TABLE III

SUMMARY OF PROPERTIES

| Compound | M.p., °C. | Analyses, % | | |
|---|---|---|---|---|
| | | | Calcd. | Found |
| $CF_3(CF_2)_3COOEt$ | ...[a] | F, | 58.5 | 58.2 |
| $CF_3CF_2CONH_2$ | 95–96 | F, | 58.3 | 58.3 |
| $CF_3CF_2CONHBr$ | 69 | Br, | 30.03 | 29.84 |
| $CF_3(CF_2)_2CONHBr$ | 80 | Br, | 27.37 | 27.43 |
| $CF_3(CF_2)_3CONHBr$ | 87 | Br, | 23.35 | 23.36 |
| *o*-$BrC_6H_5NHCOCF_2CF_3$ | 126 | Br, | 24.65 | 24.43 |
| | | N, | 4.35 | 4.32 |
| *o*-$BrC_6H_5NHCOCF_2CF_2CF_3$ | 139 | Br, | 21.36 | 21.09 |
| | | N, | 3.74 | 3.82 |
| *o*-$BrC_6H_5NHCOCF_2CF_2CF_2CF_3$ | 133 | Br, | 18.84 | 19.02 |
| | | N, | 3.30 | 3.29 |

[a] B.p. 110° (627 mm.), $n^{20}_{\rm D}$ 1.3060.

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## Unsymmetrical Tetraalkylmethanes. I. Coupling of Alkylmagnesium Bromides with Tertiary Bromides[1]

BY NORMAN RABJOHN AND M. J. LATINA[2]

RECEIVED NOVEMBER 20, 1953

The coupling reaction of Grignard reagents with tertiary alkyl bromides was investigated as a means of obtaining unsymmetrical tetraalkylmethanes which contain a minimum of sixteen carbon atoms. A number of other investigators[3,4] have employed this procedure, but have worked with compounds of lower carbon content and apparently have made only quaternary hydrocarbons in which at least two of the alkyl groups are similar.

We have found, in agreement with others, that the coupling process is not clean-cut and the yields of the desired hydrocarbons are low. Two $C_{16}$-hydrocarbons were prepared in the present study in yields of 10 and 15% and a $C_{20}$-hydrocarbon, 5-ethyl-5-octyldecane, was obtained in 16% yield. However, attempts to prepare a $C_{24}$- and a $C_{30}$-hydrocarbon by coupling *n*-dodecylmagnesium bromide with 5-ethyl-5-bromodecane and 7-butyl-7-bromotetradecane, respectively, failed. Treatment of 5-ethyl-5-bromodecane with *n*-propyllithium also led to negative results.

The solidification points of the three unsymmetrical tetraalkylmethanes which were prepared were found to be in the range of −70 to −75°.

### Experimental[5]

**Tertiary Alcohols.**—These compounds were synthesized in 40–60% yields in the typical fashion from the appropriate Grignard reagents and ketones. Ethyl-*n*-propyl-*n*-butylcarbinol was obtained from the reaction of *n*-propylmagnesium bromide with ethyl *n*-butyl ketone; b.p., 101–103° (20 mm.), $n^{19}_{\rm D}$ 1.4385; lit.[6] b.p., 88.8–89.6° (15 mm.), $n^{20}_{\rm D}$ 1.4378. Methylethyl-*n*-amylcarbinol was prepared from ethylmagnesium bromide and methyl *n*-amyl ketone; b.p. 100–102° (30 mm.), $n^{20}_{\rm D}$ 1.4321; lit.[7] b.p. 80–81° (15 mm.), $n^{20}_{\rm D}$ 1.4315. Ethyl-*n*-butyl-*n*-amylcarbinol resulted from the condensation of *n*-amylmagnesium bromide with ethyl *n*-butyl ketone; b.p. 119–120° (20 mm.), $n^{18}_{\rm D}$ 1.4430; lit.[8] $n^{20}_{\rm D}$ 1.4424. *n*-Butyl-*n*-hexyl-*n*-heptylcarbinol was prepared by treating *n*-butyl *n*-hexyl ketone with *n*-heptylmagnesium bromide in the usual manner. The product was isolated in 66% yield, b.p. 157–159° (1 mm.), $n^{19}_{\rm D}$ 1.4520.

*Anal.* Calcd. for $C_{18}H_{38}O$: C, 79.92; H, 14.16. Found: C, 79.90; H, 14.05.

**Tertiary Bromides.**—The bromides were prepared essentially by the procedure of Halse[9] as modified by Whitmore and Williams[7] for tertiary chlorides. The tertiary alcohols were saturated with hydrogen bromide at ice-bath temperature and the resulting bromides were separated from the water which had formed. Excess hydrogen bromide was removed on a water aspirator and the products were washed with an equal volume of concentrated sulfuric acid. They were allowed to stand over anhydrous sodium carbonate and sodium sulfate in a refrigerator for 12–15 hours. After removing the drying agents, the tertiary bromides resulted in yields of 70–80%. Since the bromides could not be distilled without decomposition, they were used without further purification. The following bromides were obtained in the above manner: (a) 5-ethyl-5-bromodecane, $n^{20}_{\rm D}$ 1.4650. *Anal.* Calcd. for $C_{12}H_{25}Br$: C, 57.82; H, 10.11. Found: C, 57.81; H, 10.20.

(b) 3-Methyl-3-bromoöctane, $n^{20}_{\rm D}$ 1.4545. *Anal.* Calcd. for $C_9H_{19}Br$: C, 52.20; H, 9.25. Found: C, 52.28; H, 9.46.

(c) 4-Ethyl-4-bromoöctane, $n^{20}_{\rm D}$ 1.4635. *Anal.* Calcd. for $C_{10}H_{21}Br$: C, 54.30; H, 9.57. Found: C, 54.30; H, 9.65.

7-Butyl-7-bromotetradecane could not be prepared by this process since the corresponding carbinol solidified at ice-bath temperature. Accordingly, hydrogen bromide was introduced into the carbinol at room temperature, and the resulting product failed to give satisfactory analytical data.

**Coupling of Grignard Reagents with the Tertiary Bromides.**—The method of preparation of 6-ethyl-6-butyltetradecane is illustrative and similar to that of Campbell and Eby.[4] *n*-Octylmagnesium bromide was prepared from 24 g. (1 gram atom) of magnesium, 193 g. (1.0 mole) of *n*-octyl bromide and 500 ml. of anhydrous ether. The bromide was added over a period of 2 hours and the reaction mixture was stirred for an additional hour. The ether was removed by distillation and the temperature of the reaction mixture was raised to 140°; then 200 g. (0.8 mole) of 5-ethyl-5-bromodecane was added within 2 hours. A white slurry formed and stirring became difficult. The mixture was heated for 4 more hours and allowed to stand overnight. Water was added slowly with cooling and stirring, followed by 10% hydrochloric acid solution until all solids had dissolved. The mixture was extracted several times with ether and the combined extract was washed with water, 10% sodium bicarbonate solution, again with water and dried over anhydrous sodium sulfate. The ether was removed by distillation and the residual oil was distilled from a Clark flask. The higher boiling fraction was purified through a medium bore Todd column to give 38 g. (16%) of a colorless liquid; b.p. 179–183° (18 mm.), $n^{20}_{\rm D}$ 1.4480, $d^{20}_4$ 0.799; *MR* calcd. 94.6, found 94.7.

*Anal.* Calcd. for $C_{20}H_{42}$: C, 85.02; H, 14.98. Found: C, 85.16; H, 14.86.

The sixteen-carbon hydrocarbon, 5-ethyl-5-propyldecane, was obtained by coupling *n*-hexylmagnesium bromide with 5-ethyl-5-bromoöctane in the above manner. There was isolated 39 g. (15%) of a colorless liquid, b.p. 136–138° (20 mm.), $n^{20}_{\rm D}$ 1.4420, $d^{20}_4$ 0.788; *MR* calcd. 76.1, found 76.0.

*Anal.* Calcd. for $C_{16}H_{34}$: C, 84.86; H, 15.14. Found: C, 85.08; H, 15.27.

In an analogous fashion, 18 g. (10%) of 6-methyl-6-ethyltridecane was obtained from the reaction of 3-methyl-3-bromoöctane with *n*-heptylmagnesium bromide. The colorless liquid boiled at 139–142° (15 mm.), $n^{20}_{\rm D}$ 1.4418, $d^{20}_4$ 0.780; *MR* calcd. 76.1, found 76.8.

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(1) This work was supported in part by a grant from the Lubrizol Corporation.

(2) From the Ph.D. thesis of M. J. Latina, 1953.

(3) C. R. Kinney and W. L. Spliethoff, *J. Org. Chem.*, **14**, 71 (1949).

(4) K. C. Campbell and L. T. Eby, THIS JOURNAL, **62**, 1798 (1940).

(5) The semimicro analyses were performed by Mr. P. D. Strickler and Mr. Y. N. Lee.

(6) F. C. Whitmore and H. M. Woodburn, THIS JOURNAL, **55**, 361 (1933).

(7) F. C. Whitmore and F. E. Williams, *ibid.*, **55**, 406 (1933).

(8) O. R. Quayle and K. O. Smart, *ibid.*, **66**, 935 (1944).

(9) O. M. Halse, *J. prakt. Chem.*, [2] **89**, 451 (1914).

*Anal.* Calcd. for $C_{16}H_{34}$: C, 84.86; H, 15.14. Found: C, 84.33; H, 14.56.

When 155 g. (0.62 mole) of 5-ethyl-5-bromodecane was caused to react with *n*-dodecylmagnesium bromide, prepared from 200 g. (0.8 mole) of *n*-dodecyl bromide and 19.2 g. (0.8 gram atom) of magnesium, the following fractions were obtained on distillation: 200 ml., b.p. 95–125° (15 mm.); 10 ml., b.p. 125–235° (15 mm.); and 30 ml., b.p. 235–241° (15 mm.). The latter solidified on cooling and after crystallization from acetone melted at 49–50°. The literature[10] reports the melting point of tetracosane to be 51°.

Similar results were obtained in an attempt to condense *n*-dodecylmagnesium bromide with crude 7-butyl-6-bromotetradecane. The major product isolated distilled at 132–133° (1 mm.), $n^{20}D$ 1.4460, and presumably consisted of octadecenes. In addition, the residue from the distillation solidified and yielded a compound which melted at 49–50° after crystallization from acetone.

Treatment of a solution of *n*-propyllithium, prepared from 0.7 g. (0.1 gram atom) of lithium, 6.2 g. (0.05 mole) of *n*-propyl bromide and 30 ml. of anhydrous ether, with 13 g. (0.05 mole) of 5-ethyl-5-bromodecane gave only a mixture of low-boiling compounds.

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(10) J. H. Hildebrand and A. Wachter, THIS JOURNAL, **51**, 2487 (1929).

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## Pyrolysis of the Windaus Acid

BY RICHARD B. TURNER

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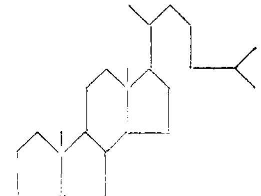
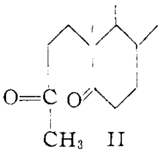
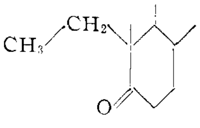
Some time ago, in connection with experiments directed toward the preparation of labeled cholestenone,[1] the barium salt of the Windaus acid (I) was subjected to pyrolysis in the presence of barium acetate in the hope that the diketone II might be obtained. There was formed instead, in 45% yield, a neutral monoketone, m.p. 55–55.5°, $[\alpha]_D$ +9.5° (chloroform), for which structure III was proposed. The same product resulted from pyrolysis of the barium salt of I in the absence of added barium acetate. Analytical values for carbon and hydrogen (found: C, 83.40; H, 12.17) were satisfactory for the formula $C_{25}H_{44}O$ (Calcd.: C, 83.26; H, 12.30), and the substance furnished an oxime, m.p. 142.5–143° (*Anal.* Calcd. for $C_{25}H_{45}ON$: C, 79.94; H, 12.07; N, 3.73. Found: C, 79.66; H, 11.82; N, 4.07.) Apart from routine examination of the infrared spectrum, the substance was not further investigated.



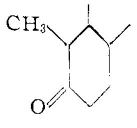
I



II



III



IV

More recent consideration of this product and of its mode of formation suggested that it might alternatively be formulated as IV, previously obtained as an oil by Inhoffen and Huang-Minlon[2] from the oxidation of 1,4-cholestadien-3-one. The carbon and hydrogen content of IV (C, 83.07; H, 12.12) and of the corresponding oxime (C, 79.48; H, 11.89; N, 4.03) is such that a clear choice between structures III and IV cannot be made on the basis of the available analytical data.

In 1951, a crystalline, though somewhat impure, preparation (m.p. 42°) of the Inhoffen ketone was obtained in the Oxford laboratories by Dr. R. P. A. Sneeden.[3] Through the courtesy of Sir Robert Robinson a more highly purified specimen, m.p. 52°, has recently been made available for direct comparison with the ketone derived from I. The two samples give no mixed melting point depression and show identical absorption in the infrared. The identity of the two substances was further confirmed by comparison of the corresponding semicarbazones, m.p. 224–225° dec.[2] Pyrolysis of the barium salt of I thereby constitutes an additional example of reversal of the Michael reaction.[4]

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(1) R. B. Turner, THIS JOURNAL, **72**, 579 (1950).

(2) H. H. Inhoffen and Huang-Minlon, *Ber.*, **72**, 1686 (1939).

(3) *Cf.* A. R. Pinder and R. Robinson, *Nature*, **167**, 484 (1951).

(4) NOTE ADDED IN PROOF.—A discussion of the cleavage of 1,5-dicarbonyl compounds and a conversion somewhat analogous to the one described above have now been reported by S. A. Julia, A. Eschenmoser, H. Heusser and N. Tarköy, *Helv. Chim. Acta*, **36**, 1885 (1953).

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## A New Method of Preparation for Alkoxysilanes*

BY LEONARD M. SHORR

RECEIVED OCTOBER 29, 1953

This paper concerns itself with a new procedure for the alkoxylation of halosilanes which is rapid, efficient and does not yield hydrogen halide by-products. Ethyl orthoformate has been found to react with halosilanes in the manner

$$\equiv Si—X + HC(OR)_3 \longrightarrow \equiv Si—OR + RX + HCOOR$$

Presumably, other orthoesters would behave similarly. Chlorosilanes may be ethoxylated more easily than fluorosilanes.

This reaction is similar to that of ethyl orthoformate with hydrogen chloride[1,2]

$$HCl + HC(OC_2H_5)_3 \longrightarrow HOC_2H_5 + C_2H_5Cl + HCOOC_2H_5$$

In the usual preparation of alkoxysilanes employing the reaction of alcohols with variously substituted halosilanes, difficulties are often incurred because the hydrogen halides formed may react deleteriously in several side reactions. In the presence of an alcohol it may cause disproportionation with a different alkoxy group already attached to the silicon atom[3]; it may react with alcohol to produce an alkyl halide and sufficient water to cause

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* Contribution from the Multiple Fellowship at Mellon Institute sustained by the Corning Glass Works and Dow Corning Corporation.

(1) M. Arnhold, *Ann.*, **240**, 195 (1887).

(2) W. Lippert, *ibid.*, **276**, 177 (1893).

(3) D. F. Peppard, W. G. Brown and W. C. Johnson, THIS JOURNAL, **68**, 70 (1946).