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Arylation and 1-Alkenylation on α-Position of Ketones *via* Tributyltin Enolates Catalyzed by Palladium Complex

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The reaction of tributyltin enolates, prepared from tributyltin methoxide and enol acetates *in situ*, with aryl and 1-alkenyl bromides in the presence of dichlorobis(tri-*o*-tolylphosphine)palladium was found to give α-aryl and α-(1-alkenyl) ketones, respectively, in good yields with essentially complete retention of the enol acetate regiochemistry.

Aryl and 1-alkenyl halides, except those bearing electron-withdrawing groups at the ortho and/or para positions, are usually unreactive toward nucleophilic displacement reactions, and thus fail to react with metal enolates under usual conditions.[1] Various methods of α-phenylation[2] and α-vinylation[3] of metal enolates are now developed. However, these require the strong basic conditions or multistep operations.

While organotin enolates have been shown to react both with carbonyl compounds to give addition products[4] and with alkyl halides to give coupling products,[4,5] there is no example of the reaction with aryl and 1-alkenyl halides. In our previous communications, we briefly reported that tributyltin enolates, irrespective of their tautomeric structures, α-stannyl ketones or enol stannyl ethers, reacted with aryl and 1-alkenyl halides in the presence of a catalytic amount of dichlorobis(tri-*o*-tolylphosphine)palladium to give α-aryl and α-(1-alkenyl) ketones in good yields.[6] Trial for similar coupling reaction with enol silyl ether *via* tin enolates was also reported by Kuwajima *et al.*[7] This paper describes the details of our results. The reaction is thought to proceed through the oxidative-adduct of the halides to palladium, followed by metathesis with tin compounds, and then reductive elimination.

Results and Discussion

Acetonylation of Aryl Bromides. Initial studies were focused on the palladium-catalyzed acetonylation of aryl bromides with the isolated acetonyltributyltin. The yield of phenylacetone, however, is rather low and substantial amounts of acetone are produced. These imply that the desired coupling competes with thermal decomposition of acetonyltributyltin under the prolonged heating conditions. Then, it may be desirable that relative concentration of acetonyltributyltin to organic halides is kept as small as possible. Indeed the best procedure was found to be the method in which acetonyltributyltin was prepared *in situ*.

$$\mathrm{Bu_3SnOMe + AcOCMe{=}CH_2 \longrightarrow [Bu_3SnCH_2COMe] + AcOMe}$$

$$\mathrm{[Bu_3SnCH_2COMe] + ArBr \xrightarrow{[Pd]} ArCH_2COMe + Bu_3SnBr}$$

Table 1. Pd-Catalyzed acetonylation of aryl bromides *via* acetonyltributyltin

$R\text{-}C_6H_4\text{-}Br$	Catalyst	Yield of $ArCH_2COMe$/%[a]		
H-	$Pd(Ph_3P)_4$		(22)	
H-	$PdCl_2(Ph_3P)_2$		(15)	
H-	$PdCl_2[(o\text{-}MeC_6H_4)_3P]_2$	78	(83)	(30)[b] (0)[c]
H-	$PdCl_2[(p\text{-}MeC_6H_4)_3P]_2$		(16)	
H-	$PdCl_2[(o\text{-}ClC_6H_4)_3P]_2$		(68)	
H-	$PdCl_2[(Me_3C_6H_2)_3P]_2$		(0)	
o-Me-	$PdCl_2[(o\text{-}MeC_6H_4)_3P]_2$	91		
m-Me-		88		
p-Me-		80		(27)[b]
o-Me-		90		(61)[b]
p-MeO-		51		
o-Cl-		80		
p-Cl-		73		
p-Me_2N-		71		
2,4,6-Me_3-		94		
o-Ac-		0		
p-Ac-		64		
p-CN-		0		
p-NO_2-		0		

a) Isolated yield based on bromide, GLC yield in parenthesis.
b) Reaction with PhI. c) Reaction with PhCl.

The procedure is quite simple. Thus, just heating of a stirred solution of tributyltin methoxide (15 mmol), isopropenyl acetate (15 mmol), aryl bromide (10 mmol), and palladium complex (0.1 mmol) in toluene (5 ml) under argon at 100 °C for 5 h, followed by usual work up gave arylacetone. The results are shown in Table 1.

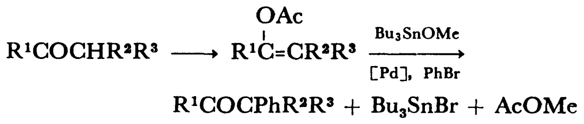
The reaction was fairly sensitive to the nature of the ligand on the dichloropalladium catalyst. The best ligand was tri-*o*-tolylphosphine. The reaction using dichlorobis(tri-*p*-tolylphosphine)palladium as a catalyst, gave only poor yield, although tri-*p*-tolylphosphine may have an electronic effect resembling to that of tri-*o*-tolylphosphine. Tris(*o*-chlorophenyl)phosphine ligand providing almost the same steric situation around palladium with that of tri-*o*-tolylphosphine was the next better ligand, but more bulkier trimesitylphosphine was not proper as ligands. Tri-*o*-tolylphosphine was previously demonstrated by Heck *et al.* to be more suitable ligand than triphenylphosphine for the palladium-catalyzed vinylation of aryl halides.[8] They explained this in terms of difference in easiness of phosphonium salt formation between the two ligands. However, even with triphenylphosphine, it was found that aryl bromide did not form phosphonium salt effectively although aryl iodide did.[9] Then, phosphonium salt formation seems not to be an essential factor influencing the efficiency of the catalyst. Although the reason why tri-*o*-tolylphosphine was effective for the present reaction is not made clear comprehensively, we feel that steric situation around palladium provided by ligand is responsible.

As shown in Table 1, among halobenzenes, bromobenzene was the best substrate. Chlorobenzene did not react with this reagent, and iodobenzene which was considered to be more reactive, gave the product in poor yields. The isolated yields were reasonably high irrespective of the substituent (Me_2N–, MeO–, Me–, Cl–, or Ac–) in aryl bromide, indicating that the reaction can be used for the preparation of arylacetone. However, there were some limitations, that is, the reaction cannot be applied to the bromide having *p*-NO_2, *p*-CN, and *o*-Ac. The presence of nitrobenzene in the reaction mixture for the acetonylation of bromobenzene did not affect the yield of phenylacetone. This means that the presence of nitro group in reacting systems does not disturb the catalytic cycle. Since the aryl bromide bearing electron-withdrawing substituent easily reacts with palladium to form the oxidative-adduct,[10] these substituent groups seem to retard subsequent steps, metathesis or reductive-elimination.

The reaction can be carried out with the substrates bearing Me–, MeO–, and Cl– at an ortho position, and even with mesityl bromide. Thus, the reaction is not sensitive to the steric effect of ortho substituents, except *o*-Ac– group, in aryl bromides.

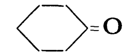
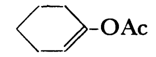
Stepwise acetonylation of *p*- and *m*-dibromobenzene could be attained by changing the molar ratio of the reactants. Usage of three molar excess of the tin enolates gave the diacetonylbenzene in 81 and 84% yield based on the corresponding dibromobenzene, respectively, while usage of three molar excess of dibromobenzenes gave *p*- and *m*-acetonylbromobenzenes in 65 and 57% yields based on the reagent, respectively. The reaction of *o*-dibromobenzene was rather complicated. Under the conditions of monoacetonylation, *o*-acetonylbromobenzene was obtained in 56% yield, but under the conditions of double acetonylation the sole isolated product was phenylacetone (13%), indicating that *o*-acetonylbromobenzene once formed was reduced under the conditions.

α-Phenylation of Ketones. Even though the α-arylation of ketones has received much attention,[2] there is still a need for a simple and regio-controlled procedure for this conversion. Since arylated acetone was effectively produced by palladium-catalyzed reaction between α-stannylacetone and aryl bromide, we tried to extend the reaction to various stannyl ketones, and to utilize the reaction for α-phenylation of ketones by the following two steps.



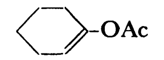
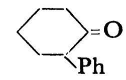
$$R^1COCHR^2R^3 \longrightarrow R^1\overset{\overset{OAc}{|}}{C}{=}CR^2R^3 \xrightarrow[\text{[Pd], PhBr}]{Bu_3SnOMe} R^1COCPhR^2R^3 + Bu_3SnBr + AcOMe$$

Table 2. Preparation of enol acetate

Ketone	Method[a)]	Enol acetate	Yield/%[b)]
$MeCOBu^t$	A	$CH_2{=}C(OAc)Bu^t$	44
MeCOPh	A	$CH_2{=}C(OAc)Ph$	69
$MeCOCH{=}CMe_2$	A	$CH_2{=}C(OAc)CH{=}CMe_2$	78
	A		88
MeCOEt	C	$CH_2{=}C(OAc)Et$	—
	A	$Me(AcO)C{=}CHMe$	47
$MeCOPr^i$	A	$CH_2{=}C(OAc)Pr^i$	34
	B	$Me(AcO)C{=}CMe_2$	76

a) A: Reaction with ketene. B: Reaction with acetic anhydride and perchloric acid. C: See Experimental part. b) Isolated yield.

Table 3. Pd-Catalyzed α-phenylation of ketones *via* tributyltin enolates

Enol acetate	Product	Yield/%[a)]
$CH_2{=}C(OAc)Bu^t$	$PhCH_2COBu^t$	86
$CH_2{=}C(OAc)Ph$	$PhCH_2COPh$	90
$CH_2{=}C(OAc)CH{=}CMe_2$	$PhCH_2COCH{=}CMe_2$	64
		54
$CH_2{=}C(OAc)Et$	$PhCH_2COEt$	(67)
$Me(AcO)C{=}CHMe$	MeCOCHPhMe	60
$CH_2{=}C(OAc)Pr^i$	$PhCH_2COPr^i$	87
$Me(AcO)C{=}CMe_2$	$MeCOCPhMe_2$	33(38)

a) Isolated yield, GLC yield in parenthesis.

The first step has been investigated thoroughly, including its regiochemistry.[11] The following method was particularly useful to prepare enol acetates used here: (A) treatment of ketone with ketene and (B) treatment of ketone with acetic anhydride and perchloric acid. Enol acetates thus prepared are shown in Table 2.

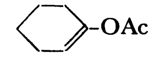
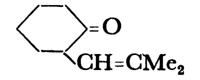
The second step is a one-pot reaction involving tributyltin enolates prepared *in situ* from the enol acetates and tributyltin methoxide as cited above. The tin enolate which would be formed *in situ* have been known to exist in either or both of tautomeric structures, α-stannyl ketones or enol stannyl ethers.[12] α-Phenyl ketones, irrespective of the tautomeric structure of the tin reagents, were obtained in reasonably high yields with complete retention of the acetate regiochemistry.

Thus, as shown in Table 3, the reaction with 2-acetoxy-1-butene and -2-butene gave exclusively 1-phenyl and 2-phenyl-butanone, respectively. Low yields from enol acetates bearing methyl substituents on the reaction site (particularly 3-methyl-2-acetoxy-2-butene) may be due to the steric hindrance. The enol ester of aldehyde cannot be used, because the produced α-phenyl aldehyde adds tributyltin methoxide.

Thus, α-arylation of ketones with complete retention of the acetate regiochemistry could be attained by two steps starting from ketones.

1-Alkenylation on α-Position of Ketones. The

Table 4. Pd-Catalyzed 1-alkenylation on α-position of ketones *via* tributyltin enolates

Enol acetate	Bromide	Product	Yield/%$^{a)}$
CH$_2$=C(OAc)Me	Me$_2$C=CHBr	Me$_2$C=CHCH$_2$COMe	62
CH$_2$=C(OAc)Bu^t	CH$_2$=CMeBr	CH$_2$=CMeCH$_2$COBu^t	53
	Me$_2$C=CHBr	Me$_2$C=CHCH$_2$COBu^t	81
	Me$_2$C=CMeBr	Me$_2$C=CMeCH$_2$COBu^t	86
	(*E*) MeCH=CMeBr	(*E*) MeCH=CMeCH$_2$COBu^t	76
	(*Z*) MeCH=CMeBr	(*Z*) MeCH=CMeCH$_2$COBu^t	90
CH$_2$=C(OAc)Ph	Me$_2$C=CHBr	Me$_2$C=CHCH$_2$COPh$^{b)}$	74
			32
CH$_2$=C(OAc)Et		Me$_2$C=CHCH$_2$COEt	(53)
Me(AcO)C=CHMe		MeCOCHMeCH=CMe$_2$	35
CH$_2$=C(OAc)Pr^i		Me$_2$C=CHCH$_2$COPr^i	74
Me(AcO)C=CMe$_2$		MeCOCMe$_2$CH=CMe$_2$	(8)

a) Isolated yield based on bromide, GLC yield in parenthesis. b) α,β-Unsaturated ketone was detected by NMR. (*ca.* 5%).

success of α-arylation of ketones *via* tin enolates catalyzed by palladium complex suggests that similar reaction can be applied to the reaction between tin enolates and 1-alkenyl bromides, which may give allylic ketones. We found that various allylic ketones were obtained in good yields under the conditions similar to those for the reaction of aryl bromide. Results are shown in Table 4.

The reaction seems sensitive to steric hindrance caused by substituent on enol acetate. The reaction of enol acetates bearing terminal methylene gave the 1-alkenylated ketones generally in high yields, while lower yields were obtained for the substrates having substituents on the reaction site. Number and position of substituents on 1-alkenyl bromide seem not to give the serious effect on the product yield. The configuration of 1-alkenyl bromide was completely retained. Thus from (*E*)- and (*Z*)-2-bromo-2-butene, (*E*)- and (*Z*)-2,2,5-trimethyl-5-hepten-3-one were obtained exclusively, respectively.

Experimental

Materials. Tributyltin methoxide was prepared by the reaction of tributyltin chloride with sodium methoxide.[13] *o*-Bromotoluene,[14] *o*-chlorobromobenzene,[15] *o*-bromoanisole,[15] mesityl bromide,[16] 2-bromopropene,[17] 3-methyl-2-bromo-2-butene,[18] 2-methyl-1-bromo-2-propene,[18] (*E*)-2-bromo-2-butene,[18] (*Z*)-2-bromo-2-butene,[17] triarylphosphines,[19] tetrakis(triphenylphosphine)palladium,[20] and dichlorobis(triarylphosphine)palladium[21] were prepared from the method described in literatures. 3,3-Dimethyl-2-acetoxy-1-butene, α-acetoxystyrene, 1-cyclohexenyl acetate, 4-methyl-2-acetoxy-1,3-pentadiene, 2-acetoxy-2-butene, and 3-methyl-2-acetoxy-1-butene were prepared by treatment of the corresponding ketones with ketene in the presence of small amounts of sulfuric acid.[11a] 3-Methyl-2-acetoxy-2-butene was prepared by treatment of the ketone with acetic anhydride and perchloric acid.[11b] 2-Acetoxy-1-butene which could be prepared by treatment of the ketone with triphenylmethyllithium followed by acetic anhydride was not obtained by the method.[11c,d] Then it was prepared by the addition of acetic acid to 1-butyne in the presence of mercury(II) acetate.[11e] Other substrates were available commercially and used after distillation or recrystallization.

Reaction Procedures. A stirred solution of tributyltin methoxide (15 mmol), a particular enol acetate (15 mmol), bromobenzene or 1-alkenyl bromide (10 mmol), and PdCl$_2$[(*o*-MeC$_6$H$_4$)$_3$P]$_2$ (0.1 mmol) in toluene (5 ml) was heated under argon at 100 °C for 5 h. After evaporation of the solvent and methyl acetate, column chromatograph of the residue (silica gel; cyclohexane followed by diethyl ether as eluants) provided the α-phenyl or α-(1-alkenyl) ketone in the ethereal elute, from which the products were isolated by distillation under reduced pressure. Some α-(1-alkenyl) ketones were obtained by distilling the reaction mixture directly under reduced pressure.

Products. The structure of the products were deduced based on the analytical and spectroscopic data recorded here. Boiling points were uncorrected.

Phenylacetone: Bp 88—92 °C/15 mmHg (1 mmHg=133.322 Pa). IR Aldrich 742A.[22] ^{1}H NMR (CCl$_4$) δ=2.00 (s, 3H), 3.50 (s, 2H), and 7.30 (s, 5H).

o-*Tolylacetone*: Bp 97—99 °C/16 mmHg. IR (neat) 1718 (C=O), 1605 (C=C), and 1498 cm^{-1} (C=C). ^{1}H NMR (CCl$_4$) δ=2.01 (s, 3H), 2.25 (s, 3H), 3.62 (s, 2H), and 7.14 (s, 4H). MS (20 eV) *m/e* (rel intensity) 148 (M$^+$, 73), 106 (82), 105 (100), and 43 (100). Found: C, 81.16; H, 8.08%. Calcd for C$_{10}$H$_{12}$O: C, 81.08; H, 8.16%.

m-*Tolylacetone*: Bp 95—97 °C/14 mmHg. IR (neat) 1715 (C=O), 1605 (C=C), and 1490 cm^{-1} (C=C). ^{1}H NMR (CCl$_4$) δ=2.04 (s, 3H), 2.31 (s, 3H), 3.51 (s, 2H), and 6.80—7.35 (m, 4H). MS (20 eV) *m/e* (rel intensity) 148 (M$^+$, 98), 106 (100), 105 (100), and 43 (100). Found: C, 80.67; H, 8.05%. Calcd for C$_{10}$H$_{12}$O: C, 81.04; H, 8.16%.

p-*Tolylacetone*: Bp 122—125 °C/35 mmHg. IR (neat) 1710 (C=O), 1605 (C=C), and 1512 cm^{-1} (C=C). ^{1}H NMR (CCl$_4$) δ=2.00 (s, 3H), 2.30 (s, 3H), 3.49 (s, 2H), and 7.00 (s, 4H). MS (30 eV) *m/e* (rel intensity) 148 (M$^+$, 15), 106 (32), 105 (100), and 43 (100). Found: C, 81.38; H, 8.46%. Calcd for C$_{10}$H$_{12}$O: C, 81.04; H, 8.16%.

p-*Methoxyphenylacetone*: Bp 88—90 °C/3 mmHg. IR (neat) 1710 (C=O), 1610 (C=C), 1512 (C=C), and 1248 cm^{-1} (C-O-C). ^{1}H NMR (CCl$_4$) δ=2.02 (s, 3H), 3.49 (s, 2H), 3.80 (s, 3H), and 6.61, 6.94 (ABq, *J*=9 Hz, 4H). MS

(20 eV) *m/e* (rel intensity) 164 (M^+, 7) 149 (10), 121 (33), and 43 (100). Found: C, 72,77; H, 7.43%. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37%.

o-*Methoxyphenylacetone*: Bp 118 °C/15 mmHg. IR (neat) 1718 (C=O), 1603 (C=C), 1498 (C=C), and 1250 cm^{-1} (C-O-C). ^{1}H NMR (CCl_4) δ=2.00 (s, 3H), 3.55 (s, 2H), 3.80 (s, 3H), and 6.67—7.35 (m, 4H). MS (20 eV) *m/e* (rel intensity) 164 (M^+, 100), 122 (100), 121 (100), and 43 (100).

p-*Chlorophenylacetone*: Bp 115—117 °C/15 mmHg. IR (neat) 1717 (C=O), 1598 (C=C), and 1491 cm^{-1} (C=C). ^{1}H NMR (CCl_4) δ=2.05 (s, 3H), 3.51 (s, 2H), and 6.97, 7.20 (ABq, J=8 Hz, 4H). MS (20 eV) *m/e* (rel intensity) 170 (M^+, 3), 168 (10), 127 (9), 125 (30), and 43 (100). Found: C, 64.15; H, 5.56%. Calcd for C_9H_9OCl: C, 64.11; H, 5.38%.

o-*Chlorophenylacetone*: Bp 119 °C/18 mmHg. IR (neat) 1726 (C=O), 1573 (C=C), and 1473 cm^{-1} (C=C). ^{1}H NMR (CCl_4) δ=2.09 (s, 3H), 3.71 (s, 2H), and 7.05—7.60 (m, 4H). MS (20 eV) *m/e* (rel intensity) 168 (1), 127 (9), 125 (27), and 43 (100).

p-*(Dimethylamino)phenylacetone*: Bp 103—104 °C/2.5 mmHg. IR (neat) 1710 (C=O), 1610 (C=C), 1520 (C=C), and 1350 cm^{-1} (C-N). ^{1}H NMR (CCl_4) δ=1.95 (s, 3H), 2.95 (s, 6H), 3.44 (s, 2H), and 6.61, 7.01 (ABq, J=9 Hz, 4H). MS (20 eV) *m/e* (rel intensity) 177 (M^+, 13), 134 (100), and 43 (7).

p-*Acetylphenylacetone*: Bp 128—130 °C/2.5 mmHg, mp 43—44 °C. IR (neat) 1718 (C=O), 1680 (C=O), 1603 (C=C), and 1508 cm^{-1} (C=C). ^{1}H NMR (CCl_4) δ=2.01 (s, 3H), 3.45 (s, 3H),3.59 (s, 2H), and 7.16, 7.79 (ABq, J=8 Hz, 4H). MS (30 eV) *m/e* (rel intensity) 176 (M^+, 2), 161 (9), 134 (100), 133 (10), 119 (20), 91 (49), and 43 (100). Found: C, 75.17; H, 6.85%. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H 6.86%.

Mesitylacetone: Bp 130 °C/10 mmHg, mp 60 °C. IR (neat) 1720 (C=O), 1611 (C=C), and 1487 cm^{-1} (C=C). ^{1}H NMR (CCl_4) δ=1.98 (s, 3H), 2.20 (s, 9H), 3.53 (s, 2H), and 6.75 (s, 2H). MS (20 eV) *m/e* (rel intensity) 176 (M^+, 24), 134 (16), 133 (100), and 43 (18). Found: C, 81.81; H, 9.54%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

p-*Diacetonylbenzene*: Bp 118 °C/0.5 mmHg, mp 46—47 °C. IR (neat) 1715 (C=O), 1610 (C=C), and 1511 cm^{-1} (C=C). ^{1}H NMR (CCl_4) δ=2.07 (s, 6H), 3.58 (s, 4H), and 7.10 (s, 4H). MS (20 eV) *m/e* (rel intensity) 190 (M^+, 13), 148 (78), 147 (13), 105 (40), and 43 (100). Found: C, 75.75; H, 7.65%. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%.

m-*Diacetonylbenzene*: Bp 127 °C/2 mmHg. IR (neat) 1712 (C=O), 1602 (C=C), and 1487 cm^{-1} (C=C). ^{1}H NMR (CCl_4) δ=2.08 (s, 6H), 3.59 (s, 4H), and 6.93—7.28 (m, 4H). MS (20 eV) *m/e* (rel intensity) 190 (M^+, 9), 148 (18), 147 (21), 105 (21), and 43 (100). Found: C, 75.57; H, 7.24%. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%.

p-*Bromophenylacetone*: Bp 91—92 °C/1 mmHg. IR (neat) 1718 (C=O), 1592 (C=C), and 1488 cm^{-1} (C=C). ^{1}H NMR (CCl_4) δ=2.10 (s, 3H), 3.58 (s, 2H), and 7.05, 7.47 (ABq, J=9 Hz, 4H). MS (20 eV) *m/e* (rel intensity) 214 (M^+, 27), 212 (28), 171 (32), 169 (30), and 43 (100). Found: C, 50.62; H, 4.71%. Calcd for C_9H_9OBr: C, 50.73; H, 4.26%.

m-*Bromophenylacetone*: Bp 83 °C/0.3 mmHg. IR (neat) 1718 (C=O), 1591 (C=C), and 1471 cm^{-1} (C=C). ^{1}H NMR (CCl_4) δ=2.10 (s, 3H), 3.59 (s, 2H), and 7.05—7.50 (m, 4H). MS (20 eV) *m/e* (rel intensity) 214 (M^+, 63), 212 (64), 171 (14), 169 (14), and 43 (100).

o-*Bromophenylacetone*: Bp 88—92 °C/0.6 mmHg. IR (neat) 1722 (C=O), 1597 (C=C), and 1472 cm^{-1} (C=C). ^{1}H NMR (CCl_4) δ=2.11 (s, 3H), 3.73 (s, 2H), and 6.90—7.70 (m, 4H). MS (20 eV) *m/e* (rel intensity) 171 (100), 169 (100), and 43 (100).

1-Phenyl-2-butanone: Bp 102—103 °C/15 mmHg. IR Aldrich 742C.[22] ^{1}H NMR (CCl_4) δ=0.96 (t, J=7 Hz, 3H), 2.35 (q, J=7 Hz, 2H), 3.55 (s, 2H), and 7.19 (s, 5H).

3-Phenyl-2-butanome: Bp 94—95 °C/14 mmHg. (107 °C/22 mmHg)[23] IR (neat) 1718 (C=O), 1600 (C=C), and 1496 cm^{-1}(C=C). ^{1}H NMR (CCl_4) δ=1.35 (d, J=7 Hz, 3H), 1.97 (s, 3H), 3.68 (q, J=7 Hz, 1H), and 7.25 (s, 5H). MS (20 eV) *m/e* (rel intensity) 148 (M^+, 29), 133 (9), 106 (25), 105 (100), and 43 (100). Found: C, 80.62; H, 8.25%. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16%.

1-Phenyl-3-methyl-2-butanone: Bp 114—115 °C/25 mmHg. IR (neat) 1712 (C=O), 1602 (C=C), and 1496 cm^{-1} (C=C). ^{1}H NMR (CCl_4) δ=1.05 (d, J=7 Hz, 6H), 2.61 (h, J=7 Hz, 1H), 3.61 (s, 2H), and 7.18 (s, 5H). MS (20 eV) *m/e* (rel intensity) 162 (M^+, 27), 119 (5), 92 (22), 91 (100), 71 (100), 44 (19), and 43 (100). Found: C, 81.79; H, 8.45%. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70%.

3-Phenyl-3-methyl-2-butanone: Mp 99—101 °C/16.5 mmHg, Ir, (neat) 1710 (C=O), 1599 (C=C), and 1495 cm^{-1} (C=C). ^{1}H NMR (CCl_4) δ=1.43 (s, 6H), 1.81 (s, 3H), and 7.19 (s, 5H). MS (20 eV) *m/e* (rel intensity) 162 (M^+, 6), 120 (36), 119 (100), 43 (25), and 15 (9). Found C, 80.86; H, 8.78%. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70%.

1-Phenyl-3,3-dimethyl-2-butanone: Bp 110—111 °C/18 mmHg. IR (neat) 1710 (C=O), 1600 (C=C), and 1493 cm^{-1} (C=C). ^{1}H NMR (CCl_4) δ=1.15 (s, 9H), 3.70 (s, 2H), and 7.20 (s, 5H). MS (20 eV) *m/e* (rel intensity) 176 (M^+, 2), 119 (1), 92 (26), 91 (28), 85 (100), 58 (25), and 57 (100). Found: C, 82.14; H, 9.00%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

2-Phenylcyclohexanone: Bp 143—145 °C/14 mmHg, mp 58—59 °C (155 °C/13 mmHg, 60 °C)[24] IR Aldrich 742E.[22]

1-Phenyl-4-methyl-3-penten-2-one: Bp 80—81 °C/1.5 mmHg. IR (neat) 1685 (C=O), 1618 (C=C), and 1496 cm^{-1} (C=C). ^{1}H NMR (CCl_4) δ=1.79 (s, 3H), 2.07 (s, 3H), 3.52 (s, 2H), 5.88 (s, 1H), and 7.19 (s, 5H). MS (20 eV) *m/e* (rel intensity) 174 (M^+, 14), 119 (3), 92 (3), 91 (34), 83 (100), 56 (5), and 55 (69). Found: C, 82.37; H, 8.26%. Calcd for $C_{12}H_{14}O$: C, 82.77; H, 8.10%.

Phenylacetophenone: Bp 115—117 °C/1 mmHg, mp 54—55 °C (160 °C/5 mmHg, 56 °C)[25] IR Aldrich 748E.[22]

5-Methyl-4-hexen-2-one: Bp 43—45 °C/17 mmHg. IR (neat) 1720 cm^{-1} (C=O). ^{1}H NMR (CCl_4) δ=1.65 (s, 3H), 1.73 (s, 3H), 2.06 (s, 3H), 2.98 (d, J=7 Hz, 2H), and 5.23 (t, J=7 Hz, 1H). MS (20 eV) *m/e* (rel intensity) 112 (M^+, 100), 97 (100), 70 (100), 69 (100), 43 (100), and 15 (13). Found: C, 75.31; H, 11.12%. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78%.

4,5-Dimethyl-4-hexen-2-one: Bp 53 °C/21 mmHg. IR (neat) 1712 cm^{-1} (C=O). ^{1}H NMR (CCl_4) δ=1.69 (s, 9H), 2.01 (s, 3H), and 3.01 (s, 2H). MS (20 eV) *m/e* (rel intensity) 126 (M^+, 93), 111 (100), 84 (100), 83 (100), 43 (100), and 15 (8). Found: C, 75.83; H, 11.18%. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18%.

6-Methyl-5-hepten-3-one: IR (neat) 1718 cm^{-1}(C=O). ^{1}H NMR (CCl_4) δ=1.03 (t, J=7 Hz, 3H), 1.67 (s, 3H), 1.79 (s, 3H), 2.38 (q, J=7 Hz, 2H), 3.01 (d, J=7 Hz, 2H), and 5.30 (t, J=7 Hz, 1H). MS (20 eV) *m/e* (rel intensity) 126 (M^+, 10), 97 (7), 70 (2), 69 (23), 57 (100), and 29 (74). Found: C, 75.63; H, 11.20%. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18%.

3,5-Dimethyl-4-hexen-2-one: Bp 56—58 °C/20 mmHg. IR (neat) 1715 cm^{-1} (C=O). ^{1}H NMR (CCl_4) δ=1.05 (d, J=7 Hz, 3H), 1.73 (s, 6H), 3.29 (d of q, J=10 and 7 Hz, 1H), and 4.98 (d, J=10 Hz, 1H). Found: C, 76.34; H, 11.51%. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18%.

2,6-Dimethyl-5-hepten-3-one: Bp 69—70 °C/20 mmHg. IR (neat) 1712 cm^{-1} (C=O). ^{1}H NMR (CCl_4) δ=1.09 (d, J=7 Hz, 6H), 1.62 (s, 3H), 1.74 (s, 3H), 2.55 (h, J=7 Hz, 1H), 3.05 (d, J=7 Hz, 2H), and 5.27 (t, J=7 Hz, 1H). MS (20 eV) *m/e* (rel intensity) 140 (M^+, 69), 97 (59), 71 (100), 70 (63), 69 (100), 44 (93), and 43 (100). Found: C, 76.85; H, 11.44%. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50%.

3,3,5-Trimethyl-4-hexen-2-one: IR (neat) 1709 cm^{-1} (C=O). ^{1}H NMR (CCl_4) δ=1.17 (s, 6H), 1.49 (s, 3H), 1.71 (s, 3H), 2.02 (s, 3H), and 5.27 (s, 1H). MS (20 eV) *m/e* (rel intensity) 140 (M$^+$, 37), 95 (100), and 43 (62). Found: C, 76.65; H, 11.70%. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50%.

2,2,5-Trimethyl-5-hexen-3-one: Bp 62—63 °C/34 mmHg. IR (neat) 1713 cm^{-1} (C=O). ^{1}H NMR (CCl_4) δ=1.15 (s, 9H), 1.71 (s, 3H), 3.11 (s, 2H), 4.67 (s, 1H), and 4.81 (s, 1H). MS (20 eV) *m/e* (rel intensity) 140 (M$^+$, 53), 85 (100), 83 (100), 58 (38), 57 (100), 56 (38), and 55 (68). Found: C, 76.81; H, 11.63%. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50%.

2,2,6-Trimethyl-5-hepten-3-one: Bp 72—73 °C/19 mmHg. IR (neat) 1710 cm^{-1} (C=O). ^{1}H NMR (CCl_4) δ=1.10 (s, 9H), 1.60 (s, 3H), 1.73 (s, 3H), 3.11 (d, J=7 Hz, 2H), and 5.24 (t, J=7 Hz, 1H). MS (20 eV) *m/e* (rel intensity) 154 (M$^+$, 4), 97 (19), 85 (77), 70 (18), 69 (46), 58 (18), and 57 (100). Found: C, 77.93; H, 11.95%. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76%.

2,2,5,6-Tetramethyl-5-hepten-3-one: Bp 79—80 °C/16 mmHg. IR (neat) 1715 cm^{-1} (C=C). ^{1}H NMR (CCl_4) δ=1.17 (s, 9H), 1.58 (s, 6H), and 1.70 (s, 3H). MS (20 eV) *m/e* (rel intensity) 168 (M$^+$, 19), 111 (29), 85 (99), 84 (28), 83 (64), 58 (28), and 57 (100). Found: C,78.42; H, 11.97%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

(*E*)*-2,2,5-Trimethyl-5-hepten-3-one*: Bp 70—71 °C/15 mmHg. IR (neat) 1710 cm^{-1} (C=O). ^{1}H NMR (CCl_4) δ= 1.15 (s, 9H), 1.58 (s, 3H), 1.60 (d, J=7 Hz, 3H), 3.08 (s, 2H), and 5.15 (t, J=7 Hz, 1H). ^{13}C NMR 26.4 (q), 214 (s), 47 (t), 130 (s), 123 (d), 13.5 (q), 16.1 (q), and 44.4 (s), MS (20 eV) *m/e* (rel intensity) 154 (M$^+$, 20), 97 (64), 85 (100), 70 (82), 69 (100), 58 (79), and 57 (100). Found: C, 77.72; H, 11.79%. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76%.

(*Z*)*-2,2,5-Trimethyl-5-hepten-3-one*: Bp 67—69 °C/14 mmHg. IR (neat) 1711 cm^{-1} (C=O). ^{1}H NMR (CCl_4) δ= 1.16 (s, 9H), 1.50 (d, J=7 Hz, 3H), 1.60 (s, 3H), 3.12 (s, 2H), and 5.30 (q, J=7 Hz, 1H). ^{13}C NMR 26.4 (q), 44.5 (s), 213 (s), 39.3 (t), 129.9 (s), 123.0 (d), 13.5 (q), and 24.1 (q). MS (20 eV) *m/e* (rel intensity) 154 (M$^+$, 15), 97 (61), 85 (100), 70 (75), 69 (97), 58 (71), and 57 (100). Found: C, 77.62; H, 11.78%. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76%.

2-(2-methyl-1-propenyl)cyclohexanone: Bp 95—97 °C/15 mmHg. IR (neat) 1710 cm^{-1} (C=O). ^{1}H NMR (CCl_4) δ=1.60 (s, 3H), 1.75 (s, 3H), 1.50—2.15 (m, 6H), 2.15—2.50 (m, 2H), and 2.70—3.55 (m, 1H). MS (20 eV) *m/e* (rel intensity) 152 (M$^+$, 15), 137 (26), 109 (36), 95 (37), 93 (30), 81 (57), 67 (100), and 43 (36).

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