**Insight into the shift and rearrangement of carbocation in
Friedel-Crafts alkylation of unsaturated fatty acids revealed by
GC-MS**

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14 **ABSTRACT:**

15 We observed that Friedel-Crafts alkylation of unsaturated fatty acids yielded diverse
16 products because of the shift and rearrangement of carbocation. However, these shifts
17 and rearrangement rules of carbocation in Friedel-Crafts alkylation were unclear. For
18 a better understanding of these rules, the product diversity of Friedel-Crafts alkylation
19 of oleic acid with phenyl was studied by GC-MS. The product structures were
20 identified by the characteristic m/z obtained in electron impact ionization and the
21 relative contents of diverse isomers were calculated by the normalization method of
22 integration areas in extracted ion and total ion chromatograms. The results suggested
23 there were 11 isomeric compounds, 7~17- phenyl stearic acids with relative contents
24 ranging from 2.9% to 16.4%. The inhibition factor of the shift and rearrangement of
25 carbocation was also being investigated. The carbocation was easily quenched by
26 oxygen-containing compounds such as ester, ether, and alcohol. Intramolecular
27 quenching stopped the carbocation shifting and inhibited 2~6- phenyl stearic acids
28 formation. The study contributed to the understanding of the shift and rearrangement
29 of carbocation, diversity of produced isomers and inhibitors in Friedel-Crafts
30 alkylation of the unsaturated fatty acids, which were helpful in preparing and
31 manufacturing relative unsaturated fatty acids by alkylation.

32 **Keywords:** Friedel-Crafts alkylation; Quenching of carbocation; Rearrangement of
33 carbocation; Oleic acid; GC-MS

34 **1. Introduction**

35 Unsaturated fatty acids are important renewable resources that have gained
36 attention as raw stocks to prepare bio-based surfactants[1-3]. However the double
37 bonds in the unsaturated fatty acids are unstable, usually requiring modification in
38 oleochemicals preparation using alkylation[4, 5], hydroxylation and epoxidation[6].

For example, oleic acid was hydro-alkylated with 1-propyl chloroformate to give a 1:1 mixture of 9- and 10-isopropylstearic acids[5]. Friedel-Crafts alkylation[7-11] with great significance for organic synthesis was used as a common method for the alkylation of unsaturated fatty acids[12]. But the product of Friedel-Crafts alkylation of oleic acid was a series of isomers instead of only 9- and 10-benzene stearic acids, due to the shift and rearrangement of carbocation.

There were many researches about the shift and rearrangement of carbocation in reaction in the last decades. For example, via rearrangement of carbocation intermediates, the diamondoids could be synthesized by the reaction of an organic precursor and a super acid catalyst in the lab[13-15]. The stereoselective ring openingmediated rearrangement of epoxides could be efficiently carried out with Lewis and Bronsted acid[16]. Alkylation of cyclohexene and 1-pentyl chloroformate in the presence of triethylsilane yielded mixtures of 2- and 3-cyclohexylpentane in a ratio of 1.3:1, due to the Wagner-Meerwein rearrangement[5]. The isomeric compounds of alkyl chain might be generated through rearrangement of carbocation in Friedel-Crafts alkylation[17-19]. The cyclobutene skeleton was formed from cyclopropyl group by rearrangement of carbocation under Lewis acid conditions[20]. Several mechanisms about skeletal rearrangement was extremely studied by density functional theory[21, 22]. Though much attention have been paid to the rearrangement of carbocation, the shift and rearrangement of carbocation in Friedel-Crafts alkylation of unsaturated fatty acids was not been studied ever.

In this study, the Friedel-Crafts alkylation of oleic acid and phenyl was

researched. The diversity, structure and relative content of the product were studied by GC-MS. The shifts and rearrangement rules of carbocation and the inhibition factor were discussed.

2. Material & method:

2.1 Materials

The oleic acid (AR, Tokyo Chemical Industry Co., Ltd, Tokyo, Japan), benzene (AR, Shanghai Lingfeng Chemical Reagent Co., Ltd, Shanghai, China), AlCl_3 (99%, Aladdin, Shanghai, China), methanol (AR, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China), *n*-hexane (AR, Shanghai Lingfeng Chemical Reagent Co., Ltd, Shanghai, China), sulfuric acid (AR, Shanghai Lingfeng Chemical Reagent Co., Ltd, Shanghai, China), diethylene oxide (AR, Shanghai Tianlian Chemical Technology Co., Ltd, Shanghai, China), methenyl trichloride (AR, Shanghai Lingfeng Chemical Reagent Co., Ltd, Shanghai, China), acetic acid (AR, Shanghai Lingfeng Chemical Reagent Co., Ltd, Shanghai, China), ethyl acetate (AR, Shanghai Tianlian Chemical Technology Co., Ltd, Shanghai, China), acetylacetone (AR, Shanghai Lingfeng Chemical Reagent Co., Ltd, Shanghai, China) were used without further purification.

2.2 Friedel-Crafts alkylation

The phenyl stearic acid was prepared in the presence of anhydrous AlCl_3 [5] by the Friedel-Crafts reaction of oleic acid with benzene in a flask, in which the molar ratio of oleic acid (5.00 g), benzene and anhydrous AlCl_3 was 1:5:1. The mixture was heated to 65 °C and maintained for 6 h with stirring. The resulted mixtures were then cooled to 0 °C, and equal volume of 6 mol/L HCl was added slowly into the flask. The

organic layer was separated and evaporated under reduced pressure to obtain phenyl stearic acids[2].

2.3 Quenching reaction

Methanol, diethylene oxide, methenyl trichloride, acetic acid, ethyl acetate and acetylacetone, as quenching reagents with double molar ratio of oleic acid were put into the reactors, respectively. Then the oleic acid, benzene and anhydrous AlCl_3 were added into the flask successively, with the molar ratio 1:5:1. The alkylation conditions were the same as mentioned in section 2.2.

2.4 Esterification

The resulted mixtures of Friedel-Crafts alkylation or quenching reaction (0.500 g) and 10 mL mixed sulfuric acid and methanol solution (1:9 in volume) were heated at 60 °C with stirring for 30 min[23-25]. Then 9 mL deionized water was added into the flask, and then the products were extracted with *n*-hexane (1 mL). The organic solution was washed with deionized water three times and then dried with sodium sulfate.

2.5 Analysis of the products

The structures of the products were characterized by Gas Chromatography Mass Spectrometry (GC-MS), recorded on Agilent 6890N Network GC system and 5978 inter Mass Selective Detector. The gas chromatograph was equipped with a capillary column HP-5MS (30 m×0.25 mm), which film thickness was 0.25 μm. The ion source temperature and the injector temperature were 230 °C and 280 °C, respectively. The temperature was programmed from 50 °C (2 min) to 230 °C at 40 °C/min and

then to 250 °C at 10 °C/min and then to 280 °C at 20 °C/min (keeping this temperature for 10 min). With split ratio 50:1, 0.20 µL of sample was injected.

3. Result and discussion

3.1 Yields and structural analyses

Scheme. 1 The route of Friedel-Crafts reaction of oleic acid with phenyl

The route of Friedel-Crafts reaction of oleic acid with phenyl was showed in Scheme 1. The GC chromatogram of methyl oleate, phenyl methyl stearate were shown in Fig. 1, in which peak A, B and C indicated the methyl oleate, methyl stearate and phenyl methyl stearate, respectively. Line 1 showed the products of esterification of oleic acid sample. There was little stearic acid in this sample, which could be used as the internal standard for the calculation of yields of Friedel-Crafts reaction. Line 2 indicated the result of Friedel-Crafts reaction of oleic acid. The conversion of alkylation was calculated by a formula:

$$\eta = \frac{A_R \times A'_I - A'_R \times A_I}{A_R \times A'_I}$$

where A_R is the peak area of methyl oleate before the alkylation; A'_R is the peak area of methyl oleate after the alkylation; A_I is the peak area of methyl stearate before the alkylation; A'_I is the peak area of methyl stearate after the alkylation. Fig. 1 showed that the oleic acid was completely expended in the alkylation, and it yielded 97.7%. Fig. 2 suggested the MS spectrogram of phenyl methyl stearate isomers, in which the molecular weights were 374.

Fig. 1 GC chromatogram of methyl oleate, phenyl methyl stearate

Line 1 showed the products of esterification of oleic acid sample. Line 2 showed the result of Friedel-Crafts alkylation of oleic acid. Peak “A” was methyl oleate, peak “B” was methyl stearate and peak “C” was phenyl methyl stearate.

There was only one peak for methyl oleate, whose molecular weight was 296 (Line 1 in Fig. 1), but 6 peaks (C1~C6) for phenyl methyl stearate isomers, whose

molecular weights equal 374 (Line 2 in Fig. 1). Besides, all these 6 peaks contained a same characteristic m/z , 91, the characteristic m/z of positive benzyl, as shown in Fig. 2. Other m/z numbers were obtained by using MS method for all these 6 peaks in GC chromatogram of phenyl methyl stearate. Since all the peaks had same characteristic m/z , 91 and 374, but differed in other characteristic m/z numbers, any difference in their structures should arise from the connecting position of phenyl to the alkyl group. This phenomenon illustrated that the products of the Friedel-Crafts alkylation of oleic acid and phenyl were skeletal isomers. Another interesting phenomenon was found that the difference of the characteristic m/z numbers for the 5 small neighboring GC peaks (C2~C6) was 14 (the molecular weight of methylene), which demonstrated that the connecting positions of phenyl group to alkyl chain were consecutively adjacent for the 5 small peaks.

Fig. 2 The MS spectrogram of phenyl methyl stearate isomers

The characteristic m/z numbers obtained by the splitting in electron impact ionization were applied for the identification of the isomers. The m/z of fragments of all isomers were calculated by two formulas m/z (a) and m/z (b-c), showed in Fig. 3. For example, Fig. 4 showed the generation of fragments from 13- phenyl methyl stearate. In electron impact ionization of alkyl chain, the C-C bond connected with more substituent groups split easily, which meant that the single bonds “a” and “b” were the primary splitting positions. The conjugated system increased the stabilization of fragments, leading to higher abundances, as conjugative effect was the most important factor for the stabilization of fragments. Hence, the m/z numbers of the stable fragments with phenyl group, 161 and 271, were applied as the characteristic

m/z for 13- phenyl methyl stearate. Other fragments were not stable enough, leading to not remarkable abundances. Besides, smaller molecule, methanol, was generated by neutral radical[26, 27]. Combined with the fragments' characteristic m/z , the isomers were identified as 13- phenyl methyl stearate, 14- phenyl methyl stearate, 15- phenyl methyl stearate, 16- phenyl methyl stearate and 17- phenyl methyl stearate for the small peaks C2~C6 (Fig. 1), respectively. In addition, because of the highest stabilization of positive benzyl generated by splitting of both "a" and "b" bonds, characteristic m/z , 91, had the maximal abundance for all the isomers except 17- phenyl methyl stearate. For 17- phenyl methyl stearate, the splitting probability of single bond "b" was low, resulting in the generation of positive phenylethylene, $m/z=105$.

Fig. 3 The formulas of fragments m/z numbers

m/z (a) was calculated as the left part of the single bands "a"; m/z (b-c) was calculated as the middle part between the single bands "b" and "c".

Fig. 4 The forming mechanism of fragments from 13- phenyl methyl stearate

For the peak C1, there were not obvious characteristic m/z at the top, except 91 and 374. However, from the bottom and middle of the peak, in close proximity to the neighboring small peak, m/z were found as 175 and 257 for 12- phenyl methyl stearate, 189 and 243 for 11- phenyl methyl stearate, based on the fragments' characteristic m/z , showed in Fig. 2. To the best of our knowledge, the position of double bond for oleic acid is 9, showed in scheme 1. We wondered whether 2~10- phenyl methyl stearates existed, since 11~17- phenyl methyl stearates were found. Extract ion spectrogram (EIS) was used to search 2~10- phenyl methyl stearates according to the fragments' characteristic m/z listed in Table 1 from the whole GC chromatogram. Table 1 exhibited the result, 7~10- phenyl methyl stearates existed in the peak C1 showed as "M" in Fig. 2, while 2~6- phenyl methyl stearates were not

found out. So the peak C1 contained 7~12- phenyl methyl stearates isomers, which can't be separated by GC because of the close boiling points and characteristics.

Table 1. The m/z characteristic number and relative amount of isomers

isomers	structure	m	n	m/z characteristic number		relative amount
				m/z (a)	m/z (b-c)	
2- phenyl methyl stearate		0	15	315	117	0%
3- phenyl methyl stearate		1	14	301	131	0%
4- phenyl methyl stearate		2	13	287	145	0%
5- phenyl methyl stearate		3	12	273	159	0%
6- phenyl methyl stearate		4	11	259	173	0%
7- phenyl methyl stearate		5	10	245	187	11.50%
8- phenyl methyl stearate		6	9	231	201	7.64%
9- phenyl methyl stearate		7	8	217	215	11.02%
10- phenyl methyl stearate		8	7	203	229	15.52%
11- phenyl methyl stearate		9	6	189	243	16.39%
12- phenyl methyl stearate		10	5	175	257	14.28%
13- phenyl methyl stearate		11	4	161	271	7.64%
14- phenyl methyl stearate		12	3	147	285	5.25%
15- phenyl methyl stearate		13	2	133	299	3.47%
16- phenyl methyl stearate		14	1	119	313	2.87%
17- phenyl methyl stearate		15	0	105	327	4.41%

The products of the Friedel-Crafts alkylation of oleic acid with benzene were 11 isomers. However, the position of double bond in oleic acid molecular is constant,

between 9th and 10th carbon atoms. It meant that the carbocation was mobile along the carbon chain during the Friedel-Crafts alkylation, but not standing at one specific position. When it shifted to one position of the alkyl chain, for example, secondary end position, the carbocation could connect with benzene, to form 17- phenyl stearic acid. H-NMR was carried out for the phenyl stearic acid isomers in CDCl₃, which was showed in Fig. 5.

Fig. 5 H-NMR of phenyl stearic acid isomers

3.2 Relative contents of isomers

The relative contents of all isomers were shown in Table 1, which was calculated by normalization method of extracted ion chromatograms for isomers in C1 and total ion chromatograms of C2~C6. The result suggested that there were no 2~6- phenyl methyl stearates. And the relative contents of 7~12- phenyl methyl stearates were higher than that of 13~17- phenyl methyl stearates. Because of the destabilization of the carbocation, the longer way it shifted, the smaller relative content of the

corresponding product generated.

Since the carbocation was shifting along the whole alkyl chain instead of standing at the initial position, the products generated should be 2~17- phenyl stearic acids in the Friedel-Crafts alkylation, theoretically. However, there were no 2~6- phenyl stearic acids from the result. The connecting points of methyl group to the alkyl chain were 2~18, when oleic acid was isomerized and hydrogenated to prepare for methyl iso-oleate in the previous study[28], in which the branching methyl group has several possible positions as the double bonds shifted. The difference connecting points of phenyl group to alkyl chain in this study might be explained by two reasons. One was that because of the larger space of phenyl group, the sterical hindrance increased, leading to the Friedel-Crafts alkylation can't carry out when the carbocation shifted near the carboxyl group. While the other was that the carbocation could be quenched by the carboxyl group when it shifted near the carboxyl group. The polar carboxyl group could form a circular structure near to a carbon atom in the alkyl chain by chain bending because of the C-C bond's rotation, and then the carbocation could be quenched by the intramolecular carboxyl group when it shifted along the alkyl chain. As there was not plentiful evidence for the quenching of carbocation, some Friedel-Crafts reactions were performed with polar reagents to test whether the carbocation would be quenched by the polar carboxyl group.

3.3 Quenching of carbocation

Table 2 listed the yields of Friedel-Crafts alkylation with quenching reagents, which were 96.6 %, 20.4 %, 13.7 %, 13.6 %, 9.84 % and 6.70 % for methenyl

trichloride, acetic acid, methanol, ethyl acetate, diethylene oxide and acetylacetone. Table 3 indicated the relative amounts of 4 isomers with quenching reagents, acetic acid and ethyl acetate, respectively.

Table 2. The yield of the Friedel-Crafts alkylation with or without quenching reagents

Quenching reagent	no	methenyl trichloride	acetic acid	methanol	ethyl acetate	diethylene oxide	acetylacetone
yield	97.7%	96.6%	20.4%	13.7%	13.6%	9.84%	6.70%

Since it was the shift of carbocation that made the products 11 isomers, the decrease of carbocation number may result in less isomers generated. In view of this, a series experiments were set to quench part of carbocation before carrying out the Friedel-Crafts alkylation. As a result, the yields of Friedel-Crafts alkylation decreased considerably with quenching reagents except methenyl trichloride as shown in Table 2. The weak-polar methenyl trichloride molecule would not quench the carbocation. Other polar quenching reagents containing oxygen atoms can provide pair electrons to the carbocation, thus resulting in considerable decrease of the product yields, which may indicate that the Friedel-Crafts alkylation was not completed in the presence of oxygen-containing polar reagents. Besides, the relative amounts of isomers far from initial position decreased with acetic acid and ethyl acetate as quenching reagents showed in Table 3, which meant that when it shifted a longer way, the chance of the carbocation quenched by quenching reagents increased. Table 1 suggested there were no 2~6- phenyl methyl stearates without quenching reagents, while the carbocation should be theoretically present at 2~17 position along the alkyl chain when it shifted from the initial position. That meant the carbocation could be quenched by the

intramolecular oxygen-containing polar carboxyl group when it shifted near the carbon atom which the carboxyl group closed to by alkyl chain bending, showed as Scheme 2. And the carbocation was also quenched even the polar carboxyl group was esterified by methanol before the alkylation.

Scheme. 2 The quenching mechanism of carbocation by carboxyl group

Table 3. The relative amounts of 4 isomers with quenching reagents- acetic acid and ethyl acetate

isomers	acetic acid	ethyl acetate
14- phenyl methyl stearate	4.38%	3.85%
15- phenyl methyl stearate	2.82%	2.82%
16- phenyl methyl stearate	2.55%	2.88%
17- phenyl methyl stearate	2.36%	3.24%

4. Conclusion:

The products of Friedel-Crafts alkylation of oleic acid were successfully characterized by GC/MS. Owing to the shift and rearrangement of carbocation, 11 isomeric compounds, 7~17- phenyl stearic acids with contents ranging from 2.9% to 16.4%, have been produced in the Friedel-Crafts reaction of oleic acid with phenyl.

Since the carbocation would be quenched by the oxygen atom in oleic acid, there were no 2~6- phenyl stearic acids generated by intramolecular quenching. The yields of Friedel-Crafts reaction decreased considerably with oxygen-containing reagents, such as ester, ether and alcohol. The study shed light on the product diversity of alkylation of unsaturated compound with a long chain and was instructive for preparing and manufacturing relative compounds by alkylation.

Acknowledgements

This research was supported by National Science Foundation of China (Grant No.51574125, 21203063) and the 863 program (Grant No.2013AA064403), and the Fundamental Research Funds for the Central Universities of China.

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