[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

Unsymmetrical Tetraalkylmethanes. V.[1] A Study of the Possibility of Rearrangements during Synthesis

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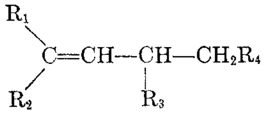
Received January 7, 1960

It has been shown that two alcohols, 5-ethyl-5-methyl-3-decanol and 6-ethyl-6-methyl-4-decanol, which are typical intermediates in a general method of synthesis of tetraalkylmethanes, may be dehydrated over potassium bisulfate to mixtures of olefins without rearrangement of the carbon skeletons.

The previous paper[1] in this series described a general method for the synthesis of tetraalkylmethanes. It was alleged that the dehydration of the intermediate secondary alcohols afforded only mixtures of olefins in which the quaternary carbon atom structure remained intact.

The acid catalyzed rearrangements of a number of related materials have been described,[4] and Mosher and Cox have shown that in the dehydration of 4,4-dimethyl-3-ethyl-2-pentanol, 43% of 4,4-dimethyl-3-ethyl-2-pentene and 57% of 2,4-dimethyl-3-ethyl-3-pentene are obtained. They explained the formation of the latter as due to a 1,3-shift of a methyl group rather than to a series of 1,2-rearrangements.

The present study was undertaken to investigate the possibility of skeletal rearrangements of the initially mentioned carbinols, of the general structure $R_1R_2R_3CCH_2CHOHCH_2R_4$, during dehydration by means of potassium bisulfate. If rearrangements had occurred, mixtures of olefins of the type



$$(R_1)(R_2)C{=}CH{-}CH(R_3){-}CH_2R_4$$

where R_1, R_2 and R_3 may occupy either carbon 1 or 3 would have resulted, which obviously would have led to mixtures of hydrocarbons which were not tetraalkylmethanes.

Since the tetraalkylmethane, 5-ethyl-5-methyldecane, had been prepared[5] previously by a sequence of reactions which did not involve any known rearrangements, it was felt that a comparison of its physical properties with those of the material which would result from the general method of synthesis of tetraalkylmethanes[1] should afford evidence of rearrangements in the process. The latter may be varied so that alkyl groupings of the final hydrocarbons can be introduced in different sequences. Accordingly, it was decided to synthesize the 5-ethyl-5-methyldecane from both 5-ethyl-5-methyl-3-decanol (Route A) and 6-ethyl-6-methyl-4-decanol (Route B). Since the structures of carbonium ions formed during the dehydration of these carbinols would be different, the end products of the reactions would be expected to be dissimilar if rearrangements took place.

To obtain still additional evidence, the 5-ethyl-5-methyldecane was synthesized not only from 2-(β-cyanoethyl)2-ethylhexanol[5] (Route C), but also by two variations of the mixed-Kolbe reaction. In the first of these (Route D), 3-ethyl-3-methyloctanoic acid was coupled with butyric acid, while in the second method (Route E), 4-ethyl-4-methyloctanoic acid was caused to react with butyric acid also to give the desired hydrocarbon directly.

The by-products of the mixed-Kolbe reactions, 6,9-diethyl-6,9-dimethyltetradecane and 5,10-diethyl-5,10-dimethyltetradecane respectively, were of interest since they contain two quaternary carbon atom systems. They are liquids with solidification points below −60°, and have infrared spectra almost identical with that of 5-ethyl-5-methyldecane.

The values for specific gravity, viscosity, refractive index, boiling point, and melting point of the five independently synthesized samples of 5-ethyl-5-methyldecane were all within experimental error of each other, and the infrared spectra appeared to be identical. Samples from Routes A, B, and D were examined by gas chromatography and gave single sharp peaks in their spectra at the same points.

Gas chromatographic studies of 5-ethyl-5-methyl-2(3)-decene (from Route A) and 6-ethyl-6-methyl-3(4-)-decene (from Route B) showed only three distinct peaks in each of their spectra. These apparently were the *cis* and *trans*-beta and *trans*-alpha olefins, with respect to the quaternary carbon atoms. The lack of *cis*, alpha olefins might be explained on the basis of the fact that models of these compounds reveal that the *cis* configurations are

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[1] Paper IV. N. Rabjohn, L. V. Phillips, and R. J. DeFeo, *J. Org. Chem.*, **24**, 1964 (1959).

[2] Abstracted in part from the Ph.D. thesis of R. J. DeFeo, 1958.

[3] Lubrizol Foundation Fellow, 1956–58.

[4] For leading references see W. A. Mosher and J. C. Cox, Jr., *J. Am. Chem. Soc.*, **72**, 3701 (1950); D. J. Cram in M. S. Newman's *Steric Effects in Organic Chemistry*, John Wiley and Sons, New York, 1956, Chap. 5.

[5] N. Rabjohn and H. H. Farmer, *J. Org. Chem.*, **23**, 522 (1958).

highly hindered structures, which suggests that they might be formed with considerable difficulty.

The preceding data support strongly the quaternary carbon atom structures which were assigned to the tetraalkylmethanes described in the previous study.[1]

EXPERIMENTAL[6]

Materials. (a) *Ethyl 2-cyano-3-ethyl-3-methylheptanoate* was prepared from ethyl 2-cyano-3-methyl-2-pentenoate[7] and *n*-butylmagnesium bromide in the presence of cuprous iodide in 70% yield;[8] b.p. 158–160°/17 mm., n_D^{25} 1.4435; lit.,[9] b.p. 160–162°/21 mm., n_D^{25} 1.4435.

(b) *Ethyl 2-cyano-3-ethyl-3-methyloctanoate* was obtained (76%) in a similar fashion from ethyl 2-cyano-3-ethyl-2-pentenoate and *n*-amylmagnesium bromide; b.p. 168–170°/17 mm., n_D^{25} 1.4446; lit.,[9] b.p. 168–170°/20 mm., n_D^{25} 1.4449.

(c) *3-Ethyl-3-methylheptanenitrile* was synthesized in 82% yield by the hydrolysis and decarboxylation of ethyl 2-cyano-3-ethyl-3-methylheptanoate; b.p. 105–107°/17 mm., n_D^{25} 1.4332; lit.,[9] b.p. 112–113°/22 mm., n_D^{25} 1.4328.

(d) *3-Ethyl-3-methyloctanenitrile* was prepared in an analogous manner from ethyl 2-cyano-3-ethyl-3-methyloctanoate; yield, 56%, b.p. 119–121°/17 mm., n_D^{25} 1.4354; lit.,[9] b.p. 127–130°/23–25 mm., n_D^{25} 1.4358.

(e) *3-Ethyl-3-methyloctanoic acid* was prepared in 96% yield by the hydrolysis of 3-ethyl-3-methyloctanenitrile with potassium hydroxide in diethylene glycol; b.p., 158–159°/15 mm., n_D^{25} 1.4427; lit.,[9] b.p. 157–160°/15 mm., n_D^{25} 1.4426.

(f) *4-Ethyl-4-methyloctanoic acid* was obtained from 2-(β-cyanoethyl)-2-ethylhexaldehyde in 73% yield[5]; b.p. 132–135°/2 mm., n_D^{25} 1.4456.

5-Ethyl-5-methyl-3-decanone. A Grignard reagent was prepared from 24.3 g. (1 g.-atom) of magnesium and 109 g. (1 mole) of ethyl bromide in 200 ml. of dry ether. To this was added 91 g. (0.54 mole) of 3-ethyl-3-methyloctanenitrile in 100 ml. of ether. There was obtained 92 g. (86%) of ketone which boiled at 127–129°/15 mm.; n_D^{25} 1.4371.

Anal. Calcd. for $C_{13}H_{26}O$: C, 78.72; H, 13.21. Found: C, 78.80; H, 13.21.

5-Ethyl-5-methyl-3-decanol. The reduction of 84 g. (0.42 mole) of 5-ethyl-5-methyl-3-decanone with 19 g. (0.5 mole) of lithium aluminum hydride was carried out in the usual manner. There resulted 82 g. (97%) of alcohol; b.p. 131–132°/15 mm., n_D^{25} 1.4470.

Anal. Calcd. for $C_{13}H_{28}O$: C, 77.93; H, 14.08. Found: C, 77.92; H, 14.13.

5-Ethyl-5-methyl-2(3)-decene. A mixture of 77 g. (0.38 mole) of 5-ethyl-5-methyl-3-decanol and 10 g. (0.07 mole) of potassium bisulfate was heated under reduced pressure at 150–160° for 24 hr. After working up the reaction mixture in the usual way, there was obtained 60 g. (87%) of olefins; b.p. 101–103°/15 mm., n_D^{25} 1.4390.

Anal. Calcd. for $C_{13}H_{26}$: C, 85.63; H, 14.37. Found: C, 85.59; H, 14.21.

6-Ethyl-6-methyl-4-decanone. A Grignard reagent was prepared from 30.4 g. (1.25 g.-atoms) of magnesium and 154 g. (1.25 moles) of *n*-propyl bromide in 250 ml. of dry ether. To this was added 113 g. (0.74 mole) of 3-ethyl-3-methylheptanenitrile. There was obtained 130 g. (89%) of ketone; b.p. 124–126°/15 mm., n_D^{25} 1.4363.

Anal. Calcd. for $C_{13}H_{26}O$: C, 78.72; H, 13.21. Found: C, 78.85; H, 13.00.

6-Ethyl-6-methyl-4-decanol. A mixture of 19 g. (0.5 mole) of lithium aluminum hydride and 114 g. (0.58 mole) of 6-ethyl-6-methyl-4-decanone was caused to react in the usual manner to give 105 g. (91%) of the desired carbinol; b.p. 129–131°/15 mm., n_D^{25} 1.4463.

Anal. Calcd. for $C_{13}H_{28}O$: C, 77.93; H, 14.09. Found: C, 77.92; H, 14.13.

6-Ethyl-6-methyl-3(4)-decene. The dehydration of 100 g. (0.5 mole) of 6-ethyl-6-methyl-4-decanol with 10 g. (0.07 mole) of potassium bisulfate afforded 82 g. (90%) of olefins; b.p. 99–100°/15 mm., n_D^{25} 1.4380.

Anal. Calcd. for $C_{13}H_{26}$: C, 85.63; H, 14.37. Found: C, 85.52; H, 14.18.

5-Ethyl-5-methyldecane. Method A. The hydrogenation of 54 g. (0.29 mole) of 5-ethyl-5-methyl-2(3)-decene in 75 ml. of methylcyclohexane with 12 g. of Raney nickel catalyst at 180° and 3200 p.s.i. of hydrogen yielded 45 g. of alkane; b.p. 102–103°/15 mm., n_D^{25} 1.4290; lit.,[5] b.p. 101–103°/18 mm., n_D^{25} 1.4291.

Method B. The above procedure was repeated using 37 g. (0.2 mole) of 6-ethyl-6-methyl-3(4)-decene, 10 g. of Raney nickel catalyst and 75 ml. of methylcyclohexane. There was obtained 31 g. (84%) of an alkane which distilled at 102–103°/15 mm., n_D^{25} 1.4290.

Method C. A mixture of 148 g. (0.75 mole) of 6-ethyl-6-methyl-3-decanone, 105 ml. (1.8 moles) of 85% hydrazine hydrate, 700 ml. of diethylene glycol, 175 g. (2.6 moles) of 85% potassium hydroxide and 150 ml. of water was caused to react in the previously described manner.[5] There was obtained 44 g. (32%) of the desired hydrocarbon; b.p. 101–103°/15 mm., n_D^{25} 1.4291.

Method D. A mixture of 119 g. (0.64 mole) of 3-ethyl-3-methyloctanoic acid, 352 g. (4 moles) of *n*-butyric acid, 500 ml. of petroleum ether (b.p. 60–80°), 2 g. of sodium, which had been dissolved in about 100 ml. of methanol, and sufficient methanol to bring the volume to 1900 ml., was electrolyzed at approximately 5.5 amp. for 29 hr. under the conditions described previously.[10] At the end of this time, the solution was light tan with no odor of butyric acid. Approximately 1 l. of solvent was removed and 132 g. (2 moles) of 85% potassium hydroxide in 500 ml. of water was added. Distillation was continued until another 1 l. of distillate had been collected. At this point, 250 ml. of water and 500 ml. of petroleum ether (b.p. 60–70°) were added, and the layers were separated. The aqueous layer was extracted twice with 500-ml. portions of a petroleum ether-ether mixture, the oil layers were combined, washed twice with water, dried over anhydrous sodium sulfate, and distilled to remove solvent.

The residue was distilled, and the portion which boiled at 95–105°/15 mm. was collected. It was washed three times with 100-ml. portions of cold concd. sulfuric acid and taken up in petroleum ether. The solution was washed with water, 10% sodium bicarbonate solution, water, and dried over anhydrous sodium sulfate. After removing the solvent, the residue was distilled to give 62 g. (51%) of an alkane which boiled at 100–101°/14 mm., n_D^{25} 1.4290.

The high-boiling residue from the distillation of the original reaction mixture was distilled, and that portion, 7 g., which boiled at 170–180°/15 mm. was taken up in petroleum ether, washed three times with concd. sulfuric acid, and treated then as above. The residue was distilled to yield 4 g. of the dicoupling product; b.p. 176–178°/15 mm., n_D^{25} 1.4481.

Anal. Calcd. for $C_{20}H_{42}$: C, 85.02; H, 14.98. Found: C, 84.77, H, 14.70.

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(6) All melting points and boiling points are uncorrected. The carbon-hydrogen analyses were performed by Mr. Arthur Mendel of this laboratory and by Drs. Weiler and Strauss, Oxford, England.

(7) A. C. Cope, C. M. Hofmann, C. Wyckoff, and E. Hardenberg, *J. Am. Chem. Soc.*, **63**, 3452 (1941).

(8) N. Rabjohn, L. V. Phillips, and R. J. DeFeo, *J. Org. Chem.*, **24**, 1964 (1959).

(9) F. S. Prout, *J. Am. Chem. Soc.*, **74**, 5915 (1952).

(10) N. Rabjohn and H. H. Farmer, *J. Org. Chem.*, **24**, 359 (1959).

Method E. The preceding procedure was followed. A mixture of 119 g. (0.64 mole) of 4-ethyl-4-methyloctanoic acid, 352 g. (4 moles) of *n*-butyric acid, 500 ml. of petroleum ether (b.p. 60–70°), 2 g. of sodium, dissolved in about 100 ml. of methanol, and sufficient methanol to bring the volume to 1900 ml., was electrolyzed at about 5 amp. for 21 hr. There was obtained 29 g. (25%) of an alkane which boiled at 101–103°/15 mm., n_D^{25} 1.4291.

The high-boiling residue was treated as above to give 4 g. of coupling product, b.p. 182–184°/15 mm., n_D^{25} 1.4480.

Anal. Calcd. for $C_{20}H_{42}$: C, 85.02, H, 14.98. Found: C, 85.31; H, 14.87.

Physical constants of 5-ethyl-5-methyldecane. In addition to the constants given above, the following values were determined for each of the five samples of the hydrocarbon: sp. gr. 20/4, 0.7705–0.7707; solidification point, −80°; viscosity in centistokes, 1.71 (100° F.) 1.10 (115° F.), and 0.77 (210° F.); and viscosity index 92.5.

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[CONTRIBUTION FROM THE JOHN STUART RESEARCH LABORATORIES OF THE QUAKER OATS CO.]

2-Methoxy-5-methylfuran: Preparation, Properties, and Proof of Structure[1]

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Received January 7, 1960

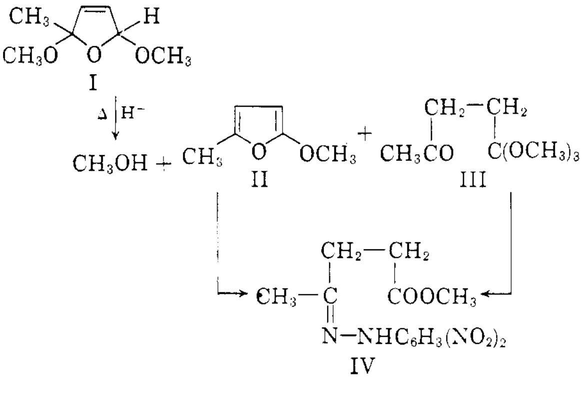
2-Methoxy-5-methylfuran (II) has been prepared in 68% yield by acid-catalyzed pyrolysis of 2,5-dimethoxy-2,5-dihydro-2-methylfuran. Other products obtained in the pyrolysis are methanol (64%), trimethyl ortholevulinate (III) (5–6%) and an unidentified polymer (*ca.* 10% by weight). The structure of II was confirmed by the following sequence of reactions: II + maleic anhydride ⟶ 3-methyl-6-methoxy-3,6-*endo*-oxo-1,2,3,6-tetrahydrophthalic anhydride (V) (84%) ⟶ 3-methyl-6-methoxyphthalic anhydride (VI) (48%) ⟶ the known 4-methoxybenzene-1,2,3-tricarboxylic acid (VII) (85%).

Samples of 2,5-dimethoxy-2,5-dihydro-2-methylfuran (I), prepared by electrolytic methoxylation of 2-methylfuran according to a modification of the method due to Clauson-Kaas *et al.*[2] (ammonium bromide electrolyte), have been found to contain traces of halogen (Beilstein test). Redistillation of stored specimens of I has invariably given rise to small amounts of methanol and a compound, boiling at *ca.* 130°, which from its physical properties and odor appeared to be methyl furfuryl ether.

Finding it practically impossible to explain the formation of methyl furfuryl ether from either methylfuran or I under the conditions of the aforementioned methoxylation or redistillation, we undertook to investigate the true structure of this substance. However, before tackling this problem, it seemed desirable to prepare deliberately the unknown compound in reasonable yield.

On the assumption that hydrogen halide, having its origin in the halogen contamination, was effecting the observed transformation of I, we tested catalytic amounts of strong acids (hydrogen chloride, *p*-toluenesulfonic acid, etc.) in a series of preliminary experiments. Subsequently, the unknown compound (II) was obtained in 68% yield together with a second product (III), by incremental addition of I to hot (*ca.* 250°) dimethyl phthalate containing a few drops of concentrated sulfuric acid, while removing the volatile products continuously by entraining in a gentle stream of nitrogen.

Analysis provided an empirical formula of $C_5H_5O(OCH_3)$, and the infrared spectrum revealed a furan structure for the compound. It was distinguished from the isomeric methyl furfuryl ether by facile formation of an adduct (V) with maleic anhydride, m.p. 111–112.5°, (84.3% yield). Methyl furfuryl ether sluggishly forms a maleic anhydride adduct melting at 97°.[3] From the orientation of substituents in the precursor (I), and the formation of methyl levulinate 2,4-dinitrophenylhydrazone (IV) on treatment with the hydrazine reagent, the structure of the compound was almost unequivocally established as 2-methoxy-5-methylfuran (II).



Further confirmation of the identity of II was achieved by the following sequence of reactions, culminating in 4-methoxybenzene-1,2,3-tricarboxylic acid (VII) which has been described.[4]

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(1) This article, in its entirety, was presented as a portion of a paper of broader scope at the 127th National ACS Meeting in Cincinnati, Ohio, March 1955.

(2) N. Clauson-Kaas, F. Limborg, and P. Dietrich, *Acta Chem. Scand.*, **6**, 545 (1952).

(3) M. G. Van Campen and J. R. Johnson, *J. Am. Chem. Soc.*, **55**, 430 (1933).

(4) D. Gardner, J. F. Grove, and D. Ismay, *J. Chem. Soc.*, 1817 (1954).