[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY, THE UNIVERSITY OF CHICAGO]

Reactions of Atoms and Free Radicals in Solution. XL. Reaction of Grignard Reagents with 1-Bromooctane in the Presence of Cobaltous Bromide

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The reaction of Grignard reagents with 1-bromooctane in the presence of cobaltous bromide has been employed to study the interaction of octyl radicals with radicals of differing reactivities. On the basis of yields of octenes and octane, the radicals investigated can be arranged in the following order of decreasing reactivity: methyl, isopropyl, *tert*-butyl. Phenylmagnesium bromide reacts to give an approximately equimolar mixture of octene and octane, which suggests that phenyl radicals do not participate in this reaction. The C_8 olefins produced in these reactions consist of 1- and 2-octene. Formation of the latter may be due to isomerization of 1-octene.

Alkyl free radicals in solution may react in different ways. (A) They may attack the solvent. (B) They may donate a hydrogen atom to another component of the reaction system (which may be another free radical). Such a reaction between two like free radicals is termed disproportionation. (C) They may combine with other free radicals including those of their own kind.

It has been shown that short-lived free radicals differ greatly in their relative reactivities, and an ordered series has been proposed.[1] The free methyl radical is so highly reactive that in most systems it will abstract a hydrogen or halogen atom from a donor molecule. Thus, this radical is termed an oxidant. On the other hand, the *tert*-butyl radical is far less reactive in this sense and may be considered a reductant in view of its tendency to donate a hydrogen atom to another component of the reaction system. Intermediate in reactivity is the isopropyl radical, which may act as either oxidant or reductant.

The present study was undertaken to explore the possibility of comparing free radical reactivities on a more quantitative basis. If two different radicals, R· and R′·, could be caused to interact (reaction B, above), the nature of the reaction products should indicate relative oxidizing or reducing tendencies. In the case of alkyl radicals, an oxidant would be expected to abstract a hydrogen atom from a reductant, leading to the formation of a saturated hydrocarbon derived from the oxidant and an olefin derived from the reductant. Furthermore, various free radicals might be compared on the basis of reaction with a suitable standard free radical.

A convenient method of generating free radicals for this purpose is the reaction of Grignard reagents with alkyl halides in the presence of cobaltous bromide (or other suitable transition metal salt). The course of this reaction has been represented in the following manner.[2]

$$\mathrm{RMgX} + \mathrm{CoX_2} \longrightarrow \mathrm{RCoX} + \mathrm{MgX_2} \qquad (1)$$

$$\mathrm{RCoX} \longrightarrow \mathrm{R\cdot} + \mathrm{CoX} \qquad (2)$$

$$\mathrm{CoX} + \mathrm{R'X} \longrightarrow \mathrm{R'\cdot} + \mathrm{CoX_2} \qquad (3)$$

Wilds and McCormack[3] have proposed an alternate path involving metallic cobalt as the reactive intermediate rather than univalent cobalt (as CoX).

$$2\mathrm{RMgX} + \mathrm{CoX_2} \longrightarrow \mathrm{CoR_2} + 2\mathrm{MgX_2} \qquad (4)$$

$$\mathrm{CoR_2} \longrightarrow \mathrm{Co} + 2\mathrm{R\cdot} \qquad (5)$$

$$\mathrm{Co} + 2\mathrm{R'X} \longrightarrow \mathrm{CoX_2} + 2\mathrm{R'\cdot} \qquad (6)$$

Of the many possible reactions which the free radicals R· and R′· may undergo, only the following interactions are dealt with in the present study.

$$2\mathrm{R\cdot} \longrightarrow \mathrm{R}_{(+\mathrm{H})} + \mathrm{R}_{(-\mathrm{H})} \qquad (7)$$

$$2\mathrm{R'\cdot} \longrightarrow \mathrm{R'}_{(+\mathrm{H})} + \mathrm{R'}_{(-\mathrm{H})} \qquad (8)$$

$$\mathrm{R\cdot} + \mathrm{R'\cdot} \longrightarrow \mathrm{R}_{(+\mathrm{H})} + \mathrm{R'}_{(-\mathrm{H})} \qquad (9a)$$

$$\mathrm{R\cdot} + \mathrm{R'\cdot} \longrightarrow \mathrm{R'}_{(+\mathrm{H})} + \mathrm{R}_{(-\mathrm{H})} \qquad (9b)$$

Reactions 7 and 8 lead to formation of equimolar amounts of paraffin and olefin by disproportionation of R· and of R′·. The yields of products from reaction 9, however, depend on the relative reactivities of the two radicals. If R· is the stronger oxidant, Reaction 9a will predominate. Thus there will be formed more paraffin than olefin derived from R· and less paraffin than olefin derived from R′·. The converse will be true if R′· is the stronger oxidant, and Reaction 9b will predominate.[4] It is recognized, of course, that paraffins may be formed by radical attack on the solvent. Furthermore, polymerization may reduce the apparent yield of olefin.[5] These side reactions, however, apparently are relatively unimportant in the case of

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* Deceased.

(1) M. S. Kharasch, M. Zimmermann, W. Zimmt, and W. Nudenberg, *J. Org. Chem.*, **18**, 1045 (1953).

(2) M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, New York, 1954, p. 123.

(3) A. L. Wilds, and W. B. McCormack, *J. Org. Chem.*, **14**, 45 (1949).

(4) The authors are grateful for an alternative explanation, suggested by a referee, that the relative importance of reactions 9a and 9b may be due to the stabilizing effects of substituents on the incipient double bond.

(5) M. S. Kharasch, D. W. Lewis, and W. B. Reynolds, *J. Am. Chem. Soc.*, **65**, 495 (1943).

TABLE I

REACTIONS OF GRIGNARD REAGENTS WITH 1-BROMOOCTANE IN THE PRESENCE OF COBALTOUS BROMIDE

Grignard Reagent	C_8 Hydrocarbons Yield, %	Octenes in C_8 Hydrocarbons, % w	1-Octene: *trans*-2-octene Mole Ratio	1-Octene Yield, %	2-Octene[a] Yield, %
CH_3MgBr	69	75.5	85:15	42	10
i-C_3H_7MgBr	84	43.4	83:17	28	8
t-C_4H_9MgBr	88	31.0	70:30	17	10
C_6H_5MgBr	56	52.3	74:26	20	9

[a] *Cis* and *trans*.

octyl radicals under the experimental conditions here reported, since the expected trends in yields have been observed.

The present investigation deals mainly with the reactions of methyl-, isopropyl-, *tert*- butyl-, and phenylmagnesium bromide with 1-bromooctane in the presence of cobaltous bromide. Attention was focussed primarily on the relative yields of octane and octenes, since these products could be most easily separated and analyzed. According to Reaction 9, a highly reactive (oxidizing) radical derived from the Grignard reagent should lead to the formation of more octene than octane, while a less reactive (reducing) radical should lead to the opposite result. Thus, the decreasing yields of octene relative to octane (Table I.) clearly indicate decreasing reactivity in the series: methyl, isopropyl, *tert*-butyl.

Gaseous products derived from these radicals correspond roughly to the observed yields of octene and octane. However, in the case of methylmagnesium bromide the mixture of gases appears to consist of ethane and ethylene in addition to the expected major product, methane. This may be attributed to the reaction of methyl radicals with the ether solvent.[6] In the case of *tert*-butylmagnesium bromide, an apparently low yield of isobutylene is obtained. This may be due to loss of the olefin by polymerization.[5]

The reaction of phenylmagnesium bromide is believed to differ from the reactions of the alkyl Grignard reagents.[7] Presumably the aryl Grignard reagent reacts with cobaltous bromide to give biphenyl and a reduced form of cobalt. Thus, the free phenyl radical is not produced, and the C_8 products (approximately equal yields of paraffin and olefin) are those to be expected of simple disproportionation of octyl radicals.

It is interesting that a relatively constant yield of 2-octene is obtained, regardless of the Grignard reagent used. Furthermore, little, if any, 3- or 4-octene is formed. Migration of a hydrogen atom during disproportionation of 1-butyl radicals has been suggested[8] to explain the formation of 2-butene in reactions similar to those employed in the present study. Although such a migration may, occur in the case of 1-octyl radicals, an alternate path to 2-octene by isomerization of 1-octene has been established. Methylmagnesium bromide reacts with 1-bromobutane in the presence of cobaltous bromide to give products[9] analogous to those obtained in the reaction of 1-bromooctane. When 1-octene is present during the reaction, extensive rearrangement to 2-octene occurs. Further study is required to establish whether this rearrangement is due to radical attack or to a polar reaction involving other components of the reaction system.

EXPERIMENTAL

Reagents. 1-Bromooctane (Eastman White Label) was fractionally distilled through a 100 × 1.2 cm. glass helices packed column. Only the middle cut (b.p. 91°/20 mm., n_D^{20} 1.4503) was used. 1-Bromobutane (Eastman White Label) was fractionally distilled through a 50 × 1.0 cm. tantalum spiral column, b.p. 101°, n_D^{20} 1.4384. Ethereal solutions of the Grignard reagents were prepared in the usual manner, and concentrations were determined by the acidimetric method.[10] Cobaltous bromide (City Chemical Co., anhydrous, C.P.) was used without further treatment.

Procedure. The reactions were carried out in a 1-l., three-necked flask equipped with sealed stirrer, reflux condenser, and two-way adapter with an addition tube for solids and a pressure equalized dropping funnel with gas inlet. The reaction vessel was thoroughly dried and then purged with dry nitrogen gas. A freshly prepared solution of the Grignard reagent (400 ml., 0.60 mole) was placed in the flask, followed by cobaltous bromide (3.28 g., 0.015 mole). A solution of 1-bromooctane (58 g., 0.30 mole) in an equal volume of ether was placed in the dropping funnel. The flow of nitrogen was stopped, and a gas collector containing a saturated aqueous solution of sodium chloride was connected through a calcium chloride drying tube to the reflux condenser. The solution of 1-bromooctane was added to the flask with stirring over a period of 30 min. During this period the temperature of the reaction mixture remained below 35°. Following the addition of 1-bromooctane the reaction mixture was heated under reflux for 45 min.

The mixture was allowed to cool and then was poured into a stirred mixture of crushed ice and water. Glacial acetic acid

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(6) M. S. Kharasch, F. Engelmann, and W. H. Urry, *J. Am. Chem. Soc.*, **66**, 366 (1944).

(7) M. S. Kharasch and E. K. Fields, *J. Am. Chem. Soc.*, **63**, 2316 (1941).

(8) M. S. Kharasch, F. L. Lambert, and W. H. Urry *J. Org. Chem.*, **10**, 298 (1945).

(9) The products obtained differ significantly from those reported by W. B. Smith (*J. Org. Chem.*, **23**, 509 (1958)). He obtained an appreciable yield of n-pentane and apparently no 2-butene. In contrast, we obtain 2-butene in 21% yield and less than 2% of n-pentane.

(10) M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, New York, 1954, p. 94.

(40 ml.) was added, and the mixture was allowed to separate. The ethereal layer was separated, and the aqueous solution was extracted with ether. The combined ethereal solutions were washed successively with water, a saturated solution of sodium bicarbonate, and water. The ethereal solution was dried over anhydrous sodium sulfate and then fractionally distilled through a Heli-Grid column (97 × 1.3 cm.), a tantalum spiral column (50 × 1.0 cm.), and finally a Piros-Glover spinning band column. High-boiling fractions were molecularly distilled from a Hickman pot-still.

Analyses and molecular weight determinations of gaseous products were carried out using the apparatus and method described by Kharasch, Lewis, and Reynolds.[11]

Analysis of C_8 products. The total yield of C_8 hydrocarbons was determined by distillation (b.p. 121–125°). Bromate-bromide titration was employed to determine the ratio of octenes to octane. The ratio of 1-octene to *trans*-nonterminal octene was determined by infrared analysis based on absorption maxima at 910 cm.$^{-1}$ (1-octene) and 960 cm.$^{-1}$ (*trans*-nonterminal octene). Gas chromatography through a 13 ft. × $^1/_4$ in. column containing 30–60 mesh firebrick impregnated with 30% w of tricresyl phosphate permitted estimation of octane, 1-octene, *trans*-2-octene, and *cis*-2-octene. Yields are reported on the basis of 1-bromooctane used.

Complete separation of C_8 products from the reaction of *tert*-butylmagnesium bromide was effected by gas chromatograpy through a 50 ft. × $^1/_4$ in. column containing dimethylsulfolane (26% w) on firebrick.[12] At a flow rate of 70 ml./min. of helium carrier gas and a column temperature of 80° the following emergence times were observed: octane, 87.5 min.; 1-octene, 116 min.; *trans*-2-octene, 125 min.; *cis*-2-octene, 136 min. Positive identification of these constituents was accomplished by use of authentic compounds. By employing relatively large samples (80–100 μl.), it was possible to trap enough of each constituent from the effluent gas to obtain a useful infrared spectrum. On the basis of comparable examinations of mixtures containing 3- and 4-octenes it was concluded that, at most, only traces of these isomers were produced by the reactions considered here.

It should be mentioned that the products of ozonolysis of the olefins are of limited value in the assignment of structure. Even when extreme precautions[13] are taken, as much as 5% of "abnormal" reaction occurs, leading to fragments containing one fewer carbon atom than would be expected. After experiments with pure olefins this approach was abandoned.

Higher molecular weight products, being of minor interest, were not thoroughly investigated. Characterization was limited to measurement of physical properties.

Products of the reaction of methylmagnesium bromide with 1-bromooctane. Gas: *ca.* 8.0 l., mol. wt., 17.55; unsaturation, 5%. Calculated composition: methane, 90%; ethane, 5%; ethylene, 5%. C_8 hydrocarbons: 23.5 g. (69% yield); unsaturation, 75.5%; ratio 1-octene:*trans*-2-octene, 85:15; yield 1-octene, 42%; yield 2-octene, 10%. Higher molecular weight products (primarily C_{16} hydrocarbons): 10 g. (29.5% yield); unsaturation, 19.4%; n_{D}^{20} 1.4320; mol. wt., 200.

Products of the reaction of isopropylmagnesium bromide with 1-bromooctane. Gas: *ca.* 7.5 l.; mol. wt., 43.24; unsaturation, 47.0%. Calculated composition: propane, 53%; propylene, 47%. C_8 hydrocarbons: 27.9 g. (84% yield); unsaturation, 43.4%; ratio 1-octene:*trans*-2-octene, 83:17; yield 1-octene, 28%; yield 2-octene, 8%. Higher molecular weight products: C_{11} hydrocarbons, 2.1 g. (4.5% yield); C_{16} hydrocarbons, 2.5 g. (7.4% yield).

Products of the reaction of tert-butylmagnesium bromide with 1-bromooctane. Gas: *ca.* 6.0 l.; mol. wt., 57.7; unsaturation, 35%. Calculated composition: isobutane, 65%; isobutylene, 35%. C_8 hydrocarbons: 30.0 g. (88% yield); unsaturation, 31.0%; ratio 1-octene:*trans*-2-octene, 70:30; yield 1-octene, 17%; yield 2-octene, 10%. Higher molecular weight products (primarily C_{12} and C_{16} hydrocarbons): 4.4 g.; unsaturation, 28%.

Products of the reaction of phenylmagnesium bromide with 1-bromooctane. Benzene, 16.6 g. C_8 hydrocarbons: 19.2 g. (56% yield); unsaturation, 52.3%; ratio 1-octene:*trans*-2-octene, 74:26; yield 1-octene, 20%; yield 2-octene, 9%. Higher molecular weight products: diphenyl, 22.5 g.; octylbenzene, 4.2 g. (7% yield); C_{16} hydrocarbons, 7.2 g. (21% yield).

Reaction of methylmagnesium bromide with 1-bromobutane. This experiment differed from the general procedure in several respects. A Dry Ice reflux condenser was used, and different amounts of reagents and solvent were employed. Thus a soluton of 1-bromobutane (27.4 g., 0.2 mole) in an equal volume of ether was added to an ethereal solution of methylmagnesium bromide (0.3 mole in 100 ml. of ether) containing 1.8 g. of cobaltous bromide (0.01 mole). When the reaction was complete, a total of 4.8 l. at S.T.P. of gas (assumed to be mostly methane) had been collected. The Dry Ice condenser was replaced by a condenser which was cooled with ice water. To this condenser was attached a trap cooled to −80°. The reaction mixture was heated to the boiling point and refluxed gently for 2 hr. The trapped material (*ca.* 9.0 g.) was analyzed by gas chromatography (using the dimethylsulfolane column) and found to consist of: *n*-butane, 42%; 1-butene, 30%: *trans*-2-butene, 18%; *cis*-2-butene, 9%; *n*-pentane, *ca.* 0.6%; and a trace of ether.

The reaction mixture was distilled almost to dryness, and the distillate (90 g., primarily ether) was also analyzed by gas chromatography. Traces of butane and butenes as well as *n*-pentane (*ca.* 0.14% w) were found. The residue was decomposed with dilute hydrochloric acid and extracted with ether. The ethereal extract was worked up as described previously and fractionally distilled. The fraction with b.p. 117–125° (2.0 g.) was analyzed by gas chromatography (dimethylsulfolane column): octane, 82%; 1-octene, 4%; *trans*-2-octene, 9%; *cis*-2-octene, 4%.

Product	Amount	Yield,[a] %
Methane	4.8 l. S.T.P.	ca. 100
n-Butane	3.8 g.	33
1-Butene	2.7 g.	24
trans-2-Butene	1.6 g.	14
cis-2-Butene	0.8 g.	7
n-Pentane	<0.2 g.	<1.8
n-Octane	1.64 g.	14
1-Octene	0.08 g.	0.7
trans-2-Octene	0.18 g.	1.6
cis-2-Octene	0.08 g.	0.7

[a] All yields except that of methane calculated on the basis of 1-bromobutane.

Isomerization of 1-octene in the reaction of methylmagnesium bromide with 1-bromobutane. The foregoing experiment was repeated, the only change being the addition of 1-octene (10.0 g.) to the solution of Grignard reagent before the reaction was begun. Yields of methane and C_4 products appeared to be unchanged. The C_8 fraction (7.0 g. recovered), b.p. 119–124°, n_{D}^{20} 1.4110, was analyzed by gas chromatography: *n*-octane, 12%; 1-octene, 20%; *trans*-2-octene, 45%; *cis*-2-octene, 20%; and possibly traces of other octenes. If isomerization of the added 1-octene had not occurred, the recovery had been complete, the expected composition would have been: *n*-octane, 13.7%; 1-octene, 84%: *trans*-2-octene, 1.5%; *cis*-2-octene, 0.7%.

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[11] M. S. Kharasch, D. W. Lewis, and W. B. Reynolds, *J. Am. Chem. Soc.*, **65**, 493 (1943).

[12] E. M. Fredericks and F. R. Brooks, *Anal. Chem.*, **28**, 297 (1956).

[13] The method involved ozonization at −80°, catalytic hydrogenation of ozonides, oxidation of resulting aldehydes to acids with silver oxide, reaction of silver salts of the acids with methyl iodide to form methyl esters, and gas chromatographic analysis of the esters.