New Cross Aldol Reactions. Titanium Tetrachloride-promoted Reactions of Silyl Enol Ethers with Carbonyl Compounds Containing A Functional Group

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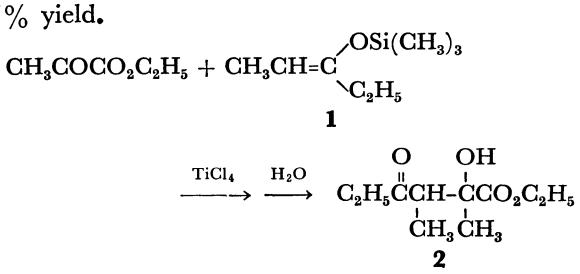
It was found that, in the presence of titanium tetrachloride, silyl enol ethers selectively react with aldehyde or ketone function of various carbonyl compounds containing another functional group giving the corresponding cross aldols in good yields. The present cross aldol reaction was successfully applied to the synthesis of ar-turmerone, one of the volatile principles of turmeric oil.

In previous paper,[1-3] it was reported that the reactions of silyl enol ethers with various simple carbonyl compounds in the presence of titanium tetrachloride proceed under mild conditions giving the desired cross aldols in good yields. According to this procedure, it was established that cross aldols are exclusively produced in most cases and no by-products, such as the di-, poly-, and self-condensation products, and α,β-unsaturated carbonyl compounds formed in the usual base-promoted aldol condensation, are produced. Therefore, it is recognized that this reaction is one of the most useful cross aldol processes among the methods reported by House[4] *et al.* and Wittig[5] *et al.*

In the present paper, the titanium tetrachloride-promoted reaction of silyl enol ethers with a variety of carbonyl compounds containing an additional functional will be described.

In the first experiment, the reaction of ethyl pyruvate with silyl enol ether (**1**) in the presence of an equimolar amount of titanium tetrachloride was attempted at room temperature. After hydrolysis, ethyl 2-hydroxy-2,3-dimethyl-4-oxohexanoate (**2**) was obtained in an 87% yield.



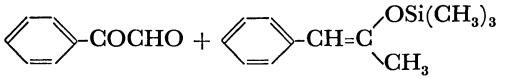
1

2

The effect of the amount of titanium tetrachloride upon the yield of **2** was investigated using the reaction of ethyl pyruvate with **1** as a model and **2** was obtained in the highest yield when an equimolar amount of titanium tetrachloride was employed.

The reactions of various silyl enol ethers with a variety of keto esters were attempted in the presence of an equimolar amount of titanium tetrachloride. These results are given in Table 1. Of these keto esters, it was found that ethyl acetoacetate did not react with silyl enol ethers under the same conditions and was recovered quantitatively.

In the next experiment, the reaction of silyl enol ethers with various dicarbonyl compounds was studied. For example, when silyl enol ether (**17**) was allowed to react with an equimolar amount of phenylglyoxal at −78 °C for 2 h, 2-hydroxy-1,3-diphenyl-1,4-pentanedione (**18**) was obtained exclusively in an 83% yield, and none of the product added to the ketone function was detected.



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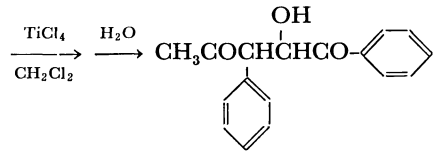
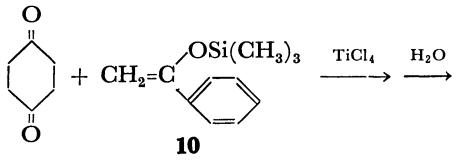


18

Unexpectedly, in the case of the reaction of 1,4-cyclohexanedione with an equimolar amount of the silyl enol ether (**10**), 1,4-bis(benzoylmethyl)-1,4-cyclohexanediol (**19**) was obtained in an 86% yield (based on **10**), and no 4-hydroxy-4-(benzoylmethyl)-1-cyclohexanone was detected by NMR and TLC analyses.



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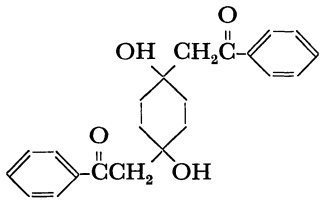
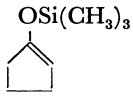
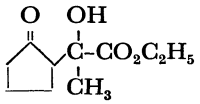
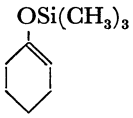
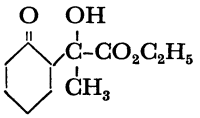
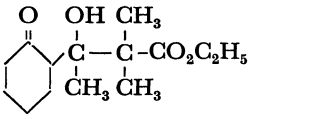
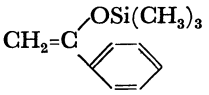
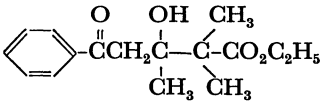
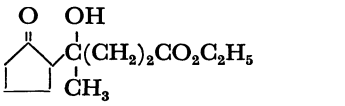
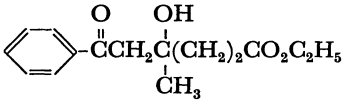
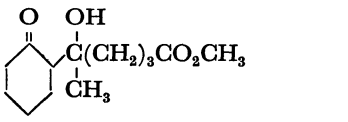


19

As described above, it should be noted that the silyl enol ether reacted only with the aldehyde function of the keto aldehyde in the presence of titanium tetrachloride at −78 °C giving the corresponding hydroxy diketone, and the silyl enol ether selectively reacted with the ketone function of the keto ester at room temperature to give the corresponding hydroxy keto ester. However, when the diketone was treated with an equimolar amount of the silyl enol ether, the latter reacted with both the ketone functions of the diketone.

Of the usual protecting groups of the carbonyl function examined,[6] it was found that only thioacetal[7] was stable and useful in the present reaction. Thus,

TABLE 1. SYNTHESIS OF HYDROXY KETO ESTERS FROM SILYL ENOL ETHERS AND KETO ESTERS

Reagents		Product	
Keto ester	Silyl enol ether	Hydroxy keto ester	Yield (%)
$CH_3COCO_2C_2H_5$	$CH_2=C(OSi(CH_3)_3)CH_3$ **3**	$CH_3C(=O)CH(OH)CH_2CO_2C_2H_5$ (CH_3) **4**	55
	 **5**	 **6**	76
	 **7**	 **8**	88
$CH_3CO-C(CH_3)(CO_2C_2H_5)-CH_3$	**7**	 **9**	52
	 **10**	 **11**	38
$CH_3CO(CH_2)_2CO_2C_2H_5$	**1**	$C_2H_5C(=O)CH(CH_3)-C(CH_3)-(CH_2)_2CO_2C_2H_5$ **12**	86
$CH_3CO(CH_2)_2CO_2C_2H_5$	**5**	 **13**	73
	10	 **14**	41
$CH_3CO(CH_2)_3CO_2CH_3$	**1**	$C_2H_5C(=O)CH(CH_3)-C(CH_3)-(CH_2)_3CO_2CH_3$ **15**	71
	7	 **16**	69

aldol formation at one of the keto groups in a diketone was performed after converting the other keto groups into its thioacetal. For example, when silyl enol ether (**3**) was allowed to react with 6,6-ethylenedithio-1-phenyl-3-heptanone in the presence of titanium tetrachloride, 7,7-ethylenedithio-4-hydroxy-4-phenethyl-2-octanone (**20**) was obtained in a 76% yield.

Next, in order to examine the influence of various functional groups on the titanium tetrachloride-promoted reaction of silyly enol ethers with carbonyl

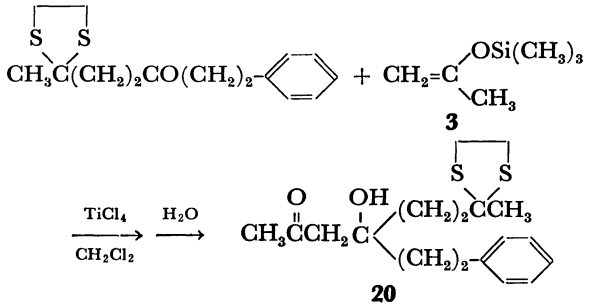


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Table 2. Synthesis of aldols from silyl enol ethers and carbonyl compounds having a functional group

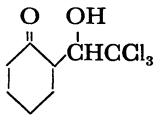
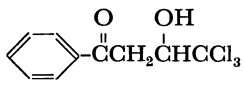
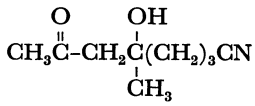
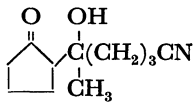
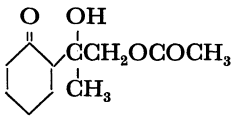
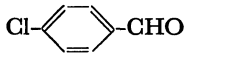
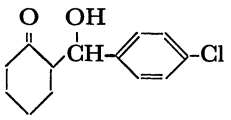
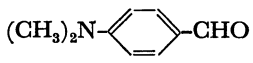
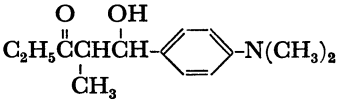
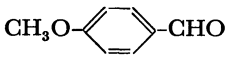
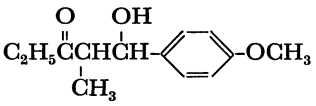
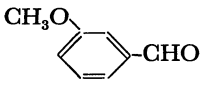
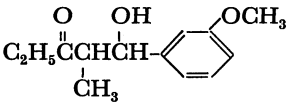
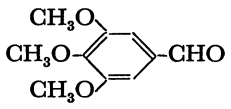
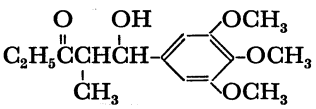
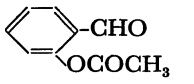
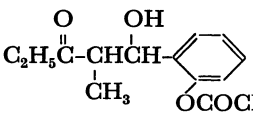
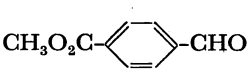
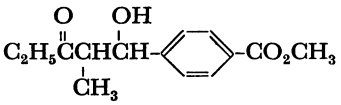
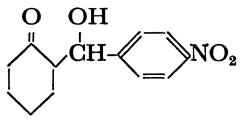
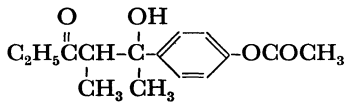
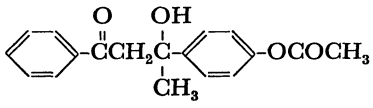
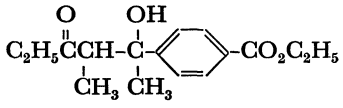
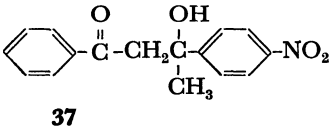
Reagents: Carbonyl compound	Reagents: Silyl enol ether	Reaction conditions: temp (°C)	Reaction conditions: time (h)	Product: Aldol	Product: Yield (%)
CCl_3CHO	**7**	−78	1	 **21**	94
	10	−78	1	 **22**	92
$CH_3CO(CH_2)_3CN$	**3**	0	1	 **23**	52
	5	0	1	 **24**	73
$CH_3COCH_2OCOCH_3$	**7**	0	1	 **25**	34
	**7**	−10	3	 **26**	86
	**1**	−10	3	 **27**	65
	**1**	−10	3	 **28**	82
	**1**	−10	3	 **29**	88
	**1**	−10	3	 **30**	82
	**1**	−10	3	 **31**	78
	**1**	−10	3	 **32**	86

TABLE 2. (Continued)

Reagents: Carbonyl compound	Reagents: Silyl enol ether	Reaction conditions: temp (°C), time (h)	Product: Aldol	Product: Yield (%)
O_2N-C$_6$H$_4$-CHO	**7**	−10, 3	 **33**	85
CH_3CO-C$_6$H$_4$-$COCH_3$	**1**	40, 3	 **34**	36
	10	40, 3	 **35**	11
$C_2H_5O_2C$-C$_6$H$_4$-$COCH_3$	**1**	Room temp, 3	 **36**	68
O_2N-C$_6$H$_4$-$COCH_3$	**10**	Room temp, 3	 **37**	52

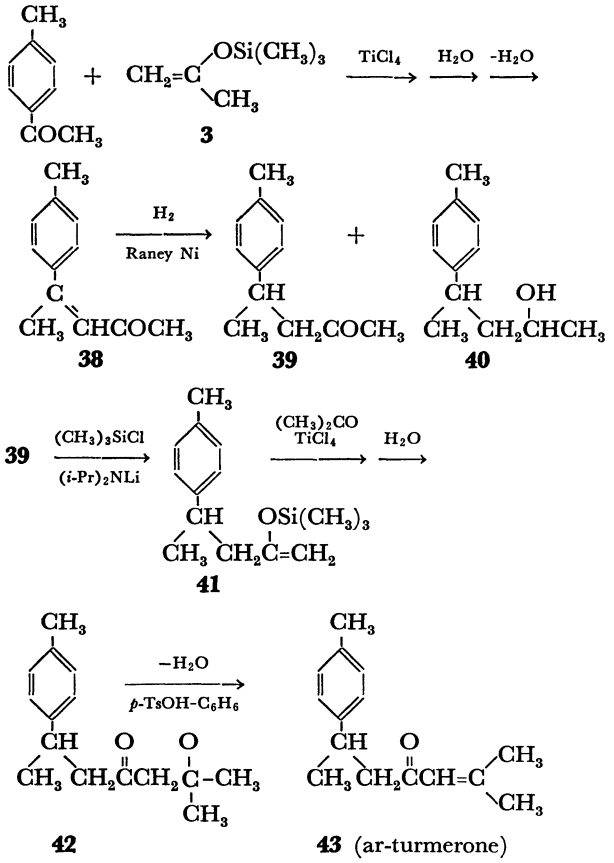
compounds, the reaction of silyl enol ethers with a variety of aliphatic and aromatic carbonyl compounds having, acyloxy, alkoxy, carboxy, amino, cyano, halogeno, hydroxy, and nitro substituents was investigated. The results are summarized in Table 2.

As shown is in Table 2, it is apparent that the titanium tetrachloride-promoted aldol reaction using silyl enol ethers is not influenced by groups such as acyloxy, alkoxyl, cyano, dialkylamino, halogeno, nitro, and thioacetal groups. However, in the cases of the carbonyl compounds containing active hydrogen, such as carboxyl, hydroxyl, primary amino, and secondary amino groups, no aldols were obtained and the silyl enol ethers were decomposed into the original carbonyl compounds. In these cases, it is believed that, at first, the carbonyl compound with active hydrogen reacted with titanium tetrachrloride to produce hydrogen chloride, which in turn rapidly reacted with the silyl enol ether to form the original carbonyl compound.

It was also established that the aldols were obtained by reactions of silyl enol ethers with various substituted aromatic aldehydes. In the cases of substituted aromatic ketones having an electron-attracting group, aldols were produced, but aromatic ketones having an electron-releasing group did not afford aldols for the same reaction procedure.

The utility of this new procedure was demonstrated by the synthesis of ar-turmerone,[8,9] 2-methy-6-*p*-tolyl-2-heptene-4-one, one of the volatile principles of turmeric oil.[10,11]

By dehydration of the reaction product of 4-methylacetophenone with the silyl enol ether (**3**) in the presence



of titanium tetrachloride, the α,β-unsaturated ketone (**38**) was obtained in a 53% yield, and the catalytic reduction of **38** over Raney nickel afforded the ketone

(**39**) and the alcohol (**40**) in 77% and 16% yields, respectively. The silyl enol ether (**41**), prepared from **39** according to the method of House *et al.*[12] was treated with acetone and titanium tetrachloride giving the aldol (**42**) in a 88% yield. This was dehydrated with *p*-toluenesulfonic acid–benzene to give racemic ar-turmerone (**43**) in a 92% yield. In summary, it is concluded that, in the presence of titanium tetrachloride, various silyl enol ethers react with a variety of aliphatic and aromatic carbonyl compounds containing an additional functional group, except for functional groups having active hydrogen, affording the corresponding aldols in good yields. The selective reaction forming an aldol in one of the carbonyl groups of a dialdehyde or a diketone occurs after converting the other carbonyl group into its thioacetal.

Experimental

Materials. Commercially available carbonyl compounds having the functional group, $TiCl_4$ and chlorotrimethylsilane were purified by the conventional procedures, recrystallization or distillation, before use. A commercial hexane solution of *n*-BuLi was used after standarization and commercially produced Raney nickel was thoroughly washed with methanol. 6,6-Ethylenedithio-1-phenyl-3-heptanone was prepared by the method of Araki *et al.*[13]

Methyl 6-oxohexanoate and 5-oxohexanenitril were prepared from ethyl acetoacetate and acrylonitrile according to a procedure in the literature.[14]

Trimethylsilyl enol ethers of ketones have been described in a previous paper.[3]

*Reaction of Ethyl Pyruvate with 3-Trimethylsiloxy-2-pentene (**1**)* To a dichloromethane (15 ml) solution of ethyl pyruvate (0.390 g, 3 mmol) and $TiCl_4$ (0.567 g, 3 mmol) was added a dichloromethane (30 ml) solution of silyl enol ether (**1**) (0.468 g, 3 mmol) at room temperature in an argon atmosphere, and the mixture was kept at room temperature for 3 h with stirring. After hydrolysis with cold water (30 ml), the resulting organic layer was extracted with ether (70 ml). The extract was washed with a saturated NaCl solution and dried over anhydrous Na_2SO_4. The ethereal solution was concentrated under reduced pressure. The aldol, ethyl 2-hydroxy-2,3-dimethyl-4-oxohexanoate (**2**), was obtained in an 87% (0.527 g) yield from the residue after purification by column chromatography (silica gel). The physical properties and analytic data of the product (**2**) are shown in Table. 3.

*Reaction of 6,6-Ethylenedithio-1-phenyl-3-heptanone with 2-Trimethylsiloxypropene (**3**).* As in the same procedure described above, 6,6-ethylenedithio-1-phenyl-3-heptanone (0.843 g, 3 mmol) reacted with silyl enol ether (**3**) (0.390 g, 3 mmol) in dichloromethane (40 ml) in the presence of $TiCl_4$ (0.567 g, 3 mmol) at 0 °C for 3 h. The reaction mixture was worked up as in the preparation of **2** to give a crude oil. It was purified by preparative TLC (silica gel) using dichloromethane to give 0.767 g (76%) of 7,7-ethylenedithio-4-hydroxy-4-phenethyl-2-octanone (**20**). The physical properties and analytical data of **20** are shown in Table 3.

Reaction of p-*Dimethylaminobenzaldehyde with 3-Trimethylsiloxy-2-pentene (**1**).* In a procedure similar to that described above, p-dimethylaminobenzaldehyde (0.450 g, 3 mmol) reacted with silyl enol ether (**1**) (0.474 g, 3 mmol) in dichloromethane (40 ml) in the presence of $TiCl_4$ (0.567 g, 3 mmol) at −10 °C for 3 h. The reaction mixture was quenched with aq. 5% K_2CO_3 (30 ml) at 0 °C, and the suspension was kept standing at room temperature for 10 min. After filtration, the filtrate was extracted with ether (100 ml). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (aluminium oxide active, neutral) to give 1-(*p*-dimethylaminophenyl)-1-hydroxyl-2-methyl-3-pentanone (**27**) in a 65% (0.458 g) yield. The physical properties and analytical data of **27** are listed in Table 3.

Reaction of p-*Acetoxyacetophenone with 1-Phenyl-1-trimethylsiloxyethylene (**10**).* A dichloromethane (10 ml) solution of 0.576 g (3 mmol) of silyl enol ether (**10**) was added dropwise into a refluxing mixture or 0.434 g (3 mmol) of *p*-acetoxyacetophenone and 0.567 g (3 mmol) of $TiCl_4$ in dichloromethane (30 ml) in an argon atmosphere within 10 min, and the reaction mixture was refluxed for 30 min. After cooling to room temperature, the reaction mixture was quenched with water (10 ml) and extracted with ether (100 ml). The resulting crude product was analyzed by chromatography on silica gel. Elution with benzene and dichloromethane (1 : 1) gave 0.098 g (11%) of 3-hydroxy-1-phenyl-3-(p-acetoxyphenyl)-1-butanone (**35**).

*Synthesis of ar-Turmerone. Preparation of 4-*p*-Tolyl-3-pentene-2-one (**38**):* A dichloromethane (40 ml) solution of 5.20 g (40 mmol) of silyl enol ether (**3**) was added to a refluxing mixture of 2.68 g (20 mmol) of *p*-methylacetophenone and 3.78 g (20 mmol) of $TiCl_4$ in dichloromethane (50 ml) in an argon atmosphere over a period of 10 min, and the reaction mixture was refluxed for 3 h. After a similar work-up, a benzene solution (50 ml) of the resulting crude was refluxed for 1 h in the presence of *p*-TsOH (0.2 g). After removal of the solvent and the unreacted starting material by distillation, **38** was isolated in a 53% (1.84 g) yield by column chromatography (silica gel) [bp 150—154 °C/25 mmHg. IR (neat): 1680, 1600 cm^{-1}. NMR (CCl_4): δ 2.20 (s, 3H), 2.37 (s, 3H), 2.50 (s, 3H), 6.45 (s, 1H), 7.0—7.7 (m, 4H)].

*Reduction of 4-*p*-Tolyl-3-pentene-2-one (**38**).* A methanol (50 ml) solution of 3.48 g (20 mmol) of **38** was treated with hydrogen for 2 h at −10 °C in the presence of commercially produced Raney nickel. About 490 ml of hydrogen was adsorbed. After filtering off the Raney nickel, the filtrate was evaporated and the residual oil was purified by column chromatography (silica gel) using dichloromethane as a developer to give 2.71 g (77%) of 4-*p*-tolyl-2-pentanone (**39**). [Found: C, 81.93; H, 9.18%. Calcd for $C_{12}H_{16}O$: C, 81,77; H, 9.15%. IR (neat): 1720 cm^{-1}. NMR (CCl_4): δ 1.25 (d, J=7 Hz, 3H), 2.01 (s, 3H), 2.38 (s, 3H), 2.68 (d, J=7 Hz, 2H), 3.0—3.5 (m, 1H), 7.15 (s, 4H)], and 0.56 g (16%) of 4-*p*-tolyl-2-pentanol (**40**) [IR (neat): 3400 cm^{-1}. NMR ($CDCl_3$): δ 1.0—1.4 (m, 6H), 1.5—2.1 (m, 2H), 2.33 (s, 3H), 2.5—4.0 (m, 2H), 7.17 (s, 4H)].

*Silylation of 4-*p*-Tolyl-2-pentanone (**39**).* A hexane solution (30.8 ml) containing 55 mmol of *n*-BuLi was mixed with 500 ml of THF. The resulting solution was cooled to −10 °C and treated with 5.5 g (55 mmol) of diisopropylamine. To this solution, 8.8 g (50 mmol) of 4-*p*-tolyl-2-pentanone (**39**) was added dropwise over a 20 min period with stirring. After stirring the mixture at the same temperature for 30 min, 6.0 g (55 mmol) of chlorotrimethylsilane was added. The reaction mixture was stirred for 30 min, diluted with 300 ml of ether, and washed rapidly with two 100 ml portions of cold aqueous 10% $KHSO_4$ and then cold aqueous 5% $NaHCO_3$. The organic layer was dried and concentrated. Fractional distillation of the residue through a spinning Teflon-band column gave fraction 1, 9.4 g (76%), bp 152—155/3.2 mmHg, containing pure 4-*p*-tolyl-2-trimethyl-

TABLE 3. PHYSICAL PROPERTIES AND ANALYTICAL DATA OF THE PRODUCTS

Product	IR (cm^{-1})	NMR (δ)	Anal. Found (%) (Calcd) C	H	N
2	[a]3505, 1730, 1700	[c]0.99(t, J=7 Hz, 3H), 1.20(t, J=7 Hz, 3H), 1.42(s, 1H), 1.43(d, J=7 Hz, 3H), 3.58 (b, 1H)[e]	59.13 (59.38)	8.97 (8.97)	
4	[a]3505, 1735, 1715	[c]1.27(t, J=7 Hz, 3H), 1.31(s, 3H), 2.12 (s, 3H), 3.57(b, 1H)[e]	54.84 (55.16)	8.40 (8.10)	
6	[a]3490, 1760, 1710	[c]1.29(t, J=7 Hz, 3H), 1.46(s, 3H), 1.5—2.8(m, 7H), 3.88(b, 1H)[e]	59.95 (59.98)	8.05 (8.05)	
8	[a]3505, 1730, 1700	[c]1.16(s, 3H), 1.23 and 1.26(t, J=7 Hz, 3/2 and 3/2H), 1.4—3.0(m, 9H), 3.16 (b, 1H)[e]	61.30 (61.66)	8.81 (8.47)	
9	[a]3500, 1725, 1700	[c]1.2—1.4(m, 12H), 1.5—3.0(m, 9H), 3.18(b, 1H)[e], 4.16(q, J=7 Hz, 2H)	65.21 (65.59)	9.60 (9.44)	
11	[a]3480, 1715, 1670	[c]1.26(t, J=7 Hz, 3H), 1.29(s, 9H), 4.30 (b, 1H)[e], 7.0—8.0(m, 5H)	68.92 (69.04)	8.01 (7.97)	
12	[a]3500, 1735, 1705	[c]1.02(t, J=7 Hz, 3H), 1.05(d, J=7 Hz, 3H), 1.14(s, 3H), 1.25(t, J=7 Hz, 3H), 3.35(b, 1H)[e]	— (62.58)	— (9.63)	
13	[a]3500, 1770, 1725	[c]1.11(s, 3H), 1.26(t, J=7 Hz, 3H), 1.5—2.5(m, 11H), 3.55(b, 1H)[e]	63.51 (63.13)	8.69 (8.83)	
14	[a]3490, 1730, 1670	[c]1.23(t, J=7 Hz, 3H), 1.26(s, 3H), 3.98 (b, 1H)[e], 7.4—8.1(m, 5H)	68.48 (68.16)	7.60 (7.63)	
15	[a]3505, 1740, 1700	[c]0.99(t, J=7 Hz, 3H), 1.04(d, J=6 Hz, 3H), 1.14(s, 3H), 3.46(b, 1H)[e], 3.61(s, 3H)	— (62.58)	— (9.63)	
16	[a]3500, 1740, 1700	[c]1.12 and 1.14(s, 3/2 and 3/2H), 1.3—2.6(m, 15H), 3.40(b, 1H)[e], 3.61(s, 3H)	64.31 (64.44)	9.43 (9.15)	
18	[a]3430, 1720, 1685	[c]2.03 and 2.08(s, 3/2 and 3/2H), 4.35 (b, 1H)[e], 7.1—8.1(m, 10H)	75.78 (76.10)	6.43 (6.01)	
19	[b]3490, 1655	[d]1.5—2.1(m, 8H), 3.10(s, 4H), 4.00(s, 1H)[e], 7.4—8.1(m, 10H)	74.74 (74.97)	6.79 (6.86)	
20	[a]3480, 1700	[c]1.75(s, 3H), 2.11(s, 3H), 3.30(s, 4H), 3.60(b, 1H)[e], 7.19(s, 5H)	64.12 (63.88)	7.80 (7.74)	
21	[b]3395, 1695	[d]1.6—3.2(m, 9H), 3.29(d, J=5.5 Hz, 1H)[e], 4.99(d, d, J=5.5 and 2.0 Hz, 1H)	39.10 (39.13)	4.60 (4.52)	
22	[b]3440, 1680	[c]3.47(d, J=5.5 Hz, 2H), 4.83(t, J=5.5 Hz, 1H), 4.92(b, 1H)[e], 7.1—8.0(m, 5H)	45.27 (44.89)	3.40 (3.39)	
23	[a]3430, 2250, 1720	[c]1.23(s, 3H), 2.12(s,3H), 5.39(b, 1H)[e],	63.91 (63.88)	8.75 (8.94)	8.05 (8.28)
24	[a]3500, 2250, 1740	[c]1.10(s, 3H), 1.3—2.9(m, 13H), 3.96(b, 1H)[e]	67.32 (67.66)	8.69 (8.78)	6.95 (7.17)
25	[a]3450, 1740, 1700	[c]1.13 and 1.19(s, 3/3 and 6/3H), 1.2—2.5(m, 11H), 2.03(s, 3H), 3.34 and 3.73(s, 1/3 and 2/3H)	61.18 (61.66)	8.65 (8.47)	

Table 3. (Continued)

Product	IR (cm^{-1})	NMR (δ)	Anal. Found (%) (Calcd) C	H	N
26	[b]3440, 1695	[d]1.1—3.2(m, 9H), 3.93(d, J=2.5 Hz, 1H)[e], 4.71(d, d, J=2.5 and 8.0 Hz, 1H), 7.1—7.8(m, 4H)	65.76 (65.41)	6.06 (6.33)	
27	[a]3460, 1705	[c]0.76 and 0.82(d, J=7 Hz, 3/3 and 6/3H), 2.90(s, 6H), 6.45(d,d, J=9 and 2 Hz, 2H), 7.02(d,d, J=9 and 2 Hz, 2H)	71.93 (71.45)	9.11 (9.00)	6.28 (5.95)
28	[a]3480, 1710	[d]0.94(d, J=7 Hz, 3H), 1.04(t, J=7 Hz, 3H), 3.73(s, 3H), 6.97(d, J=9Hz, 2H), 7.37(d, J=9 Hz, 2H)	70.32 (70.24)	8.15 (8.16)	
29	[a]3460, 1710	[c]0.83 and 0.86(d, J=7 Hz, 3/2 and 3/2H), 1.03(t, J=7 Hz, 3H), 3.77(s, 3H), 4.63 and 4.91(b, 1/2 and 1/2H)[e], 6.6—7.4(m, 4H)	70.64 (70.24)	8.07 (8.16)	
30	[a]3500, 1710	[c]0.7—1.2(m, 6H), 3.76(s, 9H), 4.20(b, 1H)[e], 6.43(d, J=1.5 Hz, 2H)	63.38 (63.81)	7.92 (7.85)	
31	[a]3400, 1705	[c]0.80 and 0.90(d, J= Hz, 3/2 and 3/2H), 0.94(t, J=7 Hz, 3H), 2.32(s, 3H), 3.62 (b, 1H)[e], 7.2—7.8(m, 4H)	— (67.18)	— (7.25)	
32	[a]3490, 1710	[c]0.84 and 0.90(d, J=7 Hz, 3/2 and 3/2H) 0.94(t, J=7 Hz, 3H), 3.62(b, 1H)[e], 3.83(s, 3H), 7.27(d, J=8 Hz, 2H), 7.86(d, J=8 Hz, 2H)	67.17 (67.18)	7.28 (7.25)	
33	[a]3440, 1700	[d]1.3—3.0(m, 9H), 4.15(d, J=4.5 Hz, 1H)[e] 5.42(d, d, J=4.5 and 7 Hz, 1H), 7.1—7.9 (m, 9H)	62.86 (62.64)	6.13 (6.07)	5.64 (5.62)
34	[a]3480, 1755, 1690	[c]0.81(d, J=7 Hz, 3H), 1.02(t, J=7 Hz, 3H), 1.44(s, 3H), 2.22(s, 3H), 4.10(b, 1H)[e], 6.9—7.8(m, 4H)	67.72 (68.16)	7.85 (7.63)	
35	[a]3470, 1755, 1670	1.56(s, 3H), 2.20(s, 3H), 4.60(b, 1H)[e], 6.8—8.0(m, 9H)	72.88 (72.46)	6.00 (6.08)	
36	[a]3500, 1755, 1680	[c]0.98(t, J=7 Hz, 3H), 1.04(d, J=7 Hz, 3H), 1.14(t, J=7 Hz, 3H), 1.82(s, 3H), 3.61 (b, 1H)[e], 7.27(d, J=8 Hz, 2H), 7.86(d, J=8 Hz, 2H)	— (69.44)	— (7.97)	
37	[b]3485, 1670	[d]1.57(s, 3H), 3.47(d, J=17 Hz, 1H), 3.59 (d, J=17 Hz, 1H), 4.76(b, 1H)[e], 7.2—8.1(m, 9H)	67.20 (67.36)	5.33 (5.30)	4.96 (4.91)

a) Neat, b) KBr disk, c) in CCl_4, d) in $CDCl_3$, e) exchanged with D_2O.

siloxy-1-pentene (**41**) [IR (neat): 1620 cm^{-1}. NMR (CCl_4): δ 0.17 (s, 9H), 1.20 (d, J=7 Hz, 3H), 2.30 (s, 3H), 3.90 (s, 2H), 7.34 (s, 4H)] and fraction 2, 2.2 g bp 156—159 °C/3.2 mmHg, containing **41** and an unknown compound.

*Preparation of 2-Hydroxy-2-methyl-6-*p*-tolyl-4-heptanone (**42**).* To a dichioromethane (40 ml) solution of acetone (0.580 g, 10 mmol) and $TiCl_4$ (1.89 g, 10 mmol) was added a dichloromethane (10 mmol) solution of silyl enol ether (**41**) (1.24 g, 5 mmol) at 0 °C, and the reaction mixture was stirred for 1 h. After the usual work-up, the resulting crude product was analyzed by chromatography on silica gel. Elution with dichloromethane afforded 1.03 g (88%) of 2-hydroxy-2-methyl-6-*p*-tolyl-4-heptanone (**42**) [IR (neat): 3470, 1700 cm^{-1}. NMR (CCl_4): δ 1.10 (s, 6H), 1.21 (d, J=7 Hz, 3H), 2.30 (s, 3H), 2.37 (s, 2H), 2.59 (d, J=7 Hz, 2H), 3.0—3.5 (m, 1H), 3.35 (b, 1H), 7.05 (s, 4H)].

*Preparation of 2-Methyl-6-*p*-tolyl-2-heptene-4-one.* (**43**: ar-turmerone). A benzene (50 ml) solution of 2-hydroxy-2-methyl-6-*p*-tolyl-4-heptanone (**42**) (0.468 g, 2 mmol) was refluxed for 1 h in the presence of *p*-TsOH (0.2 g) with a conventional Dean Stark apparatus. After removal of the solvent, the resulting crude product was analyzed by chromatography on silica gel. Elution with benzene gave 0.420 g (97%) of 2-methyl-6-*p*-tolyl-2-heptene-4-one (**43**: ar-turmerone) [Found: C, 83.09; H, 9.35%. Calcd for $C_{15}H_{20}O$: 83.28; H, 9.32%. IR (neat): 1690, 1620 cm^{-1}. NMR (CCl_4): δ 1.23 (d, J=7 Hz, 3H), 1.80 (s, 3H), 2.30 (s, (3H), 2.56 (d, J=7 Hz, 2H), 3.0—3.5 (m, 1H), 5.93 (s, 1H), 7.06 (s, 4H)].

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