

Preparation of 2,4-dimethyldecane, 5-*n*-propylnonane, 2-methyl-5-ethylnonane, and 3- and 4-ethyldecanes

Alan R. Katritzky,* Satheesh K. Nair, Stephane Ledoux,
Rachel M. Witek, Novruz G. Akhmedov, Peter A. Gordon,[§] and Margaret M. Wu[§]

*Center for Heterocyclic Compounds, Department of Chemistry, University of Florida,
Gainesville, FL 32611-7200*

[§]*Corporate Strategic Research, ExxonMobil Research & Engineering, Annandale, NJ, USA
E-mail: Katritzky@chem.ufl.edu*

Dedicated to Professor Rodney Rickards on his 70th anniversary
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Abstract

Paraffins **8**, **15**, **24**, **35**, and **41** were each prepared in three steps from the respective carbonyl precursors. Structural elucidation of these was performed using detailed ¹³C NMR analysis.

Keywords: Paraffins, Grignard reaction

Introduction

Simple branched alkanes are common components of petroleum fuels and derivatives. During the 1930's and 1940's, many syntheses of alkanes¹⁻³ were carried out to provide data on the heats of formation, heats of combustion, and general physical properties of paraffins. Recent interest in branched alkanes concerns their use as fuel additives⁴, their importance as moieties in microemulsion-forming surfactants⁵, and their synthesis as components of natural products, particularly insect hormones⁶⁻¹⁰.

Methods of synthesizing alkanes include: i) the classical alcohol-olefin-paraffin conversion¹⁻³, ii) reduction of olefins prepared from acyl cyanides¹¹ or ketones⁶, iii) halopolycarbon homologation employing α,ω -dihalides and Grignard reagents⁷, and iv) protonolysis of trialkylboranes¹². In general, the most accessible route to branched alkanes is the classical route. The appropriately substituted alcohols required can be readily obtained from reaction of Grignard reagents with ketones. Simple dehydration of these alcohols yields olefin mixtures, which can be hydrogenated by a variety of catalysts. Reduction of olefins can be carried out in a

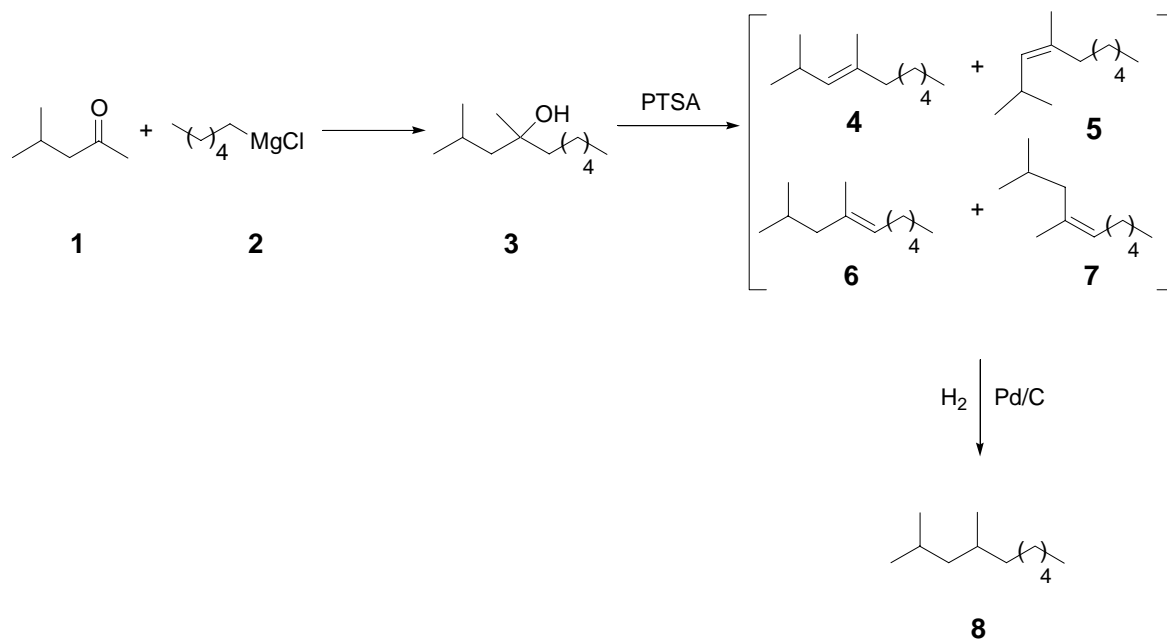
[§] E-mail: peter.a.gordon@exxonmobil.com

hydrogen atmosphere over Raney-nickel^{11,13}, Pd-C^{6,14}, PBI-PdCl₂¹⁵, polymer-supported Rh(CO₂)(pd)¹⁶, HNaY zeolite¹⁷, or platinum oxide^{1,18}. Use of Raney-nickel or HNaY zeolite often requires high pressures, while platinum oxide and palladium-based catalysts function at or near 1 atm.

In this paper, we disclose the synthesis of 2,4-dimethyldecane (**8**), 5-*n*-propyl-nonane (**15**), 2-methyl-5-ethylnonane (**24**), 4-ethyldecane (**35**), and 3-ethyldecane (**41**) following the general alcohol-olefin-paraffin route using Pd-C as catalyst in the final reduction step.

Results and Discussion

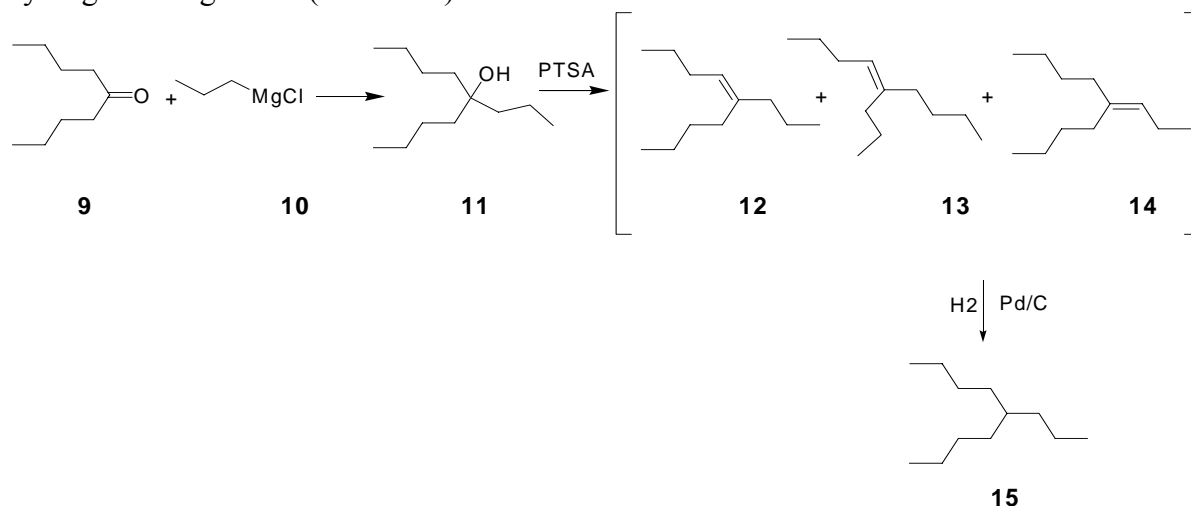
Synthesis of these alkanes was designed through a disconnection approach. The initial disconnected fragments for 2,4-dimethyldecane were 2-octanone and isobutylmagnesium bromide. However, addition of isobutylmagnesium bromide to 2-octanone gave a considerable amount of the reduction product, 2-octanol, as well the desired addition product **3**. So this disconnection was abandoned and 4-methyl-2-pentanone and hexylmagnesium chloride were selected as the new fragments, which gave the alcohol **3** in good yield. The alcohol intermediate **3** was subjected to acid catalyzed dehydration to give a mixture of alkenes, **4–7**; which after hydrogenation provided only the desired alkane **8** (Scheme 1).



Scheme 1

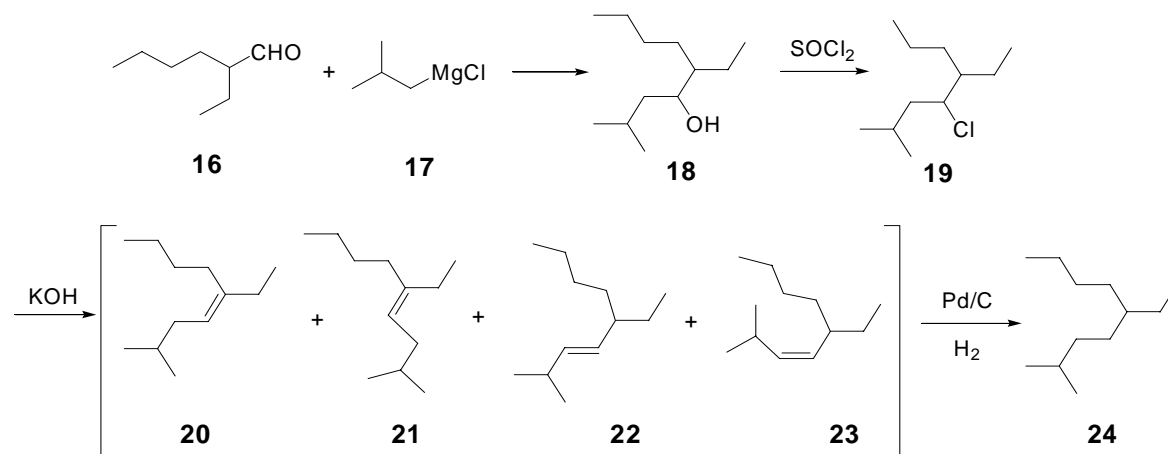
The pathway to **15** was similar to that used to prepare **8**. The ketone **9** (5-nonanone) reacted with the *n*-propyl Grignard reagent **10** to generate the alcohol intermediate **11**. Under acidic

elimination conditions, the alcohol was transformed into a mixture of alkenes **12–14**, which after hydrogenation gave **15** (Scheme 2).



Scheme 2

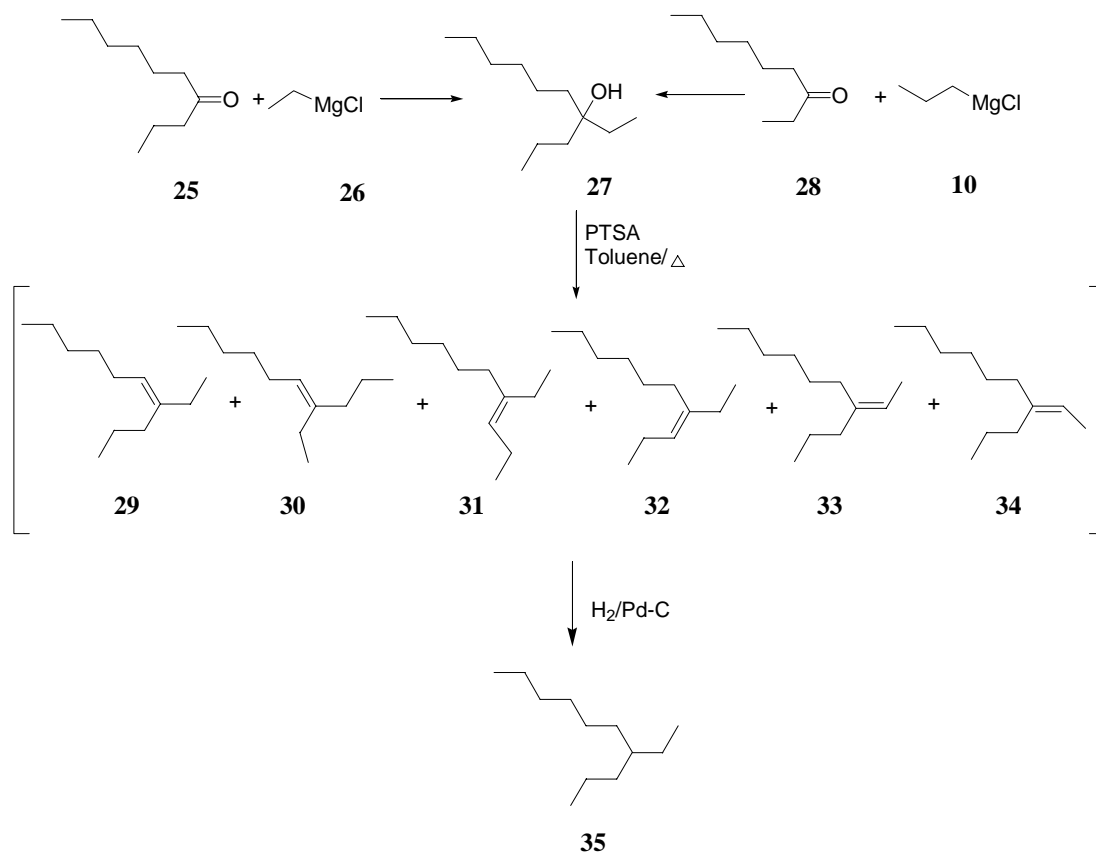
In the case of **24**, alcohol **18** was prepared by the reaction of Grignard reagent **17** with the carbonyl component **16**. However, since **18** is a secondary alcohol, the elimination reaction was unsuccessful. Thus, **18** was converted into the corresponding chloride **19**, by a standard method¹⁹, and was subjected to dehydrohalogenation by treatment with KOH in ethanol. Finally, the mixture of alkenes **20–23** was hydrogenated to the paraffin **24**, under the same conditions as for the previous compounds (Scheme 3).



Scheme 3

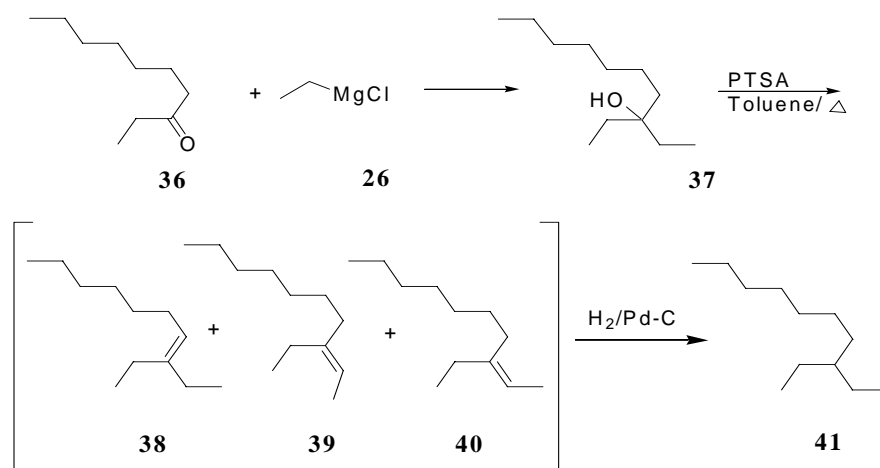
In the case of 4-ethyldecane (**35**), the intermediate alcohol **27** was prepared by two different routes; route a) used 4-decanone and ethylmagnesium chloride as the fragments while route b) used 3-nonanone and 3-propylmagnesium chloride as the reactive units. Alcohol **27** on acid

catalyzed elimination afforded a mixture of six alkenes **29-34**, which was hydrogenated under the same condition used previously, to afford the paraffin **35**.



Scheme 4

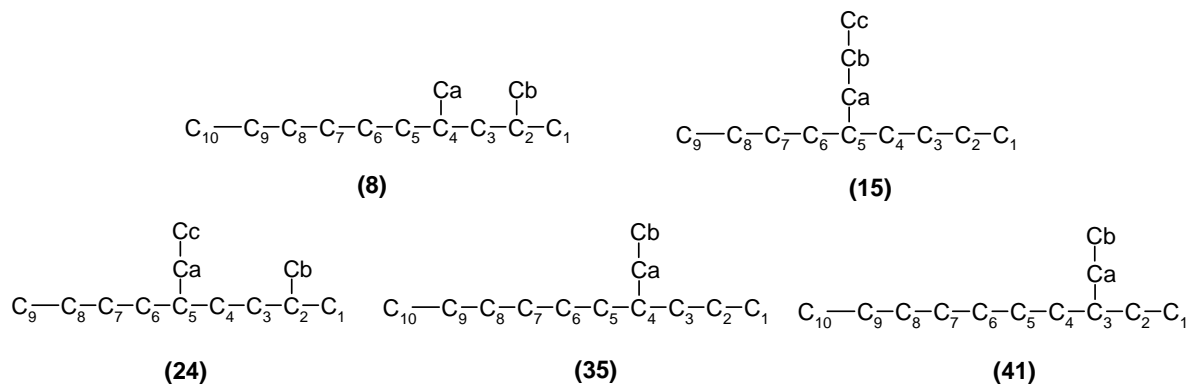
Similarly, 3-ethyldecane²⁰ (**41**) was prepared from 3-decanone (**36**) and ethylmagnesium chloride as depicted in Scheme 5.



Scheme 5

Characterization by NMR spectra

In the ^1H NMR spectra, the number of CH, CH_2 and CH_3 protons corresponded to those expected from the structures of the alkanes, but the multiplicity patterns provided no useful information. The structural determination of paraffins by ^{13}C NMR is particularly useful as the carbon chemical shifts are spread over 50 ppm. The structures of all the paraffins were confirmed through detailed ^{13}C investigations. ^{13}C -DEPT experiments differentiated the CH, CH_2 and CH_3 carbons. Two-dimensional carbon-hydrogen correlation spectra also provided useful information about each structure. Table I (Scheme 6) reports the detailed assignment of carbon signals to the paraffins.



Scheme 6

Table 1. ^{13}C Assignments to the structures of paraffins

Paraffin	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	Ca	Cb	Cc
(8)	22.31	25.25	46.90	30.29	37.48	29.74	27.01	32.02	22.74	14.14	19.81	23.46	–
(15)	14.17	23.23	28.99	33.44	37.21	33.44	28.99	23.23	14.17	–	36.19	19.88	14.55
(24)	22.71	28.47	36.01	32.95	39.10	30.83	29.07	23.20	14.18	–	25.91	22.74	10.87
(35)	14.53	19.87	35.67	38.66	33.23	26.72	29.86	31.99	22.73	10.84	25.90	14.11	–
(41)	10.91	25.48	40.44	32.82	26.84	29.47	30.68	32.00	22.75	14.12	25.48	10.91	–

Experimental Section

General procedure for the preparation of alkanes. A solution of the appropriate ketone or aldehyde (0.5 mol) in anhydrous ether (50 mL) was added dropwise to the appropriate Grignard reagent (2M sol. in ether, 250 mL, 0.5 mol) at rt. After the addition, the reaction mixture was stirred for 5 h; after which, the reaction mixture was poured into saturated ammonium chloride solution and extracted with diethyl ether (2 x 50 mL). The combined ethereal layers were dried over anhydrous sodium sulfate, and the ether was removed under vacuum. The corresponding alcohols were obtained as colorless liquids in 63–76% yields.

The crude alcohol (for **8** and **15**, 70 g, 0.38 mol) was dissolved in toluene (300 mL) and a catalytic amount (0.5 g) of *p*-toluenesulfonic acid (PTSA) was added. The mixture was refluxed overnight under a Dean-Stark trap. Ethyl acetate was added and the organic layer washed with water, dried over sodium sulfate and concentrated. The alkenes were obtained in 88–95% yields. In the case of **24**, the crude alcohol (0.5 mol scale) was treated with SOCl₂ and the intermediate chloride was treated with KOH in refluxing ethanol to afford a mixture of alkenes **20–23**.

In a three-necked flask, the alkene mixture (0.34 mol) was mixed with MeOH (200 mL), and then Pd/C 5% (3 g) was added. The reaction mixture was stirred under a hydrogen atmosphere for 100 h; the progress of the reaction was monitored by NMR of aliquots. When reduction was complete, the catalyst was filtered off and methanol was removed under reduced pressure. Distillation afforded the desired alkanes in 65–95% yields.

2,4-Dimethyldecane (8). Prepared from 4-methyl-2-pentanone and hexylmagnesium chloride, following the above general procedure. Yield 95%; colorless liquid. ¹H NMR δ 0.81–0.89 (m, 12 H), 0.92–1.15 (m, 3H), 1.16–1.36 (m, 9H), 1.37–1.52 (m, 1H), 1.53–1.71 (m, 1H).

5-*n*-Propylnonane (15). Prepared from 5-nonanone and *n*-propylmagnesium chloride, following the above general procedure. Yield 93%; colorless liquid. ¹H NMR δ 0.85–0.91 (m, 9H), 1.18–1.32 (m, 17H).

2-Methyl-5-ethylnonane (24).²¹ Prepared from 2-ethylhexanal and isobutylmagnesium chloride, following the above general procedure. Yield 65%; colorless liquid. ¹H NMR δ 0.83 (t, *J* = 7.5 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 9H), 1.09–1.52 (m, 14H).

4-Ethyldecane (35). Prepared from 4-decanone and ethylmagnesium chloride, following the above general procedure. Yield 95%; colorless liquid. ¹H NMR δ 0.80–0.90 (m, 9H), 1.22–1.31 (m, 17H).

3-Ethyldecane (41).²⁰ Prepared from 3-decanone and ethylmagnesium chloride, following the above general procedure. Yield 95%; colorless liquid. ¹H NMR δ 0.84 (t, *J* = 7.2 Hz, 6H), 0.89 (t, *J* = 6.6 Hz, 3H), 1.23–1.33 (m, 17H).

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