Coupling Reactions of 1-Chloro-5,5,7,7-tetramethyloctene-2[1]

S. WAWZONEK, H. J. BLUHM,[2] B. STUDNICKA,[2] R. E. KALLIO, AND EVA J. MCKENNA

Departments of Chemistry and Microbiology, University of Iowa, Iowa City, Iowa

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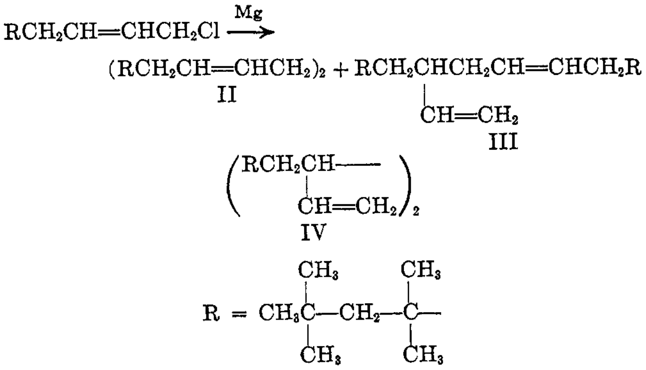
Coupling of 1-chloro-5,5,7,7-tetramethyloctene-2 (I) with magnesium in tetrahydrofuran gave equal amounts of 2,2,4,4,13,13,15,15-octamethyl-6,10-hexadecadiene (II) and 8,8,10,10-tetramethyl-3-(2,2,4,4-tetramethylpentyl)-1,5-undecadiene (III). The reaction in ether gave III and II in a ratio of 5:1. Catalytic reduction of the dienes gave 2,2,4,4,13,13,15,15-octamethylhexadecane (V) and 6-ethyl-2,2,4,4,11,11,13,13-octamethyltetradecane (VI). Coupling of I with phenyllithium gave a 60:40 mixture of *trans*-1-phenyl-5,5,7,7-tetramethyl-2-octene (VII) and 1-phenyl-2-(2,2,4,4-tetramethylpentyl)cyclopropane (VIII). Complete hydrogenation of the mixture gave 1-cyclohexyl-5,5,7,7-tetramethyloctane (IX). A similar coupling reaction using phenylmagnesium bromide and I gave an 88:12 mixture of *trans* VII and 3-phenyl-5,5,7,7-tetramethyl-1-octene (X). Diimide reduction of the last two compounds gave 1-phenyl-5,5,7,7-tetramethyloctane (XI) and 2,2,4,4-tetramethyl-6-phenyloctane (XII), respectively. Compounds V, VI, VII, IX, and XI were not oxidized by microorganisms.

In a continuation of the study of the mechanism of oxidation of saturated hydrocarbons by microorganisms[3] hydrocarbons containing terminal neopentyl groups were required for correlating structures susceptible to bacterial oxidation.

The present work describes the preparation of compounds with this group by the coupling of the readily available 1-chloro-5,5,7,7-tetramethyloctene-2 (I) with itself and with phenyllithium and phenylmagnesium bromide.

Coupling of the chloride (I) with magnesium in ether proceeded slowly and gave a 24% yield of products in 48 hr. Substitution of tetrahydrofuran for the ether gave a 78% yield of coupled products. The promotion of the magnesium coupling reaction by tetrahydrofuran has also been observed by others.[4]

Analysis by gas chromatography indicated that isomers II and III were present in equal amounts in



$$RCH_2CH{=}CHCH_2Cl \xrightarrow{Mg} \underset{II}{(RCH_2CH{=}CHCH_2)_2} + \underset{III}{RCH_2\underset{\substack{|\\CH=CH_2}}{CH}CH_2CH{=}CHCH_2R}$$

$$\underset{IV}{\left(RCH_2\underset{\substack{|\\CH=CH_2}}{CH}-\right)_2}$$

$$R = CH_3\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-$$

the product from the reaction in tetrahydrofuran as a solvent and in a ratio of 1:5 when ether was involved.

Isomers II and III were separated by fractional distillation and identified by their infrared spectra. Isomer III gave bands at 10.05 and 11.04 μ as well as an overtone at 5.5 μ which are all characteristic of a vinyl group. In addition a band was observed at 10.33 μ for a *trans* double bond. The presence of this band excludes structure IV as a possibility for this material.

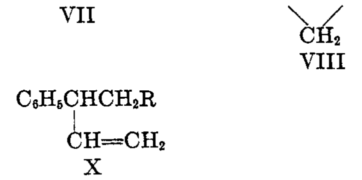
The spectrum of II shows only a band for a *trans* double bond at 10.34 μ which is more intense than that of III since there are two *trans* double bonds/molecule.

The absence of isomer IV in the product mixture is not surprising since compounds with a similar structure are known to undergo thermal rearrangement to isomers corresponding to II and III.[5] Distillation of the product mixture at the elevated temperatures used could have brought about this change.

The above results are similar to those found by others for the coupling of butenyl chloride[6,7] and cinnamyl chloride[5] in ether. No examples of coupling comparable allylic halides in tetrahydrofuran have been reported.

Catalytic, high-pressure hydrogenation of isomers II and III using platinum oxide gave 2,2,4,4,13,13,15,15-octamethylhexadecane (V) and 6-ethyl-2,2,4,4,11,11-13,13-octamethyltetradecane (VI). Raney nickel at 120° and 150 atm. of hydrogen had no effect. These saturated hydrocarbons, as might be expected, gave quite similar infrared spectra. The most marked difference was the intensity of the methylene band at 13.85 μ. Isomer V has eight adjacent methylene groups and isomer VI has only four.

Since the separation of isomers II and III was effected only with difficulty, an attempt was made to obtain coupling without rearrangement. Phenyllithium was added to 1-chloro-5,5,7,7-tetramethyloctene-2 in an attempt to effect halogen-metal interconversion. The resulting lithium derivative, if formed, could then couple with excess chloride to give the desired product. The reaction produced instead *trans*-1-phenyl-5,5,7,7-tetramethyl-2-octene (VII) and 1-phenyl-2-(2,2,4,4-tetramethylpentyl)cyclopropane (VIII). None of the isomeric alkene X was isolated.



$$C_6H_5Li + I \longrightarrow \underset{VII}{C_6H_5CH_2CH{=}CHCH_2R} + \underset{VIII}{CH_{65}CH-CHR \text{ (}CH_2\text{)}}$$

$$\underset{X}{C_6H_5\underset{\substack{|\\CH=CH_2}}{C}HCH_2R}$$

The ratio of the cyclopropane VIII to olefin VII by gas chromatographic analysis on a Carbowax column

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[2] Abstracted in part from the Ph.D. Thesis, Feb. 1963, of H. J. Bluhm and Ph.D. Thesis, Feb. 1966, of B. Studnicka.

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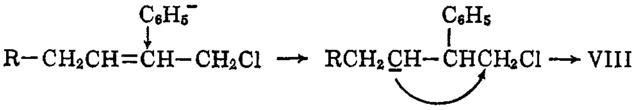
was 40:60. Separation of the two compounds could not be effected by fractional distillation but the cyclopropane VIII could be obtained pure by oxidizing the mixture with potassium permanganate. Its infrared and n.m.r. spectra were in agreement with its structure.

The cyclopropane VIII is probably formed by a reaction similar to the SN2′ reaction with attack of the phenyl carbanion occurring on the β-carbon atom instead of the γ-carbon. The resulting anion then undergoes an intramolecular reaction with displacement of the halogen.



$$R{-}CH_2CH{=}\overset{C_6H_5^-}{CH}{-}CH_2Cl \longrightarrow RCH_2\underline{C}H{-}\overset{C_6H_5}{C}HCH_2Cl \longrightarrow VIII$$

Phenyl cyclopropanes have also been isolated from the reaction of phenyllithium with allyl and crotyl chlorides.[8]

Further proof for the cyclopropane derivative VIII was the catalytic hydrogenation of the mixture VII and VIII using platinum to 1-cyclohexyl-5,5,7,7-tetramethyloctane (IX). Diimide reduction of the mixture gave a mixture of 1-phenyl-5,5,7,7-tetramethyloctane (XI) and the cyclopropane VIII.

The olefin VII could be prepared pure by coupling phenylmagnesium bromide with 1-chloro-5,5,7,7-tetramethyloctene-2. This reaction gave olefins consisting of 88% VII and 12% isomer X which could be separated by distillation.

Diimide reduction of isomer VII and isomer X gave 1-phenyl-5,5,7,7-tetramethyloctane (XI) and 2,2,4,4-tetramethyl-6-phenyloctane (XII), respectively.

Microbial utilization of 1-phenyl-5,5,7,7-tetramethyloctane (XI), 1-phenyl-5,5,7,7-tetramethyloctene-2 (VII), and 1-cyclohexyl-5,5,7,7-tetramethyloctane (IX) was assessed by determining if growth would occur at the expense of the hydrocarbons in an otherwise mineral medium using 19 test organisms (species of *Pseudomonas*, *Mycobacterium*, *Micrococcus*, and *Nocardia*) all of which grew at the expense of *n*-hexadecane and 1-phenyldecane. No growth of test organisms was noted after 4 weeks' incubation on a gyratory shaker at 30°. Enrichment cultures using VII, IX, or XI as substrates with a variety of inocula were uniformly unsuccessful; *i.e.*, there was no growth of any organisms.

Similar tests demonstrated that 2,2,4,4,13,13,15,15-octamethylhexadecane (V) and 6-ethyl-2,2,4,4,11,11,-13,13-octamethyltetradecane (VI) were refractory to microbial attack; again enrichment cultures were unsuccessful. Failure of enrichments to yield organisms from sewage, river muds, oil field soils, etc., is significant, since it broadens the scope of the assay to all organisms in these environments. Neopentyl groups thus constitute an insurmountable obstacle to microbial oxidation of alkyl chains[9]; the failure of enrichment cultures further demonstrates that there are no organisms capable of initiating oxidation of phenyl (or cyclohexyl) alkanes at the ring.

Since biodegradation of alkylbenzenesulfonates begins at the alkyl side chain and not the ring,[10] data from the hydrocarbon growth tests are applicable to alkylbenzenesulfonates and, thus, neopentyl or quaternary carbon atoms in the alkyl chains render the detergents nondegradable.

Experimental[11]

Coupling of 1-Chloro-5,5,7,7-tetramethyloctene-2 (I)[12] with Magnesium.—A suspension of magnesium turnings (6.38 g.) in tetrahydrofuran (25 ml.) was treated with a small amount of freshly distilled 1-chloro-5,5,7,7-tetramethyloctene-2 (I). After the reaction had started, additional tetrahydrofuran and chloride (I) were added over a 3-hr. period until approximately 350 ml. of solvent and 106 g. of chloride (I) had been added. The mixture was refluxed for 28 hr. with continued stirring and then decomposed with dilute hydrochloric acid. The organic layer was washed with a saturated sodium chloride solution and dried, and the tetrahydrofuran was removed by distillation. The residual oil was distilled through a Vigreux column: b.p. 115–119° (0.18 mm); yield, 68 g. Gas chromatography (see below) indicated the presence of two components in approximately equal amounts. Several fractionations using a spinning-band column gave pure samples of the two components.

2,2,4,4,13,13,15,15-Octamethyl-6,10-hexadecadiene (II) was a clear colorless liquid, b.p. 112–113° (0.10 mm), n^{20}_D 1.4678, d^{20}_4 0.8245. Infrared spectrum showed medium-to-strong bands at 3.45, 6.80, 7.18, 7.22, 7.34, 8.10, and 10.34 μ.

Anal. Calcd. for $C_{24}H_{46}$: C, 86.14; H, 13.86. Found: C, 86.07; H, 14.16.

8,8,10,10-Tetramethyl-3-(2,2,4,4-tetramethylpentyl)-1,5-undecadiene (III) was a clear, colorless liquid, b.p. 103–104° (0.08 mm.), n^{20}_D 1.4665, d^{20}_4 0.8235. Infrared spectrum showed medium-to-strong bands at 3.45, 6.09, 6.80, 7.17, 7.21, 7.33, 8.07, 10.05, 10.33, and 11.04 μ.

Anal. Calcd. for $C_{24}H_{46}$: C, 86.14; H, 13.86. Found: C, 86.55; H, 13.40.

Using a Perkin-Elmer Model 154 vapor fractometer with a 2-m. Apieson L column, the retention times for II and III were found to be 13.8 and 10.2 min., respectively. Experimental conditions were as follows: oven temperature, 228°; column temperature, 325°; helium pressure, 25 p.s.i.g.; sensitivity, 1; detector voltage, 7; helium flow rate 50 cc./min.

Using ether as a solvent and a reaction time of 48 hr. gave a 24% yield of the two hydrocarbons in which the ratio of III and II was 5:1. The remainder of the distillate was 1-chloro-5,5,7,7-tetramethyloctene-2 (I).

Hydrogenation of the Dienes II and III.—Hydrogenation in acetic acid using platinum oxide as a catalyst and 1800 p.s.i. of hydrogen at 100° gave a quantitative yield of the alkanes V and VI.

2,2,4,4,13,13,15,15-Octamethylhexadecane (V) was a clear, colorless liquid, b.p. 123–124° (0.13 mm.), n^{20}_D 1.4562, d^{20}_4 0.8152. Infrared spectrum showed medium-to-strong bands at 3.45, 6.82, 7.19, 7.23, 7.34, 8.10, and 13.92 μ.

Anal. Calcd. for $C_{24}H_{50}$: C, 85.12; H, 14.88. Found: C, 84.84; H, 14.72.

6-Ethyl-2,2,4,4,11,11,13,13-octamethyltetradecane (VI) was a clear, colorless liquid, b.p. 113–114° (0.13 mm.), n^{20}_D 1.4574, d^{20}_4 0.8176. Infrared spectrum showed medium-to-strong bands at 3.45, 6.82, 7.18, 7.22, 7.34, and 8.10 μ.

Anal. Calcd. for $C_{24}H_{50}$: C, 85.12; H, 14.88. Found: C, 85.42; H, 14.92.

Retention times in v.p.c. analysis using conditions given under the olefins were 15.65 (V) and 12.25 min. (VI), respectively.

Coupling of Phenyllithium with 1-Chloro-5,5,7,7-tetramethyloctene-2 (I).—A stirred solution of 1-chloro-5,5,7,7-tetramethyloctene-2 (I) (106 g.) in dry ether (200 ml.) under nitrogen was treated with a solution of phenyllithium during the course of 90 min. The phenyllithium was prepared by the addition of bromobenzene (81.8 g.) in ether (100 ml.) to lithium (7.3 g.) in ether (100 ml.) The resulting solution was refluxed for an additional

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[9] E. J. McKenna and R. E. Kallio, "Principals and Application in Microbiology," H. Heukelekian and N. Dondero, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964.

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[11] All boiling points are uncorrected. The infrared spectra were obtained using films of undetermined thickness between sodium chloride windows and a Perkin-Elmer Model 21 infrared spectrophotometer.

[12] W. D. Niederhauser, U. S. Patent 2,689,873 (1954).

5 hr. and then decomposed with cold dilute hydrochloric acid. The ether layer after washing with saturated sodium chloride solution and drying gave upon removal of the solvent a yellow oil. Distillation through a Vigreux column gave 1-chloro-5,5,7,7-tetramethyloctene-2 (I, 31.9 g.), b.p. 47–49° (0.15 mm.), and a mixture of 1-phenyl-5,5,7,7-tetramethyl-2-octene (VII) and 1-phenyl-2-(2,2,4,4-tetramethylpentyl)cyclopropane (VIII, 65.2 g.), b.p. 88–92° (0.15 mm.). Gas chromatography using Carbowax column in an F & M 500 chromatograph indicated that these materials were present in a ratio of 60:40. Retention times of 32 and 34 min., respectively, were obtained using a 10-ft. column containing 15% Carbowax 20M on Chromosorb P. Conditions used were a column temperature of 225° and a helium flow rate of 43 cc./min. with a pressure of 40 p.s.i. The sensitivity was 4, the block temperature was 300°, the injection port temperature was 325°, and the injection port voltage was 70 v.

1-Phenyl-2-(2,2,4,4-tetramethylpentyl)cyclopropane (VIII).—The coupling products (27.5 g.) from phenyllithium and 1-chloro-5,5,7,7-tetramethyloctene-2 (I) were refluxed with potassium permanganate (300 g.) in acetone (400 ml.) until gas chromatography indicated the absence of the olefin VII. The permanganate was added in aliquots of 50 g. After the addition of 200 g. of potassium permanganate, the manganese dioxide was removed by filtration and washed with acetone and the oxidation was resumed. The resulting mixture was filtered and washed with acetone and the solvent was removed. The crude product was dissolved in pentane and chromatographed through alumina. Elution with pentane gave 1-phenyl-2-(2,2,4,4-tetramethylpentyl)cyclopropane (VIII, 8.45 g.) which distilled at 90° (0.24 mm.), $n^{20}\text{D}$ 1.5047.

Anal. Calcd. for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.29; H, 11.26.

The infrared spectrum showed a peak at 1028 cm.$^{-1}$ for the cyclopropane ring. The n.m.r. peaks occurred in the aromatic region and between 0.6 and 1.6 p.p.m.

1-Cyclohexyl-5,5,7,7-tetramethyloctane (IX).—The mixture of olefin VII and cyclopropane VIII (16 g.) in glacial acetic acid using a platinum oxide catalyst and hydrogen (1000 p.s.i.) at 75° gave the cyclohexyl derivative IX. Distillation gave a clear, colorless liquid, 13.2 g., b.p. 92–93° (0.32 mm.), $n^{20}\text{D}$ 1.4615, d^{20}_{4} 0.8349. Infrared spectrum showed medium-to-strong bands at 3.52, 6.82, 6.91, 7.19, 7.23, 7.34, and 8.10 μ.

Anal. Calcd. for $C_{18}H_{36}$: C, 85.63; H, 14.37. Found: C, 85.94; H, 13.99.

This sample was analyzed by mass spectrometry, infrared, and gas chromatography techniques by the Atlantic Refining Co. and found to be 100% 1-cyclohexyl-5,5,7,7-tetramethyloctane (IX).

Reduction using the diimide method[13] converted only the olefin VII to the phenylalkane XI. The cyclopropane VIII was not affected.

Coupling of Phenylmagnesium Bromide with 1-Chloro-5,5,7,7-tetramethyloctene-2 (I).—A stirred solution of 0.386 mole of phenylmagnesium bromide in dry benzene (250 ml.) was treated with 39.45 g. of 1-chloro-5,5,7,7-tetramethyloctene-2 (II) in 50 ml. of benzene over the course of 2 hr., and the resulting solution was refluxed for an additional 2 hr. Decomposition of the reaction mixture with 3 *N* hydrochloric acid followed by distillation of the benzene layer gave 37.5 g. of a mixture of phenyloctenes, b.p. 100–114° (1.2 mm). Gas chromatography showed that two compounds were present in amounts of 88 and 12%, respectively. Fractionation through a spinning-band column (40 plates) gave *trans*-1-phenyl-5,5,7,7-tetramethyl-2-octene (VII) as the main component, b.p. 81–82° (0.17 mm.), $n^{20}\text{D}$ 1.4980, d^{20}_{4} 0.8764. Infrared spectrum showed medium-to-strong bands at 3.50, 6.23, 6.68, 7.18, 7.23, 7.34, 8.06, 9.33, 9.73, 10.34, 13.48, and 14.41 μ.

Anal. Calcd. for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.20; H, 11.48.

The minor component, 3-phenyl-5,5,7,7-tetramethyl-1-octene (X), was a clear, colorless liquid, b.p. 82–82.5° (0.37 mm.), $n^{20}\text{D}$ 1.4990, d^{20}_{4} 0.8842. Infrared spectrum showed medium-to-strong bands at 3.45, 6.10, 6.23, 6.70, 6.80, 6.89, 7.18, 7.21, 7.33, 8.05, 9.33, 9.73, 10.05, 11.04, 13.28, and 14.33 μ.

Anal. Calcd. for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.27; H, 11.83.

Using an F & M Model 500 gas chromatograph with a 6-ft. Carbowax 20 M column and the conditions mentioned earlier gave retention times of 12.3 and 8.6 min. for VII and X, respectively.

Diimide Reduction of Phenylalkenes VII and IX.—3-Phenyl-5,5,7,7-tetramethyl-1-octene (IX, 4.7 g.) and 95% hydrazine (1.7 g.) was stirred in absolute ethanol (40 ml.) in the presence of an oxygen and a trace of copper ions at 40° for 40 hr. Addition of water was followed by extraction with ether and gave 4.4 g. of yellowish brown oil. Distillation gave 2,2,4,4-tetramethyl-6-phenyloctane (XII, 3.5 g.) with a retention time of 6.8 min. on a 6-ft. Carbowax 20 M column using an F & M 500 chromatograph. Experimental conditions were as follows: column temperature, 210°; detector block, 325°; injection port variac, 59.5 (300°); column heater variac, 100; helium pressure, 30 p.s.i.g.; helium flow rate, 45 cc./min., bridge power, 150 ma. This compound was a clear, colorless liquid, b.p. 84.85° (0.50 mm.), $n^{20}\text{D}$ 1.4992, d^{20}_{4} 0.8714. The infrared spectrum showed medium-to-strong bands at 3.45, 6.23, 6.70, 6.80, 6.89, 7.18, 7.21, 7.27, 7.33, 8.05, 9.20, 9.71, 13.23, and 14.33 μ.

Anal. Calcd. for $C_{18}H_{30}$: C, 87.73; H, 12.27. Found: C, 87.42; H, 12.28.

The reduction of 1-phenyl-5,5,7,7-tetramethyl-2-octene (VII) was carried out in the same manner but required three such treatments with the third one being carried out at 55°. Distillation gave a homogeneous product (XI) with a retention time of 12.1 min. on a Carbowax column. This compound was a clear, colorless liquid, b.p. 95–96° (0.37 mm.), $n^{20}\text{D}$ 1.4885, d^{20}_{4} 0.8685. The infrared spectrum showed medium-to-strong bands at 3.45, 6.23, 6.68, 6.82, 7.18, 7.23, 7.34, 8.10, 9.31, 9.73, 13.46, and 14.42 μ.

Anal. Calcd. for $C_{18}H_{30}$: C, 87.73; H, 12.27. Found: C, 87.89; H, 12.47.

Acknowledgment.—The authors wish to thank the Atlantic Refining Company for the analyses cited in this paper.

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