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SUBSTITUTION REACTION WITH PARTICIPATION OF ORGANOALUMINUM COMPOUNDS

3.* CROSS-COMBINATION OF ALLYL ACETATES WITH TRIALKYLALANES

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547.256.2

In continuation of our studies on the synthesis of allenes from acetates of tertiary acetylenic alcohols [1], we investigated the reaction of alkylalanes with allyl acetates. In reaction of this type, Mg and Li compounds are actively used as organometallic reagents [2, 3].

Possible allylation of alkylalanes by allyl acetates was shown in the reactions of acetates of geraniol and cis, trans-carveols with organoaluminum compounds (OAC) of type R_3Al (R = Me, Et, i-Bu) [4, 5]. The reactions proceeded under mild conditions (−78°C) and led to alkylation products in a yield of 66-85%. We extended this method to other allyl substrates, and compared the behavior in this reaction of primary and secondary allyl acetates, and also acetates containing electron-donor substituents at the γ-position of the leaving group. As starting compounds, we selected allyl (I), crotyl (II), cinnamyl (III), sorbyl (IV), 2,7-octadienyl (V), 2-pentenyl (VI), 2-cyclohexenyl acetates (VII), and trialkylalanes R_3Al (R = Et, i-Bu, n-C_6H_{13}).

The reaction conditions were selected using as an example the reaction of OAC with acetate V, which is interesting in synthesis, since 1,6-alkadienes based on it can be used in the synthesis of several pheromones [6]. It was found that the optimal molar ratio of the reagents is ROAc : R_3Al = 1 : 2. The reaction proceeds in hexane or in CH_2Cl_2 at ~20°C for several hours. In ether and in THF, the reaction products are formed after 24 h in trace amounts. The experimental data (Table 1) show that the ratio between the two competing paths, i.e., alkylation and nucleophilic attack by alkyl on the carbon atom of the carbonyl group, is appreciably dependent

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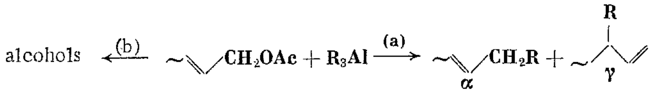
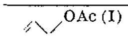
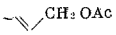
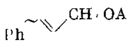
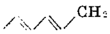
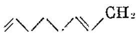
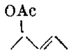
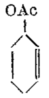
*For article 2, see [1].

Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1146-1151, May, 1983. Original article submitted June 18, 1982.

TABLE 1. Reaction of Allyl Acetates with Organoaluminum Compounds



Acetate	R_3Al	Yield of hydrocarbons, %*	Ratio of α/γ isomers, %†
 (I)	$(C_6H_{13})_3Al$	Traces	
 (II)	$(C_6H_{13})Al$	»	
 (III)	$(i\text{-}Bu)_3Al$	100	72/28
(III)	$(C_6H_{13})_3Al$	82	54/42
 (IV)	$(i\text{-}Bu)_3Al$	100	
 (V)	$(Et)_3Al$	41	70/30
(V)	$(i\text{-}Bu)_3Al$	75	82/18
(V)	$(C_6H_{13})_3Al$	26	90/10
 (VI)	$(i\text{-}Bu)_3Al$	100	
(VI)	$(C_6H_{13})_3Al$	81	
 (VII)	$(i\text{-}Bu)_3Al$	100	
(VII)	$(C_6H_{13})_3Al$	69	

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*According to GLC data.

†According to GLC and PMR data.

TABLE 2. Catalysis of Allylation of Trialkylalanes by CuBr and $FeCl_3$ (solvent CH_2Cl_2, in the case of (VII) – hexane)

Acetate	R_3Al	Catalyst	Yield of hydrocarbons, %*	Ratio of α/γ isomers, %*
(I)	$(C_6H_{13})_3Al$	$FeCl_3$	55	
(II)	$(C_6H_{13})_3Al$	$FeCl_3$	63	75/25
(V)	Et_3Al	$FeCl_3$	89	96/4
(V)	$(i\text{-}Bu)_3Al$	$FeCl_3$	91	97/3
(V)	$(C_6H_{13})Al$	CuBr	86	98/2
(VI)	$(C_6H_{13})Al$	$FeCl_3$	100	
(VII)	$(C_6H_{13})Al$	CuBr	80	

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*According to GLC data.

on the structure of the allyl substrate. The reaction of allyl acetates (I) and (II) with tris-hexylaluminum (VIII) generally does not lead to combination products. The reaction mixtures consist mainly of hexylmethyl- and dihexylmethylcarbinols.* From acetate (V) and trialkylalane (VIII), hydrocarbons are obtained in a yield of 26%, and from (V) and Et_3Al in a yield of 41%. Electron-donor groups at the double bond favor the formation of the combination products. For example, the reaction of geranyl acetate with Et_3Al leads, according to data in [4], to hydrocarbons in a yield of 75%. We observed quantitative yields of hydrocarbons in the case of acetates (III) and (IV) (effect of π-conjugation). For secondary acetates (VI) and (VII), their reaction with (VIII) and $(i\text{-}Bu)_3$-Al leads almost quantitatively to cross-combination products. The data in Table 1 show that the reactions of alkylalanes with acetates (III) and (V) under the above conditions were characterized by high regioselectivity. In the case of sorbyl acetate (IV), together with the main product 8-methyl-2,4-nonadiene (IX) (86%), an inappreciable amount of unidentified isomeric hydrocarbons is formed.

It is known [3, 7] that in reactions of allyl electrophiles with Grignard reagents, catalysis by Cu(I) is used. It is thus possible to obtain cross-combination products under mild conditions in high yields, and to in-

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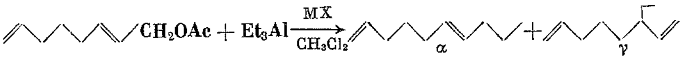
*Analysis of the alcoholic fractions obtained showed that, irrespective of the structure of the acetates, in their reaction with alkylalane (VIII), the above alcohols are mainly formed; the reaction of acetate (V) with Et_3Al and $(i\text{-}Bu)_3Al$ leads to 2,7-octadienol.

TABLE 3. Catalytic Activity of Cu(I), Cu(II), and Fe(III) Salts



MX	Yield of hydrocarbons, %*	Ratio of α/γ, isomers, %*	MX	Yield of hydrocarbons, %*	Ratio of α/γ isomers, %*
CuBr	90	90/10	Cu(acac)$_2$	90	69/31
CuCl	90	86/14	FeCl$_3$	89	96/4
CuBr$_2$	78	91/9	Fe(acac)$_3$	96	94/6

*According to GLC data.

fluence the stereo- and regioselectivity of the processes. We have already shown that Cu(I) and Fe(III) salts are effective catalysts in the reaction of propargyl acetates with OAC [1]. We also studied the catalytic activity of the above salts in the allylation reaction. Cuprous bromide and ferric chloride were studied most. The data obtained are shown in Table 2. Reactions with CuBr were carried out in hexane or in CH_2Cl_2. The compositions of the products in the mixtures differed inappreciably. Ferric chloride had catalytic activity in CH_2Cl_2 only. For each of the substrates, 7-10 mole % of the catalyst was used. Optimal results for yield of hydrocarbons and regioselectivity of the reaction were thus obtained.

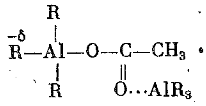
The data in Table 2 show that by using CuBr and $FeCl_3$ the selective nucleophilicity of the organometallic reagents could be appreciably changed. For example, the yield of hydrocarbons in the reaction of acetates (I) and (II) with OAC (VIII) exceeded 50%. In the reaction of trialkylalanes with acetate (V), a considerable increase in both the yield of the cross-combination products, and the regioselectivity of the reaction is observed. The use of salts was found to be ineffective in the case of acetates (III) and (IV). The ratio between the isomeric hydrocarbons thus remained as before. It should be noted that $FeCl_3$ exhibits a higher catalytic activity than CuBr in directing the reaction to the combination path. When CuBr is used in the reaction of acetates (I) and (II) with OAC (VIII), the hydrocarbons are formed in trace amounts. In the reaction of acetate (V) with Et_3Al or secondary acetate (VI) with alkylalane (VIII) in the presence of CuBr, the ratio of the hydrocarbon to the alcoholic fraction was 88 : 12 and 83 : 17, respectively (according to GLC data), while in the presence of $FeCl_3$, the yield of the hydrocarbons was 100%.

We also studied the catalytic activity of Cu(I), Cu(II) and Fe(III) (CuCl, $CuBr_2$, Cu(acac)$_2$, Fe(acac)$_3$) in the reaction of acetate with Et_3Al. The reactions were carried in CH_2Cl_2 (Table 3).

The data in Table 3 show that the catalytic activity of the salts is independent of metal counterion. An exception was only Cu(acac)$_2$, for which a low regioselectivity of the reaction was noted. Since with Cu(I) and Fe(III) salts it was impossible to attain a definite regioselectivity of the reactions of trialkylalanes with acetates (II), (III), and (IV), we also studied Pd(0) as catalyst. In recently obtained data [8, 9], a Pd(PPh$_3$)$_4$-catalyzed stereo- and regiospecific combination of allyl electrophiles (including allyl acetates) with alkenyl derivatives of aluminum has been reported. However, alkylmetals, for example, Me_3Al, could not be introduced into this reaction [8]. In our case, when the reaction was carried out in CH_2Cl_2 in the presence of 5 moles % of Pd(PPh$_3$)$_4$, acetate (II) entered the cross-combination reaction with OAC (VIII) to form α/γ-isomeric hydrocarbons in a ratio of (%) 78 : 22 (GLC). The reaction mixture obtained in the reaction of acetate (V) with Et_3Al also consisted of hydrocarbons. In this case, the ratio of α/γ-isomers was 76 : 24. A catalytic system consisting of Pd(acac)$_2$ and PPh_3 in a molar ratio of 1 : 4 led to the same result. Addition of 5 mole % of Pd(PPh$_3$)$_4$ in the reaction of acetates (III) and (IV) with (i-Bu)$_3$Al did not influence the composition of the products.

It follows from the above examples that during catalysis with Pd(PPh$_3$)$_4$ the regioselectivity of the reactions is poorer than in the presence of CuBr and $FeCl_3$.

It has already been noted that the alkyl substrates that we studied enter the reaction with trialkylalanes in the absence of catalysts also. The catalytic action of transition metals consists, in particular, in that they influence the selective nucleophilicity of the organometallic reagent, thus causing an appreciable change in the composition of the reaction mixtures in the direction of formation of hydrocarbons. The different selective nucleophilicity of trialkylalanes in the catalytic and noncatalytic reactions agrees with modern concepts on the participation of OAC in nucleophilic substitution reactions [2, 5], and on the participation of transition metal salts in the cross-combination reactions of organometallic compounds, mainly Grignard reagents [10, 11]. The noncatalytic combination of trialkylalanes with allyl acetates can be considered within the bounds of the S_N-1 substitution, in which the nucleophilic attacking particle is the complex anion



$$\overset{-\delta}{R}-\underset{R}{\overset{R}{Al}}-O-\underset{O\cdots AlR_3}{C}-CH_3\ .$$

In catalysis by Cu (I) and Fe (III) salts, a catalytic cycle, including a transition metal in a low-valent state, probably takes place in our case also.

EXPERIMENTAL

The UV and IR spectra were recorded on "Specord UV VIS" (alcoholic solution) and UR-20 spectrophotometers (in thin layer); PMR spectra – on the "Tesla BS-487B" apparatus (60 MHz) with reference to TMS. The mass spectra were obtained on MX-1306 spectrometer at 70 eV, with the temperature of the ionization chamber of 150°C. The GLC analysis was carried out on the "Chrom-5" apparatus, on a 1.2 m × 3 mm column with 5% SE-30 on Chromatone N-AW-DMCS, gas carrier – helium (50 ml/min). The preparative separation was carried out on a "Perkin-Elmer F-21" apparatus, on a 5 m × 18 mm column with 5% SE-30 on Chromatone N-AW, gas carrier – helium (300 ml/min).

The compositions of the mixtures of the isomeric hydrocarbons obtained were analyzed by PMR spectra and GLC. When isomeric hydrocarbons were isolated, the sum of the spectra of the individual compounds corresponded to the spectrum of the reaction mixture.

The OAC (VIII) was obtained by transalkylation of 1-hexene by a method described in [12]. Acetates (II), (III), (VI) and (VII) were obtained from the corresponding alcohols by standard acetylation with Ac_2O in pyridine, acetate (V) by telomerization of butadiene with AcOH by the method described in [13]. Acetate (IV) was obtained from sorbic acid by its methylation and reduction of methyl sorbate with $LiAlH_4$, according to [14]; the acetylation of the alcohol was carried by the above procedure.

Palladium tetrakis-triphenylphosphine was obtained by the method described in [15].

Reaction of Allyl Acetates with Trialkylalanes. Trialkylalane (0.02 mole; 1.5-2 M solution in hexane or CH_2Cl_2) was added dropwise in an Ar atmosphere at ~25°C to a solution of the acetafe (0.01 mole) in hexane or CH_2Cl_2. In the case of a catalytic reaction, 7-10 mole % of the catalyst were first added to the acetate. In the course of the addition, slight heating of the reaction mixture was observed. The end of the reaction was recorded by means of TLC on Al_2O_3 (activity grade II) (eluent – benzene). Depending on the reagents, the reaction finished immediately after addition, or after a few hours at ~25°C. The reaction mixture was diluted with ether and decomposed by H_2O, and with 10% HCl. The mixture was extracted by ether, washed with a solution of sodium carbonate, and then H_2O, and dried over $MgSO_4$. After the evaporation of the solvent, the residue was analyzed by GLC.

Reaction of Acetate (III) with $(i\text{-}Bu)_3Al$ and OAC (VIII). 5-Methyl-1-phenyl-1-hexene (X), 5-methyl-3-phenyl-1-hexene (XI), 1-phenyl-1-nonene (XII), and 3-phenyl-1-nonene (XIII) were obtained by the above procedure without the addition of a catalyst. Isomers (X)-(XIII) were obtained by preparative GLC.

Compound (X), n_D^{20} 1.5195. IR spectrum (ν, cm^{-1}): 970, 1500, 1600, 1650, 3030, 3065, 3090. PMR spectrum (δ, ppm): 0.8 d (6H, $\begin{smallmatrix}Me\\Me\end{smallmatrix}\!\!>\!C$), 1.4 m (3H, CH_2), 2.1 m (2H, $CH_2C=C$), 6.0 m (2H, $CH=CH$), 7.0 m (5H, C_6H_5). m/z 174.

Compound (XI), n_D^{20} 1.4961. IR spectrum (ν, cm^{-1}): 920, 1000, 1500, 1600, 1640, 3010, 3030, 3065, 3090. PMR spectrum (δ, ppm): 0.8 d (6H, $\begin{smallmatrix}Me\\Me\end{smallmatrix}\!\!>\!C$), 1.45 m, (3H, CH_2), 3.2 m (1H, CHC_6H_5), 4.8 m (2H, $CH_2=C$), 5.45-6.1 m (1H, $CH=CH$), 7.0 m (5H, C_6H_5). m/z 174.

Compound (XII), n_D^{20} 1.5142. IR spectrum (ν, cm^{-1}): 970, 1500, 1600, 1660, 3050, 3080, 3100. PMR spectrum (δ, ppm): 0.9 t (3H, CH_3), 1.35 m (10H, CH_2), 2.2 m (2H, $CH_2C=C$), 6.1 m (2H, $CH=CH$), 7.2 m (5H, C_6H_5). m/z 202.

Compound (XIII), n_D^{20} 1.4935. IR spectrum (ν, cm^{-1}): 910, 990, 1500, 1600, 1640, 3020, 3050, 3080, 3100. PMR spectrum (δ, ppm): 0.8 t (3H, CH_3), 1.0-1.7 m (10H, CH_2), 3.1 m (1H, CHC_6H_5), 4.9 m (2H, $CH_2=C$), 5.6-6.2 m (1H, $CH=CH$), 7.2 m (5H, C_6H_5). m/z 202.

Reaction of Acetate (IV) with $(i\text{-}Bu)_3Al$. Hydrocarbon (IX) was obtained by the procedure without addition of catalyst, yield 77%*, bp 178-180°C, n_D^{20} 1.4583. UV spectrum: λ_{max} 228 nm (ε 21,000). IR spectrum (ν, cm^{-1}):

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*The yield, physical constants, and spectral characteristics are given for a reaction mixture with 86% content of (IX).

1000, 1610, 1640, 3025. PMR spectrum (δ, ppm): 0.8 d (6H, $\genfrac{}{}{0pt}{}{Me}{Me}\!>\!C$), 1.0-1.5 m (3H, CH_2), 1.7 d (3H, $CH_3C=C$), 1.9 m (2H, $CH_2=C$), 4.8-6.2 m (4H, $CH=CH$). m/z 138.

Combination of Acetate (V) with Et_3Al, $(i\text{-}Bu)_3Al$, and OAC (VIII). Hydrocarbons (XIV)-(XVII) were obtained in presence of catalysts listed in Table 2.

1,6-Decadiene (XIV), yield 68%, bp 174-176°C, n_D^{20} 1.4352. IR spectrum (ν, cm^{-1}): 915, 980, 1000, 1650, 3085. PMR spectrum (δ, ppm): 0.9 t (3H, CH_3), 1.1-1.7 m (4H, CH_2), 2.0 m (6H, $CH_2C=C$), 4.9 m (2H, $CH_2=C$), 5.2-6.0 m (3H, $CH=CH$). m/z 138.

6-Vinyl-1-octene (XV) was isolated by preparative GLC, n_D^{20} 1.4340. IR spectrum (ν, cm^{-1}): 920, 1000, 1650, 3085. PMR spectrum (δ, ppm): 0.8 t (3H, CH_3), 1.25 m (6H, CH_2), 1.9 m (3H, $CH_2C=C$), 4.8 m (4H, $CH_2=C$), 5.0-6.0 m (2H, $CH=CH$), m/z 138.

10-Methyl-1,6-undecadiene (XVI), yield 74%, bp 61-63°C (6 mm), n_D^{20} 1.4430. IR spectrum (ν, cm^{-1}): 920, 980, 1000, 1650, 3085. PMR spectrum (δ, ppm): 0.8 d (6H, $\genfrac{}{}{0pt}{}{Me}{Me}\!>\!C$), 1.0-1.6 m (5H, CH_2), 1.9 m (6H, $CH_2C=C$), 4.7 m (2H, $CH_2=C$), 5.0-5.8 m (3H, $CH=CH$). m/z 166.

1,6-Tetradecadiene (XVII), yield 86%, bp 83-83.5°C (6 mm), n_D^{20} 1.4465. IR spectrum (ν, cm^{-1}): 920, 980, 1000, 1650, 3085. PMR spectrum (δ, ppm): 0.8 t (3H, CH_3), 1.2 m (12H, CH_2), 1.8 m (6H, $CH_2C=C$), 4.4-4.8 m (2H, $CH_2=C$), 4.8-5.7 m (3H, $CH=CH$). m/z 194.

Reaction of Acetate (VI) with $(i\text{-}Bu)_3Al$ and OAC (VIII). In the reaction hydrocarbons (XVIII) and (XIX) were obtained.

4,6-Dimethyl-2-heptene (XVIII), yield 70%, bp 60°C (20 mm), n_D^{20} 1.4135. IR spectrum (ν, cm^{-1}): 980, 1660, 3040. PMR spectrum (δ, ppm): 0.8 d, 0.9 d (9H, CH_3), 1.2 m (3H, CH_2), 1.6 m (3H, $CH_3C=C$), 2.0 m (1H, $CHC=C$), 5.25 m (2H, $CH=CH$). m/z 126.

4-Methyl-2-decene (XIX), yield 67%, bp 75-77°C (20 mm), n_D^{20} 1.4270. IR spectrum (ν, cm^{-1}): 975, 1650, 3035. PMR spectrum (δ, ppm): 0.9 m (6H, CH_3), 1.2 m (10H, CH_2), 1.6 m (3H, $CH_3C=C$), 1.9 m (1H, $CHC=C$), 5.25 m ($CH=CH$). m/z 154.

Reaction of Acetate (VII) with $(i\text{-}Bu)_3Al$ and OAC (VIII). In the reaction hydrocarbons (XX) and (XXI) were obtained.

2-Isobutyl-1-cyclohexene (XX), yield 80%, bp 68-70°C (20 mm), n_D^{20} 1.4547. IR spectrum (ν, cm^{-1}): 730, 1655, 3030, 3075. PMR spectrum (δ, ppm): 0.9 d (6H, CH_3), 1.1-1.5 m (3H, CH_2), 1.6 m (4H, CH_2 in the ring), 1.75-2.3 m (3H, $CH_2C=C$), 5.6 m (2H, $CH=CH$). m/z 138.

2-Hexyl-1-cyclohexene (XXI), yield 63%, bp 98-99°C (20 mm), n_D^{20} 1.4550. IR spectrum (ν, cm^{-1}): 720, 1660, 3050, 3090. PMR spectrum (δ, ppm): 0.85 t (3H, CH_3), 1.25 m (10H, CH_2), 1.5-2.1 m (4H, CH_2 in the ring, 3H, $CH_2C=C$), 5.5 m (2H, $CH=CH$). m/z 166.

CONCLUSIONS

It has been shown that the structure of allyl acetates has an appreciable influence on the character of their alkylation by trialkylalanes. The presence of catalytic amounts of Cu(I), Fe(III) and $Pd(PPh_3)_4$ considerably increases the selectivity of the reaction.

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STRUCTURE OF PRODUCT OF REACTION BETWEEN PHENYLPHOSPHINE AND PHENYLDICHLOROARSINE AND PHENYLARSINE OXIDE

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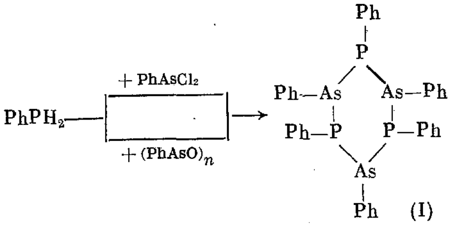
Cyclopolyphosphines and cyclopolyarsines with small and medium rings are known, and have been fairly well investigated [1-3]. Compounds with small rings (n=3, 4) containing all the possible combinations of phosphorus and arsenic atoms have been described in [3, 4]. The existence of these compounds with medium rings (n=5, 6) has not yet been shown.

1,2,3,4,5,6-Hexaphenyl-1,3,5-triphospha-2,4,6-triarsacyclohexane (I), mp 181°C, was obtained by the reaction of phenyldichlorophosphine with phenylarsine. Its elemental composition corresponded to phospharsobenzene $(PhP\text{-}AsPh)_3$, but the structure of the product has not yet been studied [5]. During recrystallization from benzene, hexaphenylcyclohexaarsane $(PhAs)_6$ separated as a precipitate, and from xylene – pentaphenylcyclopentaphosphane $(PhP)_5$. It was concluded [2] that the reaction of phenyldichlorophosphine with phenylarsine, like the reaction of phenylphosphine with phenyldichloroarsine, gives a mixture of disproportionation products, but the conditions of carrying out the experiment and the physical constants of the products were not given.

We studied the reaction of phenylphosphine with phenyldichloroarsine and phenylarsine oxide.



(I)

In both cases one and the same product was obtained, which crystallized from C_5H_5N, and whose elemental composition and melting point were identical with those given in [5]. The elemental composition and molecular weight of the product, equal to 848 for the initial sample, and 890 for a sample with a larger weight, make it possible to select between the possible structures in favor of (I) (mol. wt. 780). A certain overestimate of the experimental values may be due to the poor solubility of the material.

The mass spectra of compounds with rings consisting of P and As atoms have not been described in the literature. However, there are comprehensive data on the mass spectra of cyclopolyphosphines and cyclopolyarsines, showing that these classes of compounds have interesting mass-spectrometric features [2, 6, 7]. In

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