CONCLUSIONS

The effect of the surface concentration of Bu_4NF applied to silica gel and Aerosil on its catalytic capacity in condensation of benzaldehyde with fluorene was studied. The capacity of the Bu_4NF applied to the support to pass into DMF solution was determined by the ionometric method. In the case of monolayer application of Bu_4NF on silica gel, catalysis of the model reaction is heterogeneous in character.

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SYNTHESIS OF α-SUBSTITUTED KETONES BY REACTION OF METALLATED KETIMINES WITH ALLYL COMPOUNDS UNDER THE ACTION OF PALLADIUM COMPLEXES

U. M. Dzhemilev, D. L. Minsker,
L. M. Khalilov, and A. G. Ibragimov

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547.514.471:547.594.4

Construction of a new C—C bond in the α-position of a carbonyl group with the use of Mg or Li organometallic azomethine derivatives has been studied only with simple alkyl halides [1-3]. Information about the possibility of using allyl compounds in the above reaction is not available.

In this work we describe the reaction, catalyzed by low-valent Pd complexes, of N-, O-, and S-containing allyl substrates with 1-azaallylmagnesium halides obtained [1] by metallation of ketimines with Grignard reagents.

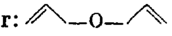
Metallation of cyclopentanone methylimine (Ia) with EtMgBr in ether proceeds through the Grignard complex of the enamine tautomer with formation of 1-azaallyl anion (IIa) which is more stable [4] than 2-azaallyl anion. The subsequent bonding of the complex (IIa) with diallyl ether, catalyzed by $Pd(acac)_2$—$2Ph_3P$ (4 mole %), leads to mono- (IIIa) and disubstituted (IVa) ketones with a yield of 90%. The ratio of ketones (IIIa) and (IVa) can change slightly depending on the ratio of the reagents and the reaction time. The yield of ketone (IIIa) is ~4 times higher with an equimolar reagent ratio and a reaction time of 5 h. In the reaction with excess EtMgBr and diallyl ether (EtMgBr:  : (Ia) = 2 : 2 : 1) the yield of ketone (IVa), which contain cis and trans isomers [Z-(IVa):E-(IVa) ~ 1:2] reaches 75%, which indicates further metallation of monosubstituted ketimine formed during the reaction. The nature of RMgX does not significantly influence the yield and composition of products (IIIa) and (IVa). For example, with the use of PrMgBr, PrMgCl, i-PrMgBr, and BuMgBr as metallizing reagents the total yield of (IIIa) and (IVa) was 80-90% and their ratio was respectively (3-5):1.

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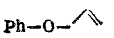
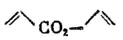
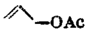
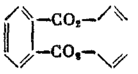
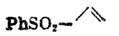
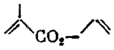
TABLE 1. Influence of Structure of Allyl Compounds on the Yield of Reaction Products [$Pd(acac)_2:Ph_3P$ = 1:2, 36-40°C, 5 h, ether]

Substance	Yield of (IIIb) + (IVb), %*	Substance	Yield of (IIIb) + (IVb), %*
	86(79)		64(55)
	81(72)		62(51)
	75(66)		60(54)
			35(26)
	68(61)		

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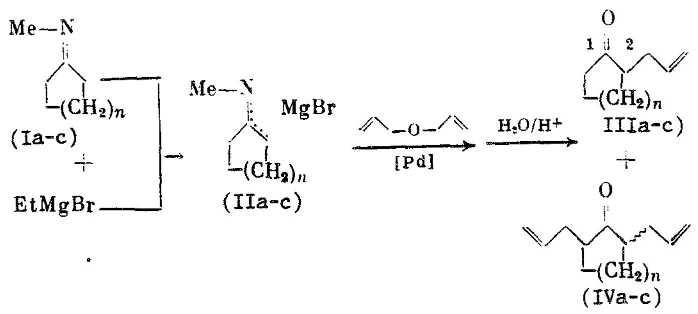
*Determined by GLC. In parentheses yields of isolated products are shown.

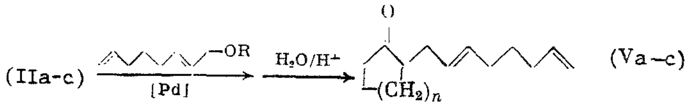


n = 1(a), 2(b), 3(c).

With equimolar amounts of diallyl ether and reagents (IIb, c) we obtained mono- (IIIb, c) and disubstituted (IVb, c) ketones in a ratio of ~4:1 with total yield of 80-85%. Ketones (IVb, c) consist of cis and trans isomers [Z-(IVb):E-(IVb) = 4:1, Z-(IVc):E-(IVc) = 8:1]. In the ^{13}C NMR spectrum of ketone (IVa) two sets of signals are observed with an intensity ratio of 1:2. According to [5], the E isomer (IVa), which gives the downfield methine signals (C^2, C^5) (49.05 ppm), predominates in this mixture. For (IVb, c) the opposite picture is observed. The lower intensity signals correspond to the more shielded carbon atoms, i.e., in the stereoisomers 2,5-diallylcyclohexanone (IVb) and 2,7-diallylcycloheptanone (IVc) and Z-isomers are prevalent. In addition to reacting diallyl ether with azaallylmagnesium bromide (IIb) we also tried phenylallyl ether, allyl acetate, diallyl phthalate, allyl methacrylate, allyl acrylate, diallyl sulfide, phenylallyl sulfone, and N-methyl-N,N-diethylallylammonium iodide. For the catalyst $Pd(acac)_2$—$2Ph_3P$ was used. The total yield of ketones (IIIb) and (IVb) was 35-86% and the ratio of mono- and disubstituted ketones was (3-5):1. The nature of the leaving group on the allyl substrate has a perceptible effect on the yield of the reaction products (Table 1).

Analysis of signal multiplicity in the ^{13}C NMR spectra of disubstituted ketones (IVa-c) indicates that gem-diallyl regioisomers are not formed (singlet signals corresponding to quaternary carbon atoms are absent).

With increase of the number of allyl substituents the yield of products does not significantly decrease. In the reaction of equimolar amounts of reagents (IIa-c) with 1-phenoxy-, 1-ethoxy-, 1-methoxy-2E,7-octadiene or 2E,7-octadienylacetate, 2-(2'E,7'-octadienyl)-1-cycloalkanones (Va-c) are obtained with yields of 62-80%.

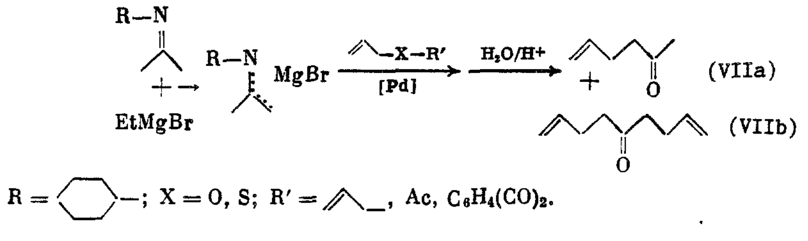


n = 1(a), 2(b), 3(c); R = Me, Et, Ph, Ac.

In the reaction of (Ia) with a two-fold excess of EtMgBr and 1-methoxy-2E,7-octadiene catalyzed by $Pd(acac)_2$—$2Ph_3P$ a mixture of ketones was obtained which contained 2-(2'E,7'-

octadienyl)- (Va) and 2,5-bis(2'E,7'-octadienyl)-1-cyclopentanone (VI) in a ratio of ~ 1:1 with total yield of 84%. The geometry of the disubstituted double bond in the octadienyl fragment of ketones (Va-c) follows from calculation of the chemical shifts by additive methods [6]. Allyl carbon signals of 29-32 ppm are typical for disubstituted trans double bonds [7], while for cis double bonds 24-26 ppm are characteristic. These signals are absent in the ^{13}C NMR spectra. Allyl isomerization of the 2E, 7-octadienyl fragment is not observed during the reaction, which is indicated by the absence in the ^{13}C NMR spectra of additional methine carbon doublets. The cis and trans isomers of ketone (VI) were not resolved. The signals of the individual steroisomers were assigned in the ^{13}C NMR spectrum of ketone (VI) on the basis of the 0.1-1.27 ppm difference in their chemical shifts.

Metallation of acetone cyclohexylimine with EtMgBr and subsequent reaction with allyl acetate, diallyl phthalate, diallyl ether, and diallyl sulfide leads to unsaturated ketones (VIIa) and (VIIb) in ~ 4:1 ratio with total yield of 45-60% (GLC).



EXPERIMENTAL

Azaallylmagnesium halides were obtained [1] by metallation of ketimines [8] with Grignard reagents. 2E,7-Octadienyl ethers were synthesized by cotelomerization of butadiene with MeOH, EtOH, PhOH, and AcOH by known methods [9, 10]. Reactions were carried out in an atmosphere of dry Ar. Ether was distilled from $LiAlH_4$ before use. GLC was performed on a Khrom-41 chromatograph in a He flow with a 1.2 × 3 mm column with 5% SE-30 on N-AW chromaton. PMR spectra were recorded in CCl_4 on a Tesla BS-467 spectrometer (60 MHz), ^{13}C NMR spectra on a Jeol-FX-90 Q spectrometer in $CDCl_3$ relative to TMS, and IR spectra on a UR-20 spectrometer (film). Mass spectra were obtained on a MX-1306 spectrometer at 70 eV and 200°C.

General Method for Reactions of Metallized Ketimines with Allyl Substrates. a) To a solution of 2.43 g (25 mmoles) cyclopentanone methylimine in 20 ml ether in an Ar flow at 0°C 30 ml of 1M EtMgBr ether solution was added. The mixture was stirred for 3 h at 36-40°C and cooled to −5°C. Then 2.45 g (25 mmoles) of diallyl ether, 0.3 g (1 mmole) $Pd(acac)_2$, and 0.52 g (2 mmoles) of Ph_3P was added. The mixture was kept for 5 h at 40°C, treated with N HCl (2 h, 50°C), and extracted with ether. The organic layer was dried with $MgSO_4$. A mixture of 1-allyl- and 2,5-diallyl-1-cyclopentanone was obtained in a ratio of 78:22 (GLC) with a total yield of 90% (yield of the products was determined by GLC with n-octane as internal standard). The reaction products were isolated by fractional distillation.

Reactions of metallized cyclohexanone, cycloheptanone, and acetone imines with the corresponding allyl substrates were carried out by the above method.

2-Allyl-1-cyclopentanone (IIIa): bp 45-46°C (5 mm), n_D^{20} 1.4594 (lit. [11]: bp 62°C (10 mm), n_D^{25} 1.4579).

2-Allyl-1-cyclohexanone (IIIb): bp 42-43°C (1 mm), n_D^{20} 1.4698 (lit. [11]: bp 91°C (18 mm), n_D^{25} 1.4666).

2-Allyl-1-heptanone (IIIc): bp 52-53°C (1 mm). IR spectrum (ν, cm^{-1}): 3080, 1705, 1005, 920. PMR spectrum (δ, ppm): 1.17-2.10 m (8H, CH_2), 2.23-2.67 m (5H, CH, CH_2), 4.78-5.00 m (3H, $CH{=}CH_2$). M^+ m/z 152.

2,5-Diallyl-1-cyclopentanone: [Z-(IVa):E-(IVa) = 1:2], bp 59-62°C (1 mm), n_D^{20} 1.4698 [see [12], bp 91°C (7 mm), n_D^{25} 1.4683]. IR spectrum (ν, cm^{-1}): 3085, 1710, 1000, 920. PMR spectrum (δ, ppm): 1.20-2.75 broad m (10H, CH, CH_2), 4.83-5.96 m (6H, $CH{=}CH_2$). ^{13}C NMR spectrum (δ, ppm): 220, 41 s (C^1), 47.75 d (C^2, C^5), 34.24 t (C^3, C^4), 25.91 t (C^6, C^9), 135.94 d (C^7, C^{10}), 116.52 t (C^8, C^{11}) (Z-isomer); 220.41 s (C^1), 49.05 d (C^2, C^5), 34.24 t (C^3, C^4), 27.06 t (C^6, C^9), 135.78 d (C^7, C^{10}), 116.42 t (C^8, C^{11}) (E-isomer). M^+ m/z 164.

2,6-Diallyl-1-cyclohexanone: [Z-(IVb):E-(IVb) = 4:1], bp 65-67°C (1 mm), n_D^{20} 1.4812 [see [13], bp 107-109°C (11 mm), n_D^{23} 1.4800]. IR spectrum (ν, cm^{-1}): 3080, 1710, 1000,

920. PMR spectrum (δ, ppm): 1.42-2.67 broad m (12H, CH, CH_2), 4.72-5.92 m (6H, $CH{=}CH_2$). ^{13}C NMR (δ, ppm): 212.50 s (C^1), 50.66 d (C^2, C^6), 34.79 t (C^3, C^5), 25.43 t (C^4), 33.68 t (C^7, C^{10}), 135.72 d (C^8, C^{11}), 116.03 t (C^9, C^{12}) (Z-isomer); 214.58 s (C^1), 48.77 d (C^2, C^6), 34.60 t (C^3, C^5), 20.37 t (C^4), 32.15 t (C^7, C^{10}), 135.91 d (C^8, C^{11}), 116.45 t (C^9, C^{12}), (E-isomer). M^+ m/z 178.

2,7-Diallyl-1-cycloheptanone: [Z-(IVc):E-(IVc) = 8:1], bp 68-69°C (1 mm). IR spectrum (ν, cm^{-1}): 3080, 1740, 1000, 975, 915. PMR spectrum (δ, ppm): 1.08-2.55 broad m (14H, CH, CH_2), 4.62-6.00 m (6H, $CH{=}CH_2$). ^{13}C NMR spectrum (δ, ppm): 216.78 s (C^1), 51.50 d (C^2, C^7), 36.95 t (C^3, C^6), 28.72 t (C^4, C^5), 31.33 t (C^8, C^{11}), 136.64 d (C^9, C^{12}), 116.52 t (C^{10}, C^{13}) (Z-isomer). M^+ m/z 192.

2-(2E',7'-Octadienyl)-1-cyclopentanone (Va): bp 86-87°C (1 mm), n_D^{20} 1.4672. IR spectrum (ν, cm^{-1}): 3080, 1740, 1000, 975, 915. PMR spectrum (δ, ppm): 1.33-1.60 m (2H, CH_2), 1.78-2.67 m (13H, CH, CH_2), 4.72-5.92 m (5H, $CH{=}CH$, $CH{=}CH_2$). ^{13}C NMR spectrum (δ, ppm): 220.70 s (C^1), 49.02 d (C^2), 32.64 t (C^3), 20.69 t (C^4), 38.25 t (C^5), 28.92 t (C^6), 127.42 d (C^7), 132.18 d (C^8), 31.92 t (C^9), 28.65 t (C^{10}), 33.16 t (C^{11}), 138.65 d (C^{12}), 114.43 t (C^{13}). M^+ m/z 192.

2-(2E',7'-Octadienyl)-1-cyclohexanone (Vb): bp 97-98°C (1 mm), n_D^{20} 1.4830 [see [14], bp 116°C (3 mm), n_D^{25} 1.4809]. IR spectrum (ν, cm^{-1}): 3080, 1710, 1000, 980, 920. PMR spectrum (δ, ppm): 1.08-1.50 m (2H, CH_2), 1.58-2.67 m (15H, CH, CH_2), 4.73-5.88 m (5H, $CH{=}CH$, $CH{=}CH_2$). ^{13}C NMR spectrum (δ, ppm): 212.54 s (C^1), 50.79 d (C^2), 33.29 t (C^3), 21.80 t (C^4), 24.94 t (C^5), 41.97 t (C^6), 34.79 t (C^7), 127.94 d (C^8), 131.99 d (C^9), 31.98 t (C^{10}), 27.94 t (C^{11}), 32.57 t (C^{12}), 138.71 d (C^{13}), 114.32 t (C^{14}). M^+ m/z 206.

2-(2E',7'-Octadienyl)-1-cycloheptanone (Vc): bp 107-109°C (1 mm). IR spectrum (ν, cm^{-1}): 3080, 1705, 1000, 980, 920. PMR spectrum (δ, ppm): 1.13-1.52 m (2H, CH_2), 1.58-2.83 m (17H, CH, CH_2), 4.80-5.56 m (5H, $CH{=}CH$, $CH{=}CH_2$). ^{13}C NMR spectrum (δ, ppm): 215.74 s (C^1), 52.22 d (C^2), 35.15 t (C^3), 24.45 t (C^4), 29.60 t (C^5), 28.69 t (C^6), 43.08 t (C^7), 30.52 t (C^8), 127.68 d (C^9), 132.38 d (C^{10}), 31.95 t (C^{11}), 28.69 t (C^{12}), 33.19 t (C^{14}), 138.74 d (C^{14}), 114.43 t (C^{15}). M^+ m/z 220.

2,5-Di-(2E',7'-octadienyl)-1-cyclopentanone: [Z-(VI):E-(VI) = 5:6], bp 149-150°C (1 mm). IR spectrum (ν, cm^{-1}): 3080, 1660, 1000, 975, 915. PMR spectrum (δ, ppm): 1.21-1.70 m (4H, CH_2), 1.75-2.80 m (18H, CH, CH_2), 4.75-6.17 m (10H, $CH{=}CH$, $CH{=}CH_2$). ^{13}C NMR spectrum (δ, ppm): 221.58 s (C^1), 49.58 d (C^2, C^5), 33.00 t (C^3, C^4), 26.96 t (C^6, C^{14}), 127.35 d (C^7, C^{15}), 132.25 d (C^8, C^{16}), 31.95 t (C^9, C^{17}), 28.72 t (C^{10}, C^{18}), 33.19 t (C^{11}, C^{19}), 138.71 d (C^{12}, C^{20}), 114.46 t (C^{13}, C^{21}) (E-isomer); 220.99 s (C^1), 48.31 d (C^2, C^5), 33.00 t (C^3, C^4), 25.85 t (C^6, C^{14}), 127.52 d (C^7, C^{15}), 132.35 d (C^8, C^{16}), 31.95 t (C^9, C^{17}), 28.72 t (C^{10}, C^{18}), 33.19 t (C^{11}, C^{19}), 138.71 d (C^{12}, C^{20}), 114.46 t (C^{13}, C^{21}) (Z-isomer). M^+ m/z 300.

1,8-Nonadiene-5-one (VIIb): bp 66-67°C (5 mm), n_D^{20} 1.4460 [see [11], bp 81°C (17 mm), n_D^{20} 1.4462].

CONCLUSIONS

Reactions of ketimines metallated with Grignard reagents with allyl N-, O-, and S-containing substrates are catalyzed by Pd complexes and result in α-substituted ketones.

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REACTIONS OF N-, P-, and S-NUCLEOPHILES WITH METHYL PROPIOLATE

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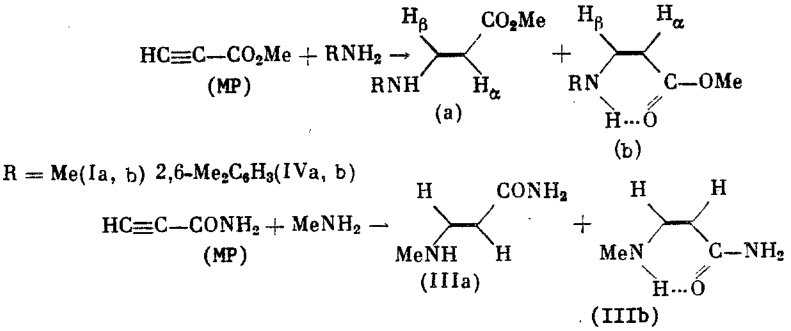
547.233

In the previous article [1], we showed the high trans-stereospecificity of the nucleophilic addition to cyanoacetylene (CA) with the formation of cis isomers when the postisomerization of the adducts was hindered by carrying out the reaction with cooling, creating steric hindrances to the isomerization by using N-nucleophiles with branched substituents, or by using nucleophiles with a weakened +M-effect of the central heteroatom.

However, already in [2] it was observed that while the reaction of CA with ethyleneimine (EI) gives only the cis product, and with dimethylamine gives a mixture of cis and trans products, under similar conditions, with methyl propiolate (MP), EI and dimethylamine preferentially form trans products. Later it was shown that the proportion of the cis product in the reaction of EI with propiolates increases in protonic solvents, ensuring an effective proton transfer to the anionic intermediate [3]. The trans products are preferentially formed also in the reactions of MP with the derivatives of aziridine-2-carboxylic acid [4] and diaziridines [5]. In the reactions of MP with sterically hindered amines i-$PrNH_2$, i-Pr_2NH, t-$BuNH_2$, the anomaly, compared with the case of usual amines, was not observed [6].

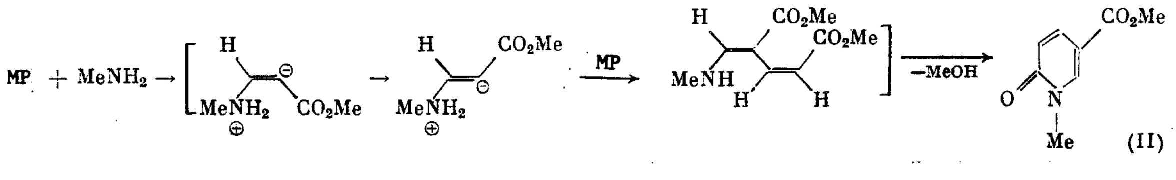
To clarify the reasons for the difference in the sterochemistry of the nucleophilic addition to CA and MP, in the present work we repeated the investigation on the reactions of MP with a series of N-nucleophiles, and for the first time with sterically highly hindered amines, mercaptan and phosphines,* and also of propiolamide (PA) with certain N-nucleophiles.

With primary amines, trans and cis isomers are formed, since the latter are stabilized by intramolecular H-bonds (cf. [3]).



$R = Me$(Ia, b) 2,6-$Me_2C_6H_3$(IVa, b)

In the reaction of $MeNH_2$ with MP, a product of a later reaction of the anoinic intermediate with MP was also obtained.



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*For previous communications, see [7].

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