THE PENNSYLVANIA STATE COLLEGE
SCHOOL OF CHEMISTRY AND PHYSICS
STATE COLLEGE, PA.

AMERICAN PETROLEUM INSTITUTE
RESEARCH PROJECT 42
THE SYNTHESIS AND PROPERTIES
OF HIGHER HYDROCARBONS
R. W. Schiessler, Director

July 13, 1954

Dr. A. W. Horton
The Kettering Laboratory
University of Cincinnati
Cincinnati 19, Ohio

Dear Wes:

In response to your letter of June 24, I am enclosing the synthetic details for the preparation of PSC 510 and PSC 174. I am sorry for the delay, but we have been very busy and I am currently ill at home. As a consequence, I have not had an opportunity to look over the details for PSC 510 carefully, Mrs. Mills having extracted this for me from one of our theses.

You will note that I have substituted the synthesis for PSC 174 (1-alpha-naphthyl pentadecane) for that of PSC 559, which you specifically requested. My reason is that the PSC 174 synthesis is more modern than that of PSC 559, and I believe it will give you better results. Of course, you can substitute the C_{11} nitrile, in order to get the C_{21} hydrocarbon which you apparently desire.

Instead of the high pressure technique reported with the PSC 174 details, you may prefer to operate at atmospheric pressure. If so, I refer you to our publication in the Journal of the American Chemical Society, 67, 2061 (1945).

If you have any further questions about these syntheses, please call on me.

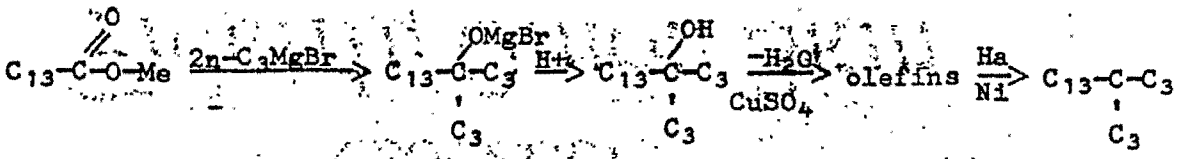
With best regards,

Sincerely,

Robert W. Schiessler/m.m.
Robert W. Schiessler
Associate Professor of Chemistry

P.S. My secretary will sign this for me in my absence.
RWS

4-n-Propylheptadecane



The procedure used in synthesizing this compound was exactly the same as that used in making 5-butylhexadecane, except that no attempt was made to isolate either the tertiary alcohol or the mixture of olefins.

n-Propylmagnesium bromide was prepared by adding 615 grams (5 moles) of n-propyl bromide, in an equal volume of anhydrous ether, to 125 grams (5 moles) of magnesium.

545 grams (2.25 moles) of methyl myristate, also in an equal volume of anhydrous ether, were then added to the Grignard reagent.

The complex was decomposed by pouring it into an ice-sulfuric acid mixture and the crude carbinol was isolated. This compound was dehydrated to the olefin mixture and the latter was hydrogenated to the corresponding paraffin. When the saturated hydrocarbon was being removed from the bomb, a considerable amount of it was lost through spilling.

Distillation of 4-n-Propylheptadecane

Column: Hy-Vac

Fract.	Time	Weight (gms.)	n_D^{20}	Boiling Point (deg.C.)	Press (mm.)	Still Temp. (deg.C.)	Bottom of Col. (deg.C.)	Top of Column (deg.C.)
---	5:25	---	---	111	0.95	160	138	120
1	6:00	36	1.4383	123	0.77	?	154	134
2	6:15	43	1.4415	132	0.77	184	157	143
3	6:30	39.5	1.4428	134	0.77	177	150	142
4	6:55	54	1.4428	134	0.77	181	152	141

In taking off cut 4., hot water had to be run through the condenser in order to liquefy a while solid which had collected.

5	7:13	49	1.4428	134	0.77	185	152	142
6	7:30	44	1.4428	134	0.77	189	153	142
7	7:50	50	1.4428	135	0.80	196	151	141
8	8:50	39	1.4428	135	0.80	196	151	141

During the distillation one of the pot heaters burned out so that near the end of the operation not enough heat could be obtained to get a small amount of material (about 20 gms.) out of the pot.

All of the fractions were placed on a window sill where it was quite cold. White crystals began forming in a number of the bottles. It was concluded, therefore that the white solid obtained in the taking off of fraction 4 was solid hydrocarbon.

Cuts 3, 4, 5, 6, 7, and 8 were combined and passed through silica gel. The compound was labeled 4-propylheptadecane.

Yield was 43.5% based on methyl myristate.

Properties:

Refractive Index: (n_D^{20}) 1.4428

Viscosity at 20 deg. C. .....8.29 centistokes

Density at 20 deg. C. .....0.7943 grams per ml.

n-Tetradecyl Bromide

$$C_{14}\text{-OH} \xrightarrow{HBr} C_{14}\text{-Br}$$

n-Tetradecyl bromide was prepared in the same manner as reported for n-decyl bromide. The synthesis was carried out on a very large scale by the author in 1945 for the work reported in his Master's Dissertation (31).

n-Tetradecyl Cyanide

$$C_{14}\text{-Br} \xrightarrow{KCN} C_{14}\text{-CN}$$

In two duplicate runs, 211 grams (3.2 g.-moles) of 98.5% potassium cyanide were dissolved in 200 ml. of water and 2.7 liters of 95% ethanol. After the addition of 886 grams (3.2 g.-moles) of pure n-tetradecyl bromide the solution was stirred for 72 hours. An additional 65 grams (1 g.-mole) of potassium syanide were added and stirring continued for 96 hours.

The two runs were combined and the majority of the solvent removed by distillation at atmospheric pressure. The addition of 3 liters of water caused separation of two layers which were stirred at reflux for several hours to insure complete solution of inorganic material. The upper organic layer was separated and washed well with water, ether being required to avoid emulsion difficulties. The water layer and the water washes were combined, ether extracted, and the solvent washed carefully with water. The ether solutions were combined, dried over anhydrous sodium sulphate, and the solvent removed by distillation.

The crude nitrile was Claisen-distilled at reduced pressure but bumping caused still liquid to be carried over with the distillate on several occasions.

An attempt was made to fractionate the nitrile through Column A-5 at reduced pressure but no appreciable through-put could be obtained. After about 100 grams of low boiling material was separated the residue was charged to the Hy-Vacuum Column.

Fractionation Data

Charge: 1250 grams of crude n-tetradecyl cyanide

Column: Hy-Vacuum

Fctn.	Temperature °C. Still	Column			B.Pt.	Press. mm. Hg	Total Wt. (grams)	$n^{20.5}D$
-	146	134	130	105	93	0.3	-	-
1	140	126	120	105	103		15	1.4402
2-4	146	130	130	120	109		62	1.4420
5-18	150	140	138	120	117	0.7	1148	1.4425
19-20	160	148	146	122	116	0.6	1230	1.4428

Residue: negligible

Fractions 5-18 were of constant index and consisted of 1086 grams, a yield of 76% based on n-tetradecyl bromide. Fractions 2-4 and 19-20 are reasonable pure nitrile and if included in the yield would raise it to 84%.

The 108 grams of lower boiling material obtained from Column A-5 which were not combined for the Hy-Vacuum fractionation had an index range of 1.4378 to 1.4417. The boiling point range is not significant as reflux was extremely low and variable. It is now evident that all of this material should have been included in the Hy-Vacuum fractionation as probably a good percentage could have been obtained as pure nitrile.

The Synthesis of 1(1-Naphthyl)pentadecane, PSC 174

n-Tetradecyl cyanide was added to 1-naphthyl magnesium bromide to yield n-tetradecyl-1-naphthyl ketone, which was reduced to 1(1-naphthyl)pentadecane by the Wolff-Kishner reaction.

n-Tetradecyl-1-naphthyl Ketone

The Grignard reagent of 1-bromonaphthalene was prepared from 122 grams (5.0 g.-atoms) of magnesium and 1035 grams (5.0 g.-moles) of the bromide at 20°C. To avoid precipitation of 1-naphthyl magnesium bromide it was necessary to prepare the Grignard reagent in 2500 ml. of anhydrous ether and 2500 ml. of distilled benzene and avoid cooling the solution below 10-15°C.

After stirring the reaction mixture for several hours, 1185 grams (5.3 g.-moles) of n-tetradecyl cyanide were added rapidly at 40°C. and the reaction allowed to stir overnight at room temperature.

Decomposition was effected with a slight excess of sulphuric acid mixed with crushed ice. The organic layer was washed with water and the solvent distilled. The residue was stirred with hot water (75°C.) for about an hour. The water was separated and the crude ketone washed with dilute bicarbonate solution and then with water.

The crude ketone was heated under water-vacuum to remove low boiling impurities and charged for fractionation.

Fractionation Data

Charge: crude n-tetradecyl-1-naphthyl ketone

Column: Hy-Vacuum

Pressure: 0.8 mm.

Fctn.	Temperature °C. Still	Column			B.Pt	Total Wt. (grams)
-	251	233	233	211	176	-
1	251	233	233	211	211	12
2	255	240	240	210	211	24
3	255	241	243	217	211	40
4	252	235	244	215	215	54
5	252	235	244	215	217	73
6	252	235	244	215	217	90
7	241	235	241	213	217	103
8	246	231	241	213	217	126
9-20	260	240	240	217	217	1099
21	321	248	252	217	220	1112
22	330	251	260	217	223	
23	360	300	277	223	226	

Residue: undetermined

Fractions 6-20, although of constant boiling point, had a viscosity range from 10.49 to 10.69 cs. at 60°C., the viscosity increasing with increasing weight-distilled. These fractions represent a yield of 60% of fairly pure ketone from naphthyl bromide.

Fractions 6-20 were combined, and a sample from the heart fraction reserved for physical property determination.

1(1-Naphthyl)pentadecane:

The reduction of 215 grams (0.60 g.-mole) of n-tetradecyl-1-naphthyl ketone was performed in a 4000 ml. autoclave (hydrogenation bomb 2-B). After mixing the ketone with 260 grams (4.8 g.-moles) of sodium methylate, 60 grams (1.2 g.-moles) of 100% hydrazine hydrate and 1600 ml. of triethylene glycol, the mixture was heated to 200°C. and shaken for eighteen hours. After cooling to 40°C., the gaseous reaction products were allowed to escape, the material removed and the bomb washed with three 300 ml. portions of n-hexane and two 500 ml. portions of warm water.

The water wash solution was warmed on the steam-bath, neutralized with dilute hydrochloric acid, and extracted with 300 ml. portions of hexane, adding the extracts to the original hexane wash solutions.

The glycol solution was diluted with an equal volume of water and extracted with the original hexane solution. After further dilution and acidification (to eliminate emulsion formations) the aqueous glycol solution was extracted with fresh hexane. The various hexane extracts were combined.

Three additional reductions were carried out on a similar scale in the same manner as above, in each case employing the same ratio of reactants and following the same procedure for treating the product.

The hexane extracts from the four runs were combined, washed well with water and concentrated by distillation. The residue, approximately 2 liters, was stirred at 65°C. with 1500 ml. of 1:1 hydrochloric acid, the organic material separated and washed several times with water. The solvent was removed by distillation and the residue Claisen-distilled at 1-3 mm. About 770 grams (2.28 g.-moles) of distilled hydrocarbon was obtained as constant boiling material from 923 grams (2.62 g.-moles) of ketone, a yield of 87%. A sample from one of the heart fractions had a setting point of 41-42°C. as compared with 39-40°C. for the fractionated ketone. When equal volumes of the two materials were mixed, the sample melted at 30-33°C. indicating that the two materials were not the same. The distilled hydrocarbon was combined and added to an ethereal solution of phenyl magnesium bromide (prepared from 0.8 g.-atoms of magnesium and excess bromobenzene) and stirred overnight. Decomposition was effected with dilute hydrochloric acid. The organic layer was separated, washed with water, and the solvent removed by distillation. The residue was charged to the Hy-Vacuum Column and carefully fractionated.

Fractionation Data

Charge: crude 1(1-naphthyl)pentadecane

Column: Hy-Vacuum

Fctn.	Temperature °C Still	Column			B.Pt.	Press. (mm.Hg)	Total Wt. (grams)	Average Eff.Time (60°C.)
-	221	212	222	193	188	0.3	-	-
1	219	210	222	193	190		13	S.Pt. 38-9°
2	221	208	212	189	190		17	S.Pt. 40°
3	225	214	216	191	191		24	S.Pt. 38-40°
4	223	213	219	193	192		39	S.Pt. 41-2°
5	221	212	219	192	192		54	S.Pt. 41-2°
6	221	210	219	192	192		71	390.7 sec.
7-9	220	210	223	194	193		128	-
10	220	210	225	194	194		170	395.7 sec.
11	221	212	223	200	201	0.5	217	-
12	221	210	224	198	202		230	396.1 sec.
13	221	211	224	196	198	0.4	282	-
14	222	212	225	198	198		338	399.1 sec.
15-17	219	197	222	191	198		410	-
18	220	206	214	189	198		423	397.6 sec.
19	230	217	219	196	197		446	-
20	232	218	221	196	197		481	398.8 sec.
21	232	219	221	197	198		518	-
22	235	222	222	197	198		568	404.1 sec.
23-28	boiling point increasing to 220°							S.Pts. depressed several degrees

Residue: negligible

It will be seen that for the majority of the distillate, the boiling point is essentially constant if the pressure variation is considered. However, the efflux times tend to increase with increasing material distilled. All the fractions had a light yellow color as a liquid but the solidified mass appeared white.

When fraction 22, efflux time 404.1 seconds, was passed through a train of silica gel, the first fraction was colorless and had an efflux time of 387.3 seconds. Re-passage through fresh silica gel had no effect on the efflux time. Fraction 6 was treated in a similar manner obtaining an efflux time of 384.5 seconds.

Fractions 10-22 (440 grams) were combined and passed through a train of silica gel. Fractions were taken, all of which had the same efflux time of 385.2-385.6 seconds. The recovery of pure hydrocarbon was 90%.