

## Quaternary-Substituted Hydrocarbons. I. A General Method of Synthesis of Hydrocarbons Interspersed with Four *gem*-Dimethyl Units

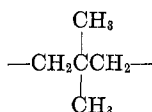
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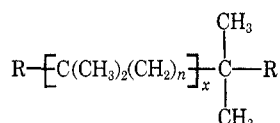
Preparation of seven high-molecular-weight ( $C_{30}$ - $C_{40}$ ) hydrocarbons containing two and four *gem*-dimethyl units interspersed in the aliphatic chain are described. Addition of mono- and difunctional Grignard reagents to ethyl isopropylidenemalonate was employed to incorporate *gem*-dimethyl units into key intermediates. The use of difunctional Grignard reagents in this reaction has not been previously reported. The acid chloride-organocadmium reaction was better for the preparation of diketone intermediates than the Grignard-nitrile reaction. A three-step procedure of reduction, dehydration, and hydrogenation to convert the diketone intermediates to the desired hydrocarbons was found to be superior to direct Wolff-Kishner reduction.

The data available to assess the effect on such properties as viscosity and thermal and oxidative stability of interspersing quaternary carbon atoms in the structure of compounds in the lubricant molecular-weight range are limited to hydrocarbons<sup>1</sup> with



recurring units and esters<sup>2,3</sup> with one or two quaternary carbons.

Of the approximately 150 reported hydrocarbons with quaternary carbons, only eight have more than 28 carbon atoms and none of these have more than two quaternary carbons. The 16 reported hydrocarbons containing two or more quaternary carbons all fall in the  $C_{18}$  to  $C_{24}$  range, and, except for 2,2,4,4,13,13,15,15-octamethylhexadecane and 6-ethyl-2,2,4,4,11,11,18,18-tetradecane,<sup>4</sup> none were prepared by unequivocal routes nor were their purities verified chromatographically.<sup>5-7</sup> To broaden the scope of these data, we prepared a number of hydrocarbons with up to four quaternary carbon atoms interspersed in the chain with the general structure below, where  $n = 4-8$  and  $x = 1$  and 3.

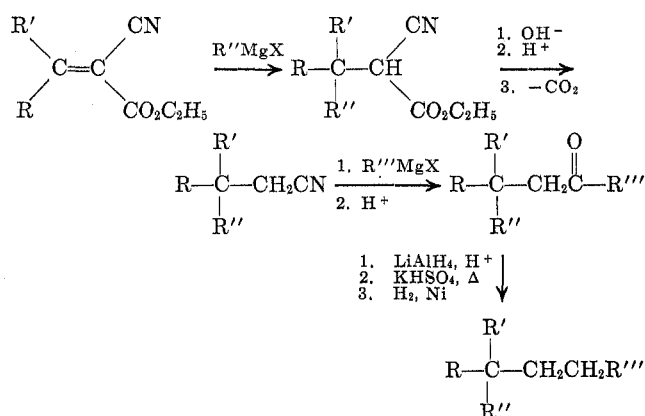


The synthesis of high-molecular-weight hydrocarbons in high purity even now presents difficulties,<sup>8</sup> and is further complicated in our case because reactions which form quaternary carbons are limited.

Desgrandchamps<sup>9</sup> has shown that of seven routes

- (1) S. F. Birch, V. E. Gripp, D. T. McAllan, and W. S. Nathan, *J. Chem. Soc.*, 1363 (1952).
- (2) W. E. Taylor, E. R. Witt, C. L. Osborn, J. L. Hugnet, and H. H. Thigpen, "The Syntheses and Evaluation of Aromatic Esters as Potential Base Stock Fluids for Gas Turbine Engine Lubricants," WADD Technical Report 60-913, March 1961.
- (3) W. E. Taylor, C. L. Osborn, and N. F. Swynnerton, ref 2, WADD Technical Report 60-913-Pt III, Jan 1962.
- (4) S. Wawzonek, H. W. Bluhm, B. Studnicka, R. E. Kallio, and E. J. McKenna, *J. Org. Chem.*, **30**, 3028 (1965).
- (5) A. I. Zakharova, G. D. Il'ina, and G. M. Murashov, *Zh. Obshch. Khim.*, **25**, 1968 (1955).
- (6) W. H. Puterbaugh and M. S. Newman, *J. Amer. Chem. Soc.*, **81**, 1611 (1959).
- (7) A. K. Hoffmann, W. G. Hodgson, D. L. Maricle, and W. H. Jura, *ibid.*, **86**, 631 (1964).
- (8) R. R. Reinhard and J. A. Dixon, *J. Org. Chem.*, **30**, 1450 (1965).
- (9) G. Desgrandchamps, A. Deluzarche, and A. Millard, *Bull. Soc. Chim. Fr.*, 264 (1961).

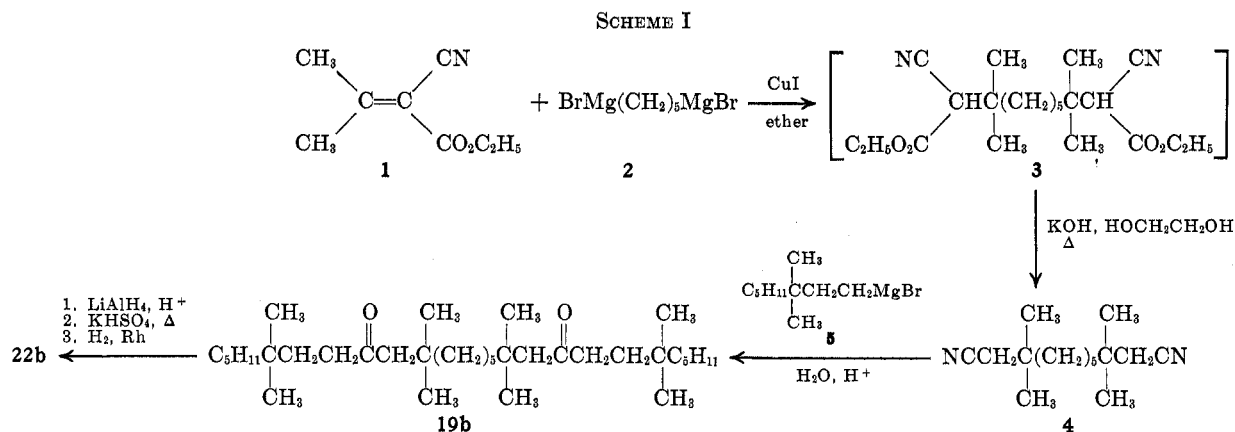
which he evaluated for the synthesis of  $C_{17}$ -tetraalkylmethanes, only one developed by Rabjohn, *et al.*,<sup>10</sup> yielded hydrocarbons of chromatographic purity. Four methods, the Blaise reaction, reactions of tertiary chlorides and alkyl sodium derivatives, reactions of alkylcadmium reagents with acid chlorides, and reactions of Grignard reagents with aldehydes did not lead to acceptable results, and the Grignard condensations of Petrov,<sup>11</sup> and the reaction of Grignard reagents with tertiary acetylenic chlorides according to Campbell and Eby<sup>12</sup> lead to contaminated products. The Rabjohn method,<sup>10,13</sup> in which the quaternary carbon is formed by 1,4 addition of a Grignard reagent to an alkylidene-cyanoacetate,<sup>14</sup> was used by Rabjohn<sup>10</sup> and Desgrandchamps<sup>9</sup> to synthesize pure, high-molecular-weight, unsymmetrical tetraalkylmethanes.



### Results and Discussion

In applying Rabjohn's method to the synthesis of 6,6,11,11,17,17,22,22-octamethylheptacosane (22b) according to Scheme I we found that in the first step the addition of pentamethylenebis(magnesium bromide) (2) to ethyl cyanoisopropylideneacetate (1) in ether afforded a complex mixture of at least five major reaction products. Hydrolysis and decarboxylation of this mixture gave only an 11% yield of pure 3,3,9,9-tetramethyl-1,11-undecanedinitrile (4). An alternate synthetic approach is the addition of Grignard reagents to

- (10) N. Rabjohn, L. V. Phillips, and R. J. DeFeo, *J. Org. Chem.*, **24**, 1964 (1959).
- (11) A. D. Petrov and E. A. Tcherishov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **6**, 1082 (1952).
- (12) K. N. Campbell and L. T. Eby, *J. Amer. Chem. Soc.*, **62**, 1798 (1940).
- (13) N. Rabjohn and R. J. DeFeo, *J. Org. Chem.*, **25**, 1307 (1960).
- (14) A. C. Cope, C. M. Hoffmann, C. Wykoff, and E. Hardenbergh, *J. Amer. Chem. Soc.*, **63**, 3452 (1941).

TABLE I.— $\beta,\beta,\beta',\beta'$ -TETRAMETHYLALKANEDIOIC ACIDS 17a-d

Compd no.	n	Bp, °C (mm)	Mp, °C	% yield	Formula	Calcd, %		Found, %	
						C	H	C	H
17a	4	180–185 (0.3)	115–116 <sup>a</sup>	35	C <sub>14</sub> H <sub>26</sub> O <sub>4</sub>	65.08	10.14	65.58	10.04
17b	5	178–180 (0.1)	96–97 <sup>b</sup>	31	C <sub>15</sub> H <sub>28</sub> O <sub>4</sub>	66.14	10.36	66.20	10.23
17c	6	185–190 (0.3)	142–143 <sup>a</sup>	49	C <sub>16</sub> H <sub>30</sub> O <sub>4</sub>	67.09	10.55	67.15	10.70
17d	8	210–220 (0.4)	124 <sup>a</sup>	46	C <sub>18</sub> H <sub>34</sub> O <sub>4</sub>	68.74	10.89	68.80	10.93

<sup>a</sup> Recrystallized from benzene. <sup>b</sup> Recrystallized from hexane.

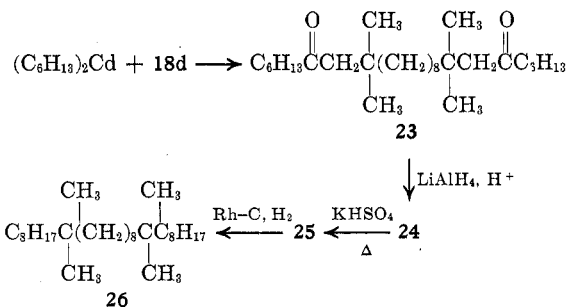
alkyldenemalonates.<sup>15</sup> The inverse addition of pentylmagnesium bromide to ethyl isopropylidenemalonate using cuprous iodide catalysis gave yields of ethyl 1,1-dimethylhexylmalonate (7) in the range of 65–70%. These yields approach those reported by Hook and Robinson<sup>16</sup> and Rabjohn, *et al.*,<sup>10</sup> for the inverse addition of Grignard reagents to ethyl cyanoisopropylideneacetate using cuprous iodide catalyst. Lower yields, 30–40%, of *t*-alkylmalonic esters were reported by Widequist<sup>16</sup> for the normal addition of methyl- and *n*-butylmagnesium bromide to ethyl isopropylidenemalonate without using cuprous iodide catalysis. The inverse addition of di-Grignard reagents to ethyl isopropylidenemalonate (Table I) gave, after hydrolysis and decarboxylation, the  $\beta,\beta,\beta',\beta'$ -tetramethylalkanedioic acids (17a–d) in yields of 31–49% compared with yields of only 11% for 3,3,9,9-tetramethyl-1,11-undecanedinitrile. Approximately 15% of the malonate is converted to the dihydro dimer during this reaction. Although di-Grignard reagents have been used widely,<sup>17</sup> this is the first report to our knowledge of di-1,4 addition of such a reagent.

In the third step of Scheme I although the reaction of 3,3,9,9-tetramethyl-1,11-undecanedinitrile (4) with 3,3-dimethyloctylmagnesium bromide (5) gave a good, 61%, yield of 6,6,11,11,17,17,22,22-octamethyl-9,19-heptacosanedione (19b), this route proved to be inferior to the organocadmium-acid chloride reaction. The addition of di(3,3-dimethyloctyl)cadmium (16a) to the chlorides of the  $\beta,\beta,\beta',\beta'$ -tetramethylalkanedioic acids gave diketones (19a–d) with four quaternary carbon atoms in yields of 80% and in high purity (Table II). The acid chlorides (18a–d) were used in this reac-

tion without final purification by vacuum distillation because decomposition began at around 125° (pot temperature) when distillation was attempted. Some of the 3,3-dimethyloctyl bromide (10), used in excess, coupled in the preparation of the cadmium compounds to yield 15–20% 6,6,11,11-tetramethylhexadecane (11).

Similar results were obtained in the reaction of the acid chlorides with di(4,4-dimethylnonyl)cadmium (15b) which was obtained as shown in Scheme II from 3,3-dimethyloctyl bromide (10) by conventional methods.

Although our synthetic work was directed primarily toward the synthesis of hydrocarbons containing four *gem*-dimethyl groups, one hydrocarbon with only two, 9,9,18,18-tetramethylhexacosane (26), was also prepared. The intermediate diketone, 9,9,18,18-tetramethyl-7-20-hexacosanedione (23), was prepared in 88% yield by the reaction of dihexylcadmium with 3,3,12,12-tetramethyl-1,14-tetradecanedioyl chloride (18d).



In an attempt to reduce the diketones directly to the hydrocarbons we selected from the many methods for

(15) S. Widequist, *Ark. Kemi, Mineral. Geol.*, **B23**, No. 4 (1946).

(16) W. H. Hook and R. Robinson, *J. Chem. Soc.*, 1952 (1944).

(17) E. Buchta and E. Weidinger, *Justus Liebigs Chem. Ann.*, **580**, 109 (1953).



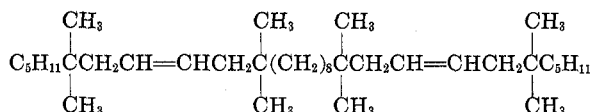
TABLE II.—*gem*-DIMETHYLALKANEDIONES 19a-f

Compd no.	m	n	Bp, °C (mm)	n <sub>D</sub> <sup>20</sup>	% yield	ν, cm <sup>-1</sup>		Formula	Calcd, %		Found, %	
						C=O	-C(CH <sub>3</sub> ) <sub>2</sub> - <sup>b</sup>		C	H	C	H
19a	2	4	198 (0.2)	1.4625	83	1694	1355-1373	C <sub>34</sub> H <sub>66</sub> O <sub>2</sub>	80.56	13.12	80.27	13.04
19b	2	5	210-215 (0.2)	1.4630	86	1692	1355-1373	C <sub>35</sub> H <sub>68</sub> O <sub>2</sub>	80.69	13.15	80.58	13.05
19c	2	6	198-201 (0.05)	1.4630	90	1692	1355-1373	C <sub>36</sub> H <sub>70</sub> O <sub>2</sub>	80.82	13.19	80.59	13.07
19d	2	8	198 (0.15)	1.4636	88	1692	1355-1373	C <sub>38</sub> H <sub>74</sub> O <sub>2</sub>	81.06	13.25	80.69	12.99
19e	3	5	225 (0.15)	1.4630	82	1700	1358-1380	C <sub>37</sub> H <sub>72</sub> O <sub>2</sub>	80.95	13.22	80.94	13.03
19f	3	8	210-218 (0.3)	1.4635	88	1710	1360-1380	C <sub>40</sub> H <sub>78</sub> O <sub>2</sub>	81.28	13.30	81.40	13.75
23 <sup>c</sup>			208 (0.3)	1.4631	88	1690	1350-1370	C <sub>50</sub> H <sub>98</sub> O <sub>2</sub>	79.93	12.96	79.60	12.68

<sup>a</sup> Capillary. <sup>b</sup> Range for two bands. <sup>c</sup> 9,9,18,18-Tetramethyl-7,20-hexacosanedione (23).

the reduction of hindered or masked carbonyl groups and which uses in the hydrazone formation acid rather than base catalysis and a large (66:1) mole ratio of hydrazine hydrate to carbonyl group,<sup>23</sup> also gave a yield of the desired hydrocarbon after chromatography on alumina of only 35%. This is about the same yield reported for direct reduction of a C<sub>94</sub> diketone to tetra-nonacontane using acid catalysis for hydrazone formation in 1-octanol, followed by decomposition of the hydrazone to hydrocarbon using sodium octylate.<sup>8</sup> These poor yields and the formation of by-products which necessitates tedious purification procedures may result from the conversion of the diketones to azines rather than hydrazones, since these high-molecular-weight diketones have limited solubility in conventional Wolff-Kishner solvents.

Since the Wolff-Kishner reduction proved unsatisfactory, we returned to the three-step method of reduction, dehydration, and hydrogenation reported by Rabjohn, *et al.*<sup>10</sup> This procedure afforded the desired hydrocarbons (22a-f) as illustrated in Scheme II, in high yield and purity. The *gem*-dimethylalkanedions (20a-f) listed in Table III were obtained in excellent yields (82-99%) *via* lithium aluminum hydride reduction. These diols were dehydrated to diolefin mixtures listed in Table IV in high yields (90-97%) using potassium hydrogen sulfate at 150-160° under reduced pressure. The infrared spectra of these diolefins exhibited no trace of an absorption band for the hydroxyl function and an intense band at 970 cm<sup>-1</sup> indicative of principally *trans* double bonds. The high ratios of methylene to vinylic protons in the nmr spectra of the diolefins indicate that double bond formation equidistant from the *gem*-dimethyl groups is preferred. In fact, the ratio of methylene protons to vinylic protons of 2.00 in the nmr spectra of the C<sub>38</sub> diolefin (21d) shows that only the less strained olefin is formed.



These results are consistent with the observations of Brown and Berneis<sup>24</sup> that the preferred olefin is the one which has the lowest steric requirements with respect to the *cis*-methyl and *t*-butyl groups in 2,4,4-trimethyl-2-pentene.

(23) W. Nagate and H. Itazoki, *Chem. Ind. (London)*, 1194 (1964).

(24) H. C. Brown and H. L. Berneis, *J. Amer. Chem. Soc.*, **75**, 10 (1953).

The *gem*-dimethylalkanes (22a-f) listed in Table V were obtained in excellent yields (82-95%) *via* hydrogenation using 5% rhodium on carbon at elevated temperatures (180°) and pressures of 3200 psi. The infrared spectra of these hydrocarbons exhibited an increase in the intensity of the absorption band due to recurring methylene units and no trace of an absorption band for unsaturation. Their nmr spectra showed no trace of unsaturation and agreed satisfactorily with their proposed structures. The purities of the intermediate diketones, diolefins, and the final quaternary hydrocarbons all exceeded 99% by glc analysis.

### Experimental Section<sup>25</sup>

**3,3,9,9-Tetramethyl-1,11-undecanedinitrile (4).**—A Grignard solution was prepared from 1,5-dibromopentane (114 g, 0.5 mol), magnesium (24.3 g, 1 g-atom) and 1200 ml of ether. This reagent was added to ethyl cyanoisopropylideneacetate (1)<sup>26</sup> (153 g, 1 mol) in a 1200-ml mixture of ether and cuprous iodide (5 g/mol of ester) over 2 hr. The reactants were mixed for 16 hr, refluxed for 1 hr, and decomposed with ice and dilute hydrochloric acid. The aqueous layer was washed several times with ether; the ether solutions were combined and dried (MgSO<sub>4</sub>). The filtered solutions were concentrated on a steam bath and distilled. The collected forerun was identified as starting material and monoaddition products, bp 105° (1.0 mm) maximum. The pot residue, consisting of crude diaddition reaction product 3 (90 g, 0.238 mol), was refluxed for 3 hr at 135° with potassium hydroxide (56.5 g, 1 mol) and 240 ml of ethylene glycol. This solution was cooled, diluted with 300 ml of water, and extracted with water and a saturated solution of sodium chloride, and dried (MgSO<sub>4</sub>). The solution was filtered, concentrated on a steam bath, and distilled.

3,3,9,9-Tetramethyl-1,11-undecanedinitrile (4) (12.9 g), bp 135-139° (0.2 mm), n<sub>D</sub><sup>20</sup> 1.4569, was obtained in 11% yield in purity greater than 99.5% by glc analysis.

*Anal.* Calcd for C<sub>15</sub>H<sub>26</sub>N<sub>2</sub>: C, 76.86; H, 11.18; N, 11.95. Found: C, 76.59; H, 11.48; N, 11.73.

**Reaction of 3,3-Dimethyloctylmagnesium Bromide (5) and 3,3,9,9-Tetramethyl-1,11-undecanedinitrile (4).**—A solution of 4 (11.7 g, 0.048 mol) dissolved in 100 ml of ether was added over a 20-min period to a Grignard reagent prepared from 10 (61 g,

(25) All boiling points and melting points were uncorrected. Microanalysis were performed by Gailbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were determined as a thin film using a Beckman IR-5 spectrometer. All nmr spectra were determined in carbon tetrachloride containing 5% tetramethylsilane as an internal standard using a Varian A-60 nmr spectrometer. Analytical gas-liquid chromatographs were determined using an F & M 720 dual column gas chromatograph. The dual columns were 20 ft, 0.25-in. o.d. packed with 12% Dow Corning high vacuum grease dispersed on 45-50 mesh Chromosorb P. Column temperatures were generally in the range of 250-275° using a helium flow of 70 ml/min. Sample sizes of 0.1 μl were used at maximum attenuation to obtain optimum resolution and detection of any trace impurities for the compounds in the C<sub>35</sub>-C<sub>50</sub> molecular-weight range reported herein.

(26) S. Wideqvist, *Acta Chem. Scand.*, **3**, 303 (1949).

TABLE III.—*gem*-DIMETHYLLALKANEDIOLS 20a-f

Compd no.	m	n	Bp, °C (mm)	n <sub>D</sub> <sup>20</sup>	% yield	-C(OH) <sub>2</sub> <sup>a,b</sup>		Formula	Mol wt		Calcd, %		Found, %		
						O—H	-C—OH <sup>b</sup>		Calcd	Found	C	H	C	H	
20a	2	4	225-227 (0.02)	1.4692	99	3278	1358-1379	1041-1069	C <sub>34</sub> H <sub>70</sub> O <sub>2</sub>	510	506	79.92	13.81	79.98	13.91
20b	2	5	226 (0.1)	1.4696	97	3246	1355-1373	1041-1069	C <sub>35</sub> H <sub>72</sub> O <sub>2</sub>	522	528	80.07	13.82	80.15	13.56
20c	2	6	225-233 (0.02)	1.4696	97	3246	1355-1373	1036-1069	C <sub>36</sub> H <sub>74</sub> O <sub>2</sub>	539	532	80.22	13.84	80.44	13.72
20d	2	8	240-242 (0.02)	1.4698	99	3246	1355-1373	1036-1052	C <sub>38</sub> H <sub>78</sub> O <sub>2</sub>	567	560	80.48	13.86	80.27	13.75
20e	3	5	245 (0.07)	1.4693	97	3246	1355-1373	1036-1069	C <sub>37</sub> H <sub>76</sub> O <sub>2</sub>	553	551	80.35	13.85	80.45	13.88
20f <sup>c</sup>	3	8	245-255 (0.05)		90	3246	1355-1373	1036-1052	C <sub>40</sub> H <sub>82</sub> O <sub>2</sub>	595	589	80.73	13.89	80.60	14.03
24 <sup>d</sup>	3	8	210-215 (0.02)	1.4675	82	3246	1352-1373	1035-1060	C <sub>30</sub> H <sub>68</sub> O <sub>2</sub>	454	448	79.22	13.74	79.35	13.65

<sup>a</sup> Capillary. <sup>b</sup> Range for two bands. <sup>c</sup> Semiwaxy diol. <sup>d</sup> 9,9,18,18-Tetramethyl-7,20-hexacosanediol (24).

TABLE IV.—*gem*-DIMETHYLLALKADIENES 21a-f

Compd no.	m	n	Bp, °C (mm)	n <sub>D</sub> <sup>20</sup>	% yield	-C(CH <sub>3</sub> ) <sub>2</sub> <sup>a,b</sup>		Formula	Mol wt		Calcd, %		Found, %		
						C=C	Nmr α-CH <sub>2</sub> C=C		Calcd	Found	C	H	C	H	
21a	2	4	200-205 (0.02)	1.4658	96	1358-1377	970	1.74	C <sub>34</sub> H <sub>66</sub>	475	480	85.99	14.00	86.07	13.97
21b	2	5	205-210 (0.1)	1.4662	90	1366-1385	972	1.70	C <sub>35</sub> H <sub>68</sub>	488	477	85.97	14.02	86.20	13.79
21c	2	6	195-210 (0.02)	1.4660	93	1355-1373	968	1.84	C <sub>36</sub> H <sub>70</sub>	502	502	85.96	14.03	85.69	13.93
21d	2	8	215-222 (0.04)	1.4662	97	1355-1373	969	2.00	C <sub>37</sub> H <sub>74</sub>	530	533	85.96	14.04	85.89	13.85
21e	3	5	202-205 (0.02)	1.4660	74	1360-1380	969	1.50	C <sub>37</sub> H <sub>72</sub>	517	523	85.96	14.04	85.91	14.02
21f	3	8	215-220 (0.08)	1.4662	98	1360-1380	970	1.42	C <sub>40</sub> H <sub>78</sub>	559	566	85.93	14.07	85.87	14.04
25 <sup>c</sup>	3	8	178-180 (0.02)	1.4614	93	1355-1373	970	1.68	C <sub>30</sub> H <sub>58</sub>	418	430	86.03	13.96	85.79	13.84

<sup>a</sup> Capillary. <sup>b</sup> Range for two bands. <sup>c</sup> 9,9,18,18-Tetramethyl-(6)7,19(20)-hexacosadiene (25).

TABLE V.—*gem*-DIMETHYLLALKANES 22a-f

Compd no.	m	n	Bp, °C (mm)	n <sub>D</sub> <sup>20</sup>	% yield	d <sub>4</sub> <sup>20</sup>	-C(CH <sub>3</sub> ) <sub>2</sub> <sup>a,c</sup>		Formula	Mol wt		Calcd, %		Found, %	
							-(CH <sub>2</sub> ) <sub>n</sub> <sup>b</sup>	-(CH <sub>2</sub> ) <sub>n</sub> <sup>b</sup>		Calcd	Found	C	H	C	H
22a	2	4	190-194 (0.02)	1.4570	95	0.8278	1369-1388	725	C <sub>34</sub> H <sub>70</sub>	479	483	85.27	14.73	85.50	14.46
22b	2	5	189-194 (0.03)	1.4568	85	0.8230	1366-1385	724	C <sub>35</sub> H <sub>72</sub>	493	492	85.28	14.72	85.48	14.65
22c	2	6	195-200 (0.02)	1.4575	82	0.8226	1369-1388	726	C <sub>36</sub> H <sub>74</sub>	507	510	85.29	14.71	85.55	14.42
22d	2	8	212-215 (0.02)	1.4580	94	0.8351	1369-1388	725	C <sub>38</sub> H <sub>78</sub>	535	536	85.30	14.70	85.62	14.33
22e	3	5	202-205 (0.04)	1.4587	79		1355-1372	720	C <sub>37</sub> H <sub>76</sub>	521	526	85.29	14.70	85.27	14.72
22f	3	8	220-225 (0.03)	1.4600	84		1369-1388	720	C <sub>40</sub> H <sub>82</sub>	563	552	85.32	14.68	85.37	14.70
11 <sup>d</sup>	3	8	136-140 (1.4)	1.4430	15-20 <sup>e</sup>		1370-1389	721	C <sub>30</sub> H <sub>62</sub>	282	286	85.01	14.98	84.73	15.00
26 <sup>f</sup>	3	8	180 (0.03)	1.4528	86	0.8149	1370-1389	721	C <sub>30</sub> H <sub>62</sub>	422	430	85.27	14.72	85.50	14.48

<sup>a</sup> Capillary. <sup>b</sup> Increased methylene absorption. <sup>c</sup> Range for two bands. <sup>d</sup> 6,6,11,11-Tetramethylhexadecane (11). <sup>e</sup> Average per cent yield of 11 obtained in preparation of 16a. <sup>f</sup> 9,9,18,18-Tetramethylhexacosane (26).

0.276 mol), 600 ml of ether and magnesium. The reactants were gently refluxed for 18 hr, cooled, and hydrolyzed with 500 g of ice and 180 ml of concentrated hydrochloric acid. The hydrolyzed reaction mixture was warmed on a steam bath with excess ether (1 l.) for 1 hr with stirring. The aqueous layer was extracted with ether; the ether layers were combined and washed with water, 10% sodium bicarbonate, and finally with water until the washings tested neutral. The dried ether extracts ( $\text{MgSO}_4$ ) were filtered and concentrated on a steam bath and the concentrates vacuum distilled. The fraction boiling principally at 199–202° (0.05 mm), 15.2 g (61% yield),  $n_D^{20}$  1.4628, had identical glc retention time and infrared spectrum as those observed for 6,6,11,11,17,17,22,22-octamethyl-9,19-heptacosanedione (19b). This diketone (19b) was also prepared *via* the organocadmium-acid chloride route. Analysis of equal concentrations of each diketone by glc showed only one peak with no shoulders showing unequivocally that these diketones are identical.

**Ethyl 1,1-Dimethylhexylmalonate (7).**—A Grignard solution was prepared from 1-bromopentane (151 g, 1 mol), magnesium (24.3 g, 1 g-atom), and 1200 ml of ether. This reagent was added to ethyl isopropylidene malonate (6)<sup>27</sup> (200 g, 1 mol) dissolved in 1200 ml of ether containing cuprous iodide (5 g/mol of ester) over 2 hr. The reactants were stirred for 16 hr, heated for 1 hr, and decomposed with ice and dilute hydrochloric acid. The aqueous layer was separated and washed several times with ether; the ether solutions were dried ( $\text{MgSO}_4$ ). The filtered ether solutions were concentrated on a steam bath and distilled. 7, bp 128–132° (3.0 mm),  $n_D^{25}$  1.4359, was obtained in 65% yield and showed no trace impurities by glc.

*Anal.* Calcd for  $\text{C}_{15}\text{H}_{28}\text{O}_4$ : C, 66.63; H, 9.69. Found: C, 66.75; H, 9.86.

**3,3-Dimethyltanoic Acid (8).**—7 (272 g, 1 mol) was added dropwise over 2 hr to a hot solution of potassium hydroxide (200 g, 3.5 mol) and water (200 ml). The mixture was refluxed at 93° for 3 hr, cooled, diluted with 200 ml of water, and distilled to collect 200 ml of ethanol forerun. Cold sulfuric acid (175 ml of concentrated  $\text{H}_2\text{SO}_4$ –450 ml of water) was added cautiously to this mixture (45–50°) before refluxing all these components for 4 hr. The cooled, aqueous layer was separated and washed with benzene; the benzene extracts were combined with the organics. The dried benzene extracts ( $\text{MgSO}_4$ ) were filtered, concentrated on a steam bath and distilled with carbon dioxide evolution. Crude 8, bp 120–125° (3.5 mm), was obtained in 94% yield. The purity of 8 was improved by distillation, bp 104° (1.0 mm),  $n_D^{25}$  1.4355.

*Anal.* Calcd for  $\text{C}_{10}\text{H}_{20}\text{O}_2$ : C, 69.72; H, 11.70. Found: C, 69.50; H, 11.80.

**3,3-Dimethyl-1-octanol (9).**—Addition of an ethereal solution of 8 (75 g, 0.43 mol) to a stirred suspension of 20.3 g of lithium aluminum hydride in 1200 ml of ether, followed by the usual procedures and distillation of the residual oil gave a total of 67.1 g (98%) of 9 boiling principally at 110–111° (2.5 mm). 9 was further purified by distillation, bp 72° (0.7 mm),  $n_D^{25}$  1.4378.

*Anal.* Calcd for  $\text{C}_{10}\text{H}_{22}\text{O}$ : C, 75.88; H, 14.01. Found: C, 75.81; H, 13.91.

**1-Bromo-3,3-dimethyloctane (10).**—A mixture of 48% hydrobromic acid (240 g, 1.4 mol), concentrated sulfuric acid (62 g, 0.34 mol), and 9 (87 g, 0.55 mol) was refluxed for 5 hr at 125°. The cooled solution was diluted with water and filtered through Hyflo Super Cel and the bromide layer separated. The crude bromide was washed with 10 ml of cold sulfuric acid, 100 ml of water and 100 ml of 10% sodium carbonate. A light brown oil was dried ( $\text{MgSO}_4$ ), filtered and distilled, bp 85–90° (2.5 mm), 85% yield. 10 was further purified by distillation, bp 69° (0.25 mm),  $n_D^{25}$  1.4575.

*Anal.* Calcd for  $\text{C}_{10}\text{H}_{21}\text{Br}$ : C, 54.29; H, 9.57; Br, 36.13. Found: C, 54.20; H, 9.66; Br, 36.14.

**3,3,9,9-Tetramethyl-1,11-undecanedioic Acid (17b).**—The ester precursor to this acid ( $n = 5$ ) was prepared by the same procedure listed for 8. A Grignard solution prepared from 1,5-dibromopentane (230 g, 1 mol) and magnesium (48.6 g, 2 g-atoms) in 1200 ml of ether was added over a period of 1 hr to 6 (440 g, 2 mol) dissolved in 1200 ml of ether containing 10 g of cuprous iodide. This mixture was stirred for 12 hr at reflux, cooled, and hydrolyzed. After distillation of the low boiling reaction products, bp 55–135° (1.4 mm), the crude ester (~250 g) in the distillation pot was saponified and decarboxylated. Crude 17b, bp 178–180° (0.1 mm), was obtained in 31% yield. Recrystal-

lization from hexane gave a white crystalline solid, mp 96–97° (*cf.* Table I).

**3,3,9,9-Tetramethyl-1,11-undecanedioyl Chloride (18b).**—17b (41 g, 0.15 mol) was added as a solid to excess thionyl chloride (71.4 g, 0.6 mol) over a period of 40 min with stirring. The mixture was refluxed for 1.5 hr at 55°; excess thionyl chloride was distilled carefully *in vacuo*, after which the crude acid chloride (18b,  $n = 5$ ) was distilled, bp 150–152° (0.2 mm), in 88% yield. Since several of the higher melting acids listed herein had limited solubility in thionyl chloride owing to the endothermic nature of the reaction, it was necessary to heat these mixtures gently at 40–45° during the addition of the acids.

**6,6,11,11,17,17,22,22-Octamethyl-9,19-heptacosanedione (19b).**—This diketone, and the *gem*-dimethylalkanediones listed in Table II, were prepared using the general procedures described by Cason and Prout.<sup>28</sup> A Grignard solution was prepared from 10 (77.5 g, 0.35 mol) and magnesium (9.7 g, 0.4 g-atom) in 600 ml of ether. Anhydrous cadmium chloride (40 g, 0.22 mol), dried in a vacuum oven at 110°, was added to the decanted Grignard solution in a dry nitrogen atmosphere at ice-bath temperature, and di(3,3-dimethyloctyl)cadmium (16a) prepared by conventional techniques.<sup>28</sup> 18b (27 g, 0.09 mol) dissolved in 50 ml of benzene was added slowly to 16a at 68° since the reaction was very exothermic. The mixture was refluxed for 2 hr, poured into a 10% solution of sulfuric acid and extracted with ether. The ether solutions were washed with water, 5% sodium carbonate, and a saturated solution of sodium chloride and dried ( $\text{MgSO}_4$ ). The reaction products were filtered, concentrated on a steam bath and distilled (*cf.* Table II). A lower boiling component, bp 136° (1.4 mm),  $n_D^{25}$  1.4330, was isolated in 18% yield. This was identified as 6,6,11,11-tetramethylhexadecane (11).

*Anal.* Calcd for  $\text{C}_{20}\text{H}_{42}$ : C, 85.01; H, 14.98. Found: C, 84.73; H, 15.00.

**6,6,11,11,17,17,22,22-Octamethyl-9,19-heptacosanediol (20b).**—This procedure is typical of those used to obtain the *gem*-dimethylalkanediols listed in Table III. A mixture of 61 g (0.16 mol) of lithium aluminum hydride in 600 ml of ether was stirred while 20.8 g (0.04 mol) of 19b in 600 ml of ether was added at a rate sufficient to cause gentle refluxing. After the addition, the mixture was stirred at ambient temperature for 14 hr and refluxed for 5 hr. Excess lithium aluminum hydride was decomposed cautiously by the dropwise addition of cold water at ice-bath temperatures, and the reaction mixture hydrolyzed with 500 ml of 10% sulfuric acid. The ether layer was removed, washed with water, 10% sodium bicarbonate, and again with water and dried ( $\text{MgSO}_4$ ). The ether solution was filtered, concentrated on a steam bath and distilled to give 20.5 g (97% yield) of 20b (*cf.* Table III).

**6,6,11,11,17,17,22,22-Octamethyl-(8)9,18(19)-heptacosadiene (21b).**—This procedure is typical of those used to obtain the *gem*-dimethylalkadienes listed in Table IV. 20b (20.5 g, 0.04 mol) was heated with anhydrous potassium bisulfate (6 g, 0.044 mol) at 150–160° for 6 hr at reduced pressure (3–5 mm). The cooled reaction product was decanted, the potassium bisulfate was washed several times with small portions of ether, and the oil and extracts were combined. The concentrate was distilled to give 17.5 g (90% yield) of 21b (*cf.* Table IV).

**6,6,11,11,17,17,22,22-Octamethylheptacosane (22b).**—The *gem*-dimethylalkanes listed in Table V were obtained by means of the typical hydrogenation procedure at elevated temperatures and pressures described herein. 21b (13.8 g, 0.028 mol), methylcyclohexane (75 ml), and 1 g of 5% rhodium-on-carbon catalyst were heated to 180° in a 300-ml bomb and rocked for 8 hr at a final pressure of hydrogen and reactants of 3200 psi. The cooled reaction mixture was filtered free of catalyst and concentrated *in vacuo*, and the concentrate distilled to yield 11.7 g (85% yield) of 22b (*cf.* Table V).

**Ethyl 4,4-Dimethylnonanoate (12).**—This ester was prepared by a procedure similar to that described by Gaertner.<sup>29</sup> A Grignard reagent prepared from 10 (442 g, 2.0 mol), magnesium (49.5 g, 2.0 g-atoms), and 2 l. of ether was added to ethyl chloroacetate (1080 g, 10 mol) in 2 l. of ether at –40° over a 4 hr period. The reactants were allowed to warm to room temperature overnight and washed with a solution of ammonium chloride and the excess ether was removed *in vacuo* with mild heating. Distillation of crude 12, bp 100–105° (1.2–1.5 mm), gave 245

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g (69% yield). Per cent yield is based on the availability of Grignard reagent since 50.5 g of the Grignard dimer 11 was also isolated from this mixture. The purity of 12 was improved by distillation, bp 108° (1.2 mm),  $n_D^{25}$  1.4302.

*Anal.* Calcd for  $C_{13}H_{26}O_2$ : C, 72.84, H, 12.22. Found: C, 72.50; H, 12.01.

**4,4-Dimethyl-1-nonanol (13).**—Addition of an ethereal solution of 198 g (0.93 mol) of 12 to a stirred suspension of 33 g of lithium aluminum hydride in 1200 ml of ether, followed by the usual procedures, gave a total of 152 g (95%) of 13, bp 105–109° (1.0 mm). The purity of 13 was improved by distillation, bp 109° (1.0 mm),  $n_D^{25}$  4.4400.

*Anal.* Calcd for  $C_{11}H_{24}O$ : C, 76.67; H, 14.04. Found: C, 76.67; H, 14.17.

**1-Bromo-4,4-dimethylnonane (14).**—A mixture of 48% hydrobromic acid (384 g, 2.24 mol), concentrated sulfuric acid (98 g, 1 mol), and 13 (152 g, 0.88 mol) was refluxed for 5 hr at 125°. The cooled solution was diluted with water and filtered through Hyflo Super Cel; the bromide layer separated. The crude bromide was washed with 10 ml of cold sulfuric acid, 100 ml of water, and 100 ml of 10% sodium carbonate. Crude 14 was dried ( $MgSO_4$ ), filtered, and distilled, bp 94° (1.0 mm),  $n_D^{25}$  1.4578, yield 75%.

*Anal.* Calcd for  $C_{11}H_{23}Br$ : C, 56.16; H, 9.85; Br, 33.97. Found: C, 56.03; H, 10.13; Br, 34.03.

**6,6,11,11,17,17,22,22-Octamethylheptacosane (22b).** **A. Huang-Minlon Modification.**—19b (20.0 g, 0.038 mol), 15 ml of 85% hydrazine hydrate, 200 ml of diethylene glycol, and potassium hydroxide (15 g, 0.27 mol) were refluxed for 16 hr at 155° before the heat was increased to 165° to collect 15 ml of low boiling components. The reaction mixture was heated at 195° for 4 hr, cooled, and diluted with ether and water; the ether extracts were collected and washed to neutrality. The dried ether extracts ( $MgSO_4$ ) were concentrated on a steam bath and the residue was distilled under vacuum to yield five fractions. The highest boiling fraction, bp 195–215° (0.2 mm), was shown by glc to be mainly 22b (10.4 g) with minor impurities. Chromatography on alumina using heptane gave 6.0 g (32% yield) of 22b in high purity (>99%), bp 220° (0.2 mm).

**B. Nagate and Itazaki Modification.**—19b (22.6 g, 0.043 mol), 85% hydrazine hydrate (287 g, 5.57 mol), hydrazine dihydrochloride (73.0 g, 0.7 mol), and triethylene glycol (980 g, 6.5 mol) were heated for 12 hr at 130–150° with a Soxhlet extractor or apparatus containing calcium oxide (50 g) fitted to the reaction flask to remove traces of water. The reaction mixture was heated for an additional 12 hr until the temperature rose to 175° and cooled; after KOH (106 g, 1.9 mol) addition, it was then heated to 175° for 6 hr and finally to 225° for 4 hr. The cooled reaction mixture was worked up by the usual procedure and 13.5 g of a crude reaction product, bp 140–185° (0.07 mm), was obtained. Chromatography on alumina using heptane gave 7.5 g (35% yield) of 22b, bp 208° (0.1 mm), in high purity (>99%) as evidenced by glc analysis.

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## High Temperature Pyrolysis of $C_1$ to $C_4$ Hydrocarbons<sup>1</sup>

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The pyrolysis of nine hydrocarbons at 1200° has been studied. The main products, which were the same for all hydrocarbons studied, were 1,3-cyclopentadiene, benzene, toluene, phenylacetylene, styrene, indene, and naphthalene. Twenty-three minor products were identified. The distribution of products can be accounted for in terms of polymerization of acetylene, produced by the pyrolysis of the hydrocarbon, and the addition of  $CH_2$  or  $CH_3$  to some of the acetylene polymers.

Pyrolyses of simple hydrocarbons have been studied previously by various investigators with the main emphasis on the kinetics and mechanism of decomposition.<sup>2–6</sup> However, these pyrolyses were usually done at relatively low temperatures (500–700°) and only the main end products were analyzed, with a few exceptions.<sup>7–11</sup> We report here pyrolysis reactions that take place at higher temperature (1200°) with particular emphasis on the product analysis. We have attempted

to describe the mechanism on the basis of the nature of the end products and their relative yields.

The pyrolysis chamber contained a hot tungsten wire, and the walls of the flask were kept cold so that high-molecular-weight compounds formed by a recombination of the initial fragmentation of the hydrocarbons were condensed on the walls of the chamber and were not subjected to further pyrolysis to a significant degree.<sup>12,13</sup> The major products from these pyrolyses are shown in Table I. The minor components are listed at the bottom of Figure 1 in order of their retention time on the gas chromatograph column.

### Results and Discussion

The pyrolysis of each of the hydrocarbons studied at 1200° leads to the same end products, but both the

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