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Celite Catalysed Alkylation of Alkenes

Irma Rojas-Oviedo,*[1] Jorge Cárdenas,[2] Carmen Márquez[2] and Lance J. Twyman[3]

[1] Departamento de Sistemas Biológicos, Universidad Autónoma Metropolitana-Xochimilco. Calzada del Hueso 1100, Col. Villa Quietud. México 04960, D.F. Tel. (52)55-54837280 irma19@correo.xoc.uam.mx.
[2] Instituto de Química. Universidad Nacional Autónoma de México, Circuito Exterior Ciudad Universitaria, Coyoacán 04510. México, D. F. rjcp@servidor.unam.mx; malonso@servidor.unam.mx
[3] The Chemistry Department, University of Sheffield, Brook Hill, Sheffield, S2 7HF, UK. l.j.twyman@sheffield.ac.uk.

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Abstract. In the presence of Celite mono and disubstituted alkenes could be alkylated with benzylic halides at room temperature. In order to form the C-C bond, it was necessary to use activated aromatics with alkenes or propargylic esters.
Key words: Celite, heterogeneous catalysis, electrophilic substitution, Friedel-Crafts

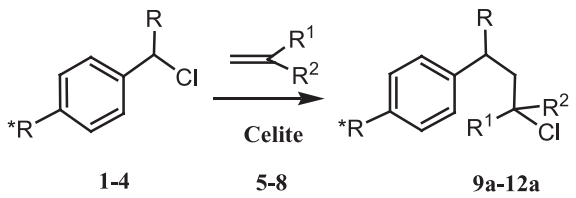
Resumen. En presencia de celita, alquenos mono- y di-sistituidos pueden ser alquilados con halogenuros de bencilo a temperatura ambiente. Para formar el enlace C-C, fue necesario usar compuestos aromáticos activados con alquenos o ésteres propargílicos.
Palabras clave: Celita, catálisis heterogénea, substitución electrofílica, Friedel y Crafts.

Introduction

Celite [1] has similar physical properties to microporous catalysts, such as silica, alumina, zeolite and montmorillonite [2]. Despite the fact that celite contains the same "active" silicium dioxide groups as silica [5], studies into its catalytic properties have so far been neglected. The silicium dioxide groups in silica are capable of catalyzing the formation of reactive benzylic cations from the appropriate benzyl halide [3,4]. With this in mind, we decided to investigate the use of celite as a heterogenous catalyst in a series of electrophilic alkylations, Scheme 1; our results are reported in this paper.

Results and Discussion

The benzylic halides **1-4** and alkenes **5-8** used in our study are shown in Table 1. Although overall yields are less than quantitative, catalytic activity was observed in most cases. For the successful reactions it was generally observed that reactions performed better when the benzylic carbocation could be stabilized by either an electron donating group, such as a methoxyl group, or a second aromatic ring. If these groups were not present then no reaction took place. For example, when 2-methylprop-1-ene was reacted with 1-(1-chloroethyl)benzene (entry 5 Table 1) no reaction took place, whilst a 71% yield of products was recorded when 2-methylprop-1-ene was reacted with chlorodiphenylmethane (entry 3, Table 1), confirming the requirement for a good stabilizing group. The functionality around the alkene is also important, for example, when 1-decene was used with 1-(chloro (methoxy)methyl)benzene an inseparable mixture of many products was obtained. Analysis of the ^{1}H NMR spectrum of this mixture indicated that none of the expected products were observed in any significant quantity, despite the presence of a good stabilizing group on the benzylic halide. Entry 7 in Table 1 shows the reaction between 4-metoxybenzylchloride and 4-allyl-2-methoxyphenol (an alkene unit possessing an aromatic side chain). In this situation the benzylic carbocation prefers to react in a Friedel Crafts fashion with the activated aromatic side chain on the alkene (rather than react with the alkene directly); therefore the only product isolated was the Friedel-Crafts compound **13d**. (Fig. 1)



1-4 **5-8** **9a-12a**

Scheme 1

When the propargylic ester 3-methylbut-3-enyl acetate [3] is reacted with 4-metoxybenzylchloride (entry 2 Table 1) the expected alkylated species **10a** is isolated as the major product, but interestingly, the Friedel-Crafts product **10d** (Figure 1) is also isolated in a low 3.4% yield. This compound forms when a 2nd benzylic carbocation adds to the alkylated product **10a**. Presumably this minor reaction occurs in the reaction described above, but the yields are too low to be recorded.

During initial attempts to optimize the yields, we also observed that different products were favored when different amounts of Celite were used. For example, the alkylated products (**9a-12a**) were favored when a 1: 20 ratio of benzylic halide to Celite was used. On the other hand, when smaller amounts of Celite were used (*i.e.* a 1:3 ratio of benzylic halide to Celite), and longer reaction times applied, the elimination

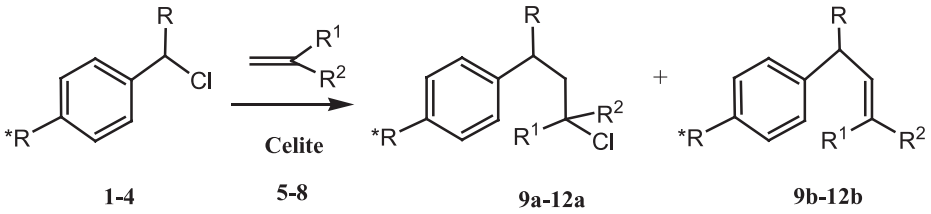


Table 1. The Celite-catalyzed alkylation of alkenes to benzylic halide in dichloromethane.

Run	R*	R	R_1	R_2	Yield %	Products	Ratio	time (days)
1[b]	OMe	H	Me	Me	42	**9a : 9b**	1 : 1	4
2[c]	OMe	H	Me	$(CH_2)_2OAc$	19	**10a :10d**	5.3 : 1	4
3[d]	H	C_6H_5	Me	Me	71	**11a : 11b : 11c**	1.4 : 1 : 2	4
4[e]	H	C_6H_5	Me	$(CH_2)_2OAc$	39	**12a : 12c**	10 : 1	4
5[f]	H	Me	Me	Me	-	-	-	20
6[g]	OMe	H	H	$(CH_2)_7CH_3$	-	-	-	4
7[h]	OMe	H	H	4-CH_2-(C_6H_3)-2-(OMe)OH	44	**13d**	-	16

[a]weight ratio of benzylic halide:olefine:celite at room temperature in dichloromethane. [b]1:0.78:20. [c]1:0.92:20.[d] 1:0.78:20 and Hofmann´s olefin **11c**. [e]1:0.78:20, there was no reaction after 20 days.[g]1:0.78:20 unidentifiable products.[h]1:1.25:20, 16 days gave a Friedel-Crafts product **13d**.

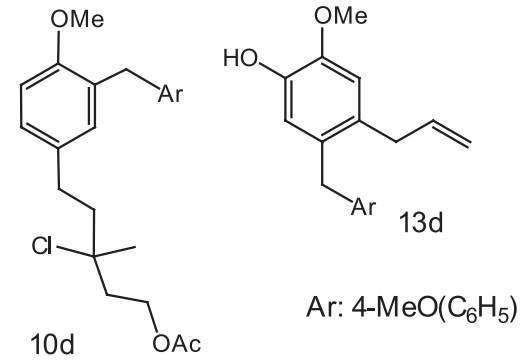


Fig. 1

products (**9b-12b**) were favored. With respect to these eliminated products the more hindered, thermodynamically stable alkene **9b** is exclusively produced (as a 1:1 mixture with **9a**) when 1-(chloromethyl)-4-methoxybenzene-chlorodiphenylethane is reacted with 2-methylprop-1-ene (entry 1 in Table 1). However, when chlorodiphenylmethane is reacted with the same alkene (entry 3 in Table 1) two alkenes **11b** and **11c** were observed (Fig. 2).

On this occasion, it appears that the least substituted alkene 11c is favored twice as much over the most substituted (thermodynamically more stable) alkene 11b (Figure 2). Even though we do not have a clear explanation for this result, it should be noticed that there is a marked preference for this isomer when a Celite catalyst is used.

Conclusions

In conclusion, we have shown that Celite is capable of promoting the formation of C-C bonds between benzylic halides and olefins under mild conditions. In some cases Friedel-Crafts products were observed, confirming that the mechanism proceeds through a carbocation intermediate. The alkylation takes place under the conditions described above only when the benzylic carbocation is stabilized by an electron withdrawing group or another aromatic ring. The amount of Celite is also important in the product distribution because the less of it is used the more of the elimination product is observed. We are currently investigating these reaction further in an attempt to understand the selectivity.

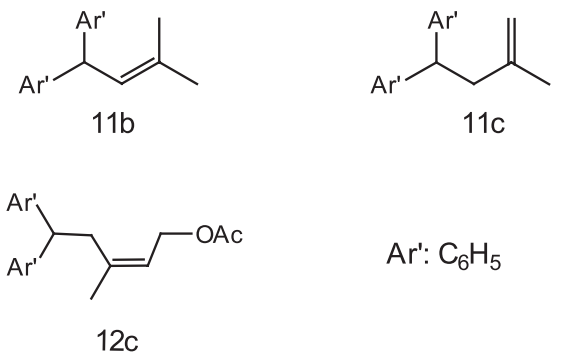


Fig. 2

Experimental

An agitator rotary shaker 110 (rpm) temperature 25-28° C SEV Mod 6090 was used. Mass spectra were recorded with a Jeol JMS AX505HA mass spectrometer. ^{1}H-NMR spectra were measured as $CDCl_3$ solutions on a Varian Gemini (200 MHz) or a Varian Unity (300 MHz) using TMS as internal standard.

Celite was purchased from Celite Mexico and dried for a period of 4 h under vacuum at 100°C. Specific surface area was calculated by N_2 adsorption at 75.25 k using a Micromeritics ASAP 2000 instrument. The specific surface area measured was 2.23 m^2g^{-1} (B.E.T. N_2) and the pore volume was 0.0030 ccg^{-1}. Dichloromethane was reagent grade (Merck) and dried under P_2O_5. The olefins were all analytical grade and used without further purification.

The benzylic halides were prepared from the corresponding alcohols by treatment with hydrochloric acid under standard conditions. The propargylic ester, 3-methylbut-3-enyl acetate, was synthesized according to the reported procedure [3].

General Procedure

A suspension of 100 mg of the benzylic halide, 15 mL of dichloromethane, 1.2 –2 equivalent of the alkene and 2.0 g of celite (1:20 w/w halide/solid ratio) were shaken at room temperature; the reaction was monitored by TLC following the disappearance of the starting material. The reaction mixture was filtered, the catalyst was washed with 20 ml of dichloromethane, and the combined solvents were evaporated under reduced pressure. The products were purified by preparative TLC (silica gel, hexane:ethyl acetate 95:5) and identified by comparison to literature spectral data [3,6-10].

3-Chloro-1-(4-methoxyphenyl)-3-3methylbutane (9a). ^{1}H NMR ($CDCl_3$) [3,6] δ 7.1 and 6.8 (AB-system, *J* = 8.6 Hz, 4H, Ar-H), 3.8 (s, 3H, CH_3O), 2.8-2.7 (m, 2H, $ArCH_2$), 2.0-1.9 (m, 2H, Ar-C-CH_2), 1.6 (s,6H,CH_3C-Cl). MS *m/z*: 212 (M^+), 176, 161 (100%),146,121,108,91.

3-Methyl-1-(4-methoxyphenyl)-3-butene (9b). ^{1}H NMR ($CDCl_3$) [7] δ 7.1 and 6.8 (AB-system, *J* 8.6 Hz, 4H, Ar-H), 5.3 (tspet. *J* 7.2, 1.4 Hz, C=CH), 3.8 (s, 3H, CH_3O), 3.3 (d, *J* 7.2 Hz, 2H, $ArCH_2$), 1.7 (sd, *J* 1.1 Hz, 3H, C=C-CH_3). MS *m/z*: 176, 121 (100%), 115, 91, 77.

3-Chloro-3-methyl-5-(4-methoxyphenyl)-pentyl acetate (10a). ^{1}H NMR ($CDCl_3$) [3] δ 7.1 and 6.8 (AA´BB´-system, 4H, Ar-H), 4.31 (t, *J* 7.3 Hz, 2H, $ArCH_2$), 3.78 (s, 3H, CH_3O), 2.77-2.71 (m, 2H, $ArCH_2$), 2.2 (dt, *J* = 14.4, 7.6 Hz, 1H, Ar-C-CH-C-Cl), 2.1 (dt, *J* 14.3, 7.6 Hz, 1H, Ar-C-CH-C-Cl), 2.08-2.0 (m, 2H, CH_2C-OCO), 2.0 (s, 3H, CH_3COO), 1.62 (s, 3H, CH_3C-Cl). MS *m/z*: 284 (M^+), 248, 224, 188, 173, 161(100%), 134, 121, 91, 77, 43.

3-Chloro-3-methyl-5-(4-methoxyphenyl-(3´-methoxybenzyl))-pentyl acetate (10d). ^{1}H NMR ($CDCl_3$) [3] δ 7.1 and 6.8 (AA´BB´-system, *J* 8.5 Hz, 4H,ArH), 7.0, 6.9 and 6.8 (ABC-system, *J* 8.7,8.7, 2.4 Hz, 3H, Ar-H), 4.3 (t, *J* 7 Hz, 2H, CH_2OCO), 3.9 and 3.8 (2s, 6H, CH_3O), 2.7-2.6 (m, 2H, Ar-CH_2), 2.2-1.9 (m, 4H, ArC-$CH_2C(Cl)CH_2$), 3.9 (s, 2H, Ar-CH_2-Ar), 2.0 (s, 3H, CH_3COO), 1.6 (s, 3H, CH_3C-Cl). MS *m/z*: 404 (M^+), 368, 308, 293, 241 (100%), 227, 187, 121, 43.

2-Chloro-2-methyl-4,4-diphenyl butane (11a). ^{1}H NMR ($CDCl_3$) [8] δ 7.3 and 7.1(2m, 10H, Ar´H), 4.17 (t, *J* 7.8 Hz, 1H, $Ar´_2CH$), 2.8 (d, *J* 7.8 Hz, 2H, CH_2-CCl), 1.4 (s, 6H, CH_3-CCl). MS *m/z*: 258,260,167 (100%).

3-Methyl-1,1-diphenyl-2-butene (11b). ^{1}H NMR ($CDCl_3$) [9] δ 7.3 and 7.1 (2m, 10H, Ar´H), 5.7 and 5.6 (dsept. *J* 9.6, 1.4 Hz, 1H, H-C=C), 4.9 (br.d, *J* =9.6, 1H, $Ar_2´CH$), 1.8 and 1.7 (2d, *J* 1.4 and 1.3 Hz, 6H, CH_3-C=C).

3-Methyl-1,1-diphenyl-3-butene (11c). ^{1}H NMR ($CDCl_3$) [10] δ 7.3 and 7.1 (2m, 10H, Ar´H), 4.7 and 4.6 (2 br.s., 2H, CH_2=C), 4.0 (t, *J* 6.7 Hz, 1H, $Ar´_2CH$), 2.6 (brd, *J* 6.7 Hz, 2H, CH_2C=C), 1.63 (s, 3H, CH_3C=C).

3-Chloro-3-methyl-5,5,-diphenylpentane (12a). ^{1}H NMR ($CDCl_3$) δ 7.3 and 7.1 (2m, 10H, Ar´H), 4.3 (t, *J* 6.3 Hz, 1H, Ar´CHAr´), 4.2 (m, 2H, CH_2OCO), 2.7 (d, *J* 6.3 Hz, 2H, CH_2CCl), 2.1-1.9 (m, 2H, CH_2C-OCO), 1.9 (s, 3H, CH_3COO), 1.3 (s, 3H, CH_3CCl). MS *m/z*: 330 (M^+), 294, 270, 234, 219, 206, 180, 167 (100%), 152, 143, 91, 43.

3-Methyl-5,5-diphenyl-2-pentenyl acetate (12c). ^{1}H NMR ($CDCl_3$) δ 7.3 and 7.1 (2m, 10H, Ar´H), 4.2 (t, *J* 6.9 Hz, 2H, Ar´CHAr´), 4.1 (t, *J* 7 Hz, 1H, C=CH), 2.4 (dd, *J* 7.0, 2.5 Hz, 2H, CH_2C=C), 2.0 (s, 3H, CH_3COO), 1.9 (m, 2H, CH_2OCO), 1.2 (s, 3H, CH_3C=C). MS *m/z*: 294 (M^+), 234, 219, 206, 167 (100%), 143, 91, 71, 43.

4-Allyl-2-methoxy-5-(4-methoxybenzyl)phenol (13d). ^{1}H NMR ($CDCl_3$) δ 7.02 and 6.79 (system AA´BB´, 4H, Ar-H), 6.67 (s, 1H, Ar''H), 6.66 (s, 1H, Ar''H), 5.87 (ddt, *J* 16.9, 10.2, 6.1 Hz, 1H, CH=C), 5.46 (br.s, 1H, OH), 5.03 (ddt, *J* 10.2, 1.7, 1.4 Hz, =CH), 4.97 (qd, *J* 16.9, 1.7 Hz, 1H, =CH), 3.84 (s, 3H, OCH_3), 3.82 (s, 2H, $ArCH_2Ar$''), 3.76 (s, 3H, OCH_3), 3.26 (dt, *J* 6.1, 1.4 Hz, 2H, $ArCH_2C$=). MS *m/z*: 284 (M^+), 267, 253,243, 225, 211, 176 (100%),161, 144, 133, 121, 115, 91, 77, 65, 41.

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