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THE PALLADIUM CATALYZED THIENYLATION OF ALLYLIC ALCOHOLS WITH 2- AND 3-BROMOTHIOPHENES AND THEIR DERIVATIVES[1]

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Abstract—Pd catalyzed reaction of allylic alcohols with 2-bromothiophene provides 3-(2'-thienyl)aldehydes or ketones selectively together with the small amounts of 2-(2'-thienyl)aldehydes and ketones. Similarly 3-(3'-thienyl)-aldehydes or ketones were obtained selectively from allylic alcohols and 3-bromothiophene. The reactivity and regioselectivity largely depend on the solvents, additives, and the structure of allylic alcohols. Generally aprotic dipolar solvent such as HMPA and DMF gave the most satisfactory results. 2-Thienyl iodide showed somewhat higher reactivity than 2-thienyl bromide. 2-Thienyl chloride was unreactive. Sodium iodide and/or triphenylphosphine were very effective as the cocatalysts especially for the reactions to give aldehydes. This thienylation reaction was also applicable to 2-bromothiophenes with a wide variety of substituents at 5-position. The synthetic utility of this catalytic reaction has been illustrated by the synthesis of 9-oxo-*trans*-2-decenoic acid (Queen substance).

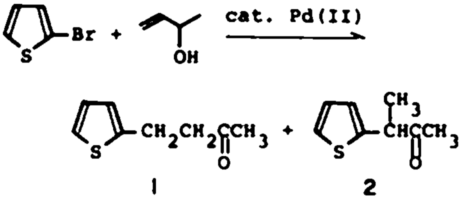
The heteroaromatics, accompanied by the current development of their ring opening procedures, have been recognized as the very useful tools for the synthesis of the natural and other products.[2] Despite this interest, little attention has been drawn to the transition metal catalyzed reactions in heteroaromatic chemistry, compared with aromatic hydrocarbon chemistry. The stoichiometric arylation of olefin by palladium with aromatic hydrocarbon and with arylmercuric compounds have been reported by Moritani *et al.*[3] and Heck,[4] respectively. Recently, as an extension of catalytic arylation of olefins with aryl iodide by Pd(II) or Pd(0),[5] the synthetically useful arylation of allylic alcohols have been reported by Heck *et al.*[6] and Chalk *et al.*,[7] where 3-arylaldehydes or ketones were obtained in high yields.

In this context, we examined the thienylation of allylic alcohols with 2- and 3-bromothiophenes catalyzed by palladium. This reaction to provide 3-thienyl aldehydes and ketones seems to be promising because it formally corresponds to the Michael type addition reaction of thienylcuprate to α,β-unsaturated aldehydes or ketones.[8]

RESULTS AND DISCUSSION

Palladium catalyzed reactions of 2- and 3-halothiophenes have been studied with 11 kinds of allylic and homoallylic alcohols in the presence of catalytic amounts of palladium salt with variations of solvents and additives. The allylic alcohols examined in this paper are allyl alcohol, α-, β- and γ-methallyl alcohols, methylpropenylcarbinol, iso-butenylmethylcarbinol, ethylvinylcarbinol, iso-propylvinylcarbinol, phenylvinylcarbinol and cyclohexen-3-ol. Allylmethylcarbinol has also been examined as a homoallylic alcohol.

After numerous attempts for optimization (*vide infra*), following conditions have been established most satisfactory in both the reactivity and the regioselectivity for most kinds of allylic alcohols. A slurry mixture of 2- or 3-bromothiophene (2 mmol), allylic alcohol (3 mmol), $Pd(OAc)_2$ (0.02 mmol), NaI (0.07 mmol) and/or triphenylphosphine (0.06 mmol) and $NaHCO_3$ (2.4 mmol) in 2 ml of HMPA (hexamethylphosphoric triamide) or DMF was heated under argon at 100–120° for an appropriate period. Triphenylphosphine or NaI was added as a cocatalyst and $NaHCO_3$ was used to neutralize hydrogen bromide produced during the reaction. Under the above conditions, the reaction was complete within 5 and 10 hr with respect to 2- and 3-bromothiophenes, respectively, except for β- and γ-methallyl alcohols and iso-butenylmethylcarbinol. The thienylation at the 3-position (of allylic alcohols) to provide 3-thienylaldehydes or ketones (1 or 3) took place selectively or preferentially over the thienylation at the 2-position (eqns 1 and 2).



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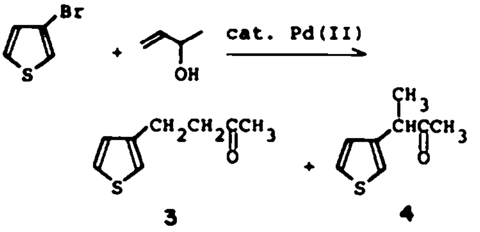

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The success in yielding the 3-alkylsubstituted thiophenes (3 and 4), probably through 3-thienylpalladium complex, is rather surprising, taking into consideration of the instability[9] and the relatively difficult availability[10] of 3-thienylmetallic compounds. 3-Bromothiophene was two or three times less reactive than 2-bromothiophene.

The results are summarized in Tables 1 and 2 for 2- and 3-bromothiophenes, respectively. The figures in these Tables are the averages of at least two independent experiments (within ±3% deviations). These Tables show that the reactivity and the selectivity largely depend on the structure of allylic alcohols. There are remarkable differences in the product distributions and

Table 1. Palladium catalyzed thienylation of allylic alcohols with 2-bromothiophene in HMPA[a]

Entries	Alcohols	Temp.[b] (°C)	Time (hr)	Conv.[c] (%)	Product distribution(%)[d] 3-Thienyl-[e] carbonyl	2-Thienyl-[e] carbonyl	2,2'-Bi Thienyl	Others
1	$CH_2=CHCH_2OH$	105	5	100	62(46)	30(25)	8	
2		90[f]	4	48	76	2	22	
3	$CH_2=C(CH_3)CH_2OH$	105	8.5	65	59(42)	0	31	10[g]
4		100[f]	9	61	25	0	56	19[g]
5	$CH_3CH=CHCH_2OH$	125	9.5	64	48(23)	0	52	
6	$CH_2=CHCH(CH_3)OH$	120	3	100	90(82)	6(5)	4(3)	
7	$CH_2=CHCH(CH_3)OH$	100[f]	9.5	92	(87)		(2)	
8	$CH_2=CHCH(C_2H_5)OH$	120	2.5	98	89(85)	9(9)	2	
9	$CH_2=CHCH(^iC_3H_7)OH$	120	5	97	93(93)	5(4)	2	
10	$CH_2=CHCH(C_6H_5)OH$	120	4	100	90(88)	—	5	5[h]
11	$CH_3CH=CHCH(CH_3)OH$	125	5	96	77(54)	3	20	
12	$(CH_3)_2C=CHCH(CH_3)OH$	130	9.5	55	24	0	76	
13	Cyclohexen-3-ol	120	9	82	65	—	29	6[h]
14	$CH_2=CHCH_2CH(CH_3)OH$	120	5	100	55	14	8	3,[h] 20[i]

[a] Unless otherwise noted, the reaction was undertaken in the following conditions: 2-bromothiophene (2 mmol), allylic alcohol (3 mmol), $NaHCO_3$ (2.4 mmol), NaI (0.07 mmol), triphenylphosphine (0.06 mmol), and $Pd(OAc)_2$ (0.02 mmol) in 2 ml of HMPA.

[b] Bath temperature controlled within ±0.5° deviation.

[c] Based on 2-bromothiophene consumed.

[d] Determined by the area intensities on VPC (SiDC 550, He). The values in the parentheses refer to the isolated yields.

[e] 3-Thienylcarbonyl and 2-thienylcarbonyl refer to 3-(2'-thienyl)aldehydes or ketones and 2-(2'-thienyl)aldehydes or ketones, respectively.

[f] The reaction was undertaken under the following conditions: 2-bromothiophene (2 mmol), allylic alcohol (6 mmol), $NaHCO_3$ (2.4 mmol), NaI (0.7 mmol) and $Pd(OAc)_2$ (0.2 mmol) in 2 ml of HMPA.

[g] β-Thienylmethacrolein.

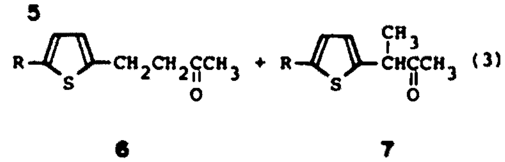
[h] Unspecified product.

[i] 1-(2'-Thienyl)penten-4-ol.

the isolated yields between the reactions which yield aldehydes and ketones. Generally thienylation to give ketones takes place selectively at the 3-position of allylic alcohols; VPC and isolated yields are in a good agreement. On the other hand, the reaction to give aldehydes is relatively slow and comparable amounts of positional isomers are obtained. The discrepancy between VPC and isolated yields may be due to the aldol condensation of products. The methyl substituent on olefinic carbons retarded the reaction. Therefore in the case of isobutenylmethylcarbinol (entries 12 and 6 in Tables 1 and 2, respectively), the reaction became unacceptably slow and the bithienyl formation became the main course of reaction. On the other hand, alkyl and aryl groups at the 1-position of allyl alcohol, independent of their bulkiness, accelerated the reaction, that is, ethylvinyl-, isopropylvinyl-, and phenylvinylcarbinols showed almost the same reactivity as methylvinylcarbinol. The competition reaction of methylvinyl and isopropylvinylcarbinols with 2-bromothiophene revealed that the former reacted only 1.4 times faster than the latter.

The effects of cocatalysts in the reaction of 2-bromothiophene with allyl alcohol and α-methallyl alcohol were examined. With α-methallyl alcohol the reaction was satisfactory without any cocatalyst; doping with NaI and/or triphenylphosphine did not cause any significant change. DIPHOS [bis(diphenylphosphino)ethane] raised the regioselectivity for 3-thienylation, though the reaction became appreciably slow (at 120° for 24 hr, 96% conversion: 92% of 3-(2'-thienyl)carbonyl, 6% of bithienyl, and 2% of unknown, *cf.* entry 6, Table 1). With allyl alcohol, triphenylphosphine was the most effective catalyst; NaI improved the turn-over of the catalyst, but not as much as triphenylphosphine. Without these additives, the reaction ceased essentially at ~50% conversion based on 2-bromothiophene and the prolonged reaction caused a decomposition of products, 3-(2'-thienyl)- and 2-(2'-thienyl)aldehydes. Again in this case, DIPHOS suppressed the reaction and raised the regioselectivity.

The problem on the regioselectivity was partly resolved by changing the solvent from HMPA to DMF or DMSO (e.g., 3-thienyl : 2-thienyl : bithienyl = 91 : 0 : 9 in DMF, and 82 : 0 : 18 in DMSO. *cf.* entry 6, Table 1). In the protic (cyclohexanol, acetic acid) and aprotic non-polar (dioxane) solvents the same kinds of products were obtained as in HMPA, though the reaction was sluggish and stopped essentially at a low conversion due to a precipitation of palladium metal. Especially in acetic acid, the reaction was very slow.[11] The reactivity order was 2-thienyl iodide ≥ Br ≫ Cl. 2-Thienyl iodide showed a relatively low selectivity, i.e. 3-(2'-thienyl)ketone : 2-(2'-thienyl)ketone : bithienyl = 70 : 8 : 16 (unknown 6%, *cf.* entry 6, Table 1). 2-Thieny chloride was unreactive under similar or even under the enforcing conditions (130°, 20 hr).



5, 6, 7a; R= CH_3
b; R= $CH_2CO_2CH_3$
c; R= H
d; R= $COCH_3$
e; R= CO_2CH_3

Table 2. Palladium catalyzed thienylation of allylic alcohols with 3-bromothiophene[a]

Entry	Alcohol	Temp.[b] (°C)	Time (hr)	Conv.[c] (%)	Product distribution[d] 3-(3'-Thienyl) carbonyl	2-(3'-Thienyl) carbonyl	3,3'-Bithienyl	Others
1	$CH_2{=}CHCH_2OH$	90	19	60	44.6(25.7)	37.1(16.3)	—	18.3[e]
2	$CH_3CH{=}CHCH_2OH$	120	16	79	51.1(23.3)	37.4(17.3)	—	11.5[e]
3	$CH_2{=}C(CH_3)CH_2OH$	100	33	24	79.3(72.8)	—	—	6.3[e] 14.4(10.7)[f]
4	$CH_2{=}CHCH(CH_3)OH$	120	10	96	90.5(89.9)	9.5(7.5)	—	
5	$CH_3CH{=}CHCH(CH_3)OH$	120	10	86	70.0(62.4)	18.0(16.1)	—	12.0(9.3)[g]
6	$(CH_3)_2C{=}CHCH(CH_3)OH$	125	62	54	33.9(21.9)	—	40.5(22.0)	25.6[h](17.2)
7	$CH_2{=}CHCH(C_2H_5)OH$	120	16	60	87.6(79.7)	7.1(6.4)	5.3	
8	$CH_2{=}CHCH(^iC_3H_7)OH$	130	8	92	87.5(87.0)	3.1(3.0)	9.4	
9	$CH_2{=}CHCH(C_6H_5)OH$	120	9	94	84.8(83)	—	8.7	6.5[e]

[a] The usual scale is 3-Bromothiophene (4.0 mmole), allylic alcohol (6.0 mmole), $Pd(OAc)_2$ (0.04 mmole), NaI (0.14 mmole), triphenylphosphine (0.12 mmole) in 3 ml of HMPA.

[b] Bath temperatures controlled within ± 0.5°.

[c] Based on 3-bromothiophene consumed.

[d] Determined by the area intensities on VPC (SiDC 550, He). The values in the parentheses refer to the isolated yields.

[e] Unspecified product.

[f] 3-(3'-Thienyl)methacrolein.

[g] 4-(3'-Thienyl)pent-4-en-2-ol.

[h] 5-(3'-Thienyl)-4-methyl-pentan-2-one.

Table 3. Palladium catalyzed thienylation of α-methallyl alcohol with 5-substituted 2-bromothiophene[a]

Entry	Thiophene	Solvent	Base	Temp. (°C)	Time (hr)	Conv. (%)	Product distribution(%)[b] 6	7	Others
1	5a	HMPA	$NaHCO_3$	120	25	93	85.7(75)	8.4	6.2[c]
2	5b	HMPA	$NaHCO_3$	120	8.5	100	70.1(44)	6.2	23.6[d]
3	5b	DMF	K_2CO_3	100	5	100	90.2(61)	2.9	6.9[d]
4	5c	HMPA	$NaHCO_3$	120	7	94	90.6(80)	6.8(5)	2.6[e]
5	5c	DMF	$NaHCO_3$	120	16	96	90.9(82)	0.5	8.6[e]
6	5d	HMPA	$NaHCO_3$	120	5	91	86.4(80)	—	7.4[e], 6.2[c]
7	5d[f]	HMPA	$NaHCO_3$	120	22	26	43		57[g]
8	5e	HMPA	$NaHCO_3$	120	9	100	100 (60)	—	—
9	5e[h]	HMPA	$NaHCO_3$	120	10	100	47 (30)[j]	—	21(10),[i] 29(14),[k] 3[c]

[a] The usual scale is 5 (4 mmole), α-methallyl alcohol (6.0 mmol), $Pd(OAc)_2$ (0.04 mmole), NaI (0.14 mmole), base (4.8 eq), triphenylphosphine (0.12 mmole) in 3 ml of solvent.

[b] Determined by the area intensities on VPC (SiDC 550, He). The values in the parentheses refer to the isolated yields.

[c] Unspecified product.

[d] Methyl (2-thienyl)acetate.

[e] 2,2'-Bithienyl.

[f] (5-Acetyl)-2-thienyl chloride was used instead of bromide 5d.

[g] 5,5'-Diacetyl-2,2'-bithienyl.

[h] With allylmethylcarbinol (2.5 mmole).

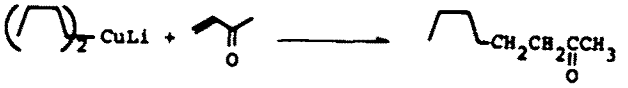
[i] 5-Carbomethoxy-2-(4'-oxo-pentyl)thiophene 9.

[j] 5-Carbomethoxy-2-(4'-oxy-pent-1'-enyl)thiophene 10.

[k] 5,5'-Dicarbomethoxy-2,2'-bithienyl.

The present reaction could accomodate a wide variety of functional groups as shown in eqn 3. With similar facility under the similar conditions to the reactions in Table 1, 5-substituted 2-bromothiophenes 5 reacted with α-methallyl alcohol to provide 3-thienyl ketones 6 selectively together with the small amounts of 2-thienyl ketones 7 (Table 3). Only with 5b, reduction to give methyl (2-thienyl)acetate was appreciable (entry 2, Table 3). This undesirable side reaction was suppressed by switching a solvent from HMPA to DMF, using K_2CO_3 as a base, and lowering the temperatures (entry 3, Table 3). 2-(5-Acetyl)thienyl chloride, in contrast to bromide 5d, reacted to give mainly 5,5'-diacetyl-2,2'-bithienyl together with a small amount of the expected product 6d (entry 7, Table 3).

This thienylation, coupled with the desulfurization with Raney nickel[12] (eqn 5), is formally equivalent to the 1,4-addition reaction of lithium dialkylcopper to the α,β-unsaturated carbonyl compounds[8] (eqn 4), but the former seems to have some advantages over the latter: (a) The manipulation is very easy (not sensitive to moisture) and applicable to large scale reaction. (b) Allylic alcohols are



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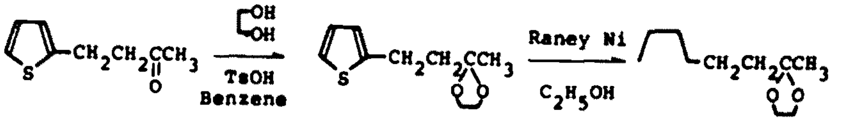

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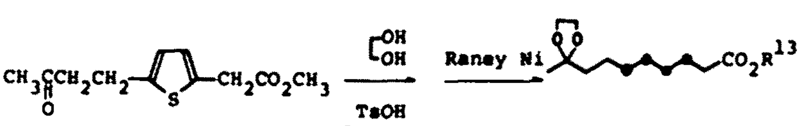
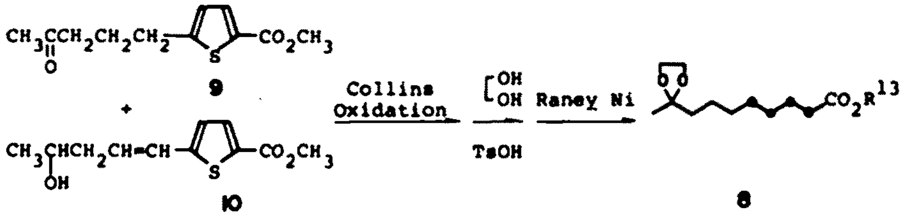


6b 8 (6)



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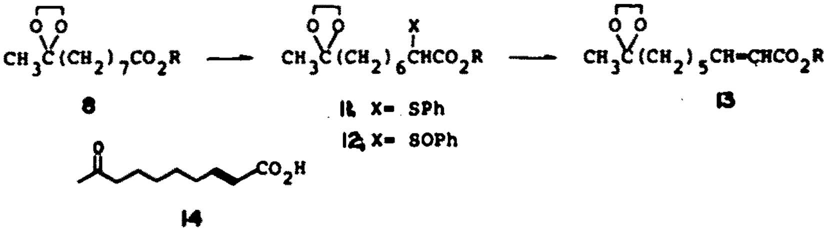


(8)

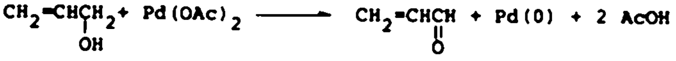
more stable and frequently more accessible than enals or enones. (c) Thiophene serves as a very useful template[2a,b] and substituents can be introduced appropriately, as necessary, on the thiophene ring before or after the present reaction.

Methyl 2-(2′-thienyl)ethylketone (entry 6, Table 1) was subjected to desulfurization with Raney nickel W-7 in refluxing ethanol, after ketalization with ethylene glycol, to give n-hexyl methyl ketone ethylene ketal in 63% isolated yield (eqn 5).

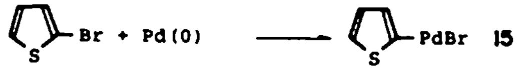
The scope and utility of this present reaction were illustrated in eqns (6) and (7), which furnished the same synthetic intermediate 8 for the synthesis of 9-oxo-*trans*-2-decenoic acid 14[14] (queen substance, a honey bee pheromone). The carbons originated from thiophene are indicated by the black spots on the structural formula of 8. Thus, methyl 5-(3′-oxo-butyl)-2-thienylacetate 6b, obtained in entry 3, (Table 3), was converted to 8 in 81.5% isolated yield following to the similar procedures to eqn (5). Similarly the mixture of 5-carbomethoxy-2-(4′-oxo-pentyl)thiophene 9 and 5-carbomethoxy-2-(4′-oxy-pent-1′-enyl)thiophene 10 (entry 9, Table 3), after Collins oxidation,[15] furnished the same product 8 in 55% isolated yield.

Queen substance 14 was prepared according to eqn (8), essentially following to the method of Trost.[16] Thus, sulfenylation (92%) and oxidation with $NaIO_4$, followed by the thermal dehydrosulfenylation gave rise to trans-ester 13 exclusively (85% from 11). The stereochemistry was determined unequivocally by NMR and IR spectroscopies ($J_{\text{olefinic protons}} = 16\,\text{Hz}$ and a weak absorption at $980\,\text{cm}^{-1}$). Hydrolysis of 13[17] gave 14 in a quantitative yield with the identical spectral data to the reported ones.

Finally it seems worthwhile to note the total profile of the thienylation reaction, exemplified by the reaction between 2-bromo-thiophene and allyl alcohol. The facts that the thienylation proceeded in the absence of NaI and that in the absence of allyl alcohol, no reaction took place and no 2,2′-bithienyl was detected suggest that allyl alcohol, not NaI, served as a reducing reagent of Pd(II) to Pd(0)[18] (eqn 9). The same conclusion, that alcohol acted as a reducing reagent, was also suggested by the quantitative formation of 2,2′-bithienyl using sec-hexyl alcohol instead of ally alcohol (entry 1 (Table 1), 96% conversion at 120° for 45 hr). By analogy with arylation reaction,[4] thienyl palladium complex 15, produced by the oxidative addition of Pd(0) to 2-bromothiophene (eqn 10), should be active species for thienylation. The addition of 15 to a double bond occurs in both senses to give the intermediates 16 and 17, giving 16 preferentially or selectively in all cases examined (eqn 11). The elimination of hydridopalladium complex from 16 gives the enol-form 18 of the major product 3-(2′-thienyl)propionaldehyde (eqn 12). Judging from the product, the intermediate 17 might have been converted to 19 via the sequential elimination and addition of hydridopalladium to give the enol-form of 2-(2′-thienyl)-propionaldehyde 20 (eqn 13). One possible mechanism for the 2,2′-bithienyl formation, which have been proposed for the oxidative coupling of arenes with palladium salts,[19] is the decomposition of 2 moles of 15 to give 1 mole of bithienyl and 2 moles of Pd(I), which might disproportionate to Pd(0) and Pd(II) (eqn 14). This mechanism is supported by the following experiment: Under the same conditions (to entry 4, Table 1) except for using 0.02 mmol of $Pd(OAc)_2$, the bithienyl formation was diminished to 1%. The similar tendency was also observed in entries 3 and 4 (Table 1). These observations that the higher the concentration of $Pd(OAc)_2$ (i.e. the higher the concen-



$$\mathrm{CH_2{=}CH\underset{OH}{\underset{|}{C}}H_2 + Pd(OAc)_2 \longrightarrow CH_2{=}CH\underset{O}{\underset{\|}{C}}H + Pd(0) + 2\,AcOH} \qquad (9)$$



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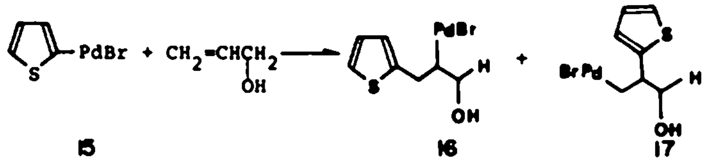

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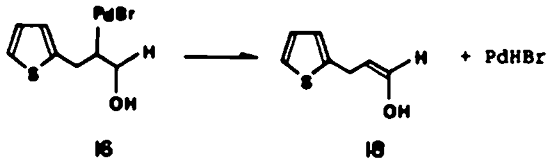

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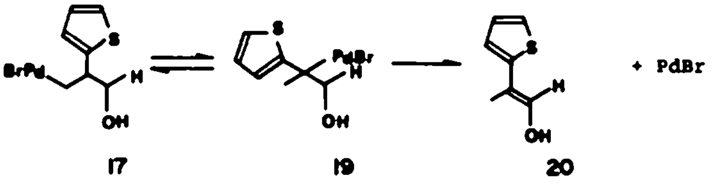

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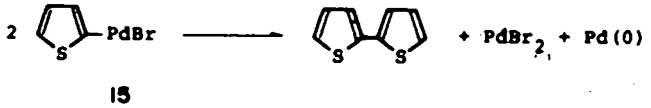


(14)

$$\mathrm{PdHBr + NaHCO_3 \longrightarrow Pd(0) + NaBr + CO_2 + H_2O} \qquad (15)$$

tration of complex 15), the more preferential the formation of bithienyl, could be rationalized by taking into consideration that the kinetics for eqn (14) is higher order than that for eqn (11) with respect to the complex 15. On this ground, the diminished formation of 3,3'-bithienyl could be rationalized (Table 2).

EXPERIMENTAL

Alcohols. Allyl, α-, β- and γ-methallyl alcohols were used after purification by distillation (over $MgSO_4$) of the commercially available samples. iso-Butenylmethylcarbinol was obtained by the reduction of mesityl oxide with $NaBH_4$ in 33 vol% aq MeOH. Ethylvinyl-, isopropylvinyl-, phenylvinyl-, methylpropenyl- and allylmethylcarbinols were prepared by the Grignard reaction (by the combinations of acrolein and EtMgBr in ether, iso-butylaldehyde and vinylmagnesium bromide in THF, acrolein and PhMgBr in ether, crotonaldehyde and MeMgI in ether, and acetaldehyde and allylmagnesium bromide in ether). Cyclohexen-3-ol was prepared by the oxidation of cyclohexene with t-butyl perbenzoate.

Halothiophenes. 2-Bromothiophene. Into a soln of thiophene (25 g, 0.3 mol) in 100 ml of ether was added gradually dioxane dibromide over a 6 hr period at 0°. After completion of addition, the mixture was refluxed for 1 hr and then poured into ice-water containing Na_2SO_3. The ether extracts were washed with satd NaCl and dried over $MgSO_4$. After evaporation of the solvent, the brown residue was distilled roughly under the reduced pressure (≤ 100° of bath temp., otherwise caused a rapid decomposition). Redistillation through a Vigreux column under the reduced pressure gave a colorless product (41 g, 84% yield). 3-Bromothiophene,[20] 2-chlorothiophene,[21] 5-methyl-2-bromothiophene,[22] 5-acetyl-2-bromo- and 5-acetyl-2-chlorothiophenes[23] and 5-carbomethoxy-2-bromothiophene[24] were prepared according to the established methods. Methyl 2-(5-bromo)thienylacetate (5b)[25] was prepared by the sequence of the chloromethylation of thiophene, substitution of Cl to CN, and hydrolysis of cyano group to methyl ester, followed by the bromination of methyl thienylacetate. The sample prepared in the similar sequence starting from 2-bromothiophene was contaminated by 18% of methyl 3-(5-bromo)thienylacetate.

Solvents. Solvents, purified by the following procedures and kept under argon, were used for all experiments. HMPA and DMSO (CaH_2), DMF (NaH), dioxane (benzophenone-Na), acetic acid (5% acetic anhydride).

General procedure of thienylation of allylic alcohol. The general procedure is exemplified by the reaction of 2-bromothiophene and α-methallyl alcohol (entry 6, Table 1). Into an argon purged mixture of $Pd(OAc)_2$ (9 mg, 0.04 mmol), NaI (21 mg, 0.14 mmol), $NaHCO_3$ (404 mg, 4.8 mmol) were added 3 ml of HMPA, α-methallyl alcohol (432 mg, 6 mmol) and 2-bromothiophene (652 mg, 4 mmol) by means of a syringe. This slurry mixture was stirred and heated at 120°. The reaction was monitored by VPC by sampling 2 μl of the mixture at an appropriate time. After 3 hr the mixture was poured into water and extracted twice with ether (20 + 10 ml). The combined ether extracts were washed twice with water and dried over $MgSO_4$. Evaporation of the solvent and subsequent distillation (102°/6 mmHg with Kugelrohr) gave a colorless oil (535 mg, 87% yield), which was analyzed by VPC (SIDC 550, 3 m, 180°, He) to be a mixture of 94% of methyl 2-(2'-thienyl)ethyl ketone and 6% of methyl 1-(2'-thienyl)ethyl ketone. Each component was separated by the preparative VPC and characterized by its spectral (NMR, IR and mass) and analytical data. Other alcohols and halothiophenes were reacted under the conditions indicated in Tables 1–3 and results were analyzed in the similar fashion. The spectral and analytical data of the products in Tables 1–3 are summarized in Table 4.

Competition reaction. α-Methallyl alcohol (3.0 mmol) and isopropylvinylcarbinol (3.0 mmol) were reacted with 2-bromothiophene (3.0 mmol) in 2.5 ml of HMPA under argon at 110° in the presence of $Pd(OAc)_2$ (0.03 mmol), NaI (0.11 mmol), $NaHCO_3$ (3.6 mmol), and triphenylphosphine (0.09 mmol). Then aliquots were sampled at an interval of 20 min and immediately after each sampling the sample were subjected to the VPC analysis. The relative reactivity of α-methallyl alcohol to isopropylvinylcarbinol was determined to be 1.4 from the relative intensities of ketones for the first 4 aliquots.

Methyl 2-thienylethyl ketone ethylene ketal. Methyl 2-thienylethyl ketone (1.32 g, 8.6 mmol), ethylene glycol (0.80 g, 12.9 mmol) were refluxed in the presence of *p*-toluenesulfonic acid (90 mg) in 20 ml of dry benzene for 2 days in a flask fitted with a water separator filled with Na_2SO_4. The mixture was washed with sat Na_2CO_3 then with sat NaCl. After drying over $MgSO_4$ and evaporation of solvent, the residue was distilled under reduced pressure (Kugelrohr 175°/16 mmHg) to give 1.58 g (93.1%) of product. $\delta^{TMS}_{CCl_4}$ 1.33 (s, 3H), 1.87 ~ 2.33 (A_2B_2 multiplet, 2H), 2.77 ~ 3.13 (A_2B_2 multiplet, 2H), 4.0 (s, 4H), and 6.7 ~ 7.35 (m, 3H). ν^{neat}_{max} 3100 (w), 3060 (w), 2970 (s), 2870 (s), 1440 (s), 1370 (s), 1250 (s), 1215 (s), 1050 (vs), 855 (s), 820 (m) and 690 (vs), *m/e* (rel. int.) 198 (P, 9), 111 (34), 97 (85), and 87 (100).

Hexyl methyl ketone ethylene ketal. Methyl 2-thienylethyl ketone ethylene ketal (1.5 g) was reacted with Raney Ni W-7, freshly prepared from 12.5 g of Raney Ni–Al-alloy [*Org. Syn.* Col. Vol. 3, p. 176], in 30 ml of refluxing abs EtOH for 7 hr. Then the mixture was washed with EtOH by means of Soxhlet apparatus. After a careful distillation of EtOH through a Vigreux column, the concentrated mixture was poured into water and extracted with pentane. The extracts were washed with sat NaCl and dried over $MgSO_4$. Vacuum distillation gave 875 mg (67.2%) of product (120°/70 mmHg, Kugelrohr). $\delta^{TMS}_{CCl_4}$ 0.7–1.75 (m, 13H), 1.3 (s, 3H) and 3.9 (s, 4H). ν^{neat}_{max} 2870 (s), 1380 (m), 1100 (m), 1070 (m) and 1045 (m). *m/e* (rel. int.) 157 ($P-CH_3$, 63), 87 (P-hexyl, 100), and 85 (21). Calcd. for $C_9H_{18}O$: C; 69.72, H: 11.70). (Found: C; 69.71, H; 11.90.

Ethyl 9-oxo-decanoate ethylene ketal 8. (a) Compound 6b (3.06 g, 13.6 mmol) was ketalyzed (ethylene glycol, 0.92 g (14.8 mmol) and TsOH, 20 mg, in 60 ml dry benzene, 17 hr, 97% isolated yield, 170–190°/5 ~ 10 mmHg) and desulfurized with Raney Ni W-7 (prepared from 17.8 g of Ni–Al alloy, in 70 ml of refluxing abs EtOH, 16 hr, 84% isolated yield, 150–160°/15 ~ 7 mmHg) to give 8, which was a mixture of methyl and ethyl ester in a ratio of 1:3.5. Methyl 5-(3'-oxo-butyl)-2-thienylacetate ethylene ketal: $\delta^{TMS}_{CCl_4}$ 1.28 (s, 3H), 1.76–2.12 (A_2B_2 m, 2H), 2.64–3.01 (A_2B_2 m, 2H), 3.67 (s, 5H), 3.88 (s, 4H), 6.55 (d, 3Hz, 1H) and 6.63 (d, 3Hz, 1H). ν^{neat}_{max} 3050 (w), 2975 (w), 2945 (m), 2870 (m), 1740 (vs), 1435 (m), 1375 (m), 1210 (m, broad), 1165 (m), 1055 (s), 950 (m), 860 (s) and 800 (m, broad). *m/e* (rel. int.) 270 (29), 255 (21), 225 (11), 211 (34), 197 (14), 183 (73), 169 (93), 123 (75) and 87 (100). (Found: C; 57.48, H; 6.99, S; 11.70. Calcd. for $C_{13}H_{18}O_4S$: C; 57.76, H; 6.71, S; 11.86%). 8 ($R=C_2H_5$): $\delta^{TMS}_{CCl_4}$ 1.09 ~ 1.96 (m, 18H), 2.03 ~ 2.39 (m, 2H), 3.83 (s, 4H) and 4.08 (q, 7Hz, 2H). ν^{neat}_{max} 2940 (m), 1740 (s), 1085 (m), 1065 (m) and 1045 (m). (Found: C; 64.98, H; 10.27 Calcd. for $C_{14}H_{26}O_4$: C; 65.09, H; 10.14%). (b) A mixture of 10 (4.13 g, 18 mmol) was oxidized by Collins oxidation (CrO_3, 2.4 g, 24 mmol), pyridine 3.8 g (48 mmol) in 60 ml of CH_2Cl_2, at r.t. for 15 min). The ppt was filtered off and washed with ether (200 ml). The ether extract was washed with 5% NaOH (40 ml), 5% HCl (40 ml), 5% $NaHCO_3$ (40 ml), and then with sat NaCl (40 ml). The crude product were ketalized and desulfurized similarly to (a) to give 8 (a mixture of methyl and ethyl esters in a ratio of 1:4) in 55% isolated yield from 9 and 10 after Kugelrohr distillation (160°/18 mmHg).

Ethyl 9-oxo-2-phenylthiodecanoate ethylene ketal.[11] Into a soln of lithium diisopropylamide (2.45 mmol) in 10 ml of freshly distilled THF cooled at −78°, was added a soln of 8 (520 mg, 2.03 mmol) in 10 ml of THF and stirred 15 min. This soln kept at −78° was transfered into a soln of diphenyl disulfide (512 mg, 2.35 mmol) in 20 ml of THF cooled at −78° gradually over a 25 min period. After 30 min stirring at −78°, the temp. was raised to r.t. gradually. The mixture was poured into water and extracted with ether. Plc purification (silica gel, benzene/ethyl acetate 8:1) gave 11 in 92% isolated yield. $\delta^{TMS}_{CCl_4}$ 1.0–1.8 (m, 18 H), 3.49 (t, 7 Hz, 1H), 3.81 (s, 4H), 4.06 (q, 7Hz, 2H) and 7.0–7.5 (m, 5H). ν^{neat}_{max} 3060 (w), 2985 (w), 2940 (s), 1730 (vs), 1490 ~ 1450 (broad peaks), 1440 (m), 1375 (m), 1155 (s), 1090 ~ 1020 (m, broad peaks), 850 (m), 750 (m) and 690 (m). Anal. Calcd. for $C_{20}H_{30}O_4S_1$: 366.18647. Found: 366.1769.

Table 4. Spectral and physical data of 2- and 3-thienylketones and aldehydes and related compounds^a

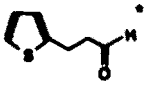
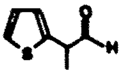
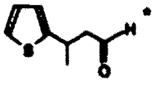
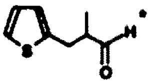
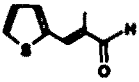
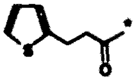
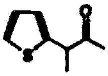
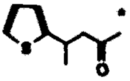
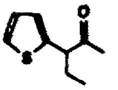
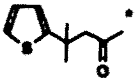
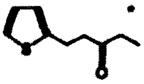
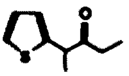
Compounds	^{1}H NMR spectra^b	IR spectra^c	Mass spectra^d	Bp °C/mmHg (Mp°C)
Compounds listed in Table 1				
	2.63-3.37(A$_2$B$_2$m, 4H), 6.7-7.3(m, 3H), 9.8 (t, ~1Hz, 1H)	3120(w), 1725(vs), 1440(m), 700(s)	140(93), 111(60) 97(100)	~140/6
	1.50(d, 7Hz, 3H), 3.9(m, 1H), 6.9-7.3(m, 3H), 9.67 (d, 2Hz, 1H)	3100(m), 1730(vs), 1420(m), 700(s)	140(20), 111(100) 97(34)	~140/6
	1.4(d, 7Hz, 3H), 2.8(d.d, 7 and 1.5Hz, 2H), 3.7 (m, 1H), 6.8-7.4(m, 3H), 9.8(t, 1.5Hz, 1H)	3100(w), 1720(vs) 1440(m), 690(s)	154(65), 125(43) 112(69), 111(100)	~150/5
	1.04(d, 8Hz, 3H), 2.33-3.33(m, 3H), 6.67-7.20 (m, 3H), 9.65(d, 1.2Hz, 1H)^f	3090(w), 1720(s) 1440(m), 695(s)	154(71), 97(100) 84(69)	~140/5
	2.13(s, 3H), 7.1-7.7 (m, 4H), 9.53(s, 1H)	3100(m), 1660(s) 1610(s), 700(s)	152(100), 137(66) 123(66), 97(59)	~140/5
	2.15(s, 3H), 2.6-3.3(A$_2$B$_2$ m, 4H), 6.74-7.21(m, 3H)	3100(m), 1715(vs), 695(s)	154(77), 111(96), 97(100)	~150/6
	1.49(d, 7Hz, 3H), 2.15 (s, 3H), 4.04(~q, 7Hz, 1H), 6.8-7.3(m, 3H)	3100(w), 1710(vs) 1460(m), 695(s)	154(17), 111(100), 97(5)	~150/6
	1.4(d, 7Hz, 3H), 2.15(s, 3H), 2.7(m, 2H), 3.67(m, 1H), 6.8-7.5(m, 3H)	3100(w), 1700(s) 1420(m), 690(s)	168(52), 151(44), 125(97), 111(100)	~150/5
	0.91(t, 7Hz, 3H), 1.6-2.2(m, 2H), 2.13(s, 3H), 3.80(t, 7Hz, 1H), 6.9-7.1(m, 2H), 7.2-7.3(m, 1H)	3080(w), 1710(vs) 1460(w), 695(vs)	168(28), 125(100), 97(88)	~150/5
	1.50(s, 6H), 1.90(s, 3H), 2.73(s, 2H), 6.8-7.3(m, 3H)	3080(w), 1705(vs) 1440(m), 690(vs)	182(26), 149(32), 125(100)	~180/5
	1.03(t, 7.5Hz, 3H), 2.4 (q, 7.5Hz, 2H), 2.5-3.2 (A$_2$B$_2$m, 4H), 6.6-7.3 (m, 3H)	3100(w), 1710(vs), 1440(m), 695(vs)	168(53), 139(28), 111(64), 97(100)	~160/20
	1.02(t, 7.2Hz, 3H), 1.49 (d, 7.0Hz, 3H), 2.50(q, 7.2Hz, 2H), 4.05(q, 7.0 Hz, 1H), 6.8-7.3(m, 3H)	3080(w), 1710(vs), 1455(m), 695(vs)	168(29), 111(100)	~160/20

Table 4. (*Contd*)

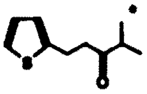
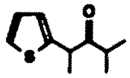
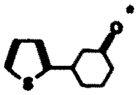
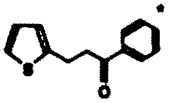
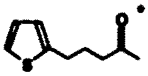
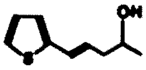
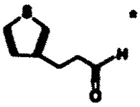
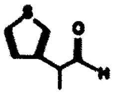
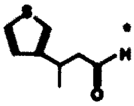
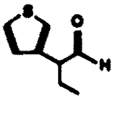
Compounds	^{1}H NMR spectra^{b}	IR spectra^{c}	Mass spectra^{d}	Bp °C/mmHg (Mp°C)
Compounds listed in Table 1				
	1.08(d, 7Hz, 6H), 2.58 (sept, 7Hz, 1H), 2.7-3.2(A_2B_2m, 4H), 6.8-7.2 (m, 3H)	3100(w), 1700(vs), 1440(m), 690(vs)	182(21), 139(49), 110(100)	∼170/20
	1.00(d, 6.6Hz, 3H), 1.09 (d, 7.0Hz, 3H), 1.46(d, 5.2Hz, 3H), 2.84(sept, 7Hz, 1H), 4.21(q, 7.2Hz, 1H), 6.8-7.3(m, 3H)	3080(w), 1710(vs), 1450(m), 695(vs)	182(23), 135(14), 110(100)	∼170/20
	1.6-3.0(m, 8H), 3.0-3.7 (m, 1H), 6.7-7.3(m, 3H)^{f}	3080(w), 1710(vs), 1450(m), 695(s)	180(70), 123(100), 110(94)	∼170/10
	3.27(s, 4H), 6.8-7.0(m, 2H), 7.0-7.2(m, 1H), 7.3-7.7(m, 3H), 7.8-8.1(m, 2H)^{f}	3110(w), 3050(w), 1680(vs), 752(vs), 708(s), 692(s)^{g}	216(82), 111(88), 105(100), 97(87)	∼170/5 (57.0-57.5)^{h}
	1.7-2.2(m, 2H), 2.06(s, 3H), 2.39(t, 6.5Hz, 2H), 2.89(t, 7Hz, 2H), 6.6-7.1(m, 3H)^{f}	3100(w), 1710(vs), 1445(m), 700(vs)	168(28), 111(41), 110(100), 97(72)	∼160/8
	1.18(d, 6.5Hz, 3H), 2.0-2.6(m, 3H), 3.6-4.0(m, 1H), 5.6-7.4(m, 5H)^{f}	3370(s), 1670(m), 960(s), 695(vs)	168(43), 151(30), 124(100), 97(54)	∼160/5
	6.9-7.3(m)	3080(w), 3015(m), 830(s), 690(vs)	166(100), 121(38)	(31-32)^{i}
Compounds listed in Table 2				
	2.56-3.10(A_2B_2m, 4H), 6.8-7.3(m, 3H), 9.72(t, 1.5Hz, 1H)^{f}	3100(m), 1720(vs), 1450(w), 775(s)	140(12), 111(28), 97(62), 43(100)	∼150/10
	1.40(d, 7Hz, 3H), 3.63 (d.q, 7 and 1.6Hz, 1H), 6.8-7.5(m, 3H), 9.53(d, 1.6Hz, 1H)^{f}	3100(m), 1720(vs), 1460(w), 780(s)	140(10), 111(100), 77(18), 43(43)	∼140/10
	1.32(d, 7Hz, 3H), 2.5-2.7(m, 3H), 3.46(t.q, 7 and 1.8Hz, 1H), 6.8-7.3 (m, 3H), 9.64(t, 1.8Hz, 1H)^{f}	3100(w), 1720(vs), 1455(m), 780(s)	154(5), 111(41) 58(13), 45(100)	∼150/10
	0.92(t, 7.4Hz, 3H), 1.90 (m, 7.4 and 7.0Hz, 2H), 3.45(d.t, 7.0 and 2.2Hz, 1H), 6.8-7.5(m, 3H), 9.50 (d, 2.2Hz, 1H)^{f}	3100(m), 1720(vs), 1455(m), 775(s)	154(19), 125(74), 111(100), 97(88)	∼150/10

Table 4. (*Contd*)

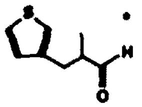
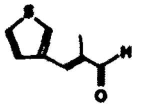
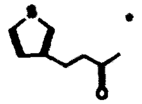
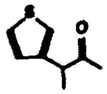
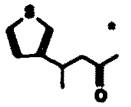
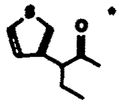
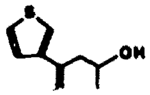
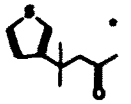
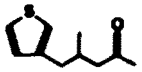
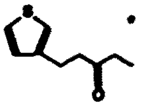
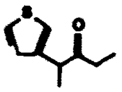
Compounds	^{1}H NMR spectra^b	IR spectra^c	Mass spectra^d	Bp °C/mmHg (Mp°C)
Compounds listed in Table 2				
 *	1.08(d, 6.6Hz, 3H), 2.4-3.2(m, 3H), 6.8-7.2(m, 3H), 9.58(d, 1.2Hz, 1H)^f	3100(w), 1720(vs), 1460(m), 770(s)	154(6), 126(30), 111(30), 97(100)	~150/10
	2.04(s, 3H), 7.0-7.5 (m, 4H), 9.44(s, 1H)^f	3100(m), 1670(vs), 1620(s), 775(s)	152(100), 124(67), 123(79), 97(78)	~160/10
 *	2.06(s, 3H), 2.52-3.02 (A_2B_2m, 4H), 6.7-7.3(m, 3H)^f	3100(w), 1710(vs), 1410(m), 770(s)	154(34), 111(100), 97(44)	~150/10
	1.33(d, 7.0Hz, 3H), 1.99 (s, 3H), 3.75(q, 7.0Hz, 1H), 6.8-7.3(m, 3H)^f	3090(m), 1708(vs), 1450(m), 785(s)	154(45), 111(100), 67(46)	~150/10
 *	1.26(d, 6.7Hz, 3H), 2.00 (s, 3H), 2.5-2.7(m, 2H), 3.1-3.7(m, 1H), 6.8-7.3 (m, 3H)^f	3090(w), 1705(vs), 1450(m), 770(s)	168(61), 125(100), 111(86), 97(54)	~150/10
 *	0.83(t, 7.4Hz, 3H), 1.99 (s, 3H), 1.4-2.2(m, 2H), 3.54(t, 7.4Hz, 1H), 6.8-7.3(m, 3H)^f	3090(w), 1705(vs), 1460(w), 775(s)	168(37), 125(96), 97(100)	~150/10
	1.15(d, 6.2Hz, 3H), 1.42 (br.s, 1H), 2.4-2.6(m, 2H), 3.7-4.0(m, 1H), 5.03(m, 1H), 5.38(d, 1.5Hz, 1H), 7.1-7.3 (m, 3H)^f	3380(br. s), 3090 (m), 1620(m), 790 (s)	168(6), 150(4), 125(45), 45(100)	~150/5
 *	1.41(s, 6H), 1.75(s, 3H), 2.57(s, 2H), 6.8-7.3(m, 3H)^f	3100(w), 1700(vs) 1360(s), 780(s)	182(40), 125(100), 97(62)	~160/10
	0.8-1.0(m, 3H), 1.7-2.6 (m, 1H), 2.01(s, 3H), 2.1-3.4(m, 2H), 2.4-2.6(m, 2H), 6.7-7.3(m, 3H)^f	3100(w), 1708(vs), 1370(s), 775(s)	182(17), 125(100), 97(77)	~170/4
 *	1.00(t, 7.2Hz, 3H), 2.33 (q, 7.2Hz, 2H), 2.4-3.1 (A_2B_2m, 4H), 6.7-7.3(m, 3H)^f	3090(w), 1710(vs), 1450(m), 775(s)	168(86), 139(25), 111(100), 97(95)	~170/10
	0.95(t, 7.2Hz, 3H), 1.36 (d, 7.0Hz, 3H), 2.34(q, 7.2Hz, 2H), 3.80(q, 7.0 Hz, 1H), 6.8-7.4(m, 3H)^f	3090(w), 1710(vs), 1455(s), 780(s)	168(48), 111(100), 58(13)	~160/10

Table 4. (*Contd.*)

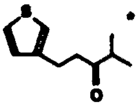
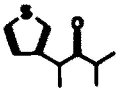
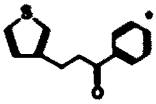
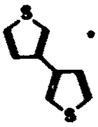
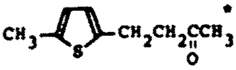
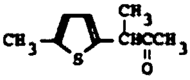
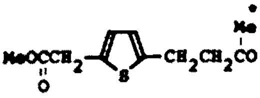
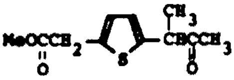
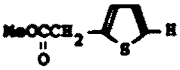
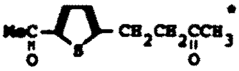
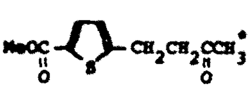
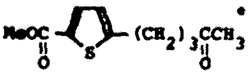
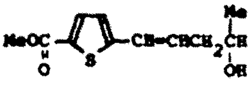
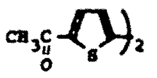
Compounds	^{1}H NMR spectra[b]	IR spectra[c]	Mass spectra[d]	Bp °C/mmHg (Mp°C)
Compounds listed in Table 2				
 *	1.02(d, 7.0Hz, 6H), 2.48 (sept, 7.0Hz, 1H), 2.5-3.0(A_2B_2m, 4H), 6.7-7.3 (m, 3H)[f]	3100(w), 1710(vs), 1470(m), 775(s)	182(53), 111(99), 97(100), 71(33)	∿170/10
	0.91(d, 7.0Hz, 3H), 1.03 (d, 7.0Hz, 3H), 1.33(d, 7.0Hz, 3H), 2.65(sept, 7.0Hz, 1H), 3.96(q, 7.0 Hz, 1H), 6.8-7.3(m, 3H)[f]	3100(w), 1712(vs) 1455(m), 768(s)	182(32), 111(100), 77(33)	∿165/10
 *	2.9-3.4(A_2B_2m, 4H), 6.9-7.3(m, 3H), 7.3-7.6(m, 3H), 7.8-8.1(m, 2H)[f]	3105(w), 3050(w), 1680(vs), 776(vs), 744(vs), 695(s)	216(73), 111(94), 105(100), 97(47)	∿180/3 (49.5-50.0)[h]
 *	7.12-7.34(m, 6H)	3100(m), 1200(m), 1090(m), 850(m), 760(s)	166(100), 121(62), 83(4)	∿180/10 (130-131)[j]
Compounds listed in Table 3				
 *	2.06(s, 3H), 2.40(s, 3H), 2.5-3.2(A_2B_2m, 4H), 6.44 (br.s, 2H)[f]	3070(w), 1712(vs), 1360(s), 800(s)	168(87), 153(10), 111(100), 97(22)	∿170/10
	1.38(d, 7.5Hz, 3H), 2.04 (s, 3H), 2.44(s, 3H), 3.79(q, 7.5Hz, 1H), 6.5-6.7(br.s, 2H)[f]	3070(w), 1708(vs), 1360(m), 800(s)	168(19), 125(100), 91(57)	∿170/10
 *	2.10(s, 3H), 2.5-3.2(A_2B_2m, 4H), 3.69(br.s, 5H), 6.56(d, 3Hz, 1H), 6.67(d, 3Hz, 1H)[f]	3075(w), 1740(vs), 1720(vs), 1440(m), 807(s)	226(63), 183(63), 167(94), 123(100)	∿155/2
	1.41(d, 7.5Hz, 3H), 2.07 (s, 3H), 3.70(s, 3H), 3.71(q, 7.5Hz, 1H), 6.66 (d, 3Hz, 1H), 6.74(d, 3Hz, 1H)[f]	3075(w), 1740(vs), 1720(vs), 1440(m), 814(s)	226(20), 183(100), 151(29), 123(56)	∿155/2
	3.69(s, 3H), 3.76(s, 2H), 6.8-7.0(m, 2H), 7.1-7.2 (m)[f]	3100(w), 1735(vs), 1440(s), 700(vs)	156(91), 97(100)	∿150/30
 *	2.11(s, 3H), 2.42(s, 3H), 2.6-3.3(A_2B_2m, 4H), 6.78 (d, 4Hz, 1H), 7.42(d, 4Hz, 1H)[f]	3080(w), 1713(s), 1660(vs), 1440(m), 810(s)	196(83), 181(92), 153(100), 111(77)	∿170/5 (74.0-74.5)[k]

Table 4. (*Contd*)

Compounds	^{1}H NMR spectra[b]	IR spectra[c]	Mass spectra[d]	Bp °C/mmHg (Mp°C)
Compounds listed in Table 3				
 *	2.13(s, 3H), 2.47-3.25 (A_2B_2m, 4H), 3.84(s, 3H), 6.76(d, 4Hz, 1H), 7.51(d, 4Hz, 1H)[f]	3080(w), 1710(vs), 1460(s), 750(s)	212(91), 169(93), 155(100), 97(45)	∼180/1
 *	1.7-2.2(m, 2H), 2.06(s, 3H), 2.41(t, 6.5Hz, 2H), 2.83(t, 7.0Hz, 2H), 3.81 (s, 3H), 6.75(d, 3.5Hz, 1H), 7.53(d, 3.5Hz, 1H)[f]	2990(w), 1705(vs), 1465(s), 1095(s), 750(m)	226(19), 169(43), 168(100), 137(87)	∼160/1
	1.21(d, 6.5Hz, 3H), 1.7-2.3(m, 2H), 2.8(br.s, 1H), 3.7(m, 1H), 3.90(s, 3H), 5.1-6.5(m, 2H), 6.80(d, 4Hz, 1H), 7.50(d, 4Hz, 1H)[f]	3450(s), 3075(w), 1700(vs), 1452(s), 960(s), 745(s)	226(11), 182(44), 168(33), 45(100)	∼160/1
	3.84(s, 6H), 7.19(d, 4Hz, 2H), 7.67(d, 4Hz, 2H)	3080(w), 1710(vs), 1445(s), 742(s)	282(12), 222(47), 220(47), 191(100)	∼180/1 (>300)
	2.59(s, 6H), 7.32(d, 4Hz, 2H), 7.55(d, 4Hz, 2H)	3070(vw), 1660(vs) 1438(m), 794(ms)	250(54), 235(100) 153(53), 121(63)	(231-232)

a) The products marked with * gave the satisfactory combustion analytical data (± 0.3% for C, H, and S).

b) Unless otherwise noted, the peaks are given in δ-value measured in $CDCl_3$ (TMS as an internal standard).

c) Unless otherwise noted, the peaks are given in cm^{-1} measured by a film method.

d) The values in parentheses refer to the relative intensities.

e) The boiling point is given as the chamber temperature (Kugelrohr distillation).

f) in CCl_4

g) KBr disk

h) Recrystallized from n-hexane.

i) Recrystallized from ethanol, lit., 33°C: O. Eberhard, Chem. Ber., 27, 2919 (1894).

j) Recrystallized from ethanol, lit., 132°C: R. Nahnsen, Chem. Ber., 17, 789 (1884).

k) Recrystallized from ethyl acetate.

l) Recrystallized from benzene-hexane.

m) Recrystallized from benzene, lit., 231-232°C: W. Steinkopf and H-J. v. Petersdorff, Ann., 543, 119 (1940).

Ethyl 9-oxo-trans-2-decenoate ethylene ketal 13. A mixture of 11 (250 mg, 0.68 mmol) and $NaIO_4$ (162 mg, 0.76 mmol) in 4 ml of MeOH and 6 ml of H_2O was stirred at r.t. for 23 hr then at 40° for 2 hr. The mixture was extracted with CH_2Cl_2 and dried over $MgSO_4$. After evaporation of solvent the mixture was purified by plc (silica gel, hexane/acetone–2:1) to give 12 in 100% yield (85% conversion), which was dehydrosulfenylated by heating in toluene at reflux for 20 min under argon. The product was subjected directly to plc purification (silica gel, benzene/ethyl acetate, 20:1) to give 13 in 85% yield. 13: $\delta^{TMS}_{CCl_4}$ 1.20 (s, 3H), 1.25 (t, 7 Hz, 3H), 1.2–1.8 (m, 8H), 2.0 ~ 2.43 (m, 2H), 3.83 (s, 4H), 4.14 (q, 7 Hz, 2H), 5.74 (d, 16 Hz, 1H) and 6.90 (d.t, 16 and 7 Hz, 1H). ν^{film}_{max} 2980 (w), 2940 (m), 1720 (vs), 1655 (m), 1375 (m), 1265 (m), 1205–1160 (m, broad peaks), 980 (w), and 880 ~ 840 (m, broad peaks). (Found: 256.1723. Calc. for $C_{14}H_{24}O_4$: 256.1673).

9-Oxo-trans-2-decenoic acid 14. Into a soln of 13 (120 mg, 0.47 mmol) in 5 ml of acetone was added 0.5 ml of 2N-HCl and stirred at r.t. for 20 hr. After the neutralization with sat Na_2CO_3 and evaporation of acetone, a soln of KOH (54 mg) in 10 ml of MeOH was added into the mixture. After refluxing for 2 hr, the mixture was acidified with 2N-HCl and extracted with ether. The ether extracts (20 + 10 + 10 ml) were washed with sat NaCl and dried over Na_2SO_4. After evaporation of the solvent, the residue was subjected to plc (silica gel, hexane/acetone 2/1) to give 85 mg of **14** (97%). **14**: $\delta^{CDCl_3}_{TMS}$ 1.15–1.78 (m, 6H), 2.06 (s, 3H), 2.15–2.54 (m, 4H), 5.76 (d.t., 16 and 0.6 Hz, 1H), 7.01 (d.t., 16 and 7 Hz, 1H) and 10.2 (br. s, 1H). ν^{neat}_{max} 2912 (s), 2840 (m), 1705 (vs), 1650 (m), 1415 (m), 1360 (m), 1280 (w), 1165 (m), 1085 (m), 1040 (w), 965 (w). *m/e* (rel. int.) 184 (32), 166 (95), 138 (43), 127 (59), 109 (76), 99 (87), 95 (84), 80 (85), 67 (90) and 58 (100). (Found: 184.1163 Calc. for $C_{10}H_{16}O_3$: 184.10994).

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