[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Orientation in the Cleavage of 2-Methoxyoctane by Organoalkali Metal Compounds[1]

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The cleavage of 2-methoxyoctane with amylsodium and with isopropyllithium was found to give 1-octene as the principal alkene. Experiments concerning the isomerization of 1- and 2-octene by these reagents are also described.

A large number of heterolytic elimination reactions caused by hydroxide and alkoxide ions have been investigated in the past. Particular attention has been directed to the reaction of unsymmetrical compounds which may lead to the formation of two different alkenes. For such cases it has been found that the less highly alkylated ethylene is the principal product in second order elimination reactions which involve the loss of $+NR_3$, $+PR_3$, $+SR_2$ and $+S\bar{O}_2R$.[2] In other cases the more highly branched ethylene is the major product.

It is well known that the very strong bases of the organoalkali metal class may also effect elimination[3] reactions; however, information concerning the course of reaction of unsymmetrical compounds has been limited. The significant cases reported are the reaction of ethyl 1-methyl ether with ethylsodium[3i] and the cleavage of some alkyl cholesteryl ethers with amylsodium.[3e] In order to gain further information about such reactions, and in particular about the reaction of a simple molecule comparable to those used in the studies of the oxide bases, we have investigated the alkene products from the reactions of amylsodium and isopropyllithium with 2-methoxyoctane.

The amylsodium reaction was carried out at low temperature in the presence of excess 2-methoxyoctane. These mild conditions were employed in order to minimize metalation by amylsodium of the octenes, which result from the elimination reaction. Such a reaction is known to occur under more vigorous conditions[4] and yields octenylsodium. On decomposition with water or alcohol, the octenylsodium could revert to a mixture of octenes different in composition from the products of the elimination reaction. As a further precaution, the reaction mixture was centrifuged before decomposition in order to separate the hydrocarbons from the insoluble sodium compounds. The octenes were then isolated by fractionation and characterized by their refractive indices and infrared spectra. It was found that the alkene product was predominately (about 96%) 1-octene.

In connection with this experiment it was of interest to know the composition of the octene fraction which would result from the decomposition of octenylsodium. Accordingly, a sample of 1-octene was metalated with amylsodium in the presence of sodium methoxide and then converted to octene with methanol. The product was largely 2-octene (about 75%).[5]

Isopropyllithium differs from amylsodium in that it is generally less reactive and is soluble in pentane, which was used as a solvent for these reactions. As with the amylsodium, however, the alkene product resulting from the reaction with 2-methoxyoctane was predominately 1-octene. The possibility that isopropyllithium had caused an isomerization of 2-octene to 1-octene may be eliminated since it was found that 2-octene was unchanged when refluxed with isopropyllithium under the conditions of the reaction.

2-Methoxyoctane, therefore, undergoes elimination in reactions with these organoalkali metal compounds in the same sense as the onium compounds and sulfones with oxide bases,[6] even though the acidity of its hydrogen atoms corresponds more to that of the alkyl halides (which give the more highly branched alkene in reactions with oxide bases).[7] It seems likely that these are concerted reactions in which the orientation is determined by the relative degree to which the C–βH and C–X bonds are broken in the transition state. Thus the less highly branched alkene (1-octene) should be the major product if the C–βH bond is more nearly broken, while the more highly branched alkene should predominate if the breakage of the C–X bond is more complete. It is reasonable that the former situation should prevail in the ether reactions for the organoalkali metal compounds contain very strong carbanion bases and the ether has a strong C–X bond. Although the reactions of the onium compounds and the sulfones involve weaker bases (alkoxide ions), proton removal may still determine the orientation as the hydrogen atoms in these molecules are comparatively acidic. If in either case the C–X bond had been more subject to ionization, the proportion of the more branched alkene should have been greater. The situation is analogous to that for the displacement reaction where the extent of racemization apparently depends upon the relative displacing power of the carbanion and the strength of the C–X bond.[8]

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(1) Presented at the meeting of the American Chemical Society in Boston, Mass., April, 1951. A portion of this work was supported by a Grant from the Abbott Fund of Northwestern University.

(2) M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. I. Woolf, *J. Chem. Soc.*, 2093 (1948).

(3) (a) A. A. Morton, S. B. Davidson and B. L. Hakan, THIS JOURNAL, **64**, 2242 (1942); (b) N. G. Brink, J. F. Lane and E. S. Wallis, *ibid.*, **65**, 943 (1943); (c) S. E. Ulrich, E. H. Gentes, J. F. Lane and E. S. Wallis, *ibid.*, **72**, 5127 (1950); (d) A. A. Morton, E. E. Magat and R. L. Letsinger, *ibid.*, **69**, 950 (1947); (e) D. H. Gould, K. H. Schaaf and W. L. Ruigh, *ibid.*, **73**, 1263 (1951); (f) H. Gilman, F. W. Moore and O. Bain, *ibid.*, **63**, 2479 (1941); (g) H. Gilman, E. A. Zoellner and W. M. Selby, *ibid.*, **54**, 1957 (1932); (h) P. Schorigin, *Ber.*, **43**, 1931 (1910); (i) W. Hückel and H. Bretschneider, *J. prakt. Chem.*, **151**, 61 (1938); (j) K. Ziegler and H. G. Gellert, *Ann.*, **567**, 185 (1950).

(4) A. A. Morton and co-workers, THIS JOURNAL, **72**, 3785 (1950).

(5) An exact assignment of the percentages was not possible since the relative amounts of *cis*- and *trans*-2-octene were not known.

(6) This orientation is similar to that observed in the ethyl 1-menthyl ether reaction, which yielded ethylene and 1-menthol.[3i] The interpretation of the orientation in the cholesteryl ether[3e] cleavages is difficult in view of the complexities of the cholesteryl radical and the possibility of rearrangements of the double bonds in these reactions.

(7) The acidity of the hydrogen atoms in methoxyoctane was probably enhanced in the course of the reaction, however, by coördination of the organoalkali metal compound with the ether.[3a]

(8) J. F. Lane and S. E. Ulrich, THIS JOURNAL, **72**, 5132 (1950).

The elimination reaction, however, appears to be an even more sensitive measure of incipient ionization at the C–X bond than the displacement reaction since, with alkoxide bases, it has been found that the second order reactions of alkyl halides give the more highly branched alkene on elimination,[2] but react with inversion without racemization on displacement.[9]

In view of these considerations, one would anticipate that the reaction of an organoalkali metal compound with a secondary alkyl halide would give the more highly branched alkene as the major elimination product.

Experimental

2-Methoxyoctane.—The potassium salt of 2-octanol was made by stirring a mixture of 117 g. (3.0 g. atom) of potassium metal with 655 g. (5.0 moles) of 2-octanol and 200 ml. of benzene at reflux for ten hours. Methyl iodide (426 g., 3.0 moles) was then added dropwise with stirring, and the mixture allowed to stand overnight. The potassium iodide was washed out with water, and the benzene solution dried with calcium sulfate. Fractionation through a three-foot helices packed column yielded 372 g. (86%) of 2-methoxyoctane; b.p. 162–163°, n^{25}_{D} 1.4071, d^{25}_{4} 0.7806; *MR*, 45.50; *MR* calcd., 45.41.

Anal. Calcd. for $C_9H_{20}O$: C, 74.93; H, 13.98. Found: C, 75.07; H, 14.04.

This procedure is adapted from that of Kenyon and McNicol[10] who reported for 2-methoxyoctane, n^{25}_{D} 1.4212; d^{25}_{4} 0.8094. Their procedure differed essentially by a laborious purification through the phthalate ester. In another preparation we followed their method, but obtained again the values we had previously found. The refractive index and density we report are in good agreement with values for 2-methoxyoctane which are extrapolated from a series of higher alkoxyoctanes also prepared by Kenyon and McNicol.

Reaction of Amylsodium and 2-Methoxyoctane.—Sodium sand (23 g., 1.0 g. atom) was prepared in a creased one-liter flask in a mineral oil dispersing medium. After the addition of a pentane fraction (b.p. 28–35°, carefully fractionated to remove any higher boiling components) to decrease the viscosity, the sand settled out and was washed three times with additional fresh portions of pentane. Amylsodium was prepared in the conventional manner by the dropwise addition of amyl chloride (53.3 g., 0.5 mole) to the sand in 500 ml. of pentane (−5°) over an hour period. High speed stirring and a nitrogen atmosphere were maintained throughout this and subsequent steps. The amylsodium was stirred an additional 30 minutes at −5°, allowed to come to room temperature, and then cooled to 0°. 2-Methoxyoctane (144 g., 1.00 mole) was then added rapidly and stirred with the amylsodium at 0–5° for 3.5 hours, during which time the mixture became quite thick. Then the mixture was siphoned into centrifuge bottles in order to separate the solids from the liquid portion. The solids were washed and centrifuged two additional times with fresh portions of pentane.

From a fractionation (through a 30-cm. Vigreux column) of the combined liquid layers were obtained octane (a broad cut, 19.25 g., b.p. 118–132°) and a fraction boiling in the region of 2-methoxyoctane (82 g.). Redistillation of the octene fraction through a Piros–Glover spinning band microstill at 743 mm. yielded the fractions listed in Table I.

TABLE I

Fraction	Wt.. g.	Boiling range. °C.	n^{25}_{D}
1	1.30	To 120.5	1.4061
2	14.60	120.5–121.0	1.4063
3	0.90	121.0–123.6	1.4079
4	0.12	123.6–126.0	1.4102
5	1.05	126.0–164.0	1.4070
Residue	0.57		

The physical constants reported for 1- and 2-octene are[11]: 1-octene, b.p. 121.27°; n^{25}_{D} 1.4063; *cis*-2-octene, b.p. 125.6°, n^{25}_{D} 1.4125; *trans*-2-octene, b.p. 125.0, n^{25}_{D} 1.4107. It is apparent, therefore, that fractions 2 and 4 are primarily 1-octene and 2-octene, respectively. As confirmation evidence, the infrared spectra of fractions 2, 3 and 4 were taken and compared with the spectra of samples of 1-octene (one sample (n^{25}_{D} 1.4063) was prepared by the action of allylmagnesium bromide on *n*-hexyl bromide; another sample was obtained by fractionating a sample of 1-octene obtained from the Humphrey-Wilkinson Company, n^{25}_{D} 1.4063) and 2-octene (prepared by the reaction of butylmagnesium bromide on crotyl chloride,[12] n^{25}_{D} 1.4117) and mixtures of the two. These data indicated that these fractions contained altogether 96% 1-octene and 4% 2-octene.

The solids from the centrifugation were stirred in pentane, cooled to 0° and decomposed with methanol. Water was then added to bring the salts into solution, and hydrochloric acid added until the solution was acidic. From the hydrocarbon layer (after drying with calcium sulfate and distillation) there was obtained 5.65 g. (b.p. 117–132°, n^{25}_{D} 1.4069) of a C-8 cut and 14.90 g. of 2-methoxyoctane. The C-8 portion was separated into the fractions listed in Table II by distillation through the Piros–Glover column.

TABLE II

Fraction	Wt.. g.	B.p.. °C.	n^{25}_{D}
1	0.38	To 121.5°	1.4067
2	2.43	121.5–122.0	1.4063
3	0.75	122.0–123.0	1.4072
4	.26	123.0–124.0	1.4086
5	.08	124.0–124.6	1.4094
Residue	.64		

Infrared spectra of fractions 2, 3, 4 and 5 showed that altogether they consisted of about 93% 1-octene and 7% 2-octene. In view of the experiment to be described and the fact that 2-methoxyoctane was also isolated, it seems that this octene must have been elimination product which had been carried along with the solids, rather than a product of the acidification of octenylsodium.

Reaction of Amylsodium with 1-Octene.—Amylsodium was prepared as before from 64 g. (0.6 mole) of amyl chloride and 28 g. (1.2 g. atom) of sodium. Methyl alcohol (3.2 g., 0.1 mole) was dropped onto the amylsodium in order to form sodium methoxide (since this salt had been formed in the metalation reaction), and then 45.1 g. (0.4 mole) of 1-octene (n^{25}_{D} 1.4063) was added. The resulting mixture was stirred vigorously for four hours at 25° and then allowed to stand for an additional 18 hours. A portion (about 420 cc.) of the viscous reaction suspension was siphoned into two large centrifuge bottles by nitrogen pressure. The remainder (about 280 cc.) was siphoned directly onto powdered Dry Ice in order to obtain the carboxylic acids, and thereby confirm the fact that octene had been metalated.

The uncarbonated portion was centrifuged, freed of the liquid layer, and washed two times with pentane (with centrifugation). The solids which remained were then decomposed with methanol and water as in the previous reaction. Distillation results (from the micro still) are shown in Table III.

TABLE III

Fraction	Wt.. g.	Boiling range, °C.	n^{25}_{D}
1	0.58	120.8–122.3	1.4074
2	1.77	122.4–124.2	1.4100
3	2.11	124.2–124.8	1.4122
4	1.64	Residue and hold up	

The boiling points and refractive indices indicate fraction 1 to be largely 1-octene and fraction 3, 2-octene, and this was confirmed by their infrared spectra. It is estimated that the ratio of 2-octene to 1-octene was three to one. It is possible that some of the 1-octene may have been carried over by adsorption on the solids during the separation.

The acids from the carbonated portion were separated by

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[9] E. D. Hughes, C. K. Ingold and S. Masterman, *J. Chem. Soc.*, 1196 (1937).

[10] J. Kenyon and R. A. McNicol, *ibid.*, **123**, 17 (1923).

[11] Report of the Am. Pet. Inst., Project 44, Table 10a, 1.

[12] A. L. Henne, H. Chanan and A. Turk, THIS JOURNAL, **63**, 3474 (1941).

conventional methods and distilled at 12 mm. As seen from the refractive indices ($n^{25}\text{D}$ 1.4149 reported for caproic acid, and $n^{25}\text{D}$ 1.4387 and $n^{25}\text{D}$ 1.4454 for the two nonenoic acids which could form[4]), the second and third fractions were largely nonenoic acids.

TABLE IV

Wt., g.	B.p., °C.	$n^{21.5}\text{D}$
1.47	70–110	1.4229
3.49	110–132	1.4354
1.34	133–137	1.4421

Reaction of 2-Methoxyoctane with Isopropyllithium.—2-Methoxyoctane (36.0 g., 0.25 mole) was added to a filtered pentane solution (300 ml.) which contained 0.33 mole of isopropyllithium. After two hours of refluxing the reaction mixture became turbid. Heating was continued for a total of 66 hours, then water was added and the organic layer separated, dried and distilled. The fractions are given in Table V.

Fraction 2 showed 100% unsaturation in a bromine titration,[3c] and gave an infrared spectrum virtually identical with that for a sample of 1-octene (Beckman IR-2T spectrophotometer).

TABLE V

Fraction	Wt., g.	B.p., °C.	$n^{25}\text{D}$
1	1.06	117.5–119.8	1.4061
2	2.57	120.0–121.0	1.4063
3	0.43	121.2–126.8	
Residue	25.62	155–177	

Reaction of Isopropyllithium with 2-Octene.—2-Octene (27.85 g., $n^{25}\text{D}$ 1.4117) was added to a solution of isopropyllithium, prepared from 9.7 g. of lithium and 39.2 g. of isopropyl chloride and refluxed in a nitrogen atmosphere for 72 hours. The solution was then decomposed on ice and worked up as before. Distillation yielded 22.6 g. of octene, b.p. 122.8–124.2° (more than 90% boiled at 124.0–124.2°), $n^{25}\text{D}$ 1.4116. The infrared analysis showed that this material was 2-octene; isomerization, if any, amounted to less than a few per cent. Therefore, the 1-octene from the reaction of isopropyllithium and 2-methoxyoctane must have resulted from the elimination reaction, and not from a subsequent isomerization of 2-octene to 1-octene *via* a metalation reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

Exchange Studies with Complex Ions. III. The Nature of the Complex Formed between Cobalt(II) and Potassium Cyanide, and its Exchange with Radiocyanide Ion in Aqueous Solution[1]

BY ARTHUR W. ADAMSON

The only solid complex that is known to form from cobalt(II) and potassium cyanide has been shown to have the empirical formula $K_3Co(CN)_5$, rather than $K_4Co(CN)_6$, as previously supposed. The solid is diamagnetic with specific susceptibility -0.196×10^{-6}, but is paramagnetic in excess aqueous cyanide, with susceptibility corresponding to one unpaired electron per cobalt. Evidence is presented which indicates that the cobalt(II) cyanide complex in excess aqueous cyanide exists primarily as a pentacyanide rather than as a hexacyanide. The complex is found to undergo complete exchange with radiocyanide ion in two minutes, but the exchange with hexacyanocobaltate(III) ion is negligible in several days. The above data, and other information available on cobalt(II) complexes, indicate that the existence of hexacovalent cobalt(II) is improbable, and this the cobalt(II) pentacyanide may exist in aqueous solution as $Co(CN)_5^{-3}$ rather than as the hexacoordinated ion $Co(H_2O)(CN)_5^{-3}$.

It is well known that cobalt(II) ion forms some type of complex cyanide. For example, on adding dilute potassium cyanide solution to one of a cobalt(II) salt, a brownish-green precipitate forms, which dissolves in excess cyanide to give a yellowish-green solution; from this solution, by the addition of alcohol, or by cooling, a violet crystalline material can be precipitated, whose formula has been reported to be $K_4Co(CN)_6$.[2]

The present investigations were initiated with the object of studying the exchange behavior of the hexacyanocobaltate(II) ion which has been supposed to be present in an aqueous solution of the violet crystals. It became apparent, however, that the evidence for the existence of this ion was questionable, and that a study of the nature of the cobalt(II) cyanide complex would be a necessary precursor to the interpretation of any exchange results, as well as a subject of interest in itself. Thus while many investigators have referred to the cobalt(II) complex as a hexacyanide,[3] this supposition appears to have been based primarily upon the reported formula for the violet solid and the reasonable assumption that the same structure would persist in solution. This argument is vitiated by the findings, reported below, that the solid actually has the empirical formula $K_3Co(CN)_5$. Moreover, Hume and Kolthoff[4] have pointed out that there is reason to believe that in moderately concentrated solutions the dominant form is a pentacyanide, which they take to be an aquopentacyanide. Thus the initial precipitate formed on addition of cyanide to a solution of a cobalt(II) salt dissolves at the point of five cyanides per cobalt. Hume and Kolthoff, in addition, found that after oxidation of the cobalt(II) complex, the observed polarographic wave corresponded to pentacyanoaquocobaltate(III) ion rather than to hexacyanocobaltate(III) ion.

[1] These investigations were carried out under contract N6 onr 23809 between the University of Southern California and the Office of Naval Research.

[2] (a) W. Biltz, W. Eschweiler and A. Bodensiek, *Z. anorg. allgem. Chem.*, **170**, 161 (1928); (b) A. Descamps, *Ann. chim. phys.*, [5] **24**, 178 (1881); (c) A. Rosenheim and I. Koppel, *Z. anorg. Chem.*, **17**, 67 (1898).

[3] (a) H. Brintzinger and H. Osswald, *ibid.*, **225**, 217 (1935); **220**, 172 (1934); (b) S. S. Bhatnagar, M. L. Khauna and M. B. Neugi, *Phil. Mag.*, **25**, 234 (1938); (c) J. Cremoux and P. Mondain-Monval, *Bull. soc. chim.*, 700 (1949); (d) H. G. Grube, *Z. Elektrochem.*, **32**, 561 (1926); (e) L. Szego and P. Ostinelli, *Gazz. chim. ital.*, **60**, 946 (1930). See also reference 4.

[4] D. N. Hume and I. M. Kolthoff, THIS JOURNAL, **71**, 876 (1949).