[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

Reactions of Organometallic Compounds with Alkyl Halides. IV. On Wurtz Syntheses with Optically Active Halides

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In earlier papers of this series[2,3] it has been shown that the action of sodium ethyl on (−)2-bromoöctane gives a small amount of optically inactive 7,8-dimethyltetradecane. On the other hand, the interaction of sodium ethyl with (+)2-chloroöctane gives rise to a small amount of (+)7,8-dimethyltetradecane. It was concluded[3] that, while the hydrocarbon is produced in each case by the interaction of sodium *s*-octyl with the alkyl halide, it is produced in the two experiments by different paths of reaction, *e.g.*

$$(-)s\text{-}C_8H_{17}Br \xrightarrow{\text{slow}} Br^{\ominus} + dl\text{-}s\text{-}C_8H_{17}^{\oplus} + dl\text{-}s\text{-}C_8H_{17}^{\ominus}Na^{\oplus} \xrightarrow{\text{fast}} dl + meso\text{-}(s\text{-}C_8H_{17})_2 + NaBr \quad (1)$$

$$(+)s\text{-}C_8H_{17}Cl + dl\text{-}s\text{-}C_8H_{17}^{\ominus}Na^{\oplus} \xrightarrow{\text{concerted}} (+) + meso\text{-}(s\text{-}C_8H_{17})_2 + NaBr \quad (2)$$

Now Morton[4] has suggested that the initial stage of the Wurtz synthesis involves the direct formation of a sodium alkyl

$$2Na + RX \longrightarrow NaX + NaR \quad (3)$$

followed by a second stage in which this sodium alkyl reacts with a second mole of halide to give the hydrocarbon (RR)

$$NaR + RX \longrightarrow RR + NaX \quad (4)$$

This second stage is, of course, precisely the kind of reaction which has been shown to give 7,8-dimethyltetradecane from optically active 2-haloöctanes in the earlier studies in this series.[2,3] If it occurs in the Wurtz reactions of these and similar optically active halides, then comparable optical behavior should be observed: namely, the action of sodium on optically active 2-bromooctane should give inactive 7,8-dimethyltetradecane, while sodium and optically active 2-chloroöctane should give active 7,8-dimethyltetradecane.

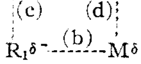
This is indeed the case. Interaction of sodium (activated with a trace of ethyl acetate) with (−)2-chloroöctane, $[\alpha]^{25}D$ − 31.84°, was found to proceed vigorously at room temperature. Fractionation of the hydrocarbon products gave octane (36%), octylene (38%) and (−)7,8-dimethyltetradecane (16%), $\alpha^{25}D$ − 1.82° (1-dm. tube, homogeneous). Sodium and (+)2-bromoöctane, $[\alpha]^{25}D$ + 27.7°, reacted much more slowly to give inactive 7,8-dimethyltetradecane in 11% yield.

Exactly similar behavior obtains with the optically active (+)2-halobutanes. Thus, from (+)2-chlorobutane, $[\alpha]^{25}D$ 13.7°, (+)3,4-dimethylhexane, $[\alpha]^{22}D$ + 0.58°, was obtained in 8% yield. (+)2-Bromobutane has, of course, already been shown by Wallis and Adams[5] to give optically inactive 3,4-dimethylhexane.

The results strongly support Morton's picture of the Wurtz reaction and render most unlikely the alternative view[6] that this reaction proceeds *via* free radicals.

It is of interest, at this point, to consider the data so far obtained by us and also by Letsinger[7,8] on the extent of racemization accompanying the replacement of halogen in secondary alkyl halides (RX) by various hydrocarbon residues derived from reactive organometallic compounds (R_1-M). For convenience of discussion these data are summarized in Table I. In general, it is seen that while replacement of chlorine is attended by little racemization, the replacement of bromine is attended by extensive or complete racemization when R_1 is alkyl and M is sodium or when R_1 is alkaryl and M is magnesium (MgBr). When, however, R_1 is alkaryl and M is sodium, or R_1 is allyl and M either sodium or magnesium, little racemization results.

The results obtained with alkyl sodium and benzyl metal compounds suggest that whether a given halide reacts according to path (1) or path (2) above depends not only on the ease of ionization of the carbon halogen bond, but also on the readiness with which the organo-metallic compound can supply the carbanion which effects substitution. Thus, the substitution process might be pictured as arising from the association of the organometallic compound, acting either as an ion-pair or a polar molecule,[9] with the carbon–halogen dipole



followed by redistribution of bonds to give RR_1 + MX. If R is to remain optically active, bond (c) must be established synchronously with the rupture of bond (a). This will be easiest when bond (a) (*e.g.*, CCl) resists ionization and bond (b) (*e.g.*, RM) is essentially ionic. If, however,

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[2] Brink, Lane and Wallis, THIS JOURNAL, **65**, 943 (1943).

[3] Ulrich, Gentes, Lane and Wallis, *ibid.*, **72**, 5127 (1950).

[4] Morton, Davidson and Hakan, *ibid.*, **64**, 2242 (1942).

[5] Wallis and Adams, *ibid.*, **55**, 3838 (1933).

[6] *Cf.* Hückel, Kraemer and Thiele, *J. prakt. Chem.*, **142**, 207 (1935); Bachmann and Clarke, THIS JOURNAL, **49**, 2089 (1927); Richards, *Trans. Far. Soc.*, **36**, 956 (1940).

[7] Letsinger, THIS JOURNAL, **70**, 406 (1948).

[8] Letsinger and Traynham, *ibid.*, **72**, 849 (1950).

[9] *Cf.* Morton, *ibid.*, **69**, 969 (1947).

TABLE I

OPTICAL ACTIVITY OF PRODUCTS (RR_1) OBTAINED BY THE ACTION OF SOME ORGANOMETALLIC COMPOUNDS (R_1M) ON OPTICALLY ACTIVE ALKYL HALIDES(RX)

Reactants				Rotations[a] (°)			
X	R	R_1	M	RX	RR_1	% Rac.	Ref.[b]
Br	$CH_3CHC_6H_{13}$-*n*	C_2H_5	Na	−30.7[c]	−0.23	97	2
		n-C_4H_9		−32.5	0.00	100	7
		$CH_3CHC_6H_{13}$		−30.7[c]	0.00	100	2
				+27.7	0.00	100	*
		$CH_2{=}CHCH_2$		−29.6	−4.73	13	8
		$C_6H_5CH_2$		+28.8	+4.53	30	7
				−32.5	−5.20	30	7
		$CH_2{=}CHCH_2$	MgBr	+30.0	+4.79	13	8
		$C_6H_5CH_2$		+30.0	+0.64	91	8
	$CH_3CHC_2H_5$	*s*-C_4H_9	Na	+10.8	0.00	100	5
		$C_6H_5CH_2$		+ 6.84	−2.25	26	7
Cl	$CH_3CHC_6H_{13}$-*n*	C_2H_5	Na	+26.4	+5.16	20	3
		$CH_3CHC_6H_{13}$		+26.4	+0.96[d]		3
				−31.8	−1.82[e]		*
	$CH_3CHC_2H_5$	*s*-C_4H_9		+13.7	+0.58[f]		*

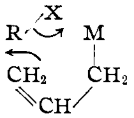
[a] $[\alpha]^{25}D$ (homogeneous) unless otherwise noted. [b] Data from this paper are marked with an asterisk. [c] $[\alpha]^{20}D$. [d] $\alpha^{23}D$ (homogeneous, 1-dm. tube). [e] $\alpha^{25}D$ (homogeneous, 1-dm. tube). [f] $[\alpha]^{22}D$.

bond (a) is easily ionized (*e.g.*, CBr) and bond (b) is appreciably covalent, the establishment of bond (c) may lag behind the rupture of bond (a) and racemization of R will occur.

The ease of ionization of the R_1M bond should decrease (1) if M is made less electropositive (*e.g.*, Na→Mg),[10] or (2) if R_1 is made more basic ($C_6H_5CH_2 \rightarrow C_2H_5$).[11] The experimental results indicate that, with the alkyl bromides, either kind of change, within relatively small limits, exerts a profound effect on the optical result of substitution.

Similar effects are observed in the reactions of alkaryl chlorides. Thus Ott[12] and Bergmann[13] have found that the action of sodium alkaryls (NaR_1) on optically active α-phenethyl chloride (RX) leads to products (RR_1) of high optical activity. Levene,[14] on the other hand, has found that the action of methylmagnesium bromide on 1-phenyl-1-chloropropane gives extensively (90%) racemized 2-phenylbutane.

It is to be noted, however, that whether (+)2-bromoöctane reacts with allylmagnesium bromide or with allyl sodium essentially the same optical result is obtained.[8] On the basis of the theory just outlined this would indicate that the ease of ionization of allyl metal bonds is great. As Letsinger[8] has pointed out, however, both allyl metal compounds may react by an entirely different (cyclic) mechanism



Clarification of this point will require further studies on this reaction which employ unsymmetrical ("tagged") alkenyl metal compounds.

Experimental

Materials.—(−)2-Chloroöctane, $[\alpha]^{25}D$ −31.84° (homogeneous), b. p. 66–67° (17 mm.), d^{25}_4 0.8607, was prepared from (+)2-octanol,[15] $[\alpha]^{25}D$ + 9.52° (homogeneous), d^{25}_4 0.816, by the method previously described[3] for the preparation of its enantiomorph. (+)2-Bromoöctane, $[\alpha]^{25}D$ + 27.7° (homogeneous), b. p. 78–79°(19 mm.), d^{25}_4 1.009 was prepared in 66% yield by the method of Shriner and Young[16] from (−)2-octanol,[16] $[\alpha]^{25}D$ −8.35° (homogeneous), d^{25}_4 0.816. (+)2-Chlorobutane, $[\alpha]^{25}D$ 13.70° (homogeneous), b. p. 69.5–69.8° (765 mm.), d^{25}_4 0.8671 was prepared in 41% yield by the method of Clark and Streight[17] from (−)2-butanol, $[\alpha]^{25}D$ −5.54° (homogeneous), d^{25}_4 0.8025, b. p. 101.2–101.6° (780 mm.), prepared by resolving *dl*-2-butanol (Eastman Kodak Co., White Label) according to Viditz.[18] The *n*-pentane used as a solvent has been described previously.[3] *n*-Dodecane (Eastman Kodak Co., White Label) was allowed to stand over sodium for several days and then washed repeatedly with concd. sulfuric acid. After having been washed with water and dried over magnesium sulfate and sodium, the product boiled at 90–91° (11 mm.), $n^{25}D$ 1.4191, now was free of unsaturates and optically inactive.

Action of Sodium on (−)2-Chloroöctane.—The apparatus was that described previously,[2,3] except that a 250-ml. reaction flask was used instead of the two-liter size. After 13 g. (0.57 g. atom) of sodium had been added in the form of small strips to 80 ml. of pentane in the reaction flask, the system was swept out with nitrogen and the sodium activated with 0.8 ml. of ethyl acetate. Over a period of about one hour, 36.8 g. (0.248 mole) of (−)2-chloroöctane $[\alpha]^{25}D$ −31.8° was added. Twenty minutes after the addition of alkyl chloride had begun, an exothermic reaction set in and it was necessary to cool the reaction flask in order to keep the temperature below 30°. Four hours later, the reaction temperature had returned to normal. The mixture, which had a deep blue color, was stirred for about three days and then refluxed for one-half

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[10] *Cf.* Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 521–524.

[11] *Cf.* Hein *et al.*, *Z. anorg. allgem. Chem.*, **141**, 161 (1924).

[12] Ott, *Ber.*, **61**, 2124 (1928).

[13] Bergmann, *Helv. Chim. Acta*, **20**, 611 (1937).

[14] Levene and Marker, *J. Biol. Chem.*, **97**, 658 (1932).

[15] Kenyon, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943. p. 418.

[16] Shriner and Young, THIS JOURNAL, **52**, 3332 (1930).

[17] Clark and Streight, *Trans. Roy. Soc. Can.*, **3**, 23, Sept. 3, 77 (1929).

[18] Viditz, *Biochem. Z.*, **259**, 294 (1933).

hour. After it was cooled, the material was treated cautiously with 100 ml. of water and stirred overnight.

The two layers were separated and in the aqueous layer was found 0.247 mole of chloride ion and 0.31 mole of base; this indicated that the alkyl chloride had reacted practically completely. After the pentane solution was dried over magnesium sulfate, the pentane was removed and the liquid remaining was fractionated through a 90-cm. Todd column. The fraction, b. p. 115–125°, weighed 20.8 g. and analyzed for 10.3 g. of octane and 10.5 g. of octene according to the method of Uhrig and Levin.[19] The residue was taken up in ether, decolorized, and the ether removed. The liquid was then distilled from a 50-ml. distilling flask; the fractions which were obtained are listed in Table II. All fractions gave negative Beilstein tests.

TABLE II

HYDROCARBON PRODUCTS BOILING BETWEEN 125–270° FROM THE REACTION OF SODIUM AND (−)2-CHLOROÖCTANE

Fraction	B. p., °C.[a]	Weight, g.	n^{20}D	α^{25}D,[b] deg.	Micro b. p., °C. (cor.) (769 mm.)
1	240	0.2	....	....	...
2	240–258	0.6	1.4363	....	...
3	258–268	3.5	1.4383	−1.82	274
4	268–270	0.3	1.4398	....	...

[a] 764 mm. (uncor.). [b] Homogeneous, 1-dm. tube.

Action of Sodium on (+)2-Bromoöctane.—In the same apparatus as in the previous experiment, 8.7 g. (0.38 g. atom) of sodium was added in small strips to 50 ml. of pentane. Nitrogen was passed through the system and 0.5 ml. of acetonitrile was added to etch the sodium. Within a five-minute period 31.0 g. (0.161 mole) of (+)2-bromoöctane, $[\alpha]^{25}$D + 27.7°, was added. A reaction set in immediately as evidenced by the appearance of a white precipitate and small black specks. The reaction was only slightly exothermic and required no external cooling. After the mixture had been stirred for five days at room temperature and two days at reflux, pieces of sodium were still present. One hundred ml. of water was added cautiously and the mixture stirred for one hour. Upon separation of the two layers, there was found 0.093 mole of bromide ion and 0.29 mole of base in the aqueous layer. These results indicated only a 58% reaction of the alkyl bromide. Consequently, the pentane solution was treated a second time with 3.0 g. (0.13 g. atom) of sodium under nitrogen with acetonitrile as the activator. The mixture was stirred for 36 hours at room temperature and two days at gentle reflux. To the cooled reaction mixture was added 50 ml. of water, and after two hours of stirring, the two layers were separated. In the aqueous layer there was found 0.046 mole of bromide ion and 0.080 mole of base; thus a total of 0.139 mole of bromide ion was determined, which represented 86% of the starting material.

After the organic layer had been dried over magnesium sulfate, the pentane was removed, the residue was taken up in dilute ethyl alcohol, 14 g. of silver nitrate was added, and the mixture refluxed for one-half hour. The silver bromide and excess silver nitrate were removed by filtration and the filtrate extracted with ether and dried over magnesium sulfate. Upon removal of the ether and alcohol much charring occurred. No octane or octene was isolated. The dark residue was taken up in pentane, washed five times with cold, concentrated sulfuric acid, three time with saturated magnesium sulfate solution, and dried over magnesium sulfate and potassium carbonate. After the pentane was removed, the liquid was distilled from a 10-ml. distilling flask. Table III lists the fractions obtained.

TABLE III

HYDROCARBON PRODUCTS BOILING BETWEEN 220-263° FROM THE REACTION OF SODIUM AND (+)2-BROMOÖCTANE

Fraction	B. p., °C.[a]	Weight, g.	n^{20}D	α^{25}D,[b] deg.	Micro b. p., °C. (cor.) (769 mm).
1	220–258	0.3	1.4369	..	...
2	258–262	1.0	1.4372	0.00	274
3	262–263	0.4	1.4378	..	...

[a] 764 mm. (uncor.). [b] Homogeneous, 1-dm. tube.

Action of Sodium on (+)2-Chlorobutane.—By a similar technique, 18.8 g. (0.203 mole) of (+)2-chlorobutane, $[\alpha]^{25}$D + 13.7° was treated with 5.9 g. (0.26 g. atom) of sodium in 25 ml. of *n*-dodecane over a period of two days at room temperature. Only a slight heat of reaction was noticed during the first few hours. After water was added, there was found 0.186 mole of chloride ion and 0.065 mole of base; thus 92% of the alkyl chloride had reacted. In order to remove the unreacted alkyl halide, the hydrocarbon solution was treated with dioxane, ethanolamine, and sodium according to the method of Rauscher.[20] After water was added, an additional 0.007 mole of chloride ion was determined in the aqueous layer and the hydrocarbon layer was dried over magnesium sulfate. Upon distillation through a 90-cm. Todd column, there was obtained 0.80 g. of material boiling between 117–119°, n^{25}D 1.4040. Egloff[21] lists the following physical constants for 3,4-dimethylhexane: b. p. 117.8°, n^{25}D 1.4038. The sample, which gave a negative Beilstein test, was diluted with 0.25 g. of petroleum ether to give a total volume of 1.5 ml. and the rotation of the solution determined in a 1-dm. tube at 22°. The observed rotation was α^{22}D + 0.31°, and therefore the specific rotation was $[\alpha]^{22}$D + 0.58°.

Summary

It has been found that the action of sodium on (−)2-chloroöctane, $[\alpha]^{25}$D − 31.84°, gives (−)-7,8-dimethyltetradecane, $[\alpha]^{25}$D − 1.82 (1-dm. tube, homogeneous). Sodium and (+)2-bromooctane, $[\alpha]^{25}$D 27.7°, give inactive 7,8-dimethyltetradecane. Similarly sodium and (+)2-chlorobutane give (+)3,4-dimethylhexane $[\alpha]^{22}$D +0.58°.

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[19] Uhrig and Levin *Ind. Eng. Chem., Anal. Ed.*, **13**, 90 (1941).

[20] Rauscher, *ibid.*, **9**, 296 (1937).

[21] Egloff, "Physical Constants of Hydrocarbons," Vol. 1, Reinhold Publishing Corp., New York, N. Y., 1939.