

Acyldemetallation of titanium(III) π -allylic complexes

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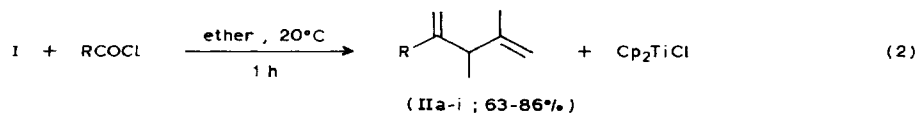
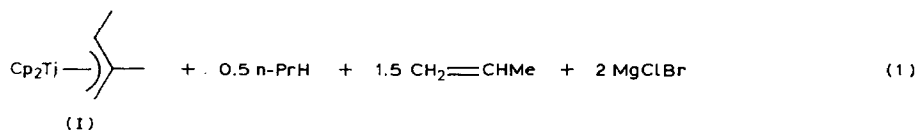
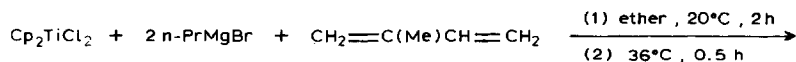
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Abstract

Titanium(III) π -allylic complexes, prepared by the interaction of 1,3-dienes or trienes with Cp_2TiCl_2 and $n\text{-PrMgBr}$, react with carboxylic acid chlorides RCOCl (R = alkyl, aryl, alkenyl) to give β , γ -unsaturated ketones in high yields. The reaction takes place at the most substituted carbon atom of the π -allylic ligand.

Simple and effective routes to organometallic compounds are achieved by olefin, diene, and acetylene hydrometallations which are presently widely employed in organic synthesis (e.g. refs. 1, 2). The hydrotitanation of 1,3-dienes in particular, results in the Ti^{III} π -allylic complexes, which can be usefully applied to regio- and stereoselective condensations with carbonyl compounds [3,4]. Here we report on our



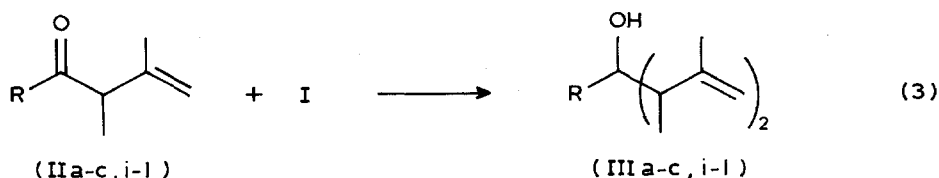
(R = Ph (a), PhCH_2 (b), 2-furyl (c),
 3-pyridyl (d), $i\text{-Pr}$ (e),
 $\text{CH}_2=\text{C}(\text{Me})$ (f), $\text{MeO}_2\text{C}(\text{CH}_2)_3$ (g),
 $\text{Br}(\text{CH}_2)_4$ (h), $i\text{-Bu}$ (i), $\text{Me}(\text{CH}_2)_4$ (j))

studies of the reactions of Ti^{III} π -allylic complexes with carboxylic acid chlorides with a view to developing some convenient methods for synthesizing asymmetrical ketones.

Complex I prepared in situ by the interaction of Cp_2TiCl_2 and n-propylmagnesium bromide in the presence of isoprene [5], has been found to react with carboxylic acid chlorides under mild conditions and, as a result, gives high yields of related β , γ -unsaturated ketones (II) (Table 1).

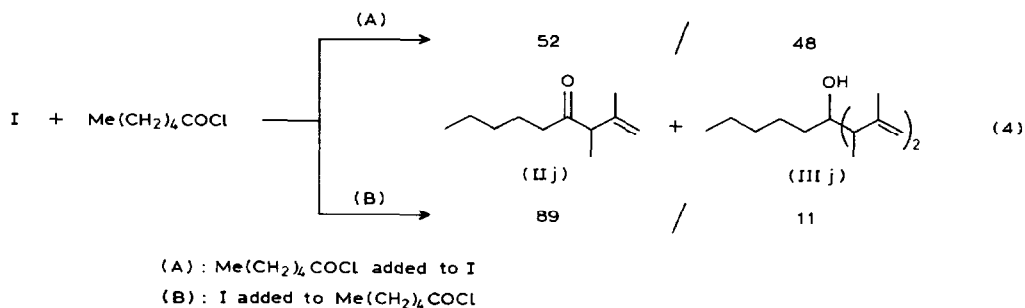
From the data obtained, it was seen that the reactions of I with chlorides of both the aromatic and the aliphatic series proceed with the exclusive involvement of the most-substituted end of the π -allylic system. The similarity in regioselectivities have been observed in reactions of Ti^{III} π -allylic complexes with aldehydes and ketones [3,6,7].

The main side-reaction is the subsequent reaction of an acyldemetallation product with organotitanium reagent to give tertiary alcohol III after the usual work-up with water and ether.

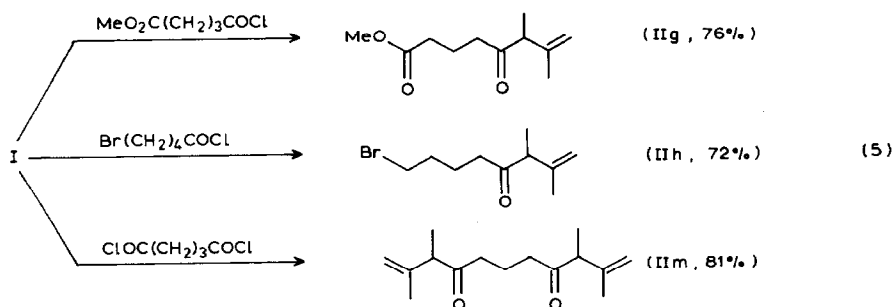


(R = Me (k), *trans*-PhCH=CH (l))

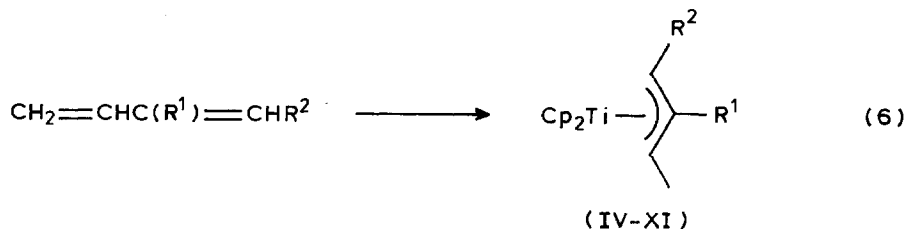
As a whole, the contribution by side-reaction 3 decreases with increase in the spatial hindrance by the initial chloride molecule. When RCOCl are added to solutions of complex I, the ratio of II/III was found to increase along this series of R: Me, *trans*-PhCH=CH < $\text{Me}(\text{CH}_2)_4$ < 2-furyl < *i*-Bu, PhCH_2 < Ph < *i*-Pr, $\text{CH}_2=\text{C}(\text{Me})$; the only tertiary alcohols (IIIk, l) were obtained from RCOCl in which R = Me, and *trans*-PhCH=CH, and the only asymmetrical ketones (IIe, f) were obtained from those with R = *i*-Pr, $\text{CH}_2=\text{C}(\text{Me})$. In reactions involving the chlorides of acetic, capronic, pyromucic acids, the yields of acyldemetallation products are increased when the order in which the reagents are mixed is changed (solution of I added to that of RCOCl) in the presence of a 1.5-fold excess of chloride.



The reactions of complex I with $\text{MeO}_2\text{C}(\text{CH}_2)_3\text{COCl}$ and $\text{Br}(\text{CH}_2)_4\text{COCl}$ favour retention of ester and halide groups of the initial compounds. The reaction of



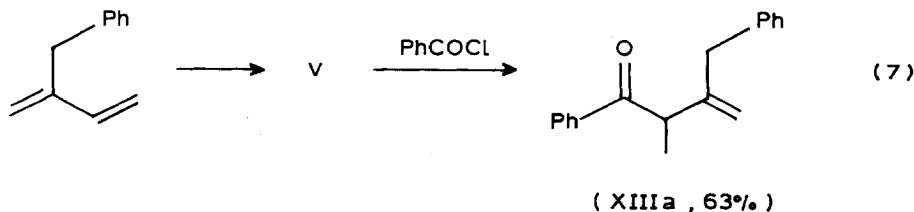
glutaric acid dichloride with two equivalents of I results in the related diketone (IIIm).



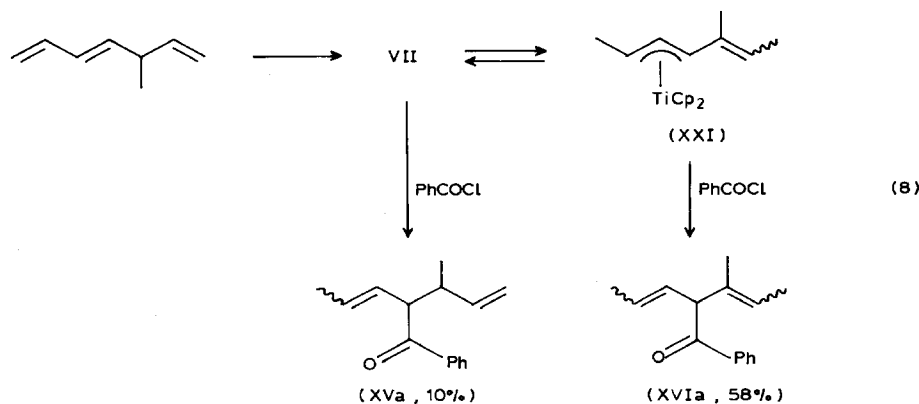
- (IV , $\text{R}^1 = \text{R}^2 = \text{H}$;
 V , $\text{R}^1 = \text{CH}_2\text{Ph}$, $\text{R}^2 = \text{H}$;
 VI , $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$;
 VII , $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}(\text{Me})\text{CH}=\text{CH}_2$;
 VIII , $\text{R}^1 = \text{CH}_2\text{CH}=\text{CH}_2$, $\text{R}^2 = \text{H}$;
 IX , $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}=\text{CH}_2$;
 X , $\text{R}^1 = \text{SiEt}_2\text{Me}$, $\text{R}^2 = \text{H}$;
 XI , $\text{R}^1 = \text{CH}_2\text{SiMe}_3$, $\text{R}^2 = \text{H}$)

In addition to complex I some other π -allylic complexes of Ti^{III} , prepared in situ by hydrotitanation of dienes [5] and trienes [8] under the same conditions as those of eq. 1, have been introduced into the reaction with carboxylic acid chlorides.

β,γ -Unsaturated ketones (XII-XX) were formed during the reaction of reagents IV-XI with RCOCl ($\text{R} = \text{Ph}$, i-Pr, i-Bu, $\text{CH}_2=\text{C}(\text{Me})$) under mild conditions (ether, 20°C , 1 h) to give 50–80% yields and 100% regioselectivity (Table 2) *.

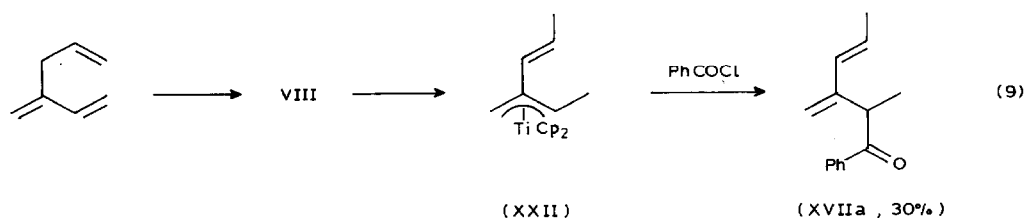


* GLC analysis data indicate that the amount of tertiary alcohols formed as in eq. 3 does not exceed 5% in each case.

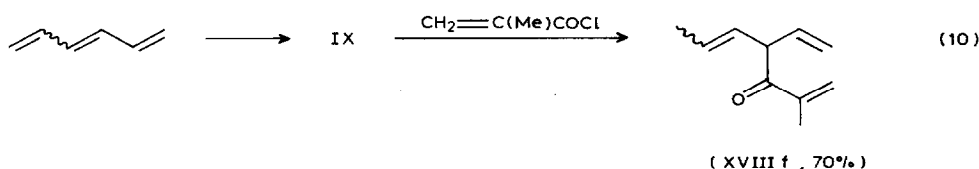


In addition to acyldemetallation products, the reactions of complex VI also gave the "dimerization" product of the initial organometallic compound, i.e. 4,5-dimethyl-2,6-octadiene in 11–34% yields (Table 2, nos. 3, 4).

Reagent VII, during its formation, is partially isomerized into XXI [8] and under the effect of PhCOCl, to give a mixture of two ketones (XVa, XVIa), XVIa without consequence, terminal double bonds being significantly prevalent in that mixture. In contrast to 5-methyl-1,3,6-heptatriene, 2-allyl butadiene is hydrotitanated so as to be transformed completely into the isomerized complex XXII, the reaction of which with PhCOCl gives ketone XVIIa containing a 1,3-diene system, along with the formation of small amount of resin.



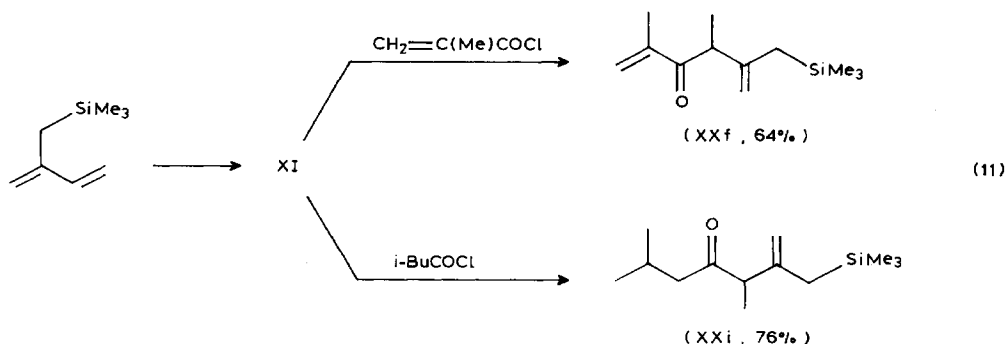
The reaction of organotitanium complex IX prepared from 1,3,5-hexatriene in each case gives only a single regioisomer, inasmuch as both reactive sites of the π -allyl fragments are represented by the secondary carbon atoms.



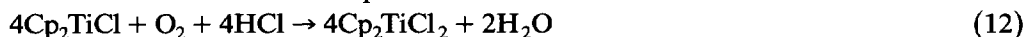
Analogous regular phenomena have been observed for the complexes VII and XXI (eq. 8).

π -Allylic complexes X, XI containing trialkylsilylic substituents react with acid chlorides to form the related organosilicon β , γ -unsaturated ketones.

It should be noted, that in each case (Tables 1, 2) after reaction was complete, the initial Cp_2TiCl_2 was isolated in more than 90% yield after treatment of the reaction



mixture with 4*N* HCl in the presence of air *.



Thus, acyldemetallation of Ti^{III} π -allylic complexes is carried out under mild conditions to give high product yields and, therefore can serve as a convenient route to the various β , γ -unsaturated ketones immediately from dienes (trienes) and carboxylic acid chlorides.

Experimental

2-Benzyl- and 2-allyl butadienes were prepared by the reaction of $\text{CH}_2=\text{C}(\text{MgCl})-\text{CH}=\text{CH}_2$ with PhCH_2Cl and $\text{CH}_2=\text{CHCH}_2\text{Br}$ [9]. 2-(Methyldiethylsilyl)butadiene

(Continued on p. 30)

Table 1

Reactions of complex I with RCOCl (ether, 20° C, 1 h)

R	Reaction conditions ^a	II/III ^b	Compound	Yield (%) ^c
Ph	A	95/5	IIa	86
PhCH ₂	A	90/10	IIb	84
2-furyl	A	73/27	IIIc	20 ^d
2-furyl	B	93/7	IIc	66
3-pyridyl	A	— ^e	IIId	63
i-Pr	A	100/0	IIe	75
CH ₂ =C(Me)	A	100/0	IIIf	70
MeO ₂ C(CH ₂) ₃	B	100/0	IIg	76
Br(CH ₂) ₄	B	100/0	IIh	72
i-Bu	A	90/10		
i-Bu	B	100/0	IIi	79
Me(CH ₂) ₄	A	52/48	IIIj	30 ^d
Me(CH ₂) ₄	B	89/11	IIj	80
Me	A	0/100	IIIk	48 ^d
Me	B	50/50	IIk	30
trans-PhCH=CH	A	0/100	IIIl	42 ^d

^a A: RCOCl was added to I solution, $\text{RCOCl}/\text{I} = 1/1$; B: a solution of I was slowly added to one of RCOCl one, $\text{RCOCl}/\text{I} = 1.5/1$. ^b II/III mole ratio was found with GLC method. ^c Yields of isolated products are given. ^d Yield calculated for the initial RCOCl . ^e II/III ratio was not determined.

* With the exception of reactions as in eq. 11, in which the treatment with acid was impossible owing to likely desilylation.

Table 2

Reactions of titanium(III) π -allylic complexes with RCOCl (ether, 20°C , 1 h, $\text{RCOCl}/\text{complex} = 1/1$) ^a

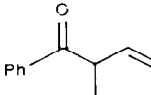
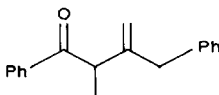
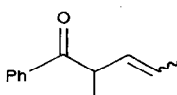
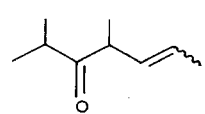
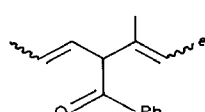
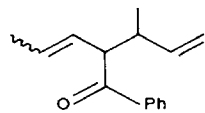
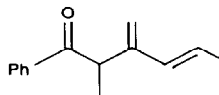
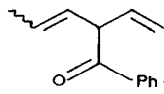
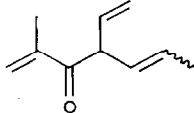
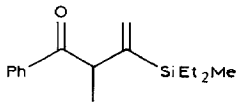
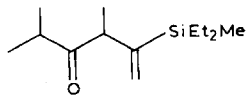
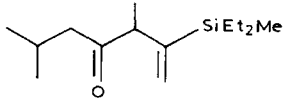
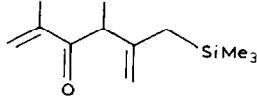
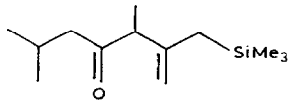
Initial diene (triene)	Complex	R	Reaction product	Yield (%) ^b
Butadiene	IV	Ph	 (XIIa)	81
2-Benzyl-butadiene	V	Ph	 (XIIIa)	63
Piperylene (<i>E/Z</i> = 93/7)	VI	Ph	 (XIVa) (<i>E/Z</i> ~ 1/1) ^c	51 34 ^d
Piperylene (<i>E/Z</i> = 93/7)	VI	i-Pr	 (XVe) (<i>E/Z</i> ~ 1/1) ^c	77 11 ^d
<i>Trans</i> -5-methyl- 1,3,6-heptatriene	VII	Ph	 (XVIa)	58
			 (XVa)	10
2-Allylbutadiene	VIII	Ph	 (XVIIa)	30 ^f

Table 2 (continued)

Initial diene (triene)	Complex	R	Reaction product	Yield (%) ^b
1,3,5-Hexatriene (<i>E/Z</i> = 65/35)	IX	Ph	 (XVIIIa) (<i>E/Z</i> ~ 3/2) ^c	80
1,3,5-Hexatriene (<i>E/Z</i> = 65/35)	IX	CH ₂ =C(Me)	 (XVIII f) (<i>E/Z</i> ~ 3/2) ^c	70
CH ₂ =C(SiEt ₂ Me)CH=CH ₂	X	Ph	 (XIXa)	70
CH ₂ =C(SiEt ₂ Me)CH=CH ₂	X	i-Pr	 (XIXe)	68
CH ₂ =C(SiEt ₂ Me)CH=CH ₂	X	i-Bu	 (XIX i)	73
CH ₂ =C(CH ₂ SiMe ₃)CH=CH ₂	XI	CH ₂ =C(Me)	 (XX f)	64
CH ₂ =C(CH ₂ SiMe ₃)CH=CH ₂	XI	i-Bu	 (XX i)	76

^a RCOCl was added to the solution of a complex in each experiment. ^b Yields of isolated products.^c According to NMR spectral data. ^d Yield of [MeCH=CHCH(Me)]₂. ^e Mixture of stereoisomers.^f Pronounced gumming.

was obtained from the reaction of 1,4-dichlorobut-2-yn and methyldiethylsilane [10]. 2-(Trimethylsilylmethyl)butadiene was synthesized with chloroprene effected by $\text{Me}_3\text{SiCH}_2\text{MgCl}$ in the presence of $\text{NiCl}_2(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)$ [11]. *Trans*-5-methyl-1,3,6-heptatriene [12], 1,3,5-hexatriene (*E/Z* = 65/35) [13], bis(cyclopentadienyl)titanium dichloride [14], and carboxylic acid chlorides were prepared by standard procedures. All reactions were carried out under dry argon. Ether was dried over LiAlH_4 immediately before use.

The samples were separated on a "Chrom-5" chromatograph with a flame-ionization detector, carrier gas He (50 ml/min); 1.2 m $\times$ 3 mm column, 5% SE-30 on Inerton-super. For the preparative separation of regioisomers, a Perkin-Elmer F-21 preparative chromatograph was used with He as carrier gas (300 ml/min) and 5 m $\times$ 8 mm column, 5% SE-30 on NAW chromaton. PMR spectra were recorded on a Tesla BS-567 (100 MHz) and Tesla BS-467 (60 MHz) spectrometers. ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer, with TMS as the internal standard. IR spectra were detected on UR-20 device with a thin layer of the sample. Mass spectra were recorded with an MX-1306 spectrometer with a lapping cylinder temperature of 100°C and ionization energies of 70 and 12 eV.

Synthesis of β,γ -unsaturated ketones by the reaction of π -allylic complexes of Ti^{III} with carboxylic acid chlorides

A solution of *n*-propylmagnesium bromide in 2.13 ml (3.2 mmol) of 1.5 *M* ether was added to 0.4 g (1.6 mmol) of a Cp_2TiCl_2 suspension in 8 ml of ether with a 1.92–2.4 mmol content of freshly distilled diene (triene) under stirring and cooling to 0°C. The mixture was stirred for 2 h at 20°C, and then boiled for 0.5 h. Carboxylic acid chloride (1.6 mmol) was added to the prepared solution of Ti^{III} π -allylic complex (or a solution of π -allylic complex was added dropwise to a solution of the chloride (2.4 mmol) in 5 ml of ether during 15 min. The reaction mixture was kept for 1 h at 20°C. After hydrolysis with 4*N* HCl (10 ml), the reaction mixture was stirred for 0.5 h in the presence of air, filtered to remove the precipitated Cp_2TiCl_2 , and extracted with ether (3 $\times$ 7 ml). The ether layer was washed with water (3 $\times$ 7 ml), dried with MgSO_4 , concentrated, and subjected to GLC. The reaction products were isolated by column chromatography on silica gel and were identified from their IR and NMR spectra.

The reactions of complexes I, IV–XI with RCOCl were carried out by the procedure described ($\text{R} = \text{Ph}$, 2-furyl-3-, pyridyl, PhCH_2 , *i*-Pr, $\text{CH}_2=\text{CH}(\text{Me})$, *i*-Bu, $\text{Me}(\text{C}_2\text{H}_4)_4$ Me, $\text{MeO}_2\text{C}(\text{CH}_2)_3$, $\text{Br}(\text{CH}_2)_4$, $\text{ClCO}(\text{CH}_2)_3$, *trans*- $\text{PhCH}=\text{CH}$) (Tables 1, 2).

In the reaction of complex I with nicotinyll chloride, the addition of 4*N* HCl and separation of Cp_2TiCl_2 was followed by the neutralization of the aqueous layer with 10 ml of NaHCO_3 saturated solution and subsequently extracted with ether (5 $\times$ 7 ml); the ether layer was treated as described above.

1-Phenyl-2,3-dimethyl-3-buten-1-one (IIa). 0.239 g (86%) isolated, R_f 0.51 (hexane/ether = 4/1). PMR spectrum (CCl_4 , $\delta(\text{ppm})$): 1.15 (d, 3H, CH_3 , *J* 7 Hz), 1.73 (s, 3H, $\text{CH}_3\text{C}=\text{C}$), 4.1(q, 1H, *J* 7 Hz), 4.87(m, 2H, $\text{CH}_2=\text{C}$), 7.1–7.55 and 7.8–8.1(m, 5H arom.). IR spectrum (ν (cm^{-1})): 3085, 3045, 1695, 1650, 1610, 1510, 920, 760, 700. Mass spectrum (m/z): 174 [M^+].

1-Phenyl-3,4-dimethyl-4-penten-2-one (IIb). 0.253 g (84%) isolated, R_f 0.51 (hexane/ether = 4/1). PMR spectrum (CCl_4 , $\delta(\text{ppm})$): 1.12 (d, 3H, CH_3 , *J* 7 Hz),

1.61(s, 3H, CH₃C=), 3.32(q, 1H, CH, *J* 7 Hz), 3.7(s, 2H, CH₂Ph), 4.9(m, 2H, CH₂=), 7.21 (m, 5H arom.). IR spectrum (ν (cm⁻¹)): 3080, 3040, 1710, 1640, 1600, 1500, 910, 720, 690. Mass spectrum (*m/z*): 188 [*M*⁺].

1-(2-Furyl)-2,3-dimethyl-3-buten-1-one (IIc). 0.173 g (66%) isolated, *R*_f 0.48 (hexane/ether = 4/1). PMR spectrum (CCl₄, δ (ppm)): 1.23 (d, 3H, CH₃, *J* 7 Hz), 1.71 (s, 3H, CH₃C=), 3.91 (q, 1H, CH, *J* 7 Hz), 4.83 (m, 2H, CH₂=), 6.35–6.6 and 7.0–7.7 (m, 3H of furane ring). IR spectrum (ν (cm⁻¹)): 3145, 3090, 1680, 1650, 1570, 1480, 900, 780. Mass spectrum (*m/z*): 164 [*M*⁺].

1-(3-Pyridyl)-2,3-dimethyl-3-buten-1-one (IIId). 0.176 g (63%) isolated, *R*_f 0.32 (hexane/ether = 4/1). PMR spectrum (CCl₄, δ (ppm)): 1.35 (d, 3H, CH₃, *J* 7 Hz), 1.73 (s, 3H, CH₃C=), 4.1 (q, 1H, CH, *J* 7 Hz), 4.9 (m, 2H, CH₂=), 7.2–7.5, 8.1–8.4, 8.5–8.9, 9.2 (m, 4H of pyridine ring). IR spectrum (ν (cm⁻¹)): 3070, 3035, 1690, 1640, 1585, 1460, 900, 780, 735, 705. Mass spectrum (*m/z*): 175 [*M*⁺].

2,4,5-Trimethyl-5-hexen-3-one (IIe). 0.168 g (75%) isolated, *R*_f 0.45 (hexane/ether = 10/1). PMR spectrum (CCl₄, δ (ppm)): 0.95 and 1.0 (d, 6H, CH₃, *J* 7 Hz), 1.08 (d, 3H, CH₃CC=, *J* 7 Hz), 1.62 (s, 3H, CH₃C=), 2.75 (qq, 1H, CH, *J*₁ = *J*₂ = 7 Hz), 3.3 (q, 1H, CH=, *J* 7 Hz), 4.8 (m, 2H, CH₂=). IR spectrum (ν (cm⁻¹)): 3085, 1710, 1640, 910. Mass spectrum (*m/z*): 140 [*M*⁺].

2,4,5-Trimethyl-1,5-hexadien-3-one (IIIf). 0.155 g (70%) isolated, *R*_f 0.43 (hexane/ether = 10/1). PMR spectrum (CCl₄, δ (ppm)): 1.15 (d, 3H, CH₃, *J* 6 Hz), 1.65 (s, 3H, CH₃C=), 1.83 (s, 3H, =C(CH₃)CO), 3.82 (q, 1H, CH, *J* 6 Hz), 4.75 (m, 2H, CH₂=), 5.63 and 5.92 (m, 2H, CH₂=CCO). IR spectrum (ν (cm⁻¹)): 3085, 1680, 1640, 900. Mass spectrum (*m/z*): 138 [*M*⁺].

1-Carbomethoxy-5,6-dimethyl-6-hepten-4-one (IIg). 0.241 g (76%) isolated, *R*_f 0.23 (hexane/ether = 3/1). PMR spectrum (CCl₄, δ (ppm)): 1.15 (d, 3H, CH₃, *J* 7 Hz), 1.66 (s, 3H, CH₃C=), 1.7–2.7 (m, 6H, CH₂), 3.23 (q, 1H, CH, *J* 7 Hz), 3.68 (s, 3H, CH₃O), 4.91 (m, 2H, CH₂=). IR spectrum (ν (cm⁻¹)): 3090, 1735, 1710, 1645, 910. Mass spectrum (*m/z*): 198 [*M*⁺].

8-Bromo-2,3-dimethyl-1-octen-4-one (IIh). 0.269 g (72%) isolated, *R*_f 0.40 (hexane/ether = 3/1). PMR spectrum (CCl₄, δ (ppm)): 1.15 (d, 3H, CH₃, *J* 7 Hz), 1.66 (s, 3H, CH₃C=), 1.65–2.0 (m, 4H, CH₂), 2.47 (t, 2H, CH₂CO, *J* 6 Hz), 3.23 (q, 1H, CH, *J* 7 Hz), 3.37 (t, 2H, CH₂Br, *J* 6.5 Hz), 4.89 (m, 2H, CH₂=). IR spectrum (ν (cm⁻¹)): 3070, 1705, 1640, 900, 730. Mass-spectrum (*m/z*): 233 [*M*⁺].

2,3,6-Trimethyl-1-hepten-4-one (IIi). 0.194 g (79%) isolated, *R*_f 0.45 (hexane/ether = 10/1). PMR spectrum (CCl₄, δ (ppm)): 0.8–1.5 (m, 7H, (CH₃)₂CH), 1.1 (d, 3H, CH₃CC=, *J* 6.5 Hz), 1.63 (s, 3H, CH₃C=), 2.23 (m, 2H, CH₂), 3.1 (q, 1H, CHC=, *J* 6.5 Hz), 4.82 (m, 2H, CH₂=). IR spectrum (ν (cm⁻¹)): 3085, 1715, 1635, 900. Mass spectrum (*m/z*): 154 [*M*⁺].

2,3-Dimethyl-1-nonen-4-one (IIj). 0.214 g (80%) isolated, *R*_f 0.41 (hexane/ether = 10/1). PMR spectrum (CCl₄, δ (ppm)): 1.1 (d, 3H, CH₃, *J* 7 Hz), 0.85–1.55 (m, 9H, CH₃(CH₂)₃), 1.63 (s, 3H, CH₃C=), 2.33 (m, 2H, CH₂CO), 3.15 (q, 1H, CH, *J* 7 Hz), 4.87 (m, 2H, CH₂=). IR spectrum (ν (cm⁻¹)): 3085, 1715, 1635, 900. Mass spectrum (*m/z*): 168 [*M*⁺].

3,4-Dimethyl-4-penten-2-one (IIk). 0.054 g (30%) isolated, *R*_f 0.40 (hexane/ether = 7/1). PMR spectrum (CCl₄, δ (ppm)): 1.12 (d, 3H, CH₃, *J* 6.5 Hz), 1.63 (s, 3H, CH₃C=), 2.06 (s, 3H, CH₃CO), 3.1 (q, 1H, CH, *J* 6.5 Hz), 4.85 (m, 2H, CH₂=). IR spectrum (ν (cm⁻¹)): 3085, 1715, 1635, 900. Mass spectrum (*m/z*): 112 [*M*⁺].

2,3,9,10-Tetramethyl-1,10-undecadien-4,8-dione (IIIm). 0.306 g (81%) isolated, *R*_f

0.23 (hexane/ether = 3/1). PMR spectrum (CCl_4 , $\delta(\text{ppm})$): 1.07 (d, 6H, CH_3 , J 7 Hz), 1.57 (s, 6H, $\text{CH}_3\text{C}=\text{C}$), 1.67 (tt, 2H, CH_2 , $J_1 = J_2 = 7$ Hz), 2.38 (t, 4H, CH_2CO , J 7 Hz), 3.11 (q, 2H, CH, J 7 Hz), 4.77 (m, 2H, $\text{CH}_2=\text{C}$). IR spectrum (ν (cm^{-1})): 3065, 1710, 1640, 900. Mass spectrum (m/z): 236 [M^+].

Bis(3-methyl-3-buten-2-yl)-2-furylcarbinol (IIIc). 0.075 g (20%) isolated, R_f 0.55 (hexane/ether = 4/1). PMR spectrum (CCl_4 , $\delta(\text{ppm})$): 1.13 and 1.23 (d, 6H, CH_3 , J 6.5 Hz), 1.46 (s, 6H, $\text{CH}_3\text{C}=\text{C}$), 2.63 and 2.82 (q, 2H, CH, J 6.5 Hz), 2.37 (s, 1H, OH), 4.4–4.85 (m, 4H, $\text{CH}_2=\text{C}$), 5.9–6.2 and 7.2 (m, 3H of furan ring). IR spectrum (ν (cm^{-1})): 3530, 3145, 3090, 1650, 1600, 1510, 900, 820, 750. Mass spectrum (m/z): 234 [M^+].

Bis(3-methyl-3-buten-2-yl)amylcarbinol (IIIj). 0.114 g (30%) isolated, R_f 0.49 (hexane/ether = 10/1). PMR spectrum (CCl_4 , $\delta(\text{ppm})$): 0.85–1.55 (m, 11H, $\text{CH}_3(\text{CH}_2)_4$), 1.0 and 1.66 (d, 6H, CH_3 , J 7 Hz), 1.78 (m, 6H, $\text{CH}_3\text{C}=\text{C}$), 2.1–2.6 (m, 2H, CH), 4.6–5.0 (m, 4H, $\text{CH}_2=\text{C}$). IR spectrum (ν (cm^{-1})): 3500, 3085, 1635, 900. Mass spectrum (m/z): 238 [M^+].

Bis(3-methyl-3-buten-2-yl)methylcarbinol (IIIk). 0.14 g (48%) isolated, R_f 0.48 (hexane/ether = 7/1). PMR spectrum (CCl_4 , $\delta(\text{ppm})$): 1.0 and 1.05 (d, 6H, CH_3 , J 7.5 Hz), 1.0 (s, 3H, $\text{CH}_3\text{C}(\text{OH})$), 1.8 (m, 6H, $\text{CH}_3\text{C}=\text{C}$), 2.1–2.6 (m, 2H, CH), 4.6–5.0 (m, 4H, $\text{CH}_2=\text{C}$). IR spectrum (ν (cm^{-1})): 3450, 3080, 1640, 900. Mass spectrum (m/z): 182 [M^+].

Trans-bis(3-methyl-3-buten-2-yl)- β -styrylcarbinol (IIII). 0.181 g (42%) isolated, R_f 0.34 (hexane/ether = 4/1). PMR spectrum (CCl_4 , δ (ppm)): 1.1 (d, 6H, CH_3 , J 7 Hz), 1.67 (s, 6H, $\text{CH}_3\text{C}=\text{C}$), 2.55 and 2.62 (q, 2H, CH, J 7 Hz), 4.5–4.95 (m, 4H, $\text{CH}_2=\text{C}$), 6.2 and 6.38 (d, 2H, CH=, J_{AB} 20 Hz), 7.18 (m, 5H arom.). IR spectrum (ν (cm^{-1})): 3450, 3070, 3030, 1640, 1600, 1500, 960, 900, 740, 690. Mass spectrum (m/z): 270 [M^+].

1-Phenyl-2-methyl-3-buten-1-one (XIIa). 0.207 g (81%) isolated, R_f 0.50 (hexane/ether = 4/1). PMR spectrum (CCl_4 , $\delta(\text{ppm})$): 1.32 (d, 3H, CH_3 , J 6.5 Hz), 4.15 (dq, 1H, CH, $J_1 = J_2 = 6.5$ Hz), 4.9–5.35 (m, 2H, $\text{CH}_2=\text{C}$), 5.6–6.3 (m, 1H, CH=), 7.2–7.6 and 7.85–8.1 (m, 5H arom.). IR spectrum (ν (cm^{-1})): 3070, 1680, 1640, 1600, 1580, 1010, 920, 730, 690. Mass spectrum (m/z): 160 [M^+].

1-Phenyl-2-methyl-3-benzyl-3-buten-1-one (XIIIa). 0.252 g (63%) isolated, R_f 0.38 (hexane/ether = 4/1). PMR spectrum (CCl_4 , $\delta(\text{ppm})$): 1.3 (d, 3H, CH_3 , J 7 Hz), 3.38 (s, 2H, CH_2), 4.0 (q, 1H, CH, J 7 Hz), 4.87 (m, 2H, $\text{CH}_2=\text{C}$), 7.05–7.45 and 7.6–7.8 (m, 10H arom.). IR spectrum (ν (cm^{-1})): 3060, 3015, 1680, 1640, 1600, 1580, 1495, 905, 730, 700. Mass spectrum (m/z): 250 [M^+].

1-Phenyl-2-methyl-3-penten-1-one (XIVa) (E/Z = 1/1). 0.142 g (51%) isolated, R_f 0.51 (hexane/ether = 4/1). PMR spectrum (CCl_4 , δ (ppm)): 1.26 (d, 3H, CH_3 , J 6.5 Hz), 1.63 and 1.72 ($d^{*,*}$, 3H, $\text{CH}_3\text{C}=\text{C}$, J 6.5 Hz), 3.8–4.55 (m, 1H, CH), 5.35–6.0 (m, 2H, CH=), 7.15–7.6 and 7.85–8.15 (m, 5H arom.). IR spectrum (ν (cm^{-1})): 3070, 3030, 1680, 1640, 1595, 1480, 965, 740, 690. Mass spectrum (m/z): 174 [M^+].

2,4-Dimethyl-5-hepten-3-one (XIVe) (E/Z = 1/1). 0.172 g (77%) isolated, R_f 0.45 (hexane/ether = 10/1). PMR spectrum (CCl_4 , $\delta(\text{ppm})$): 0.95–1.2 (m, 9H, CH_3), 1.68 and 1.75 (d^* , 3H, $\text{CH}_3\text{C}=\text{C}$, J 6.5 Hz), 2.5–2.95 (m, 1H, CH), 3.15–3.7

* Signals were assigned to various stereoisomers.

(m, 1H, CHC=), 5.35–6.0 (m, 2H, CH=). IR spectrum (ν (cm⁻¹)): 3090, 1700, 1625, 960. Mass spectrum (m/z): 140 [M^+].

1-Phenyl-2-propenyl-3-methyl-4-penten-1-one (XVa). 0.034 g (10%) isolated, R_f 0.41 (hexane/ether = 4/1). PMR spectrum (CCl₄, δ (ppm)): 0.99 and 1.04 (d*, 3H, CH₃, J 7 Hz), 1.65 and 1.68 (d*, 3H, CH₃C=, J 5 Hz), 2.78 (ddq, 1H, CH, $J_1 = J_2 = J_3 = 7$ Hz), 3.88 (dd, 1H, CHCO, J_1 7, J_2 8.5 Hz), 4.8–5.1 (m, 2H, CH₂=), 5.45–6.0 (m, 3H, CH=), 7.3–7.6 and 7.9–8.05 (m, 5H arom.). IR spectrum (ν (cm⁻¹)): 3090, 3045, 1675, 1600, 1450, 990, 960, 910, 720, 700. Mass spectrum (m/z): 214 [M^+].

1-Phenyl-2-propenyl-3-methyl-3-penten-1-one (XVIa). 0.199 g (58%) isolated, R_f 0.41 (hexane/ether = 4/1). PMR spectrum (CCl₄, δ (ppm)): 1.67 (m, 9H, CH₃), 4.55 and 4.93 (d*, 1H, CH, J 5 Hz), 5.2–5.7 (m, 3H, CH=), 7.3–7.6 and 7.9–8.05 (m, 5H arom.). IR spectrum (ν (cm⁻¹)): 3085, 3045, 1680, 1600, 1450, 960, 840, 730, 690. Mass spectrum (m/z): 214 [M^+].

Trans-1-phenyl-2-methyl-3-methylen-4-hexen-1-one (XVIIa). 0.096 g (30%) isolated, R_f 0.40 (hexane/ether = 4/1). PMR spectrum (CCl₄, δ (ppm)): 1.35 (d, 3H, CH₃, J 6 Hz), 1.83 (d, 3H, CH₃C=, J 5.5 Hz), 4.3 (q, 1H, CH, J 6 Hz), 4.7–5.05 (m, 2H, CH₂=), 5.5–6.4 (m, 2H, CH=), 7.25–7.6 and 7.8–8.1 (m, 5H arom.). IR spectrum (ν (cm⁻¹)): 3060, 3025, 1680, 1635, 1600, 1450, 990, 975, 920, 700. Mass spectrum (m/z): 200 [M^+].

1-Phenyl-2-vinyl-3-penten-1-one (XVIIIa) (E/Z = 3/2). 0.238 g (80%) isolated, R_f 0.40 (hexane/ether = 4/1). PMR spectrum (CCl₄, δ (ppm)): 1.68 and 1.73 (d*, 3H, CH₃, J 5 Hz), 4.4–5.25 (m, 3H, CH⁺=CH₂), 5.9–6.3 (m, 3H, CH=), 7.2–7.5 and 7.75–8.0 (m, 5H arom.). ¹³C NMR spectrum (CDCl₃, δ (ppm)): 18.08(q), 55.03(d), 116.91(t), 128.50(d), 128.11(d), 128.66(d), 132.94(s), 136.23(d), 199.12(s) (*E*-isomer); 13.25(q), 50.33(d), 116.62(t), 126.83(d), 127.09(d), 128.50(d), 128.66(d), 132.94(s), 135.45(d), 199.12(s). (*Z*-isomer). IR spectrum (ν (cm⁻¹)): 3080, 3030, 1680, 1640, 1600, 1460, 990, 970, 910, 730, 690. Mass spectrum (m/z): 186 [M^+].

2-Methyl-4-vinyl-1,5-heptadien-3-one (XVIIIb) (E/Z = 3/2). 0.168 g (70%) isolated, R_f 0.39 (hexane/ether = 10/1). PMR spectrum (CCl₄, δ (ppm)): 1.67 and 1.72 (d*, 3H, CH₃, J 5.5 Hz), 1.85 (s, 3H, CH₃CCO), 4.28 and 4.63 (dd*, 1H, CH, $J_1 = J_2 = 6$ Hz), 4.75–5.15 (m, 2H, CH₂=), 5.4–6.1 (m, 5H, CH= + CH₂=CMe). ¹³C NMR spectrum (CDCl₃, δ (ppm)): 17.89(q), 54.05(d), 116.26(t), 125.00(t), 128.01(d), 128.34(d), 136.43(d), 143.48(s), 200.72(s) (*E*-isomer); 12.99(q), 17.89(q), 49.28(d), 116.00(t), 124.74(t), 126.12(d), 127.35(d), 135.78(d), 143.48(s), 200.72(s) (*Z*-isomer). IR spectrum (ν (cm⁻¹)): 1675, 1630, 995, 970, 915, 860. Mass spectrum (m/z): 150 [M^+].

1-Phenyl-2-methyl-3-(methyldiethylsilyl)-3-buten-1-one (XIXa). 0.291 g (70%) isolated, R_f 0.45 (hexane/ether = 4/1). PMR spectrum (CCl₄, δ (ppm)): 0.03 (s, 3H, CH₃Si), 0.5–1.2 (m, 10H, CH₃CH₂Si), 1.2 (d, 3H, CH₃, J 7 Hz), 4.07 (q, 1H, CH, J 7 Hz), 5.37 and 5.53 (d, 2H, CH₂=, J_{AB} 2.5 Hz), 7.2–7.45 and 7.6–7.9 (m, 5H arom.). IR spectrum (ν (cm⁻¹)): 3050, 1680, 1600, 1450, 1260, 920, 800, 730, 690. Mass spectrum (m/z): 260 [M^+].

2,4-Dimethyl-5-(methyldiethylsilyl)-5-hexen-3-one (XIXe). 0.246 g (68%) isolated, R_f 0.40 (hexane/ether = 10/1). PMR spectrum (CCl₄, δ (ppm)): 0.03 (s, 3H, CH₃Si), 0.5–1.2 (m, 19H, CH₃ + CH₂), 2.5 (qq, 1H, CH, $J_1 = J_2 = 7$ Hz), 3.3 (q, 1H, CHC=, J 7 Hz), 5.37 and 5.53 (d, 2H, CH₂=, J_{AB} 3 Hz). IR spectrum (ν (cm⁻¹)): 3065, 1710, 1260, 920, 800. Mass spectrum (m/z): 226 [M^+].

2-(Methyldiethylsilyl)-3,6-dimethyl-1-hepten-4-one (XIXi). 0.28 g (73%) isolated, R_f 0.40 (hexane/ether = 10/1). PMR spectrum (CCl_4 , δ (ppm)): 0.03 (s, 3H, CH_3Si), 0.5–1.2 (m, 20H, $\text{CH}_3 + \text{CH}_2 + \text{CH}$), 2.23 (m, 2H, CH_2CO), 3.3 (q, 1H, CHC= , J 7 Hz), 5.36 and 5.54 (d, 2H, $\text{CH}_2=$, J_{AB} 3 Hz). IR spectrum (ν (cm^{-1})): 3065, 1710, 1260, 910, 800. Mass spectrum (m/z): 240 [M^+].

2,4-Dimethyl-5-methylene-6-trimethylsilyl-1-hexen-3-one (XXf). 0.215 g (64%) isolated, R_f 0.38 hexane/ether = 10/1). PMR spectrum (CCl_4 , δ (ppm)): 0.01 (s, 9H, CH_3Si), 1.1 (d, 3H, CH_3 , J 7 Hz), 1.42 (s, 2H, CH_2), 1.79 (s, 3H, $\text{CH}_3\text{C=}$), 3.67 (q, 1H, CH , J 7 Hz), 4.61 (m, 2H, $\text{CH}_2=$), 5.6 and 5.85 (m, 2H, $\text{CH}_2=\text{CCO}$). IR spectrum (ν (cm^{-1})): 3060, 1675, 1625, 1260, 890, 850. Mass spectrum (m/z): 210 [M^+].

1-Trimethylsilyl-2-methylene-3,6-dimethylheptan-4-one (XXi). 0.275 g (76%) isolated, R_f 0.40 (hexane/ether = 10/1). PMR spectrum (CCl_4 , δ (ppm)): 0.01 (s, 9H, CH_3Si), 0.75–1.0 (m, 7H, $(\text{CH}_3)_2\text{CH}$), 1.05 (d, 3H, CH_3 , J 7 Hz), 1.4 (s, 2H, CH_2Si), 2.15 (m, 2H, CH_2), 2.88 (q, 1H, CH , J 7 Hz), 4.65 (m, 2H, $\text{CH}_2=$). IR spectrum (ν (cm^{-1})): 3060, 1710, 1640, 1260, 890, 850. Mass spectrum (m/z): 226 [M^+].

References

- 1 U.M. Dzhemilev, O.S. Vostrikova and G.A. Tolstikov, J. Organomet. Chem., 304 (1986) 17.
- 2 F. Sato, J. Organomet. Chem., 285 (1985) 53.
- 3 F. Sato, S. Iijima and M. Sato, Tetrahedron Lett., 22 (1981) 243.
- 4 Y. Kobayashi, K. Umeyama and F. Sato, J. Chem. Soc., Chem. Commun., (1984) 621.
- 5 H.A. Martin and J. Jellinek, J. Organomet. Chem., 12 (1968) 149.
- 6 F. Sato, Y. Suzuki and M. Sato, Tetrahedron Lett., 23 (1982) 4589.
- 7 B. Klei, J.H. Teuben and J.H.L. Meijer, J. Chem. Soc., Chem. Commun., (1981) 342.
- 8 H. Lehmkuhl and S. Fustero, Liebigs Ann. Chem., (1980) 1353.
- 9 A.A. Pashayan, S.A. Vorskayan, Zh.A. Tchobayan and Sh.O. Badanyan, Arm. Khim. Zhur., 34 (1981) 133.
- 10 D.G. Batt and B. Ganem, Tetrahedron Lett., 36 (1978) 3323.
- 11 H. Sakurai, A. Hosomi, M. Saito, K. Sasaki, H. Iguchi, J. Sasaki and Y. Araki, Tetrahedron, 39 (1983) 883.
- 12 T. Sato, Y. Uchida and A. Misono, Bull. Chem. Soc. Japan, 37 (1964) 105.
- 13 Sintezy organicheskikh preparatov, v. 12, Inostrannaya Literatura, 1964, p. 18.
- 14 G. Wilkinson and J.M. Birmingham, J. Am. Chem. Soc., 76 (1954) 4281.