pivaloyl bromide (0.01 mol) was added dropwise to a solution of pivaloylethoxyacetylene **1** in dichloromethane (5 ml). After 20–24 hours, the solvent was removed in vacuum and the residue was distilled. The yield after distillation 60%, bp 69–71 at 0.1 torr. IR: ν_{max} 1960 (C=C=C), 1760 cm^{-1} (C=O); δH (CD_2Cl_2), 3.6 (2H, q, CH_2O), 1.1 (3H, t, Me), 0.8 (9H, s, *t*-Bu), 0.9 (9H, s, *t*-BuO); δC ($CDCl_3$), 174.47 (1C, C=O), 171.66 (1C, =C=), 135.84 (1C,–C=), 115.28 (1C, =C–), 68.19 (1C, CH_2O), 39.18, 36.29 (2C, *t*-Bu, t-BuO), 27.36, 26.81 (6C, *t*-Bu and *t*-BuO), 14.14 (1C, Me). Anal. found: C, 52.90; H, 7.56. $C_{14}H_{23}BrO_3$ requires C, 52.67; H, 7.26%.

1,1,4,4-Tetraphenyl-2,5-dipivaloyl-1λ^5,4λ^5-diphosphacyclohexa-1,4-diene-3,6-dione (**8**)

Diphenylchlorophosphine (0.01 mol) was added dropwise to a stirred solution of 0.01 mol acetylene (**1**) in 5 ml dichloromethane at −10°C. The reaction mixture was kept for 24 hours at 20°C. The ^{31}P NMR spectrum displayed formation of **8** in 60% yield, δP 8.82. After 2 days at −20°C, crystalline **8** was isolated in 39% yield, mp 168–170°C. IR: ν_{max} 1740, 1700 cm^{-1} (C=O); δC ($CDCl_3$), 204.75 (2C, m, CO), 174.81 (2C, m, PC=O), 132.65, 132.05, 128.58 (20C, Ph), 124.32 (4C, d, $^1J_{PC}$ 95.6 Hz, C ipso in Ph), 94.96 (2C, m, C=P), 43.49 (2C, s, *t*-Bu), 25.27 (6C, s, *t*-Bu). Anal. found: C, 72.67; H, 6.21; P, 10.37. $C_{38}H_{38}O_4P_2$ requires C, 73.54; H, 6.17; P, 9.98%.

REFERENCES

[1] H. Steller, K. Kiehs, *Chem. Ber., 98*, 1965, 1181.
[2] J. A. Hyatt, P. L. Feldman, R. J. Clemens, *J. Org. Chem., 49*, 1984, 5105.
[3] R. J. Clemens, J. S. Witzeman, *J. Am. Chem. Soc., 111*, 1989, 2189; J. S. Witzeman, *Tetrahedron Lett., 31*, 1990, 1401.
[4] L. Copuano, K. Djohar, N. Schneider, C. Wamprecht, *Liebigs Ann. Chem.*, 1987, 183.
[5] V. A. Nikolaev, Yu. Frenh, I. K. Korobitsyna, *Zh. Org. Chem. Engl. Transl., 14* 1978, 1069.
[6] O. L. Chapman, C. L. McIntosh, *J. Am. Chem. Soc., 92*, 1970, 7001.
[7] V. Dvorak, J. Kolc, J. Michl, *Tetrahedron Lett.*, 1972, 3443.
[8] C. Wentrup, H.-W. Winter, G. Gross, K. P. Netsch, G. Kollenz, W. Ott, A. G. Biedermann, *Angew. Chem., 96*, 1984, 791; C. Wentrup, K.-P. Netsch, *Angew Chem., 96*, 1984, 792.
[9] G. Maier, H. P. Reisenauer, T. Sayrac, *Chem. Ber., 115*, 1982, 2192.
[10] B. Freiermuth, C. Wentrup, *J. Org. Chem., 56*, 1991, 2286.
[11] V. A. Nikolaev, Yu. Frenh, I. K. Korobitsyna, *Zh. Org. Khim. Engl. Transl., 14*, 1978, 1338.
[12] C. O. Kappe, R. A. Evans, C. H. L. Kennard, C. Wentrup, *J. Am. Chem. Soc., 113*, 1991, 4234.

[13] D. C. England, *J. Org. Chem.*, *46*, 1981, 147, 153; *J. Org. Chem.*, *49*, 1984, 4007.

[14] I. V. Efimova, M. A. Kazankova, I. F. Lutsenko, *J. Gen Chem USSR*, *55*, 1985, 1465.

[15] N. V. Lukashev, O. I. Artushin, E. I. Lazhko, E. V. Lusikova, M. A. Kazankova, *J. Gen. Chem. USSR 60*, 1990, 1374.

[16] N. V. Lukashev, A. A. Fil'chikov, Yu. N. Lusikov, M. A. Kazankova, *J. Gen Chem USSR*, *60*, 1990, 1492.

[17] N. V. Lukashev, A. A. Fil'chikov, P. E. Zhichkin, M. A. Kazankova, I. P. Beletskaya, *J. Gen Chem USSR*, *61*, 1991, 920.

[18] G. Himbert, L. Henn, *Tetrahedron Lett.*, *22*, 1981, 2637; *Org. Prep. Proced. Int.*, *14*, 1982, 189.

[19] S. V. Ponomarev, I. F. Lutsenko, *Vestnik MGU, Ser. Chim.*, *28*, 1987, 3.

[20] Yu. I. Baukov, I. F. Lutsenko, *Organomet. Chem. Rev. A. 6*, 1970, 355.

[21] N. V. Lukashev, O. I. Artushin, E. I. Lazhko, V. A. Tafeenko, M. A. Kazankova, I. F. Lutsenko, *J. Gen. Chem. USSR*, *58*, 1988, 278.

[22] M. A. Kazankova, I. F. Lutsenko, *Vestnik MGU, Ser. Chim.*, *24*, 1983, 315.