[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS
INSTITUTE OF TECHNOLOGY]

PYROLYSIS OF AMYLSODIUM AND THE ISOMERIZATION OF ALKENES BY ORGANOSODIUM REAGENTS[1]

AVERY A. MORTON AND EDWARD J. LANPHER

Received February 16, 1955

Previous work (1, 2) in this laboratory upon the pyrolysis of amylsodium has shown its instability and the influence of associated salts. In the present work this organosodium compound was pyrolyzed as a dry solid under a vacuum in order to observe if both pentane and pentene were present or (4) if the hydrocarbon were only the alkene, as had been observed in the pyrolysis of butyllithium (3). Pentane proved to be present in large amount. Pentene-1 was found at 90° and 75° but, surprisingly, *trans*-pentene-2 was found also, and in increasing amounts as the temperature fell. At 50° this *trans* isomer was the sole olefin. Pentene-1 might have changed to *trans*-pentene-2 if it had remained long enough on the surface to be metalated by pentenylsodium, $C_2H_5CH\overset{\cdots}{-}CH\overset{\cdots}{-}C\overset{-}{H_2}\overset{+}{N}a$, which, in turn, had been made by metalation of pentene by amylsodium. The necessary steps would be very rapid. An alternative way might be by mere contact or coordination on the surface of the solid reagent. In order to explore the possible course of such an isomerization, pentene-1 and other olefins were exposed as liquids to the action of pentenylsodium at room temperatures and were found to be isomerized very readily. The velocity, in fact, was so great as to rival that induced by the traditional acid catalysts.

In the midst of this broad study of isomerization of unsaturated compounds, the paper by Pines, Vesely, and Ipatieff (4) appeared. They found that butene-1 and decene-1 were isomerized during several hours exposure under pressure to sodium metal at 150–170°, preferably in the presence of *o*-chlorotoluene or anthracene. They also regarded an alkenylsodium compound as an intermediate. It seems desirable, therefore, to record the results obtained to date in this laboratory. Attention should also be drawn to the work of Shatensteĭn and coworkers (5) who isomerized pentene-1, hexene-1, and octene-1 with potassium amide in liquid ammonia.

Table I shows the results obtained in the pyrolysis of amylsodium. At each of three temperatures the gas from the first period of pyrolysis was predominantly pentane, a fact which accords with the view that the escape of pentene was delayed because it was being metalated. With longer time at 90° and 75° the proportion of pentane fell. This difference in the appearance of alkane and alkene products agrees with that found by Carothers (6) in the pyrolysis of ethylsodium, although the explanation is different. At 90° the amount of pentene-1 exceeded that of *trans*-pentene-2. At 70° it always was less. At 50° no pentene-1 was detected.

---

[1] This work was performed as a part of the research project sponsored by the Federal Facilities Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

TABLE I

Pyrolysis of Amylsodium

Temp., °C.	Fract. No.	Time, hours	Yield, mg.	Pentane, %	Pentene	
					—1 %	—2 %
90	1	0.7	820	61	18	18
	2	1.3	1320	45	33	22
	3	2.3	510	26	55	19
	4	3.3	330	31	46	23
	5	5.3	390			
	6	8.3	120			
	Total		3490[a]			
75	1	2	470	50	18	32
	2	4	446	38	20	42
	3	6	378	20	26	54
	4	8	394	34[b]	15	51
	5	11	331	0	25	75
	6	14	150			
	7	21	218	5	12	83
	Total		2387[c]			
50		48	295[d]	82		18

[a] This quantity equals 48.5 m.e. of C_5 hydrocarbons from an original sample of 60.2 m.e.

[b] This value appears out of line, possibly because the process was discontinued overnight and pentane accumulated in the system.

[c] This quantity equals 33.2 m.e. out of an original value of 49.9 m.e. of amylsodium.

[d] This quantity equals 4.1 m.e. of C_5 hydrocarbons from 19.2 m.e. of amylsodium.

Table II shows the isomerization of a number of unsaturated hydrocarbons under the influence of pentenylsodium. Straight chain olefins isomerized very readily. Only 2 mole-% of the organosodium reagent was required for a noticeable evolution of heat and only a part of that insoluble aggregate could have entered into the reaction. A branched chain or cyclic system was isomerized more slowly. Diallyl and 4-phenylbutene-1 were isomerized very slowly.

Sodium reagents, found capable of causing isomerization of pentene-1, are recorded in Table III in the order of decreasing activity. All of the organosodium compounds except phenylsodium were prepared by metalating the corresponding hydrocarbon with amylsodium. Traces of this metalating agent may still be present in triphenylmethylsodium and allylsodium, although the preparation time was as long as with diallyl and fluorene where only slight isomerizing activity developed. The three phenylsodium reagents with the halide salts indicated were made from the corresponding halobenzenes.

The supposition that each molecule of olefin actually passes through an organosodium intermediate on its way to the isomer deserves careful consideration. Whether in the pyrolysis or the isomerization tests only a trace of pentenylsodium would be needed. That such a metalation can occur was proven by tests

TABLE II

CONVERSION OF UNSATURATED HYDROCARBONS TO MORE STABLE ISOMERS BY MEANS OF PENTENYLSODIUM

Hydrocarbon	Evol. of heat	Time, min.	Product,	Yield, %
Pentene-1	Yes	30	*trans*-Pentene-2	95
Pentene-2	No	60	No change	
Hexene-1	Yes	30	*trans*-Hexene-2	95
Octene-1	Yes	30	*trans*-Octene-2	95
2-Ethylhexene-1	No	1440	3-Methylheptene-2[a]	95
β-Pinene	No	20	α-Pinene	51
		1440	α-Pinene	95
Diallyl	No	1440	—[b]	30
4-Phenylbutene-1	No	1440	4-Phenylbutene-2	23

[a] The product may be a heptene-2 or heptene-3 but in either event the terminal vinyl group has disappeared.

[b] The structure is unknown but a conjugated hexadiene should form ultimately. The percentage change has been judged largely by the increase in the terminal CH_3 group.

TABLE III

ISOMERIZATION OF PENTENE-1 BY VARIOUS ALKALI METAL REAGENTS

Reagent-sodium	Time for noticeable heat, min.	Total time, min.	Isomerization, %
Pentenyl-[a]	2	20	95
Benzyl-	4	20	95
Octenyl-	4	20	83
Amyl-	8	20	71
Phenyl-(NaCl)	20	60	54
Phenyl- (NaBr)	20	60	23
Phenyl- (NaI)		120	13
Triphenylmethyl-		90	22
Allyl- (Alfin)[b]		1440	92
Fluorenyl-		120	0
Fluorenyl-		1440	72
Diallyl-		1440	39
-hydride		2880	0
-hydroxide[c]		1440	0

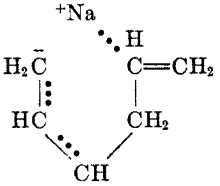
[a] Made from either pentene-1 or pentene-2.

[b] Hexene-1 was used in this test in place of pentene-1.

[c] Potassium hydroxide instead of sodium hydroxide was used.

of pentenylsodium with octene-1. Around 26% change of the ionic aggregate to octenylsodium occurred in 30 minutes, 63% within 24 hours. If the reaction can penetrate so far into an aggregate during these times, the surface of the organosodium reagent should have been affected almost immediately. Hence, for pyrolysis or isomerization, metalation could be functioning in a catalytic sense to produce a *trans*-alkene-2 isomer from an alkene-1.

Several other facts should be clarified, however, before this opinion is regarded as proven. Amylsodium is unquestionably the most powerful metalating agent of the group because it acts irreversibly in metalating all olefins and alkylaryl compounds. Yet this reagent was only fourth in isomerizing activity. Benzylsodium, which is second in the list, would not ordinarily be chosen as a metalating agent for olefins and triphenylmethylsodium and fluorenylsodium even less so because of the difference in *p*K value (7, 8) of the hydrocarbons. The very strong halide salt influence in the three phenylsodium tests is reminiscent of the salt influence in the polymerization of butadiene by phenylsodium (9) and in the Alfin catalysts (10), where metalation seems of less importance than orientation on the surface (11). Diallylsodium was surprisingly inactive for an alkenylsodium type of compound but intramolecular coordination about sodium, as shown in the formula, might account for the reduced isomerizing activity. Alkalimetal amides, as used in Shatenstein's (5) experiments are not ordinarily regarded as metalating agents for olefins in view of Wooster's (12) inability to get benzylsodium in liquid ammonia, although a potassium cation was not present in Wooster's work.



EXPERIMENTS

Pyrolysis of amylsodium. A measured volume of amylsodium, prepared in the usual way, (13, 14) was added to a round-bottom flask and the pentane was removed by a rapid stream of nitrogen with some heating. The dry solid then was kept under the vacuum of an oil pump for several hours to remove traces of pentane and decane. The flask then was surrounded by a water-bath and the volatile products were collected in a trap cooled in liquid nitrogen. The weight and infrared absorption of nearly all fractions collected were measured. The results are recorded in Table I.

Hydrocarbons. Pentene-1 was the Phillips Petroleum Company pure grade and was claimed to be 99 mole-% pure. Hexene-1 was Phillips Petroleum Company research grade and claimed to be 99.5% pure. Pentene-2 was Phillip's grade and boiled at 36–37°, n_D^{25} 1.3759. Octene-1, from the Humphrey-Wilkinson Company, boiled 120.5–121.5°. 2-Ethylhexene-1 was from the same company and boiled at 118–119°. Diallyl was from a sample in the laboratory (13) which had been made from allyl chloride and magnesium turnings. It boiled at 60.5–61.5° and had n_D^{25} 1.4010. 4-Phenylbutene-1 was made from benzyl chloride and allylsodium and boiled at 176–177°. β-Pinene and α-pinene were obtained through the courtesy of the Naval Stores Station, Olustee, Florida. Both were reported as distilled through a 100-plate column and were middle cuts.

All hydrocarbons were tested for peroxide. If the surface of a drop of mercury was only slightly tarnished, sodium hydride alone was used for purification. If larger amounts of peroxide were present, a ferrous sulfate wash, followed by drying and fractionation, was employed. The final drying was always with sodium hydride which caused no isomerization.

Analysis by infrared absorption. All measurements were made on a Spectrophotometer by Dr. Nagy, to whom the authors are indebted. The reference cell was a salt block. The sample cell was 0.031-mm. thick. The pure liquids were observed before isomerization. The product of each isomerization contained as much as 10% heptane, in which the sodium reagent had been suspended.

The following bands were used in this study: 6.06–6.25 for the double bond, 10.10 and 11.00 for the terminal vinyl group, 10.22–10.37 for the *trans*-alkene-2, 14.8–15.7 for *cis*-alkene-2, and 7.27 for a terminal methyl. As an illustration, the spectrum of pentene-1 has from 5–15% transmission at 6.13, 10.12 and 11.00. The isomerization product has only a weak band at 6.1 μ, none at 10.1 and only a slight hump at 11.0 μ, but has a very strong band (5–10% transmission) at 10.42 μ. Also increased absorption takes place at 7.27 μ and a new but weak band appears at 14.4 μ. The band at 6.1 shifts very slightly to shorter length. If the band at 6.1 is due to residual alkene-1, only about 95% of alkene-1 is converted to alkene-2. If the weak band in the 6.1 region is due to *cis*- or *trans*-alkene-2, then the isomerization is approximately 100%.

Also in these calculations the possibility of an equilibrium must be considered. The free energies (15) of formation at 25° are 18.96, 17.17, and 16.76 for pentene-1, *cis*-pentene-2, and *trans*-pentene-2. Hence the value of K_2/K_1 from $F = 2.3\ RT \log K_2/K_1$ is 50 for the free energy difference between pentene-1 and *trans*-pentene-2. Accordingly 2% of pentene-1 might be present in the final product. The expressions "nearly complete" or above 95% are used in this paper to cover such a possibility. By a similar calculation about 10% of the pentene-2 would be *cis*. At higher temperatures the equilibrium would shift to more pentene-1. Preliminary experiments have not confirmed that an equilibrium really exists.

Preparation of pentenylsodium. Phillip's pentene-1 (175 g.), reported as 99% pure, was added to amylsodium prepared in the standard way (13, 14) from 1 g.-atom of sodium and 0.5 mole of amyl chloride in heptane. Previous experience in metalating olefins has indicated that a five-fold excess of olefin would insure consumption of the amylsodium, as judged by carbonation. The suspension was stirred slowly for 40 hours and then was transferred to a bottle under nitrogen and diluted with heptane to a volume of 700 ml. A sample then was removed and centrifuged. An infrared absorption of the clear hydrocarbon layer showed that nearly all of the pentene-1 had been converted to *trans*-pentene-2.

Isomerization of pentene-1 by pentenylsodium. The pentenylsodium suspension (50-ml. portion), amounting to approximately 0.017 mole, was centrifuged, the hydrocarbon layer was removed, and the solid reagent was washed three times with heptane which had been previously dried over sodium hydride. An atmosphere of dry nitrogen was present always. The last washing showed no unsaturation by infrared analysis. Moreover, in a parallel experiment, 130 ml. of the suspension was carbonated after the last washing. Fractionation of the neutral hydrocarbon layer in a 6 x 900 mm. Podbielniak spinning band column yielded no material which boiled within the range of pentene or showed evidence of unsaturation.

To the above washed solid from the 50 ml. of pentenylsodium was added 100 ml. of pentene-1. After about five minutes the evolution of heat was noticeable and enough to cause boiling of the pentene. After 20 minutes the bottle was centrifuged. Infrared analysis of the clear hydrocarbon layer showed that conversion to *trans*-pentene-2 had been complete or nearly so. The hydrocarbon layer therefore was removed and replaced by a fresh 100-ml. portion of pentene-1. Once again the mixture boiled and isomerization to *trans*-pentene-2 was similarly complete. In these two experiments the pentenylsodium had converted 100 times its mole quantity of pentene-1 to *trans*-pentene-2 rapidly enough to be noticeably exothermic.

Isomerization of unsaturated hydrocarbons. In each experiment 5 ml. of the pentenylsodium suspension was put in a 15-ml. centrifuge tube and all trace of pentene was removed by three centrifugings and washings with heptane. After the last wash, 10 ml. of an olefin or unsaturated hydrocarbon was added to the solid. If some heat was evolved, the sample for infrared absorption was taken in 30 minutes. Otherwise the reaction time was as much as 24 hours. The results are recorded in Table I.

Isomerization by various sodium reagents. The reagent from pentene-1 was made from the reaction of 200 ml. of the hydrocarbon with 500 ml. of amylsodium, which had previously been made by the process regularly employed in this laboratory (13, 14). Such a preparation usually contains about 0.5 m.e. per ml.

Similarly sodium compounds were prepared from pentene-2, octene-1, toluene, and diallyl in the proportion of 100 ml. of the hydrocarbon with 250 ml. of the amylsodium suspension.

Triphenylmethylsodium and fluorenylsodium were prepared respectively by addition of 30 g. (0.12 mole) of triphenylmethane and 25 g. (0.15 mole) of fluorene to 250 ml. (approximately 0.13 mole) of amylsodium in pentane. In these cases, as in the previous ones, the hydrocarbons were added to the bottle which contained the amylsodium and the mixtures were allowed to stand at least several days with occasional hand shaking.

The phenylsodium preparations were made from 0.5 mole of the halobenzene with 1 g.-atom of sodium sand in cyclohexane in the customary high-speed stirring apparatus used in this laboratory. The yields were nearly identical, being 0.41, 0.40, and 0.40 mole of phenylsodium from chloro-, bromo-, and iodo-benzene respectively.

Sodium hydride was obtained from the Metal Hydrides Corporation.

Potassium hydroxide was Merck reagent grade in pellets.

The results of experiments with these reagents are recorded in Table III.

Metalation of octene by pentenylsodium. Pentenylsodium suspension (130 ml.) was freed of pentene in the manner already described and 40 ml. of octene-1 was added to the solid. After 24 hours the hydrocarbon layer was removed and fractionated in the Podbielniak column. About 2 ml. of pentene-2 (mostly *trans*), 0.7 ml. of octene, b.p. 120–121°, and 18 ml. of octene, b.p. 124–125° were collected. Infrared curves of both octene fractions showed only *trans*-octene-2. Carbonation of the sodium compounds led, after the usual method of separation, to 3.5 g. of carboxylic acids of which 63% were derived from octene.

SUMMARY

1. Decomposition of amylsodium at 90, 75, and 50° under a vacuum yielded progressively less pentene-1. At the lowest temperature the olefin was entirely *trans*-pentene-2.

2. Pentenylsodium caused the isomerization of hydrocarbons with terminal vinyl groups and the process was exceedingly rapid with any *n*-alkene-1 tested.

3. The isomerization of pentene-1 to *trans*-pentene-2 took place in decreasing velocity as pentenyl-, benzyl-, octenyl-, amyl-, phenyl-, triphenylmethyl-, and allyl- (alfin) sodium compounds were used.

4. With phenylsodium the isomerizing activity decreased as the sodium compound was made from chloro-, bromo-, and iodo-benzene.

CAMBRIDGE 39, MASS.

REFERENCES

(1) MORTON AND NEWEY, *J. Am. Chem. Soc.*, **64,** 2247 (1942).

(2) MORTON AND CLUFF, *J. Am. Chem. Soc.*, **74,** 4056 (1952); **75,** 134 (1953).

(3) ZIEGLER AND GELLENT, *Ann.*, **567,** 179 (1950).

(4) PINES, VESELEY, AND IPATIEFF, *J. Am. Chem. Soc.*, **77,** 347 (1955).

(5) SHATENSHTEĬN, VASIL'EVA, DYKHNO, AND IZRAILERICH, *Doklady, Akad. Nauk. SSSR*, **85,** 381 (1952); *Chem. Abstr.*, **46,** 9954 (1952).

(6) CAROTHERS AND COFFMAN, *J. Am. Chem. Soc.*, **51,** 588 (1929).

(7) CONANT AND WHELAND, *J. Am. Chem. Soc.*, **54,** 1212 (1932).

(8) MCEWEN, *J. Am. Chem. Soc.*, **58,** 1124 (1936).

(9) MORTON AND LETSINGER, *J. Am. Chem. Soc.*, **69,** 172 (1947).

(10) MORTON, BOLTON, COLLINS, AND CLUFF, JR., *Ind. Eng. Chem.*, **44,** 2876 (1952).

(11) MORTON, NELIDOW, AND SCHOENBERG, *Trans. Inst. Rubber Ind.*, In press.

(12) WOOSTER AND MITCHELL, *J. Am. Chem. Soc.*, **52,** 688 (1930).

(13) MORTON, *et al.*, *J. Am. Chem. Soc.*, **72,** 3785 (1950).

(14) MORTON AND BRACHMAN, *J. Am. Chem. Soc.*, **73,** 4363 (1951); **76,** 2973 (1954).

(15) ROSSINI, *et al.*, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953.