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The Methylation of Alkenes to Triptyls with Dimethyl Carbonate

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Abstract A series of methylating reagents: methanol, dimethylether and dimethylcarbonate, have been evaluated for their ability to methylate 2,3-dimethylbut-2-ene to yield triptyls (a mixture of triptane and triptene). The results presented highlight that dimethylcarbonate is a far superior methylating agent compared to methanol or dimethylether, providing a higher yield of triptyls.

Keywords Methylation · Triptyls · Dimethyl carbonate · Zeolite Y

1 Introduction

Over the past decades governments across the globe have introduced ever more stringent legislation on the presence of aromatic components in gasoline. For example, the United States environmental protection agency introduced new regulations in 2011 that lowered the allowable benzene content in gasoline from several percent to 0.62 % [1]. Typically, aromatic C_6 to C_9 components provide a significant octane boost to the final gasoline blend. However, many refineries are now forced to send these benzene-rich streams to be hydro-treated until fully saturated. These hydrogenated components can then be blended into the gasoline pool, but at a significant octane loss and with additional processing costs. A separate issue for refineries is the abundance of C_3 to C_5 hydrocarbons produced in large quantities by fluidised catalytic cracking (FCC) [2] and coking processes[2] that are becoming harder to blend into the gasoline pool due to tightening Reid vapour pressure (RVP) specifications[1]. Traditionally, these unsaturated C_3 to C_5 streams are further reacted in alkylation units which have the ability to couple these species to give a branched C_{7+} product [3]. However, the alkylation units generally employ homogeneous acid catalysts such as HF or H_2SO_4 [2].

A possible solution to these two issues is the development of a process for the production of octane-rich fuel additives (e.g. “triptyls”) from lighter olefins. Triptyls is the general term for a mixture of 2,2,3-trimethylbutane (commonly known as triptane) and 2,3,3-trimethylbut-1-ene (triptene). Triptane has a research octane number (RON) of 113 [4] and can be blended into gasoline to increase its octane number. Triptane can be produced by reacting methanol over ZnI_2 [5], InI_3 [6, 7] or by reacting DME over solid acids [8–10]. Triptene has a slightly lower RON of 108 [4] but can be easily hydrogenated to triptane [10]. The aim of these investigations is to explore how alkenes, ranging from C_3 to C_6, can be upgraded to highly branched C_7 and C_8 octane-rich blend-stocks for the gasoline pool via sequential addition of C_1 fragments. Sequential C_1 alkylation reactions, such as the well-documented methanol to gasoline (MTG) chemistry, generally give a variety of products [11]. One of the major challenges in developing such a process is understanding how to control sequential C_1 additions so that the desired C_7 to C_8 branched paraffins can be produced selectively.

As a starting point the single methylation of 2,3-dimethylbut-2-ene (DMB-2, **1**) to 2,3,3-trimethylbut-1-ene (**2**) was chosen and three methylating agents were evaluated

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methanol (MeOH), dimethylether (DME) and dimethylcarbonate (DMC), (Scheme 1).

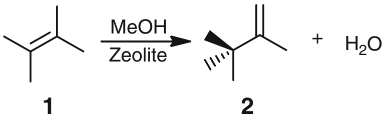
2 Experimental

2.1 General Methods and Chemicals

Zeolite Y (SAR 80) was purchased from Zeolyst International in the proton form. Zeolites FER (SAR 55), Beta (SAR 38), ZSM-5 (SAR 50) and MOR (SAR 20) were purchased from Zeolyst International in the ammonium form and were calcined in static air at 500 °C for 3 h before use. All liquid reagents were purchased from Aldrich Chemical co. and used as received. Carborundum was purchased from Fisher Scientific and sieved to 24 mesh size. Gas phase analysis was run on an Agilent CP9000 using an open tubular silica coated column (50 m × 0.32 mm i.d.), coated with a 1.2 μ thickness of CP-Sil08CB. Liquid-phase analysis was run on an Agilent CP9001 using an open tubular silica coated column (10 m × 0.53 mm i.d.), coated with a 1.0 μm thickness of CP-Sil08CB. Note that since routine GC analytical procedures cannot fully separate triptane from triptene, the total yield of these is defined in the text as ‘‘triptyls’’ [12].

2.2 General Procedure for Catalytic Tests

The zeolite catalyst was pressed into a cylindrical pellet (d = 30 mm, l = 25 mm approx.) with a force of 12 tons and finally crushed and sieved to a particle size of 250–500 μm. Then 1.8 g of these particles were placed into a quartz reactor (i.d. = 10 mm, l = 560 mm) using carborundum as a pre-heat material, separated from the catalyst with quartz wool. The reactor was placed into a vertical tubular furnace and a flow of nitrogen (50 mL min^{-1}) was introduced to the top of the reactor. A condenser was connected to the outlet of the reactor, cooled by a recirculating cooler set at −5 °C to trap any low-boiling components from the reaction. Downstream of the condenser a 40 L gas bag was attached to collect all gases from the reactor. The furnace was then heated to the desired reaction temperature at atmospheric pressure over the course of 60 min. Once at temperature a flow of methylating agent and alkene was introduced via a syringe pump to the top of the reactor. The reaction was left in this configuration for 5.0 h. Liquid and gas analysis was conducted by gas chromatography as described in the previous section. Product selectivity and catalyst activity were defined as follows:



1 **2**

Scheme 1 Methylation of 2,3-dimethylbut-2-ene to 2,3,3-trimethylbut-1-ene

$$\text{Selectivity}(\%) = \left(\frac{\text{mmol of product}}{\text{mmol of alkene fed - mmol of alkene recovered}}\right)\times 100$$

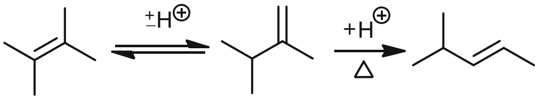
$$\text{Activity}(\text{mmol g}^{-1}) = \left(\frac{\text{mmol of alkene fed} - \text{mmol alkene recovered}}{\text{grams of catalyst}}\right)$$

$$\text{Activity per acid site} = \left(\frac{\text{mmol of alkene fed} - \text{mmol alkene recovered}}{\text{mmol of acid sites}}\right)$$

The amount of acid sites in millimoles was deduced from the mass and the SAR of each zeolite tested.

3 Results and Discussion

Initial experiments focused on the stability of the methylating components and 2,3-dimethylbut-2-ene under the reaction conditions. Previous investigations conducted by our team had highlighted that under certain conditions H-Y did not appear to be a particularly active MTG catalyst and might prove to be a useful candidate for this programme of work (unpublished results). The stability of the starting alkene, 2,3-dimethylbut-2-ene (**1**), was more difficult to control, with double bond and structural isomerisation of this intermediate over acidic catalyst being well-documented [14]. Our own investigations confirmed this by highlighting that the double bond isomerisation of 2,3-dimethylbut-2-ene (**1**) to 2,3-dimethylbut-1-ene (**3**) was facile, occurring at a temperature of 100 °C. They also showed that the skeletal rearrangement of 2,3-dimethylbut-1-ene (**3**) to 2-methylpentene isomers, such as 4-methylpent-2-ene (**4**), occurred at temperatures above 250 °C (unpublished results). These intermediates could then isomerise further over the catalyst. However, this type of methyl rearrangement was found to be significant only at temperatures above 300 °C (Scheme 2).



1 **3** **4**

Scheme 2 Isomerisation 2,3-dimethylbut-2-ene to 2,3-dimethylbut-1-ene and skeletal rearrangement of 2,3-dimethylbut-1-ene to 4-methylpent-2-ene

We then began to investigate MeOH, DME and DMC for the methylation of 2,3-dimethylbut-2-ene (**1**) over the H-Y catalyst. The analysis of the C_5–C_7 components identified the major product as 2,3-dimethylbut-1-ene (**3**) for the MeOH and DME reactions. However, for the DMC reaction the major component in the liquid-phase was triptyls, with a selectivity of 10.2 %, compared to 1.4 and 0.6 % selectivity for MeOH and DME respectively (Fig. 1; Table 1: runs 1–3). The overall activity and relative yield of liquid-phase products were also higher using DMC than when using either MeOH or DME as methylating agents. Further investigations on the H-Y/DMC system (Table 1: runs 3–6) showed that decreasing reaction temperature to 250 °C resulted in reduced activity and the selectivity to triptyls was essentially half of that at 300 °C. The decrease in triptyls selectivity suggests that the rate constant for methylation responds to temperature drop more significantly than those for the side reactions. Upon decreasing the DMC to DMB-2 ratio whilst keeping the reaction temperature at 300 °C, resulted in lower activity and reduced the selectivity to triptyls by ca. 50 %. On the other hand, increasing the DMC to DMB-2 ratio resulted in increased catalyst activity whilst the selectivity to triptyls remained approximately constant. These results suggests that the rate for methylation could be close to first order in [DMC] at low concentrations, becoming pseudo-zero order in [DMC] as the concentration of DMC increases.

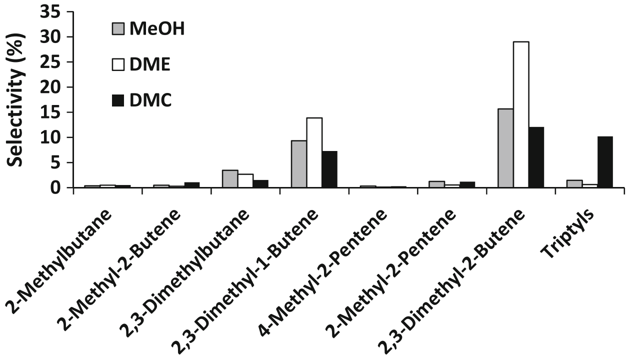


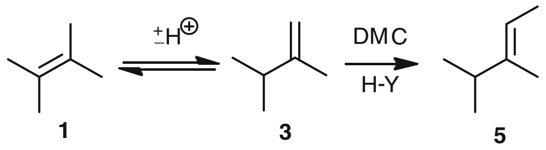
Fig. 1 Liquid-phase products of the methylation of 2,3-dimethylbut-2-ene. Comparison of MeOH, DME and DMC as methylating agents

One of the major products of the methylation reaction was the isomerised starting material DMB-1. In addition, various methyl pentene isomers were also produced as expected. However, further analysis failed to identify any methylated product resulting from 2,3-dimethylbut-1-ene, such as 3,4-dimethylpent-2-ene (**5**), (Scheme 3). To examine this observation further 2,3-dimethylbut-1-ene (**3**) was fed instead of 2,3-dimethylbut-2-ene (**1**) in the DMC methylation so that the types of methylated products could be compared to the 2,3-dimethylbut-2-ene (**1**) methylation (Fig. 2; Table 1: runs 3 and 7). The comparison of the 2,3-dimethylbut-2-ene (**1**) and the 2,3-dimethylbut-1-ene (**3**) methylation highlighted that there was very little difference between the type of products produced by each reaction, indicating that under reaction conditions, 2,3-dimethylbut-2-ene and 2,3-dimethylbut-1-ene reach equilibrium rapidly over H-Y. This is confirmed by plotting the selectivity to 2,3-dimethylbut-1-ene versus the selectivity to 2,3-dimethylbut-2-ene (Fig. 3). It is noteworthy that no product was identified that related to methylation of the terminal olefin in 2,3-dimethylbut-1-ene (**3**), (Scheme 3).

Having shown that DMC is an effective methylating agent for the methylation of DMB-2 we then turned our attention to comparing the performance of H-Y with

Table 1 Selectivity to liquid-phase products and activity in the methylation of alkenes over zeolite Y

Run Number	1	2	3	4	5	6	7	8
Temperature (°C)	300	300	300	250	300	300	300	300
Methylating Agent	MeOH	DME	DMC	DMC	DMC	DMC	DMC	DMC
Alkene	DMB-2	DMB-2	DMB-2	DMB-2	DMB-2	DMB-2	DMB-1	MB-2
MA:Alkene	5:1	5:1	5:1	5:1	2.5:1	10:1	5:1	10:1
Selectivity (%)								
2-Methylbutane	0.4	0.5	0.5	0.4	0.0	0.4	0.4	4.9
2-Methyl-2-Butene	0.5	0.3	1.1	0.3	0.6	1.3	1.1	29.6
2,3-Dimethylbutane	3.4	2.7	1.6	1.2	2.1	0.7	1.5	0.7
2,3-dimethylbut-1-ene	9.3	13.9	7.3	8.7	10.0	3.4	6.1	2.7
4-Methyl-2-Pentene	0.3	0.1	0.3	0.1	0.4	0.2	0.0	0.3
2-Methyl-2-Pentene	1.2	0.5	1.2	0.3	0.6	0.6	1.2	1.0
2,3-dimethylbut-2-ene	15.7	29.0	12.1	17.3	17.5	5.4	9.9	4.0
Triptyls (triptene)	1.4	0.6	10.2	5.2	5.2	9.5	10.0	6.8
Activity (mmol g^{-1})	24.1	22.3	25.7	24.7	24.8	27.9	27.0	12.6
Activity per acid site	59.4	55.0	63.3	60.8	61.1	68.8	66.6	31.0



Scheme 3 Isomerisation of 2,3-dimethylbut-2-ene to 2,3-dimethylbut-1-ene, which can undergo methylation to 3,4-dimethylpent-2-ene

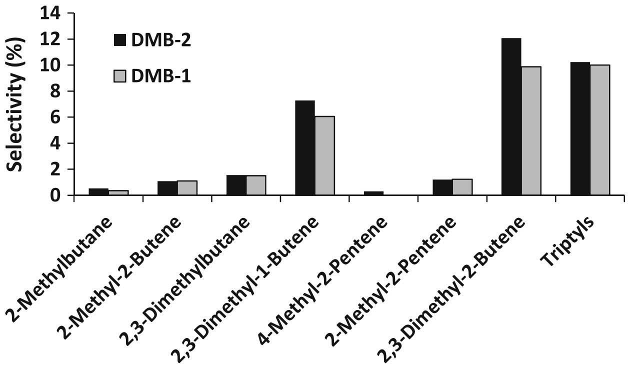


Fig. 2 DMC methylation of 2,3-dimethylbut-1-ene compared to 2,3-dimethylbut-2-ene

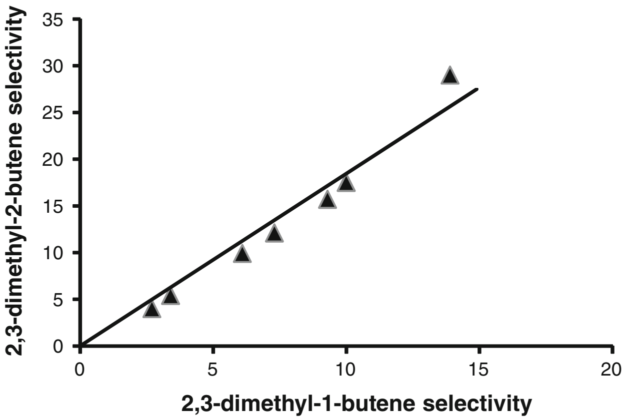


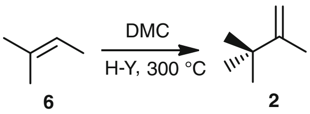
Fig. 3 Plot of the selectivity to 2,3-dimethylbut-1-ene vs. the selectivity to 2,3-dimethylbut-2-ene

respect to other zeolites with different frameworks and acidities (i.e. different SARs). Initial testing was done at 300 °C (Table 2: runs 9 and 10) and it showed that H-FER has a lower activity and much lower selectivity to triptyls than H-Y. Also the total yield of liquid produced is very low, suggesting that at this temperature H-FER possibly catalyses cracking of the alkene or MTG/MTO-type chemistries. We thus lowered the reaction temperature to 250 °C where we have previously shown that H-Y is still active and where both cracking and MTG/MTO-type chemistries are less pronounced [15] (Table 2: runs 11–15). The results show that of all the zeolites tested H-ZSM-5 exhibited the highest activity but also the lowest selectivity to triptyls while H-MOR exhibited the lowest activity and poor selectivity to triptyls. H-Y on the other hand is shown to be the best catalyst both in terms of activity per acid site and selectivity to triptyls.

Having proven that the DMC/H-Y system could effectively methylate 2,3-dimethylbut-2-ene (**1**) our attention focused on performing sequential methylations to upgrade 2-methyl-2-butene (**6**) to 2,3,3-trimethylbut-1-ene (**2**) under the same reaction conditions (Scheme 4; Table 1:

Table 2 Selectivity to liquid-phase products and activity in the methylation of DMB-2 with DMC over different zeolites

Run number	9	10	11	12	13	14	15
Temperature (°C)	300	300	250	250	250	250	250
Zeolite	H-Y	H-FER	H-Y	H-FER	H-Beta	HZSM5	H-MOR
SAR	80	55	80	55	38	50	20
Methylating agent	DMC	DMC	DMC	DMC	DMC	DMC	DMC
Alkene	DMB-2	DMB-2	DMB-2	DMB-2	DMB-2	DMB-2	MB-2
MA : Alkene	5:1	5:1	5:1	5:1	5:1	5:1	5:1
Selectivity (%)							
2-Methylbutane	0.5	0.1	0.4	0.0	2.7	11.2	0.5
2-Methyl-2-Butene	1.1	0.6	0.3	0.3	2.2	5.3	0.5
2,3-Dimethylbutane	1.6	0.0	1.2	0.1	1.1	0.5	0.8
2,3-dimethylbut-1-ene	7.3	2.1	8.7	10.8	2.1	5.6	8.8
4-Methyl-2-Pentene	0.3	0.1	0.1	0.2	0.3	0.2	0.6
2-Methyl-2-Pentene	1.2	0.3	0.3	0.7	1.1	0.7	2.7
2,3-dimethylbut-2-ene	12.1	4.3	17.3	27.3	0.8	0.5	19.1
Triptyls (triptene)	10.2	0.2	5.2	3.0	0.4	0.1	0.6
Activity (mmol g^{-1})	25.7	20.3	24.7	16.5	21.6	28.2	16.2
Activity per acid site	63.3	34.8	60.8	28.3	26.0	44.0	10.7



Scheme 4 Alkylation of 2-methylbut-2-ene to 2,3,3-trimethylbut-1-ene

run 8). From the results it can be seen that 2-methyl-2-butene (**6**) was successfully converted to 2,3,3-trimethylbut-1-ene (**2**) via two sequential methylations with a selectivity of 6.8 %. In addition both 2,3-dimethylbut-1-ene (**3**) and 2,3-dimethylbut-2-ene (**1**) were observed with a selectivity of 2.7 and 4.0 % respectively.

4 Conclusions

The methylation of 2,3-dimethylbut-2-ene (**1**) can be achieved in much higher yield using DMC as opposed to MeOH or DME reactants over an H-Y catalyst, which has been shown to be the best catalyst among a series of zeolites tested. Furthermore, it has been shown that the double bond isomerisation of 2,3-dimethylbut-2-ene (**1**) to 2,3-dimethylbut-1-ene (**3**) does not impact the selectivity of the methylation reaction towards 2,3,3-trimethylbut-1-ene (**2**). Finally, the sequential methylation of 2-methyl-2-butene (**6**) was demonstrated and highlights a route by which C_5-alkenes can be upgraded to heavier, higher octane products.

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