# Formation of $\alpha,\beta$-Unsaturated Ketones from the Gas-Phase Pyrolysis of $\alpha$-Substituted Propargyl Esters[1]

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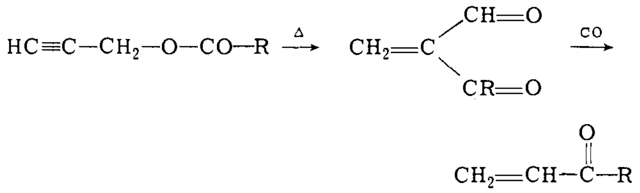
**Abstract:** Products from the low pressure ($10^{-3}$ to $10^{-5}$ Torr) gas-phase pyrolysis of the following $\alpha$-substituted propargyl esters were determined: 1-phenylpropargyl hexanoate (**1**); 1-methylpropargyl benzoate (**2**); 1,1-dimethylpropargyl benzoate (**3**); 1,1-dimethylpropargyl hexanoate (**4**); 1-propylpropargyl benzoate (**5**); 1-isopropylpropargyl benzoate (**8**); 1-ethynylcyclohexyl benzoate (**6**); 1-ethynylcyclopentyl benzoate (**7**). With the exception of **7**, all of these esters, which have the general formula $HC{\equiv}CCR_1R_2OCOR_3$, produced $\alpha,\beta$-unsaturated ketones that have the general formula $R_3COCH{=}CR_1R_2$ in yields ranging from 10 to 70%. However, the esters that possess $\beta$ hydrogen atoms (**2–8**) gave significant amounts of elimination products, the corresponding vinylacetylene and carboxylic acid. Pyrolysis of **1** at lower temperatures gave rise to the isomeric 1-phenyl-2-formyloct-1-en-3-ones. This result supports the proposed mechanism for the conversion of the propargyl esters to the $\alpha,\beta$-unsaturated ketones which involves the intermediate formation of an $\alpha$-formyl $\alpha,\beta$-unsaturated ketone. It is concluded that the thermal conversion of propargyl esters to $\alpha,\beta$-unsaturated ketones is a general reaction.

Recently we reported that the low-pressure ($10^{-3}$ to $10^{-5}$ Torr) gas-phase pyrolysis of propargyl esters gives rise to $\alpha,\beta$-unsaturated ketones in fair to good yields.[2] It was proposed that an intermediate enedione is formed which undergoes a facile decarbonylation to yield an enol which rearranges to the ketone. Only one propargyl ester that contains an $\alpha$ substituent, 1-phenylpropargyl acetate, was studied, and this ester did give a good yield (ca. 80%) of the expected $\alpha,\beta$-unsaturated ketone, 4-phenylbut-3-en-2-one.



$$HC{\equiv}C{-}CH_2{-}O{-}CO{-}R \xrightarrow{\Delta} CH_2{=}C\begin{matrix}CH{=}O\\CR{=}O\end{matrix} \xrightarrow{CO} CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}R$$

In order to establish the generality of this reaction, we have studied the pyrolysis of several propargyl esters with the general formula $HC{\equiv}CCR_1R_2OCOR_3$, where $R_1$ and $R_2$ were hydrogen atoms or simple alkyl or aryl groups, and $R_3$ was a simple alkyl or aryl group. The results of this study are reported here. It is concluded that the conversion of these esters to the expected $\alpha,\beta$-unsaturated ketones, $R_3COCH{=}CR_1R_2$, is fairly general.

## Results

1-Phenylpropargyl hexanoate (**1**), prepared by the addition of hexanoyl chloride in ether to an ether solution of 1-phenylpropargyl alcohol and triethylamine, was pyrolyzed by the procedure previously reported[3] using pyrolysis temperatures ranging from 500 to 645°. The products from a pyrolysis at 600° were shown to be the expected $\alpha,\beta$-unsaturated ketones, ($E$)- (88% rel. yield) and ($Z$)-1-phenyloct-1-en-3-ones (12% rel yield) whereas, at 500°, the proposed intermediate aldehydes, ($E$)- (90% rel yield) and ($Z$)-1-phenyl-2-formyloct-1-en-3-ones (10% rel yield) were isolated in addition to residual starting material and the $\alpha,\beta$-unsaturated ketones. Product yields from runs at various temperatures are given in Table I.

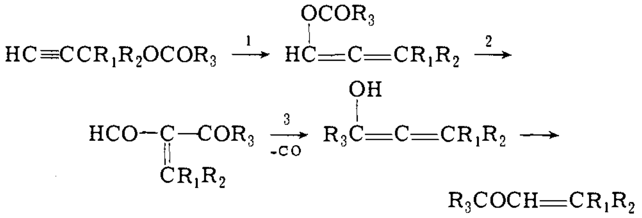
The following esters which possess $\beta$-hydrogen atoms were prepared by the addition of the acid chloride to a solution of the alcohol and pyridine:[4] 1-methylpropargyl benzoate (**2**), 1,1-dimethylpropargyl benzoate (**3**), 1,1-dimethylpropargyl hexanoate (**1**), 1-propylpropargyl benzoate (**5**), 1-ethynylcyclohexyl benzoate (**6**), and 1-ethynylcyclopentyl benzoate (**7**). 1-Isopropylpropargyl benzoate (**8**) was prepared using triethylamine instead of pyridine, which rapidly decomposes 4-methylpent-1-yn-3-ol.

Pyrolysis of all of these esters, except 1-ethynylcyclopentyl benzoate (**7**), gave the expected $\alpha,\beta$-unsaturated ketones and products arising from $\beta$-elimination of a carboxylic acid. Ester **7** gave only $\beta$-elimination products. The products obtained from these reactions and their yields are given in Table II. The temperature study of 1,1-dimethylpropargyl benzoate (**3**) showed that a maximum yield of $\alpha,\beta$-unsaturated ketone is obtained at pyrolysis temperatures of 600–700°, and therefore the other esters were pyrolyzed only within this range.

## Discussion

The mechanism proposed[2] for the conversion of propargyl esters to $\alpha,\beta$-unsaturated ketones consists of a series of symmetry-allowed, intramolecular, concerted reactions and is presented in Scheme I. Step 1 involves formation of an allenyl ester via a Claisen-type reaction, and several metal- or acid-catalyzed rearrangements of this type have been reported.[5] Step 2 involves a 1,3-acyl shift which is common for vinyl esters in the gas phase.[6] Step 3 involves a decarbonylation of the intermediate $\alpha$-formyl $\alpha,\beta$-unsaturated ketone to an enol which rearranges to the ketone. Decarbonylation of an intermediate $\alpha$-ketoaldehyde has also been proposed for the thermal rearrangement of some vinyl esters.[6c,e]

**Scheme I**



$$HC{\equiv}CCR_1R_2OCOR_3 \xrightarrow{1} H\overset{OCOR_3}{\overset{|}{C}}{=}C{=}CR_1R_2 \xrightarrow{2} HCO{-}\underset{CR_1R_2}{\underset{\|}{C}}{-}COR_3 \xrightarrow[-CO]{3} R_3\overset{OH}{\overset{|}{C}}{=}C{=}CR_1R_2 \longrightarrow R_3COCH{=}CR_1R_2$$

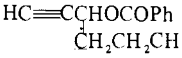
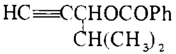
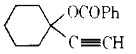
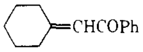
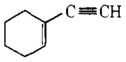
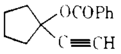
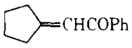
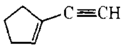
The results of the present study indicate that the conversion of propargyl esters of the general formula $HC{\equiv}CCR_1R_2OCOR_3$ to $\alpha,\beta$-unsaturated ketones, $R_3COCH{=}CR_1R_2$, is a general reaction in the cases where $R_1$, $R_2$, and $R_3$ are simple alkyl or aryl groups. Furthermore, the proposed mechanism for this rearrangement is supported by the observation that pyrolysis of 1-phenylpropargyl hexanoate at temperatures from 500 to 600° yields the

Table I. Products and Yields from Pyrolysis of 1-Phenylpropargyl Hexanoate (**1**)

| Pyrolysis temp, °C | Products and yields, %[a] | | Recovered starting material, % |
|---|---|---|---|
| | $C_5H_{11}COCH{=}CHPh$[b] | $C_5H_{11}COC(CHO){=}CHPh$[c] | |
| 500 | 20[d] | 30 | 18 |
| 545 | 49 | 24 | 5 |
| 585 | 63 | 6 | |
| 645 | 68 | Trace | |

[a] Yields were determined by NMR spectroscopy using 1,2-dibromoethane as an internal standard. [b] This product is a mixture of *E* and *Z* isomers in a ratio of approximately 8/1. [c] This product is a mixture of *E* and *Z* isomers in a ratio of approximately 9/1. [d] The yields are an average of two runs.

Table II. Products and Yields from Pyrolysis of Propargyl Esters Containing β-Hydrogen Atoms

| Substrate | Pyrolysis Temp, °C | Products and yields, %[a] | | | Recovered starting material, % | Elimn rearr[b] |
|---|---|---|---|---|---|---|
| $HC{\equiv}CCH(CH_3)OCOPh$ | | $PhCOCH{=}CHCH_3$[c] | PhCOOH | $HC{\equiv}CCH{=}CH_2$ | | |
| 1-Methylpropargyl | 620 | 41[d] | 60 | 28[e] | | 1.5 |
| benzoate (**2**) | 645 | 42 | 62 | 26 | | 1.4 |
| | 660 | 35 | 65 | 22 | | 1.8 |
| $HC{\equiv}CC(CH_3)_2OCOPh$ | | $PhCOCH{=}C(CH_3)_2$ | PhCOOH | $HC{\equiv}CC(CH_3){=}CH_2$ | | |
| 1,1-Dimethyl- | 445 | | 63 | 42 | 42 | |
| propargyl | 505 | 7 | 84 | 11 | 15 | 12.1 |
| benzoate (**3**) | 535 | 16 | 80 | 10 | 5 | 5.2 |
| | 620 | 21 | 67 | 11 | | 3.2 |
| | 700 | 17 | 82 | 4 | | 4.7 |
| $HC{\equiv}CC(CH_3)_2OCOC_5H_{11}$ | | $C_5H_{11}COCH{=}C(CH_3)_2$ | $C_5H_{11}COOH$ | $HC{\equiv}CC(CH_3){=}CH_2$ | | |
| 1,1-Dimethyl- | 600 | 26 | 65 | 54 | | 2.5 |
| propargyl | 640 | 25 | 56 | 54 | | 2.2 |
| hexanoate (**4**) | 660 | 27 | 58 | 52 | | 2.2 |
| | 675 | 24 | 58 | 51 | | 2.4 |
|  $HC{\equiv}C\underset{CH_2CH_2CH_3}{CH}OCOPh$ | | $PhCOCH{=}CHC_3H_7$[f] | PhCOOH | $HC{\equiv}CCH{=}CHC_2H_5$[g] | | |
| 1-Propyl- | 660 | 23 | 53 | | | 2.3 |
| propargyl | 680 | 22 | 52 | | | 2.4 |
| benzoate (**5**) | | | | | | |
|  $HC{\equiv}C\underset{CH(CH_3)_2}{CH}OCOPh$ | | $PhCOCH{=}CHCH(CH_3)_2$[f] | PhCOOH | $HC{\equiv}CCH{=}C(CH_3)_2$ | | |
| 1-Isopropyl- | 640 | 31 | 45 | 31 | | 1.4 |
| propargyl | 670 | 24 | 46 | 23 | | 1.9 |
| benzoate (**8**) | | | | | | |
|  | |  | PhCOOH |  | | |
| 1-Ethynyl- | 645 | 9 | 90 | 72 | | 10.0 |
| cyclohexyl | 660 | 6 | 95 | 64 | | 15.8 |
| benzoate (**6**) | | | | | | |
|  | |  | PhCOOH |  | | |
| 1-Ethynyl- | 650 | | 90 | 82 | | |
| cyclopentyl | | | | | | |
| benzoate (**7**) | | | | | | |

[a] Yields were determined by NMR spectroscopy using 1,2-dibromoethane as an internal standard. [b] This ratio was obtained by dividing the yield of carboxylic acid by the yield of α,β-unsaturated ketone at each temperature. [c] This product is a mixture of *E* and *Z* isomers in a ratio of approximately 4/1. [d] Yields are an average of two or three runs. [e] The yields of enynes are low because of their high volatility. [f] This product is a mixture of *E* and *Z* isomers, but an isomer ratio could not be determined from the NMR spectrum of the crude product mixture. [g] This vinylacetylene was removed from the product mixture by rotary evaporation before the NMR spectrum of the product mixture was recorded.

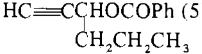
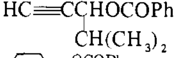
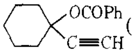
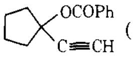
stereoisomeric α-formyl α,β-unsaturated ketones in addition to the expected stereoisomeric α,β-unsaturated ketones. Also, as the pyrolysis temperature of this reaction is increased, the yields of aldehydes decrease while the yields of ketones increase, suggesting that the ketone probably does arise from the decarbonylation of the aldehyde.

The present results also show that pyrolysis of a propargyl ester that possesses β-hydrogen atoms yields, in addition to an α,β-unsaturated ketone, mainly elimination products. Average yields of these products are summarized in Table III. No doubt the mechanism for this elimination reaction is the well established six-electron cyclic one.[7]

There does not appear to be any direct correlation between the number of β-hydrogen atoms in the propargyl ester and the amount of elimination. Decreasing the number of β hydrogens from three to two to one, as shown by a comparison of 1-methyl-, 1-propyl-, and 1-isopropylpropargyl benzoate, does not produce a corresponding decrease in the amount of elimination and therefore an increase in the yield of α,β-unsaturated ketone. Moreover, ethynylcyclohexyl and ethynylcyclopentyl benzoates appear to be anomalous when compared with the other propargyl esters since they yield little or no α,β-unsaturated ketone.

The first step for both the rearrangement reaction and

Table III. Yields of α,β-Unsaturated Ketones and Carboxylic Acids from Pyrolysis of Propargyl Esters Containing β-Hydrogen Atoms

| Propargyl ester | α,β-Unsaturated ketone, % | Carboxylic acid, % | Elimn/rearr |
|---|---|---|---|
| $HC{\equiv}CCH(CH_3)OCOPh$ (2) | 39 | 62 | 1.6 |
| $HC{\equiv}CC(CH_3)_2OCOPh$ (3) | 19 | 75 | 4.0 |
| $HC{\equiv}CC(CH_3)_2OCOC_5H_{11}$ (4) | 25 | 59 | 2.4 |
|  $HC{\equiv}CCH(CH_2CH_2CH_3)OCOPh$ (5) | 23 | 53 | 2.3 |
|  $HC{\equiv}CCH(CH(CH_3)_2)OCOPh$ (8) | 27 | 46 | 1.7 |
|  (6) | 8 | 93 | 11.6 |
|  (7) |  | 90 |  |

the elimination reaction involves relief of steric congestion at the α position; in both cases, the α-carbon atom, which is tetrahedral, goes to a trigonal carbon atom. Our results indicate that, except for the ethynylcycloalkyl esters, these two processes are competitive which must be the result of a balance of numerous subtle steric, conformational, and electronic factors.

α,β-Unsaturated ketones can be synthesized in several ways.[8] Many of these methods involve the use of organometallic reagents or base-catalyzed reactions. The preparation of α,β-unsaturated ketones by the pyrolysis of propargyl esters, which can be prepared from the corresponding carboxylic acid and propargyl alcohol, offers the advantage of not using any organometallic reagents, or strong bases or acids. Moreover, since the product is trapped in a cold trap, it is in a very unreactive state during the course of the pyrolysis reaction. Of course this method of preparing α,β-unsaturated ketones cannot be used if the starting propargyl ester is not very volatile or the desired unsaturated ketone is thermally unstable.

In several cases, this method of preparing α,β-unsaturated ketones gives yields comparable to or better than other methods. One major limitation of this method is that pyrolysis of propargyl esters containing β-hydrogen atoms produces mainly elimination products. However, although the yields of the α,β-unsaturated ketones are rather low in these cases (20–40%), the pyrolysis reaction is very clean, and the α,β-unsaturated ketone is easily separated from the elimination products.

In summary, the reaction by which propargyl esters are converted to α,β-unsaturated ketones is general and offers a useful means of preparing α,β-unsaturated ketones in reasonable yields from the corresponding carboxylic acids.

## Experimental Section

**Methods and Materials.** Most equipment and methods,[9] including the pyrolysis apparatus[3] and generalized procedure for the gas-phase pyrolyses,[10] have been described previously. Benzoyl chloride, hexanoic acid, and 2-methylbut-3-yn-2-ol were obtained from J. T. Baker Chemical Co. But-3-yn-2-ol, 1-ethynyl-1-cyclopentanol, and 4-methylpent-1-yn-3-ol were obtained from Farchan Research Labs. 1-Ethynyl-1-cyclohexanol was obtained from Aldrich Chemical Co. Hex-1-yn-3-ol was obtained from Chemical Procurement Labs. 1-Phenylpropargyl and propargyl alcohol were obtained from Chemical Samples Co.

**Hexanoyl chloride** was prepared from hexanoic acid and thionyl chloride by the method of Fierz-David and Kuster[11] in 70% yield: bp 45–47° (15 mm) [lit.[11] bp 150–153° (725 mm)]; NMR ($CCl_4$) δ 2.83 (t, 2, $CH_2CO$, $J = 2.0$ Hz), 2.00–1.10 [m, 6, $(CH_2)_3$], 0.90 (t, 2, $CH_3$, $J = 5.5$ Hz).

**Propargyl esters 1 and 8** were prepared by adding dropwise 0.08 mol of the acid chloride in 15 ml of ether to a stirred mixture of 0.08 mol of triethylamine and 0.06 mol of the alcohol in 60 ml of ether. The reaction mixture was stirred at room temperature for 1 hr and then poured into a separatory funnel containing 50 ml of water. The organic layer was separated and washed successively with three 15-ml portions of 10% hydrochloric acid, three 15-ml portions of saturated aqueous sodium bicarbonate solution, and two 15-ml portions of saturated aqueous sodium chloride solution and was dried ($MgSO_4$) and concentrated.

**1-Phenylpropargyl hexanoate (1):** bp 117–119° (1 mm); NMR ($CCl_4$) δ 7.53–7.00 (m, 5, $C_6H_5$), 6.36 (d, 1, $C{\equiv}CCH$, $J = 2.3$ Hz), 2.52 (d, 1, $HC{\equiv}C$, $J = 2.3$ Hz), 2.20 (t, 2, $CH_2CO$, $J = 6.2$ Hz), 1.92–0.60 (m, 9, $C_4H_9$); ir ($CCl_4$) 3318, 2130, 1750, 1160 $cm^{-1}$; MS *m/e* (rel intensity) 230 ($M^+$, 14.8), 115 (63.0), 114 (100.0).

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.26; H, 7.83. Found: C, 78.17; H, 7.67.

**1-Isopropylpropargyl benzoate (8):** bp 79–81° (0.45 mm); NMR ($CCl_4$) δ 8.30–7.27 (m, 5, $C_6H_5$), 5.55 (d of d, 1, $C{\equiv}CCH$, $J_1 = 5.5$, $J_2 = 2.3$ Hz), 2.48 (d, 1, $HC{\equiv}C$, $J = 2.3$ Hz), 2.44–1.75 (m, 1, $CH_3CHCH_3$), 1.12 (d of d, 6, $CH_3CCH_3$, $J_1 = 6.9$, $J_2 = 1.9$ Hz); ir ($CCl_4$) 3320, 1735, 1100, 1098 $cm^{-1}$; MS *m/e* (rel intensity) 202 ($M^+$, 1.3), 106 (11.4), 105 (100.0), 77 (39.8).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.18; H, 6.99. Found: C, 77.01; H, 6.91.

The following esters were prepared by the addition of the acid chloride to a solution of the alcohol and pyridine according to the method of Magid and Nieh.[4]

**1-Methylpropargyl benzoate (2):** bp 67–70° (0.6 mm); mp 45–47° (lit.[4] mp 46–47°); NMR ($CDCl_3$) δ 8.25–7.22 (m, 5, $C_6H_5$), 5.70 (q of d, 1, $C{\equiv}CCH$, $J_1 = 6.8$, $J_2 = 2.3$ Hz), 2.48 (d, 1, $HC{\equiv}C$, $J = 2.3$ Hz), and 1.65 (d, 3, $CH_3$, $J = 6.8$ Hz); ir ($CCl_4$) 3320, 2130, 1725, 1108, 1098 $cm^{-1}$; MS *m/e* (rel intensity) 174 ($M^+$, 11.2), 105 (100.0), 77 (26.6).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.90; H, 5.70. Found: C, 75.67; H, 5.66.

**1,1-Dimethylpropargyl benzoate (3):** bp 71–73° (0.6 mm) [lit.[12] bp 118–120° (12 mm)]; NMR ($CCl_4$) δ 8.15–7.00 (m, 5, $C_6H_5$), 2.56 (s, 1, $HC{\equiv}C$), 1.80 (s, 6, $CH_3CCH_3$); ir ($CCl_4$) 3318, 1736, 1108, 1098 $cm^{-1}$; MS *m/e* (rel intensity) 188 ($M^+$, 28.1), 105 (100.0), 77 (61.0), 67 (46.9).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.60; H, 6.38. Found: C, 76.34; H, 6.43.

**1,1-Dimethylpropargyl hexanoate (4):** bp 36–38° (0.15 mm); NMR ($CCl_4$) δ 2.45 (s, 1, $HC{\equiv}C$), 2.35–2.10 (m, 2, $CH_2CO$), 1.63 (s, 6, $CH_3CCH_3$), 1.55–0.75 (m, 9, $C_4H_9$); ir ($CCl_4$) 3319, 1753, 1250, 1137 $cm^{-1}$; MS *m/e* (rel intensity) 182 ($M^+$, 13.0), 99 (95.0), 71 (54.6), 67 (100.0).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.53; H, 9.89. Found: C, 72.35; H, 10.10.

**1-Propylpropargyl benzoate (5):**[13] bp 77–78° (0.25 mm); NMR ($CCl_4$) δ 8.20–7.13 (m, 5, $C_6H_5$), 5.61 (t of d, 1, $C{\equiv}CCH$, $J_1 = 6.3$, $J_2 = 2.0$ Hz), 2.48 (d, 1, $HC{\equiv}C$, $J = 2.0$ Hz), 2.16–0.77 (m, 7, $C_3H_7$); ir ($CCl_4$) 3316, 1730, 1108, 1098 $cm^{-1}$; MS *m/e* (rel. intensity) 202 ($M^+$, 1.0), 105 (100.0), 77 (28.5).

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.30; H, 6.94. Found: C, 77.18; H, 6.91.

**1-Ethynylcyclohexyl benzoate: (6):** bp 105–110° (0.25 mm); mp 51–53° (lit.[14] mp 54–55°); NMR ($CCl_4$) δ 8.20–7.15 (m, 5, $C_6H_5$), 2.50 (s, 1, $HC{\equiv}C$), 2.40–1.95 (m, 4, $CH_2CCH_2$), 1.95–1.22 [m, 6, $(CH_2)_3$]; ir ($CCl_4$) 3308, 2115, 1728, 1280, 1108, 1098 $cm^{-1}$; MS *m/e* (rel intensity) 228 ($M^+$, 5.5), 105 (100.0), 77 (23.0).

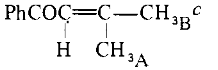
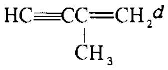
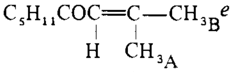
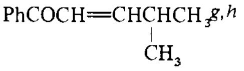
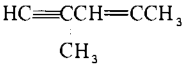
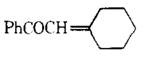
Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.95; H, 7.02. Found: C, 78.82; H, 6.94.

**1-Ethynylcyclopentyl benzoate (7):** bp 97–98° (0.24 mm); NMR ($CCl_4$) δ 8.10–7.10 (m, 5, $C_6H_5$), 2.60 (s, 1, $HC{\equiv}C$), 2.75–1.55 [m, 8, $(CH_2)_4$]; ir ($CCl_4$) 3320, 1738, 1280, 1110, 1100 $cm^{-1}$; MS *m/e* (rel intensity) 214 ($M^+$, 5.2), 105 (100.0), 91 (59.0), 77 (38.6).

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.47; H, 6.60. Found: C, 78.64; H, 6.60.

**Pyrolysis Products from 1-Phenylpropargyl Hexanoate (1).** The products from pyrolysis of **1** at 600° were washed from the trap with ether and analyzed by GLC on a 1.5 m × 6.35 mm, 20% SE-30 on Chromosorb W column (column temperature was 168°). The two major peaks were collected and identified as (*E*)- and (*Z*)-1-phenyloct-1-en-3-one from the following data.

**Table IV.** NMR Spectral Data of Products from Pyrolysis of Propargyl Esters

| Compd | Resonance | Chemical shift, δ[a] | Pattern | Coupling, Hz |
|---|---|---|---|---|
| HC≡CCH=CH$_2$[b] | HC≡C | 2.88 | s (br) | |
| Vinylacetylene | CH=CH$_2$ | 5.35–5.85 | m | |
|  $\mathrm{PhCO\underset{H}{C}{=}\underset{CH_{3A}}{C}{-}CH_{3B}}$[c] | CH$_{3A}$ | 1.99 | d | $J = 1.0$ |
| | CH$_{3B}$ | 2.19 | d | $J = 0.9$ |
| 3-Methylcrotonophenone | CH=C | 6.70 | m | |
| | Ph | 7.20–7.60 | m | |
| | | 7.75–8.00 | m | |
|  $\mathrm{HC{\equiv}\underset{CH_3}{C}{=}CH_2}$[d] | CH$_3$ | 1.88 | t | $J = 1.0$ |
| | HC≡C | 2.78 | s | |
| Isopropenylacetylene | C=CH$_2$ | 5.15–5.30 | m | |
|  $\mathrm{C_5H_{11}CO\underset{H}{C}{=}\underset{CH_{3A}}{C}{-}CH_{3B}}$[e] | C$_4$H$_9$ | 0.70–1.80 | m | |
| | CH$_2$CO | 2.18–2.60 | m | |
| 2-Methylnon-2-en-4-one | CH$_{3A}$ | 1.88 | m | |
| | CH$_{3B}$ | 2.13 | m | |
| | CH=C | 6.05 | m | |
| PhCOCH=CHCH$_2$CH$_2$CH$_3$[f,g] | CH$_3$ | 0.80–1.20 | m | |
| 2-Hexenophenone | CH$_2$CH$_2$ | 1.20–2.50 | m | |
| | CH=CH | 6.70–7.10 | m | |
| | Ph | 7.20–7.65 | m | |
| | | 7.70–8.10 | m | |
|  $\mathrm{PhCOCH{=}CH\underset{CH_3}{C}HCH_3}$[g,h] | CH$_3$CCH$_3$ | 1.00–1.50 | m | |
| | CH$_3$C*H*CH$_3$ | 2.20–2.90 | m | |
| 4-Methyl-2-pentenophenone | CH=CH | 6.70–7.10 | m | |
| | Ph | 7.20–7.70 | m | |
| | | 7.80–8.30 | m | |
|  $\mathrm{HC{\equiv}CCH{=}\underset{CH_3}{C}CH_3}$[i] | CH$_3$CCH$_3$ | 1.65–2.10 | m | |
| | HC≡C | 2.98 | m | |
| 2-Methylpent-2-en-4-yne | CH=C | 5.24 | m | |
|  | (CH$_2$)$_5$ | 1.40–1.85 | m | |
| | | 1.85–2.40 | m | |
| Cyclohexylideneacetophenone | CH=C | 6.52 | m | |
| | | 7.70–7.60 | | |
| | Ph | 7.70–8.20 | m | |

[a] The reported chemical shifts were determined from an NMR spectrum of a crude product. [b] See R. C. Hirst and D. M. Grant, *J. Am. Chem. Soc.*, 84, 2009 (1962). [c] See ref 8i. [d] See H. M. Hutton and T. Schaefer, *Can. J. Chem.*, 45, 1165 (1967). [e] See ref 8f. [f] See K. E. Schulte and F. Zinnert, *Arch. Pharm. (Weinheim, Ger.)*, 288, 60 (1955). [g] This product is a mixture of *E* and *Z* isomers, but an isomer ratio could not be determined from the NMR spectrum of the crude product mixture. [h] See W. D. Emmons, *J. Am. Chem. Soc.*, 79, 5739 (1957). [i] See P. R. Ashurst and D. R. J. Laws, *J. Chem. Soc. C*, 1615 (1966). [j] C. S. Marvel and W. L. Walton, *J. Org. Chem.*, 7, 88 (1942).

**(*E*)-Phenyloct-1-en-3-one:**[15] NMR (CCl$_4$) δ 7.58-7.00 (m, 5, C$_6$H$_5$), 6.90 (AB pattern, 2, CH=CH, $J$ = 16.0 Hz, $\Delta\nu_{AB}$ = 47.1 Hz), 2.53 (m, 2, CH$_2$CO), 1.90-0.67 (m, 9, C$_4$H$_9$); ir (CCl$_4$) 1700, 1675, 1618 cm$^{-1}$; MS *m/e* (rel intensity) 202 (M$^+$, 6.7), 146 (46.7), 131 (100.0), 103 (36.6).

Anal. Calcd for C$_{14}$H$_{18}$O: C, 83.20; H, 8.92. Found: C, 83.25; H, 8.87.

**(*Z*)-1-Phenyloct-1-en-3-one:** NMR (CCl$_4$) δ 7.58-6.92 (m, 5, C$_6$H$_5$), 6.32 (AB pattern, 2, CH=CH, $J$ = 12.8 Hz, $\Delta\nu_{AB}$ = 36.0 Hz), 2.57-1.98 (m, 2, CH$_2$CO), 1.78-0.50 (m, 9, C$_4$H$_9$); ir (CCl$_4$) 1700, 1615 cm$^{-1}$; high-resolution MS (exact mass calcd for C$_{14}$H$_{18}$O, 202.1357) 202.1397.

The products from the pyrolysis of **1** at 500° were separated by GLC and, in addition to starting material and the isomeric $\alpha,\beta$-unsaturated ketones, the isomeric 1-phenyl-2-formyloct-1-en-3-ones were collected and identified on the basis of the following data: NMR (CCl$_4$) δ 9.83 (s, 1, CHO, *Z* isomer), 9.36 (s, 1, CHO, *E* isomer), 7.68-7.24 (m, 5, C$_6$H$_5$), 7.18 (s, 1, CH=C), 2.67-2.35 (m, 2, CH$_2$CO), 1.90-0.60 (m, 9, C$_4$H$_9$); ratio of *E* to *Z* = 10/1; ir (CCl$_4$) 1724, 1693, 1622 cm$^{-1}$.

**Pyrolysis Products from 1-methylpropargyl benzoate (2)** at 640° were washed from the trap with ether and analyzed by GLC on a 1 m × 4.65 mm i.d. aluminum column packed with 10% diethylene glycol adipate (LAC 446) on 80-100 mesh Gas Pack FS (column temperature was 148°). The two major peaks were collected and identified as benzoic acid and crotonophenone:[16] NMR (CCl$_4$) δ 8.07-7.25 (m, 5 C$_6$H$_5$), 7.15-6.32 (m, 2, CH=CH), 2.10 (d of d, 3, CH$_3$, $J_1$ = 6.7, $J_2$ = 1.5 Hz, *Z* isomer), 1.92 (d, 3, CH$_3$, $J$ = 5.0 Hz, *E* isomer); ratio of *E* to *Z* = 4/1; ir (CCl$_4$) 1680, 1631, 1452, 1298, 1222 cm$^{-1}$.

**Pyrolysis products from 1-ethynylcyclohexyl (6) and 1-ethynylcyclopentyl benzoate (7)** were washed from the product trap with ether. Each ether solution was washed with saturated aqueous sodium bicarbonate solution to remove benzoic acid and was then analyzed by GLC on the LAC 446 column (column temperatures were 110 and 96°, respectively). 1-Ethynylcyclohexene and 1-ethynylcyclopentene were collected and identified on the basis of the following data.

**1-Ethynylcyclohexene:**[17] NMR (CCl$_4$) δ 6.15 (m, 1, CH=C), 2.69 (s, 1, HC≡C), 2.32-1.40 [m, 8, (CH$_2$)$_4$]; ir (CCl$_4$) 3328, 2110, 1635 cm$^{-1}$.

**1-Ethynylcyclopentene:**[18] NMR (CCl$_4$) δ 6.13 (m, 1, CH=C), 2.88 (s, 1, HC≡C), 2.73-1.55 [m, 6, (CH$_2$)$_3$]; ir (CCl$_4$) 3320, 2105, 1616 cm$^{-1}$; high-resolution MS (no M$^+$; exact mass calcd for C$_7$H$_7$, 91.0548) 91.0545.

**Pyrolysis products from the other propargyl esters** were analyzed only from the NMR spectra of the crude product mixtures. The NMR spectral data for these products are summarized in Table IV.

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(1) Based on work by S.L.E. in partial fulfillment of the requirements for the M.S. degree at Iowa State University.

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# Hindered Organosilicon Compounds. Synthesis and Properties of Di-*tert*-butyl-, Di-*tert*-butylmethyl-, and Tri-*tert*-butylsilanes

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**Abstract:** Di-*tert*-butylchlorosilane, but not di-*tert*-butyldichlorosilane, reacts slowly with alkyllithium compounds to form di-*tert*-butylalkylsilanes. With methyllithium, substitution is the only observed process. With *tert*-butyllithium, reduction competes with and is favored over substitution by 2:1. Tri-*tert*-butylsilane is prepared from *tert*-butyltrichlorosilane by reaction with *tert*-butyllithium, followed by lithium aluminum hydride reduction of the resulting mixture of products that includes di-*tert*-butyldichlorosilane, di-*tert*-butylchlorosilane, di-*tert*-butylsilane, and tri-*tert*-butylsilane, and by selective chlorination of di-*tert*-butylsilane with subsequent reaction of di-*tert*-butylchlorosilane with *tert*-butyllithium. The nature of the *tert*-butyllithium reduction process is discussed. The spectral properties of di- and tri-*tert*-butylsilanes are presented; relatively severe crowding of the *tert*-butyl groups in tri-*tert*-butylsilane is implied from C–H stretching frequencies.

Organic compounds possessing bulky *tert*-butyl groups in close proximity have received considerable attention in recent years.[2-6] Such compounds possess unusual physical and chemical properties. Intramolecular crowding of the *tert*-butyl groups in tri-*tert*-butylmethane, for example, distorts bond angles and bond lengths from their normal equilibrium values.[2a] Rotation of the *tert*-butyl groups in tri-*tert*-butylmethane is restricted, and a strain energy of 33.5 kcal/mol for this compound has been calculated.[2b] The strain present in tri-*tert*-butylmethane and its derivatives is likewise evident in the chemical reactivities of these compounds.[5,6]

Few examples are known of compounds with three *tert*-butyl groups bonded to a central atom other than carbon. Tri-*tert*-butyltin derivatives[7a-c] and tri-*tert*-butylphosphine[7d] have been recently prepared but do not appear to be severely restricted in chemical reactions that would increase the steric bulk about the central atom.[7] A silicon analog of tri-*tert*-butylsilane, $(Me_3Si)_3SiH$, and even $(Me_3Si)_4Si$ have been reported.[8] However, previous attempts to prepare tri-*tert*-butylsilane have not been successful.[9] We have found that, whereas di-*tert*-butyldichlorosilane is inert to substitution reactions by alkyllithium compounds, tri-*tert*-butyl- and di-*tert*-butylmethylsilane can be prepared from di-*tert*-butylchlorosilane and *tert*-butyl- or methyllithium. The syntheses and spectral properties of these compounds are described.

## Results and Discussion

*tert*-Butyltrichlorosilane was prepared by the procedure of Tyler, Sommer, and Whitmore.[9a] When the *tert*-butyltrichlorosilane was further treated with *tert*-butyllithium over a period of 11 days, while the reaction temperature was slowly increased from 38 to 105°, instead of observing only di-*tert*-butyldichlorosilane, five compounds were detected and analyzed (eq 1). One of these compounds was identified

$$(t\text{-Bu})SiCl_3 + t\text{-BuLi} \longrightarrow \underset{9\%}{(t\text{-Bu})_2SiH_2} + \underset{32\%}{(t\text{-Bu})_2SiHCl} + \underset{47\%}{(t\text{-Bu})_2SiCl_2} + \underset{5\%}{(t\text{-Bu})_3SiH} + \underset{7\%}{(t\text{-Bu})SiCl_2\text{-O-}t\text{-Bu}} \quad (1)$$

as tri-*tert*-butylsilane. Nearly identical results were obtained in a duplicate experiment.

The source of the tri-*tert*-butylsilane could not have been di-*tert*-butyldichlorosilane since this compound is resistant to substitution by *tert*-butyllithium under these reaction conditions and does not form tri-*tert*-butylsilane even under more drastic conditions.[9a] Likewise, although hydride displacement from organosilanes by alkyllithiums is a known