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Friedel-Crafts alkylation of benzene and toluene with olefinic C_6 hydrocarbons and esters

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Abstract

To assist our study of the reaction of toluene and other aromatic compounds with methyl oleate and other olefinic esters, benzene and toluene have been alkylated under Friedel-Crafts conditions with hex-1-ene, hex-3-ene, methyl hex-3-enoate and methyl hex-3-enedioate. The products were isolated and identified by NMR and mass spectrometric procedures.

Keywords: Friedel-Crafts alkylation; Benzene; Toluene; Hexenes; Hexenoates; NMR spectra; Mass spectra

1. Introduction

We are interested in the Friedel-Crafts reaction between methyl oleate and aromatic molecules such as toluene. Our experiments showed that the main product — a mixture of compounds containing one aromatic ring and one aliphatic chain was accompanied by other compounds with two or more aliphatic chains per aromatic ring [1]. To assist our understanding of these products, we have examined the alkylation with several unsaturated C₆ compounds.

2. Results and discussion

2.1. Reaction of hex-1-ene and benzene

Hex-1-ene and benzene reacted in the presence of aluminium chloride to give a complex reaction mixture. Gas chromatography showed many peaks arranged in clusters and GC/MS indicated that these clusters represented products in which an aromatic ring is associated with 1-4 alkyl chains. These will be referred to as the n:1 components, when n represents the number of alkyl chains.

Table 1

Products (%) of the reaction between benzene and hex-1-ene followed by a second addition of alkene

| AIkyl/aromatic ratio | 1:1 | 2:1 | 3:1 | 4:1 | Other |
|----------------------|-----|-----|-----|-----|-------|
| First reaction | 70 | 26 | 3 | 0 | 1 |
| Second reaction | 26 | 38 | 21 | 12 | 3 |

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Scheme 1.

When the reaction product was re-treated with more hex-1-ene, further alkylation occurred as shown in Table 1. The average degree of alkylation was raised from 1.3 to 2.2.

After the first reaction the product was mainly 1:1 (70%) with some 1:2 (26%); on further reaction the product was more complex with increasing quantities of higher molecular weight product and less of the 1:1 product. As already indicated, each of these products appeared as a number of GC peaks: two for the 1:1 product, six for the 2:1, five for the 3:1 and four for the 4:1. This multiplicity of products results from the differing point of attachment to the alkyl chain and from the differing orientation of the alkyl groups attached to the ring system.

The 1:1 product was a mixture of 2- and 3-phenylhexanes with no evidence of any 1-phenylhexane. These products result from the appropriate carbocations (Scheme 1) and were identified by their mass spectra after separation by gas chromatography. Both compounds (1 and 2) gave molecular ions of m/e 162 and, in common with other benzyl compounds, they also produce the tropylium cation $(C_7H_7^+, m/e 91)$. 2-Phenylhexane gave a peak at M-57, but hardly any M-15. In contrast, 3-phenylhexane gave fragments at M-29 and M-43. This pattern of fragmentation is a clear indication of the point of attachment of the aromatic ring.



The 2:1 cluster showed six peaks, all of which had a molecular ion of 246. This accords with a 2:1 product of molecular formula $C_{18}H_{30}$. From their mass spectra, there were two 2,2-dihexylbenzenes, two 3,3-dihexylbenzenes, and two 2,3-dihexylbenzenes. The two products in each case were probably *ortho* and *para* isomers, but we did not prove this. These structural conclusions were based mainly on the presence or absence of peaks corresponding to M-57 (2-substituted) and to M-43 and M-29 (3-substituted) as shown in Table 2.



Intensities and assignments for GC/MS peaks of the 2:1 hexene/benzene product

| Peak | number | 1 | 2 | 3 | 4 | 5 | 6 |
|------|---------------|----|----|----|-----|----|-----|
| m/e | ·· | | | | | | |
| 246 | Μ | 21 | 6 | 7 | 7 | 18 | 3 |
| 217 | M-Et (29) | 22 | 5 | 21 | 0 | 17 | 0 |
| 203 | M-Pr (43) | 93 | 35 | 59 | 0 | 74 | 0 |
| 189 | M-Bu (57) | 0 | 30 | 0 | 100 | 99 | 100 |
| 175 | Α | 78 | 48 | 60 | 3 | 83 | 3 |
| 147 | A + 1-Et (29) | 0 | 6 | 0 | 3 | 13 | 1 |
| 133 | A + 1-Pr (43) | 63 | 25 | 13 | 12 | 13 | 3 |
| 117 | A + 1-Bu (57) | 31 | 14 | 22 | 16 | 38 | 10 |
| 105 | В | 22 | 18 | 13 | 15 | 31 | 18 |
| 91 | A + 1-Hex | | | | | | |
| | (tropylium) | 80 | 39 | 52 | 16 | 60 | 13 |
| Base | peak (m/e) | 43 | 43 | 43 | 189 | 43 | 189 |



Peaks 1 and 3 showed M-29 and M-43 fragments and are, therefore, 3,3-dihexylbenzenes. Peaks 4 and 6 had M-57 ions as base peaks and no M-29 or M-43 fragments and are, therefore, 2,2-dihexylbenzenes. The remaining peaks (2 and 5) had M-29, M-43 and M-57 ions and are presumably 2,3-dihexylbenzenes. All these compounds showed ions of m/e 175, 105, and 91 corresponding to tropylium ions 3–5 as well as fragments resulting from further loss of ethyl, propyl or butyl groups from fragment 3.



The 3:1 cluster had five peaks (Table 3), all of which showed a molecular ion of 330 ($C_{24}H_{42}$). By virtue of the presence or absence of M-29, M-43 and and M-57 ions we consider that the first three peaks were 2-hexyl,di-3-hexylbenzene (peak 1), di-2-hexyl,3-hexylbenzene (peak 2), and tri-2-hexyl-benzene (peak 3). It was less easy to assign structures to peaks 4 and 5 and there is a possibility that these may be isomers of dodecylhexylbenzene. These would be formed if hex-1-ene was dimerised to a dodecene before reaction with benzene.

Finally, the 4:1 cluster had four peaks all with molecular ions of 414 ($C_{30}H_{54}$) (Table 4). Their mass spectra followed similar patterns to those with the compounds already discussed but it was not possible to make detailed structural assignments.

2.2. Reaction of hex-1-ene and toluene

When hex-1-ene reacted with excess of toluene in the presence of aluminium chloride, a complex mixture of products was formed. Replacement of benzene by toluene leads to additional possibilities of isomerism in the 1:1 products. The total product was separated into a number of clusters by GC. GC-MS showed the presence of up to four hexyl chains (or their equivalent with some C_{12} chains) per aromatic ring. Some of the products were identified by spectroscopic procedures.

| Table | 3 | |
|-------|---|--|
| | | |

Intensities and assignments for GC/MS peaks of the 3:1 hexene/benzene product

| Peak | number | 1 | 2 | 3 | 4 | 5 |
|-------------|---------------|----|----|----|----|----|
| m/e | | | | | | |
| 330 | М | 6 | 3 | 8 | 3 | 15 |
| 301 | M-Et (29) | 6 | 2 | 0 | 4 | 0 |
| 287 | M-Pr (43) | 23 | 5 | 0 | 1 | 0 |
| 273 | M-Bu (57) | 18 | 28 | 93 | 20 | 47 |
| 259 | С | 20 | 10 | 2 | 0 | 0 |
| 231 | C + 1-Et (29) | 3 | 1 | 0 | 12 | 5 |
| 217 | C + 1-Pr (43) | 4 | 2 | 4 | 17 | 53 |
| 203 | C + 1-Bu (57) | 7 | 3 | 3 | 26 | 67 |
| 1 89 | D | 5 | 7 | 16 | 24 | 26 |
| Base | peak (m/e) | 43 | 43 | 43 | 43 | 43 |





Intensities and assignments for GC/MS peaks of the 4:1 hexene/benzene product

| Peak | number | 1 | 2 | 3 | 4 | |
|------|---------------|----|----|----|----|--|
| m/e | | _ | | | | |
| 414 | М | 20 | 21 | 4 | 32 | |
| 385 | M-Et (29) | 15 | 12 | 0 | 0 | |
| 371 | M-Pr (43) | 12 | 11 | 0 | 0 | |
| 357 | M-Bu (57) | 11 | 21 | 6 | 37 | |
| 343 | E | 0 | 0 | 0 | 0 | |
| 315 | E + 1-Et (29) | 13 | 6 | 0 | 4 | |
| 301 | E + 1-Pr (43) | 16 | 17 | 7 | 40 | |
| 287 | E + 1-Bu (57) | 20 | 30 | 11 | 37 | |
| 273 | F | 11 | 7 | 0 | 0 | |
| Base | peaks (m/e) | 43 | 43 | 43 | 43 | |



When reaction was effected at 20° C, the product was mainly 1:1, i.e. a mixture of 3-tolyl and 2-tolylhexanes (90%) with only a little 2:1 product (7%). At 0°C, these figures were only

Table 5 Products (%) of the reaction between toluene and hex-1-ene or hex-3-ene at various temperatures

| | Hex | -1-ene | | | Hex-3-ei | ne |
|-------------------|-----|--------|-----|-----|----------|----|
| Temp (°C) | 20 | 0 | -10 | -75 | 0 | |
| Yield (%)* | 98 | 99 | 90 | 3 | 85 | |
| 1:1 3-Tolylhexane | 31 | 29 | 18 | 3 | 50 | |
| 1:1 2-Tolylhexane | 59 | 57 | 47 | 17 | 28 | |
| 2:1 | 7 | 14 | 28 | 27 | 22 | |
| 3:1 | 0 | 0 | 5 | 45 | 0 | |
| 4:1 | 0 | 0 | 0 | 3 | 0 | |
| Other | 3 | 0 | 2 | 5 | 0 | |

*Based on alkene.

slightly changed (Table 5) and the ratio of 2- to 3-tolylhexanes remained at about 2:1. At -10° C, there was more of the 2:1 product, a little 3:1, and a higher proportion of 2- to 3-tolylhexanes. This trend was even more marked in the reaction product obtained at -75° C, though here the total yield of product was much lower. It is thus possible to control the nature of the reaction product to some extent by choice of the reaction temperature.

The 2- and 3-tolylhexanes and some of the more complex products were identified by GC/MS. The results were similar to those observed in the reactions with benzene and are detailed in the experimental section.

2.3. Reaction of hex-3-ene and toluene

Hex-3-ene and toluene reacted at 0°C to give a mixture of products similar to those obtained with hex-1-ene except that the proportion of 2- and 3-tolylhexane has changed in favour of the 3-isomer (Table 5).

2.4. Reaction of cyclohexene with benzene and toluene

Reaction between cyclohexene and benzene or toluene gave the expected arylcyclohexane (6 or 7). Spectroscopic information is given in the experimental section.

2.5. Reaction of unsaturated C_6 esters and benzene

Methyl *trans*-hex-3-enoate reacted with benzene to give mainly methyl 5-phenylhexanoate (92%) on the basis of its NMR spectrum. Gas chromatography suggested the presence of some of the 4-phenyl isomer (4%) and some compounds of higher molecular weight (2-3%). There was no evidence for any of the 2- or 3-phenylhexanoates. The presence and absence of these particular isomers shows the lability of the carbocation and the greater stability of that with the charge on the penultimate carbon atom (Scheme 2).

Dimethyl hex-3-enedioate was recovered unchanged under these conditions. The two ester



Scheme 2.



Scheme 3.

groups presumably inhibit carbocation formation at any point along the chain.

2.6. Synthetic studies

To assist in our structural assignments, we synthesized samples of 2-phenylhexane (10) and 1,4-di(2-hexyl) benzene (12) by Wittig reaction between the phosphonium salt of 1-bromobutane and acetyl benzene and 1,4-diacetylbenzene (Scheme 3).

3. Experimental

3.1. General

Gas chromatography was carried out on an HP-1 non-polar WCOT column (25 m, 0.2 mm I.D., 0.11 μ m coating thickness) using helium (27 cm·s⁻¹) as carrier gas.

Mass spectra were recorded on a Finnigam Matt Incos 50 mass spectrometer with sample introduction by GC system similar to the above.

All NMR spectra were run on a Bruker AM

300 spectrometer. Samples were dissolved in deutero-chloroform with tetramethylsilane as internal standard.

3.2. Friedel-Crafts alkylation

The following description of reaction between toluene and cyclohexene represents the typical procedure employed. When the alkene is replaced by an olefinic ester, one extra mol of catalyst is required for each ester group.

Cyclohexene (5.00 g, 61 mmol) was added to a stirred suspension of aluminium chloride (0.80 g, 6 mmol) in toluene (25 ml) in an ice bath. After stirring for 3 h, ice was added to the reaction mixture. The organic product was extracted with petrolum ether (bp 40-60°C, 100 ml) and washed first with dilute hydrochloric acid (0.5 M, 100 ml) and then with water (3 \times 100 ml). The aqueous washings were extracted again with more petroleum ether (50 ml). The combined organic extracts gave the product (9.51 g) after removal of solvent. Gas chromatography showed this to be a mixture of 1:1 (70%) and 2:1 (29%) products.

3.3. Esterification

trans-Hex-3-enedioic acid and *trans*-hex-3-enoic acid were esterified with care to inhibit double bond migration.

The dibasic acid (3.00 g, 20.8 mmol), methanol (1.00 g, 31.3 mmol), 2,2-dimethoxypropane (4.50 g, 43.2 mmol) and 4-toluenesulphonic acid (0.025 g, 0.15 mmol) were stirred together at 45°C for 4 h. The mixture was then evaporated and the diester was distilled under reduced pressure (3.12 g, 87%). The monobasic acid was esterified in a similar way.

3.4. 2-Phenylhexane [2]

Triphenylphosphine (10.00 g, 38 mmol) and 1-bromobutane (7.00 g, 51 mmol) were refluxed in xylene (50 ml) for 16 h. The solution was filtered and the white phosphonium salt (11.73 g, 77%) was washed with a little petroleum ether.

Nitrogen was bubbled through dimethylsulphoxide (50 ml, dried over molecular sieve) for 30 min before adding sodium hydride (60% dispersion in mineral oil, 1.60 g, 40 mmol). This mixture was stirred under nitrogen at 65° for 1.5 h then cooled to room temperature prior to the addition of the phosphonium salt (16.0 g, 40 mmol) over 15 min. After stirring for a further 45 min acetylbenzene (4.80 g, 40 mmol) was added and the temperature raised to 50°C and held for 1 h.

The cooled reaction mixture was acidified (dil. hydrochloric acid, 0.5 M, 50 ml) and extracted with petroleum ether (bp $40-60^{\circ}$, 100 ml). The extract was washed with water (4 \times 50 ml), the solvent removed, and the residue (6.67 g) eluted from an alumina column (50 g) with petroleum ether to give 2-phenylhex-2-ene (4.68 g, 73%) as a 3:1 mixture of two diastereoisomers.

2-Phenylhexane was recovered in good yield when the olefin (1 g). in methanol solution (30 ml) was stirred with Pd/C (10%, 200 mg) in an atmosphere of hydrogen for 8 h.

3.5. 1,4-Di(2-hexyl)benzene

1,4-Diacetylbenzene was treated as above with twice the proportion of ylide. The product was mainly the result of reaction with two mol of ylide (68%) though some of the diketone had only reacted with one mol (8%). These were separated by chromatography and the di-olefinic compound was hydrogenated to 1,4-di-(2-hexyl)benzene.

| | a | Ь | с | d | e | f | g | h |
|-----------|-----------------------------|--------------------------------|---------------------|-------------------------------------|---|---|----------------------------|-------------------------------------|
| ян | 1.40 | , 1.85 | | 2.48 | | | 7.20 | |
| бC | 26.27 | 27.01 | 34.56 | 44.70 | 148.00 | 128.28 | 126.80 | 125.78 |
| | a Cycu | b b | c c | d d | , sever e | f f | g g | h |
| | a Cycu | b b | c c | d d | , sever e | f f | g g | h |
| | a | b | c | d d | , sever e | f | g | h |
| 5н | a 1.40 | b , 1.82 | c | d 2.41 | e e | f | g 5 | h 2.28 |
| 5.7. | a 1.40 | b , 1.82 | c | d 2.41 2.65 | e e | f 7.0 | g 95 | h 2.28 2.30 |
| 5н 5С° | a 1.40 26.29 | b , 1.82 27.04 | c 34.67 | d 2.41 2.65 44.27 | , sever e — 7 145.00 | f 7.0 6 123.8 | g 5 135.04 | h 2.28 2.30 20.94 |
| бн бС" | a 1.40 26.29 26.44 | b 0, 1.82 27.04 27.27 | c 34.67 34.59 | d 2.41 2.65 44.27 44.68 | , sever e — 7 145.00 3 148.00 | $\begin{array}{c} \text{al isof} \\ f \\ \hline \\ 7.0 \\ 6 \\ 123.8 \\ 0 \\ \text{to} \end{array}$ | g 5 135.04 137.60 | h 2.28 2.30 20.94 21.46 |

^aThese signals are listed in decreasing order of intensity. ^bTen signals.



| 3.8. | . 3,3 | -Dicy | cione | exyii d | oiuei | ne (a | b) | ~ | h | : |
|-------|--------|---------|--------|------------|--------------|-------|------------|-----------|----------|--------|
| | a | U | C | u | e | 1 | | g | 11 | 1 |
| δH | 1.4 | 0, 1.85 | 5 | 2.45 | | 6.8 | 35 | | 6.85 | 2.30 |
| δC | 26.32 | 27.08 | 34.63 | 44.72 | 7 147 | .9 12 | 5.14 | 137.46 | 122.61 | 21.52 |
| 3.9 | . 2-P | Pheny | lhex- | 2-en | e (9 |) | | | | |
| | а | b | c | d | e | f | g | h | i | j |
| δH | | | | | | | | | | |
| cis | 1.98 | — | 5.44 | 2.05 | 1.35 | 0.78 | | 7.20 |) | |
| trans | 5 1.98 | _ | 5.77 | 2.17 | 1.47 | 0.93 | | 7.2 | 0 | |
| δC | | | | | | | | | | |
| cis | 31.28 | 142.38 | 126.39 | 25.63 | 23.39 | 13.82 | 136. | 22 128.04 | 4 128.04 | 126.45 |

trans 30.96 144.14 125.66 25.63 22.92 13.94 134.84 127.76 127.76 126.47 Mass spectrum: peaks at 160 (M⁺, 40), 145 (M-15, 30), 131 (M-29, 100), 115 (M-45, 28) and 91 (C_7H_7 , 67).

3.10. 2-Phenylhexane (10) [2]

 δ H 1.23 2.65 1.55 1.24 1.24 0.82 7.20 δ C 22.36 39.99 38.22 29.99 22.82 14.04 147.94 128.28 126.98 125.74 Mass spectrum: peaks at 162 (M ⁺, 50), 147 (M-15, 4), (M-57, 100) and 91 (C₇H₇, 41).

3.11. 2-Tolylhexane

Mass spectrum: peaks at 176 (M⁺, 17), 120 (M-56, 95), 119 (M-57, 100), 105 (C_8H_9 , 25) and 91 (C_7H_7 , 24).

3.12. 3-Phenylhexane (11) [4]

a b c d e f g h i j C 12.22 29.83 47.77 38.99 20.81 14.20 147.86 128.19 127.73 125.79 These results were obtained from a mixture of 2and 3-phenylhexane after subtraction of data for the 2-isomer.

3.13. 3-Tolylhexane

Mass spectrum: peaks at 176 (M⁺, 13), 147 (M-29, 18), 133 (M-43, 42), 105 (C_8H_9 , 100), 104 (C_8H_8 , 96) and 91 (C_7H_7 , 12).

3.14. 1,4-Di(2-hexyl)benzene (12)

 a
 b
 c
 d
 e
 f
 g
 h

 H
 1.22
 2.63
 1.57
 1.25
 1.25
 0.83
 —
 7.09

 C
 22.82
 39.56
 38.38
 30.08
 22.88
 14.09
 145.21
 126.78

 A
 DEFT
 study allowed the distinction between the signals at 22.28 and 22.88 ppm.

Mass spectrum: peaks at 246 $(M^+, 6)$ and 189 (M-57, 100).

3.15. Dihexyltoluene

Mass spectrum of 2,2-isomer: peaks at 260 (M⁺, 6), 217 (M-43, 7), 203 (M-57, 100), 189 (M-71, 7) and 105 (C₈H₉, 8). Mass spectrum of 2,3-isomer: peaks at 260 (M⁺, 4), 231 (M-29, 13), 217 (M-43, 33), 203 (M-57, 46), 189 (M-71, 48) and 105 (C₈H₉, 25).

3.16. Trihexyltoluene

Mass spectrum: peaks at 344 (M^+ , 14), 287 (M-57, 64), 231 (M-113, 15), 217 (M-127, 12) and 203 (M-141, 10).

| | a | b | c | d | e | f | g | h | i | j | OCH ₃ |
|----|--------|-------|-------|-------|-------|-------|--------|--------|--------|--------|------------------|
| н | | 2.25 | 1.58 | 1.58 | 2.67 | 1.23 | | 7.20 | | | 3.58 |
| С | 173.88 | 34.01 | 23.13 | 37.73 | 39.75 | 22.30 | 147.09 | 128.36 | 126.91 | 125.96 | 51.31 |
| 3. | 18. | Meth | hvltr | ans- | hex- | 3-er | ioate | (14) | [6] | | |

| | a | b | с | d | e | f | OCH ₃ |
|---|--------|-------|--------|--------|-------|-------|------------------|
| Н | _ | 3.02 | 5.55 | 5.55 | 2.05 | 0.98 | 3.65 |
| С | 172.44 | 37.94 | 120.92 | 136.26 | 25.66 | 13.52 | 51.61 |

3.19. Dimethyl trans-hexenedioate (15) [7]

| | a | b | с | OCH ₃ |
|---|--------|-------|--------|------------------|
| Н | _ | 3.08 | 5.70 | 3.68 |
| С | 171.78 | 37.62 | 126.08 | 51.74 |



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sible and to Dr. S. Crook of Castrol for many valuable discussions.

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