Summary

(+)3-Methylheptane and 80 mole per cent. sulfuric acid-d_2 have been agitated together at temperatures between 25 and 70°. Exchange and racemization occur with the rate of the former being about fifteen times greater. Isomerization is slower than racemization. The rate of exchange of *n*-octane is more than one hundred times slower than that of 2- and 3-methylheptane.

These results are incompatible with those mechanisms of alkylation of olefins by isoparaffins which involve initial attack by sulfuric acid on the alkane. Possible mechanisms of the racemization-exchange reaction are discussed with most favor being given to a chain reaction with an olefin intermediate.

EVANSTON, ILLINOIS RECEIVED APRIL 3, 1948

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

Polymerization. VIII. The Action of Metalating Reagents on Rubber[1]

BY AVERY A. MORTON AND HUGH E. RAMSDEN[2]

The Alfin catalysts[3] are metalating[4] as well as polymerizing agents. Hence a knowledge of what metalation does to natural rubber and the Alfin polymer is important. The method used in this study was to subject the rubber to the metalating agent, carbonate the product and examine its solubility in water or other solvents or determine its intrinsic viscosity. Insolubility in organic solvents is taken as evidence of cross-linking. Four reagents were used: alkoxides (as a class), phenylsodium, amylsodium and 1-pentenylsodium. The first obviously does not add to carbon–carbon double bonds, the second one does not so add[5] and therefore can exert a metalating action only, the third adds to conjugated double bonds[6] but not to monoölefins and is a powerful metalating agent,[4] the fourth adds more readily to conjugated bonds[3] than does the third but obviously is a weaker metalating agent. These agents uniformly caused cross-linking in the expected order of metalating strength which is: amylsodium > phenylsodium > 1-pentenylsodium > alkoxides. The series covers a wide range, from the extremely high activity of amylsodium to the extremely low activity of the alkoxides, the latter so weak that heat and vacuum must be used to remove one component of an equilibrium after the manner used by McElvain and co-workers[7] in the action of sodium ethoxide on esters. All results are listed in Tables I to IV inclusive, and in each table the order from top to bottom is the order of increasing severity or condition of use. The gel formation follows approximately this same order. A similar series of tests, applied to Alfin polybutadiene and polyisoprene, gave, in general, similar results (see Table V).

TABLE I

EFFECT OF ALKOXIDES ON NATURAL RUBBER UNDER CONDITIONS THAT SHOULD EFFECT METALATION

Expt.	Alcohol[a]	Max. temp., °C.	Time[b]	Pres. microns	Percentage of product soluble[c] in E.	C.	B.	insol.[d] in solvents
1	Me_2CHOH	80	11 d	R[e]	60	10	Trace	..
2	EtOH	100	49 h	0.4	60	10	..	7
3	Me_2CHOH	100	46 h	1–50	60	7	20	..
4	Me_2CHOH	100	72 h	1.503.0	20	33	..	4
5	Et_2CHOH	100	45 h	1–50	40	27	13	..
6	$EtMe_2COH$	100	47 h	2.7–15	20	20	..	40
7	EtOH	150	24 h	2–5	13	7	33	53
8	EtOH	150	24 h	1.1–3.2	7	13	20	40
9	Me_2COH	150	24 h	0.7–1.5	13	13	7	53

[a] In this column Me = CH_3, Et = C_2H_5. [b] d = days; h = hours. [c] The solvents used were either (E.); chloroform (C.) and benzene (B.). [d] The blank spaces in these columns may mean that the values were undetermined. The sum of the values is not exactly 100%, because of losses or occlusion of solvent. [e] In this experiment the mixture was refluxed in benzene as a solvent.

Alfin catalysts contain also minute amounts of metallic sodium left over from the initial reaction of sodium with the alkyl halide used in preparing the catalyst. It is necessary to know whether an alkali metal will also cause cross-linking and metalation. Tests of the action of alkali metal on nat-

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[1] This work was part of the program of research carried out during the war under the sponsorship of Rubber Reserve Co.

[2] Present address: E. I. du Pont de Nemours and Co., Inc., Parlin, New Jersey.

[3] Morton, Magat and Letsinger, THIS JOURNAL, **69**, 950 (1947).

[4] Morton and Holden, *ibid.*, **69**, 1675 (1947); Morton, Brown, Holden, Letsinger and Magat, *ibid.*, **69**, 2224 (1947).

[5] Morton and Wohlers, *ibid.*, **69**, 167 (1947).

[6] Morton, Brown and Magat, *ibid.*, **69**, 161 (1947).

[7] Roberts and McElvain, THIS JOURNAL, **59**, 2007 (1937); McElvain, *ibid.*, **51**, 3124 (1929); Briese and McElvain, *ibid.*, **55**, 1697 (1933); Cox and McElvain, "Organic Syntheses," **17**, 54 (1937).

TABLE II

EFFECT OF PHENYLSODIUM ON NATURAL RUBBER[a]

				Percentage of product			
				soluble[c] in			insol. in sol-vents
Expt.	Cond.[b]	Temp., °C.	Time, hr.	E.	C.	B.	
10	Sta.	R.	24	53	13	3	
11	Sta.	R.	119	13	33		27
12	HSS.	20	5	27	33	3	7
13	HSS.	40	5	13	33	3	33
14	HSS.	60	4.5	4	3		80
15	HSS.	80	5	7	3		80

[a] The amount of rubber used was 0.022 mole, calculated on the basis of the number of C_5H_8 units. The amount of phenylsodium was the same. [b] For the conditions listed in this column, Sta. means standing and HSS. means high-speed stirring. [c] The letters E, C and B refer to ether, chloroform and benzene, respectively.

TABLE III

METALATION OF NATURAL RUBBER BY AMYLSODIUM[a] IN THE HIGH-SPEED STIRRING APPARATUS

				Percentage of product			
				soluble[c] in			insol. sol-vents
Expt.	RONa[b] mole equiv.	Temp., °C.	Time, hr.	E.	C.	B.	
16	None	20	5	3	3	33	53
17	None	40	2, 3.5[d]	3	3	1	87
18	None	60	5	7	1	1	80
19	None	80	5	3	3		87
20	0.5	20	5	3	3	3	80
21	1.0	20	5	1	3	1	80[e]

[a] The amounts of amylsodium and rubber were 0.044 and 0.022 mole, respectively, the latter being based on the amount of C_5H_8 units present. [b] R = the isopropyl radical. [c] The letters E, C and B refer to ether, chloroform and benzene, respectively. [d] In this experiment the mixture was stirred for two hours, and then allowed to stand for three and one-half hours longer. [e] The gel content of the rubber before solvent extraction was 89%, as measured in the conventional manner. The swelling volume of the gel was 11.8. An analysis of the total rubber showed C, 68.7; H, 9.4; Na, 4.4, and O (by difference) 17.5. Small portions of this rubber were alkali water-soluble. The sodium is exceedingly difficult to remove by washing because of the insolubility of the product.

TABLE IV

EFFECT[a] OF 1-PENTENYLSODIUM ON NATURAL RUBBER

			Percentage of product					
			soluble[d] in		insol. in sol-vents			
Expt.	Molal ratio RNa to R'ONa[b]	Time, hr.	E.	C.		Gel	S. V.	Int. vis.
	[Control][c]					25	77	2.0
22	None[e]	4	73		10			
23	9/1	5	69		20	36	14	1.4
24	4/1	5	7	7	73	51	19	1.0
25	1/1	5	33	3	33	57	14	1.2
26	1/2	5	1	52	33[f]	58	15	1.4

[a] The amount of 1-pentenylsodium was estimated at 0.044 mole based on a yield of 80% amylsodium and complete utilization in the metalation of 1-pentene. The natural rubber amounted to 0.022 mole referred to the number of isoprene units. The temperature of reaction was 20°. The product was carbonated at the end of each reaction but no alkali water-soluble rubber was obtained. [b] R = pentenyl radical; R' = isopropyl. [c] Values for the rubber before treatment with any reagent. [d] E. and C. have the same meaning as in the previous tables. [e] No isopropoxide was present in the experiment. [f] An ordinary gel determination of the rubber before solvent extraction showed 58.4% gel. Analysis of the rubber before solvent extraction showed C, 57.2; H, 11.2; Na, 2.0; O (by difference) 29.6. Analysis of the chloroform-soluble part showed C, 88.4; H, 10.9; O (by difference) 0.7.

TABLE V

EFFECT[a] OF VARIOUS ALFIN CATALYSTS AND ORGANOSODIUM REAGENTS ON ALFIN RUBBERS

Expt.	Polymer[b]	Catalyst[c] or reagent	Gel	S. V.	Intrinsic vis-cosity
	Polybutadiene	None	7.1	133	3.5
27		PP_1	24.5	30	2.0
28		PP	23.4	20	1.0
	Polyisoprene	None	0	...	9
29		PP[d]	50.3	6	2.3
30		P_2P[d]	40.3	12	2.3
31		Allyl Na[d]	19.3	12	2.8

[a] The reaction took place for five and one-half hours at 20°. [b] The polybutadiene was prepared with a catalyst made from 2-pentanol and 1-hexene, commonly designated[3] as a P_2H_1 catalyst. The polyisoprene was made with the PP or allylsodium–sodium isopropoxide catalyst. [c] The letters refer to the components used in making the catalyst, the first letter to the alcohol and the second to the olefin.[3] PP_1 = Propanol-2 and 1-pentene, respectively. PP = Propanol-2 and propylene, respectively. P_2P = Pentanol-2 and propylene, respectively. [d] Quantities of reagents are not equivalent.

ural rubber under heat and vacuum (Table VI) and in the high-speed stirring apparatus (Table VII) showed no cross-linking. If any change occurred, it was in the direction of lower molecular weight. Tests of the action of sodium or potassium on comparatively strong hydrocarbon acids, such as fluorene, triphenylmethane and diphenylmethane, showed that metalation could occur under appropriately vigorous conditions (Table VIII), but only with fair to poor yields, respectively. Similar tests on the less acidic toluene (Table IX) showed that metalation was slight and was not greatly facilitated by the presence of diphenyl- or triphenylmethane. Therefore the traces of metallic sodium present with the Alfin catalyst do not appear to have any influence on the formation of gel.

TABLE VI

EFFECT OF ALKALI METAL ON NATURAL RUBBER[a] AT REDUCED PRESSURE

					Percentage of product soluble[c] in		
Expt.	Metal, g.	Max. temp., °C.	Time[b] at max. temp.	Pres., microns	E.	C.	B.
32	None[d]	Room			80		
33	None	150–170 170–180 180	6 h 30 m 15 m	1–3	47	13	
34	Na 5	150–180	100 m	17–50	40	7	
35	Na 5	150	50 h	0.4–1	27	7	7
36	Na 5	230[e]	25 h	1.7–12	20	13	
37	K 5	180[e]	30 h	1.5–5.5	20	33	

[a] 1.5 g. of rubber was used in each test. [b] m = minutes; h = hours. [c] E = Ether, C = Chloroform and B = Benzene. [d] Control test of the solubility of the rubber. [e] At this temperature the metal vaporized and deposited a mirror in the neck of the flask.

TABLE VII

EFFECT OF SODIUM METAL ON NATURAL RUBBER[a] IN THE PRESENCE OF SODIUM ISOPROPOXIDE AND IN THE HIGH-SPEED STIRRING APPARATUS

Expt.	Sodium, mole	Isopropyl alcohol, mole	Solvent[b]	Temp., °C.	Time, hr.	Percentage of product soluble in E.[c]	C.	B.	insol. in solvents	Approx. mol. wt. of E. sol. fract.
38	0.088	0.017	B	80	4.5	47	3	7	33	50,000
39	.088	.017	To	109	5.5	73			Tr.	45,000
40	.088	.017	X	140	5	27	33	7	13	25,000
41	.088	.017	Cu	150	5	73	1		3	20,000
42	.30[d]	.1	Cu	150	5	20[e]	40	5	20	2,300
43	.22	.0	Cu	150	5	130[f]				13,000

[a] Rubber 1.5 g. was used. [b] B = Benzene; To = Toluene; X = Xylene; Cu = Cumene. [c] E = Ether; C = Chloroform; B = Benzene. [d] Only one gram of rubber was used in this experiment. [e] Some unsaturated (to permanganate) organic acids, soluble in water were obtained also, from this reaction. [f] The yield was over 100% for reasons not yet understood.

TABLE VIII

ACTION OF SODIUM AND POTASSIUM METAL ON HYDROCARBONS THAT PROBABLY HAVE A GREATER HYDROCARBON ACIDITY THAN DOES RUBBER

Expt.	Hydrocarbon,[a]	g.	Metal,	g.	Isopropyl alcohol, g.	Solvent[b]	React. cond.[c]	Temp., °C.	Time[d]	Product RCO_2H—[e] %
44	Tr	5	Na	1	1	B	R	80	4 d	0
45	F	5	Na	1	1	B	R	80	4 d	0
46	F	5	Na	1	1	X	R	138	11 d	0
47	F	3.7	Na	5	13	X	S	138	5 h	0
48	Tr	5.4	Na	5	6.5	X	S	138	5 h	0
49	F	3.7	Na	5	None	X	S	138	5 h	29
50	F	3.7	Na	5	6.5	X	S	138	5 h	77
51	Tr[f] F	5.4 3.7	Na	5	6.5	X	S	138	5 h	0.2 64
52	Tr	5.4	K	8.5	None	X	S	138	3.5 h	69
53	Di	3.7	K	8.5	None	X	S	138	2.5 h	3

[a] Tr = Triphenylmethane; F = Fluorene; Di = Diphenylmethane. [b] B = Benzene; X = Xylene. [c] R = Reflux; S = Stirred. [d] d = days; h = hours. [e] RCO_2H refers to the carboxylic acid derived from the hydrocarbon being treated with the metal. [f] A mixture of hydrocarbons were used in the hope that metalation of the one present in smaller amount would facilitate metalation of the other.

TABLE IX

METALATION OF TOLUENE AND OTHER HYDROCARBONS BY POTASSIUM METAL IN BOILING TOLUENE FOR FOUR HOURS

Expt.	Hydrocarbon,[a] g.	K, g.	Alcohol,[b] g.	Products, % RCO_2H[c]	$PhCH_2CO_2H$[d]
54	To	8.5	None		2.7
55	To	8.5	I 6.4		10[e]
56	To	8.5	sB 8.1		4.9
57	To	8.5	D 10.9		4.2
58	Di 0.4	8.5	I 6.4	99	1.2
59	Di 3.6	5.2	None	98	8
60	Tr 5.4	5.2	None	39	1
61	Tr 5.4	8.5	I 6.5	62	4.1

[a] To = Toluene, present as the solvent; D_1 = Diphenylmethane; Tr = Triphenylmethane. [b] I = Isopropyl; sB = *s*-butyl; D = Diethylcarbinol. [c] RCO_2H = the carboxylic acid derived from hydrocarbons other than toluene. [d] The yield was calculated on the basis of the available metal. [e] Attempts to reproduce this result yielded no higher than 4%.

Experiments

The experimental methods used are, in general, identical with those described in earlier publications as far as the preparation of phenylsodium,[8] amylsodium,[4] allylsodium[4] and the Alfin catalysts[8] are concerned. The high-speed stirring apparatus also has been described elsewhere.[9] The natural rubber was a sample of deproteinized material obtained through the courtesy of Dr. Blake.[10] Intrinsic viscosities and sol gel determinations were carried out in benzene solution by the method commonly used in the work on the rubber project.[11]

Rubber and Sodium Alkoxides.—The usual method was to dissolve 1.5 g. of rubber in benzene, add 2 g. of sodium metal and a small excess of the alcohol. The mixture was allowed to react or was refluxed, if necessary, under an atmosphere of nitrogen for a long time. In Experiment I, Table I, the mixture was poured onto Dry Ice after refluxing. In the other experiments of the table, benzene and excess alcohol were removed by an aspirator pump, the flask was transferred to a molecular still, and heat and high vacuum were applied as specified in the table. The product was carbonated by admitting carbon dioxide, cooling and adding solid carbon dioxide. When the carbon dioxide had evaporated, 200 ml. of alcohol was added to destroy traces of sodium metal that might still be present and to dissolve soluble sodium salts. After two hours of reflux the alcoholic solution was removed and treated with water and acid in order to recover any soluble portion. The residue was also treated with acid (100 ml. of 6 *N* acid) the acid subsequently removed, the rubber washed free of chlorine ion (silver nitrate test), and the residue refluxed for four hours with 200 ml. of ethyl ether. Filtration of the ether extract through

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[8] Morton and Letsinger, THIS JOURNAL, **69**, 172 (1947).

[9] Morton and Redman, *Ind. Eng. Chem.*, **40**, 1190 (1948).

[10] The authors are greatly indebted to Dr. J. T. Blake, of the Simplex Wire and Cable Company, for his coöperation.

[11] Baker, Mullen and Walker, private communication.

glass wool and evaporation yielded the ether-soluble rubber. The portion insoluble in ether was similarly treated with 100 ml. of chloroform for four hours and the residue from that treatment was extracted with 100 ml. of benzene for four hours.

Phenylsodium and Rubber.—Phenylsodium was made from 2.5 g. (0.022 mole) of chlorobenzene and sodium sand in a total volume of 160 ml. of thiophene-free benzene in the usual way. The mixture was forced by nitrogen pressure into a solution of 1.5 g. of rubber in 100 ml. of thiophene-free benzene. The viscous mixture was allowed to stand for the period given in Table II, after which it was forced onto solid carbon dioxide. Subsequent recoveries of rubber were as described in the previous section. The operations with stirring were in general the same as when the mixture was allowed to stand. Other conditions and results are given in Table II.

Amylsodium and Rubber.—The quantities of amyl chloride and sodium used for preparing amylsodium were such as to give 0.044 mole in each experiment based on an 80% yield. If isopropyl alcohol was added to this mixture in order to form the isopropoxide, enough additional amylsodium was prepared to allow for this consumption. Rubber, 1.5 g., was shredded and added to the reaction mixture. For the reaction at 20° the solvent was pentane; for the higher temperatures it was cyclohexane. The products were handled as before. The results are given in Table III.

Pentenylsodium and Rubber.—The preparation of amylsodium was carried out in the usual manner but with 1-pentene as a solvent.[4] Isopropoxide was obtained when desired by addition of the requisite quantity of isopropyl alcohol to 1-pentenylsodium. Rubber was added and the products separated as described in the previous section. The results are given in Table IV. The gel, swelling volume (S. V.) and intrinsic viscosity were determined by standard methods.

Alkali Metals and Rubber.—Sodium (5 g.) was shaken in 100 ml. of hot sulfur-free toluene. Rubber (1.5 g.) was then added and dissolved in 60°. An atmosphere of nitrogen was maintained. After removal of as much of the toluene as possible by use of an aspirator, the remainder was removed under a molecular still. Heat and vacuum was applied as described in Table VI. Carbon dioxide was then admitted, the reaction mixture cooled, and treated with solid carbon dioxide. The rubber was washed and fractionated as described below. The results are given in Table VI.

Reaction of Metals with Hydrocarbons.—The hydrocarbon in the quantities specified in Tables VII and VIII was dissolved in 40 ml. of benzene or xylene. Sodium was cut into small pieces and added. Alcohol was added as specified; the mixture was refluxed under an atmosphere of dry nitrogen. After the period of time specified in the table the mixture was carbonated by forcing it onto solid carbon dioxide. Alcohol, 100 ml., was added to destroy the sodium. Water, 13 ml., was then added and the solution heated on a water-bath to evaporate the alcohol. The aqueous solution was extracted with petroleum ether and with benzene and was then acidified with hydrochloric acid. The acid solution was then extracted with three 100-ml. portions of benzene and with three 100-ml. portions of ether.

The procedure was, in general, the same when the mixtures were stirred instead of refluxed. Usually the carboxylic acid precipitated upon the addition of hydrochloric acid and a single crystallization gave fairly good material. Triphenylacetic acid, recrystallized once from benzene, melted at 256.5–258.5° (the recorded[12] value is 264–265° dec.), fluorene-9-carboxylic acid, recrystallized once from alcohol, melted at 216–218° (a recorded[13] value is 220–222°), and phenylacetic acid, as obtained by evaporation of the ether extract, melted at 70–72° (recorded[14] value 76.7°).

Summary

When metalating agents act on natural or Alfin rubber, gel is formed. The amount of gel increases with the activity of the metalating agent and the severity of the conditions under which it is used.

Metallic sodium or potassium does not cause gel to form in natural rubber. Under very severe conditions these metals will metalate the highly active hydrocarbons, fluorene, triphenylmethane and diphenylmethane, in fair to poor amount, depending on the hydrocarbon, but they metalate toluene only slightly, even under highly favorable conditions.

[12] Schmidlin, *Ber.*, **39**, 636 (1906).

[13] Friedländer, *ibid.*, **10**, 536 (1877).

[14] Huntress and Mulliken, "Identification of Pure Organic Compounds Order I," John Wiley and Sons, New York, N. Y., 1941.

CAMBRIDGE, MASS. RECEIVED JULY 15, 1947

NOTES

The Preparation of Methyl Esters

BY R. O. CLINTON AND S. C. LASKOWSKI

There appears to be no description in the literature of an easily applicable general method for the preparation of the methyl esters of aliphatic and aromatic acids, especially for large-scale preparations. A large number of individual preparations have been described, involving in most cases the use of methanol–sulfuric acid or the Fischer methanol–hydrogen chloride method. In certain cases either of these methods gives excellent results; usually, however, the yields are of the order of 60–80%. The Fischer method generally gives the better yield, but is not easily adaptable to large-scale preparations. Other methods involving fractional distillation, such as the method of Weissberger and Kibler[1] require elaborate equipment and considerable manipulation. Baker[2] has described a procedure of apparently wide adaptability for small scale preparations, in which a mixture of the acid, methanol, chloroform (or benzene) and sulfuric acid is refluxed under a Soxhlet apparatus containing anhydrous magnesium sulfate. Baker[2b] states that continuous

[1] Weissberger and Kibler, "Organic Syntheses," **24**, 72 (1944).

[2] (a) Baker, THIS JOURNAL, **65**, 1577 (1943); (b) Baker, Querry, Safir and Bernstein, *J. Org. Chem.*, **12**, 144 (1947).