remained. An excess of strong potassium hydroxide was added to this residue, and the immiscible free pyridine base taken up in ether. The ether solution was dried, and the ether removed. Distillation gave 1.1 g. (77% yield) of a colorless liquid, b. p. 205–207° (756 mm.), $n^{20}D$ 1.4950.

The chloroplatinate came down readily and quickly as small orange needles, m. p. 183–185°.

Anal. Calcd. for $C_{20}H_{32}Cl_6N_2Pt$: Pt, 27.6. Found: Pt, 28.0.

The picrate came down very slowly from an alcohol solution, m. p. 64–65°.

Anal. Calcd. for $C_{16}H_{18}N_4O_7$: N, 14.8. Found: N, 14.5.

It was not possible to isolate the chloroaurate in a pure form. The product first formed as a liquid which did not appear to be stable. A solid was finally obtained, but this product decomposed slowly upon being heated, with liberation of free gold, m. p. 160–173°. All attempts at purification produced a yellow solid which visibly contained some free gold.

The Reaction of Isobutylmagnesium Bromide with 2-Bromopyridine.—Isobutylmagnesium bromide was prepared from 6 g. of magnesium and 31.5 g. of isobutyl bromide (b. p. 88.5–89.0) in 125 cc. of ether. To this refluxing solution was added, slowly over a period of one hour, 31.5 g. of 2-bromopyridine.[12] The solution turned brown and by the end of the addition contained a dark insoluble material. The mixture was refluxed an additional half-hour, and then acidified with dilute hydrochloric acid (vigorous reaction). The mixture was made slightly basic with potassium hydroxide and filtered through glass wool. The clear ether solution was dried and the ether removed. Fractional distillation of the residual red liquid gave 7 g., b. p. 120–130°, and 3 g. of unreacted 2-bromopyridine, b. p. 190–195°; there was a 5-g. residue. No 2-isobutylpyridine was isolated.[13]

2-Bromo-3-methylpyridine (IX).—To a 2-liter flask equipped with a low temperature thermometer and an efficient stirrer were added 230 cc. of 48% hydrobromic acid, the contents cooled to −10°, and 50 g. of 2-amino-3-methylpyridine (VIII) (Reilly Tar and Chemical Company) added. The temperature was kept below 0° as 70 cc. of bromine were added over a period of one and one-half hours. The contents of the flask became viscous, as a voluminous red solid came out of solution. A solu-

tion of 80 g. of sodium nitrite in 150 cc. of water was added slowly over a period of two hours. Stirring was continued for an additional one-half hour, and a solution of 175 g. of sodium hydroxide in 250 cc. of water added, keeping the temperature below 20°. The opaque suspension was extracted four times with 250-cc. portions of ether. The combined ether extracts were dried, the ether removed, leaving a red liquid. Vacuum distillation gave 64 g. (82% yield) of colorless liquid, b. p. 76–77°[14] at 7 mm., d^{20}_4 1.544, $n^{20}D$ 1.5680. The liquid turned yellow very slowly.

The Reaction of *n*-Butylmagnesium Bromide with 2-Bromo-3-methylpyridine.—A solution of *n*-butylmagnesium bromide was prepared from 2.7 g. of magnesium metal, 15 g. of *n*-butyl bromide (b. p. 100.0–100.8°) in 250 cc. of dibutyl ether (freshly distilled over sodium metal). To this refluxing solution were added 19 g. of 2-bromo-3-methylpyridine (IX), over a period of one hour. Refluxing was continued for another hour. There was a considerable amount of an orange tar on the sides of the flask. A saturated ammonium chloride solution was added till no more reaction was observed. The layers were separated, the ether layers washed with potassium hydroxide, and dried. Removal of the ether gave 5 cc. of a dark liquid. Distillation at atmospheric pressure gave 0.65 g. (4% yield) of colorless liquid, b. p. 205–207°, and 2.0 g. of pale yellow liquid, b. p. 212–225°. The former gave a negative Beilstein test, and formed a chloroplatinate very easily, which had a m. p. 185°. The mixed m. p. with the chloroplatinate of 2-*n*-butyl-3-methylpyridine (see above) was 183–185°. The higher boiling material give a positive Beilstein test, and probably was a mixture of some unreacted 2-bromo-3-methylpyridine and some 2-*n*-butyl-3-methylpyridine.

Summary

1. The reaction of ethyl formate with ethyl *n*-butyl ketone occurs at the methylene of the ethyl group.

2. The condensation product of cyanoacetamide with the sodium salt of 2-hydroxymethylene-3-heptanone was degraded to 2-*n*-butyl-3-methylpyridine.

3. Under the proper condition, an alkyl group can replace an α-bromo group in the pyridine series, by use of the Grignard reagent.

(12) "Organic Syntheses," Vol. XXVI, John Wiley and Sons, Inc.' New York, N. Y., 1946, p. 16.

(13) *Cf.* Mariella, ref. 1, who reported the b. p. of 2-isobutylpyridine to be 177–179°.

(14) Case, ref. 6, reported a b. p. 218–219°.

The Action of Sulfuric Acid on an Optically Active Hydrocarbon[1]

BY ROBERT L. BURWELL, JR., AND GEORGE S. GORDON, III[2]

A simple optically active hydrocarbon is very resistant to inversion of configuration. von Weber[3] reported that *d*-3-methylhexane was decomposed slowly at 400° but that the recovered hydrocarbon was unracemized. Petroleum fractions which boil above about 280° possess optical activity[4]

which survives distillation, the use of the hydrocarbons as lubricating oil in a motor vehicle and, presumably, storage for several millenia.

Racemization of a simple hydrocarbon has not been reported. Thermal racemization of certain terpenes has been claimed and seems to have been established for the case of α-pinene[5] although the process is complicated by the simultaneous occurrence of faster isomerization reactions.

In view of the reactivity of alkanes containing a

(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Chicago meeting, April 21, 1948.

(2) Standard Oil Company (Indiana) Fellow, 1946–1948.

(3) von Weber, *Z. physik. Chem.*, 179A, 295 (1937).

(4) Fenske, Carnahan, Breston, Caser and Rescorla, *Ind. Eng. Chem.*, 34, 638 (1942).

(5) Savich and Goldblatt, THIS JOURNAL, 67, 2027 (1945); Fuguitt and Hawkins, *ibid.*, 69, 319 (1947).

tertiary carbon atom as exemplified by their exchange with sulfuric acid-d_2[6] and their reaction with olefins,[7] it appeared of interest to investigate on an optically active hydrocarbon the action of catalysts known to promote this reaction. It was hoped that information so discovered, in addition to throwing some light on the mechanism of the alkylation reaction, would contribute to an understanding of the reactivity of hydrocarbons in general. This paper deals with the action of sulfuric acid and of sulfuric acid-d_2 on (+)3-methylheptane.

Experimental

Materials.—(+)3-Methylheptane was prepared from (−)2-methyl-1-butanol obtained by fractionating fermentation amyl alcohol (U. S. Industrial Chemicals) in a Podbielniak Heligrid column. In three passes one obtained an alcohol of $[\alpha]^{25}$D −5.76°. Further fractionation resulted in an increase of no more than 0.01°. Several standard methods of converting the alcohol to the bromide gave poor yields but the method employing phosphorus tribromide of Bartleson, Burk and Lankelma[8] gave yields up to 90%. To reach this value, however, the reaction mixture must stand six weeks before working up. The active amyl bromide was washed with cold concentrated sulfuric acid but not fractionated since this was found likely to result in considerable isomerization. This material, $[\alpha]^{25}$D +4.05°, was coupled with allyl bromide via the Grignard reagent to give 5-methyl-1-heptene, α^{26}D +6.84°, which hydrogenated in methanol solution with the Adams platinum oxide catalyst, extracted with water, dried and distilled, gave 3-methylheptane, $[\alpha]^{26}$D +9.34°; d^{25}_4 0.7019[9]; n^{25}D 1.3962. A repetition of this preparation resulted in material of the same physical properties.[10] The material was treated with concentrated sulfuric acid and stored over sodium. No change in rotation resulted from this treatment.

2-Methylheptane was prepared from the isoamyl alcohol of fermentation amyl alcohol by the same method. n-Octane from the Connecticut Hard Rubber Company was redistilled.

Sulfuric acid-d_2 was prepared by distilling sulfur trioxide from oleum into one side of an H-shaped vessel, placing the calculated quantity of 99.8% deuterium oxide in the other limb, closing the vessel with ground glass caps and allowing the sulfur trioxide to distil to the other side at 35°. The concentration was checked by titration.

Apparatus and Procedure.—The acid was pipetted directly, and the octane distilled under vacuum into a 50-cc. spherical flask attached to a vacuum system. Both acid and hydrocarbon were degassed before this mixture was effected. Reactions were run at atmospheric pressure under dry oxygen-free nitrogen. Openings on the manifold above the hydrocarbon storage bulb and the reaction vessel were closed by mercury-sealed ground glass caps to avoid contamination by traces of stopcock grease. The reaction vessel was maintained at ±0.5° by a small oil thermostat. Stirring was effected by rotating a magnet beneath the reaction vessel, within which was a small Pyrex tube curved to fit the bottom of the flask and into which had been sealed some iron wire. Stirring was at two rates, a swishing or an agitation violent enough to produce a temporary emulsion.

(6) Ingold, Raisin and Wilson, *J. Chem. Soc.*, 1643 (1936).

(7) First reported by Ipatieff and Grosse, THIS JOURNAL, **57**, 1616 (1935).

(8) Bartleson, Burk and Lankelma, *ibid.*, **68**, 2513 (1946).

(9) American Petroleum Project 44 at the National Bureau of Standards, Table 3a, gives n^{25}D 1.39612 and d^{25}_4 0.70176.

(10) Levene and Marker, *J. Biol. Chem.*, **91**, 761 (1931), and **92**, 455 (1931), give a higher value for the rotation but in view of their comments in the second paper no great weight need be attached to this.

Products were distilled under vacuum into a graduated tube from which they could be removed for analysis or from which they could be vaporized by a stream of dry air to a tube containing copper oxide at 700°. The resulting water was condensed by Dry Ice, refluxed with alkaline permanganate and distilled *in vacuo* to a removable sample tube. The deuterium content of the water was determined by the method of Randall and Longtin.[11] Temperatures were measured to the nearest 0.01° to obtain an accuracy of better than 0.01% in deuterium content.

Polarimeter readings were made in a 2-dm. tube to a precision of 0.02°. Infrared absorption spectra of the two isomeric octanes were measured on a Beckman Infrared Spectrophotometer. Good agreement was found with those reported by the American Petroleum Institute Research Project 44,[12] and with a spectrogram of a National Bureau of Standards standard sample of 3-methylheptane (232) run at this institution. These spectra were unfortunately such as to provide no way of determining small amounts of 2-methylheptane in 3-methylheptane. Even a content of 10% could hardly be demonstrated.

Experimental Results.—Table I summarizes the main experimental results. In preliminary runs, racemization and exchange were found to be very slow with acid of weight % less than 90. Above 97% there was too much oxidation of the hydrocarbon. With 98% acid a rather stable emulsion resulted. The others settled immediately upon cessation of stirring. Acid layers darkened rapidly and sulfur dioxide was formed when 2- or 3-methylheptanes were used, but neither of these reactions occurred with n-octane. Judging from recoveries, the extreme loss by oxidation was in the vicinity of 5–6%.

TABLE I

ACTION OF SULFURIC ACID ON 3-METHYLHEPTANE

Acid used, % by weight	Temp., °C.	Time, hours	Loss in rotation $\Delta\alpha/\alpha_0$	X_{oot}	$\dfrac{\log(1 - qX_{oot}.)}{q \log(\alpha/\alpha_0)}$
98% H$_2$SO$_4$	25	1	0	.....	..
98% H$_2$SO$_4$	50	1	0.056	.....	..
89% H$_2$SO$_4$	110	2.5	0	.....	..
80.6% D$_2$SO$_4$	110	4	0	0.00020	..
95.1% D$_2$SO$_4$	70	4	.012	.0095	0.82
95.2% D$_2$SO$_4$	50	72	.050	.036	.83
95.2% D$_2$SO$_4$	50	24	.016	.012	.79
95.2% D$_2$SO$_4$	50	141	.050	.037	.83
95.2% D$_2$SO$_4$	50	43	.015	.012	.84
95.2% D$_2$SO$_4$	70	64	.029	.024	.90
94.9% D$_2$SO$_4$	70	16	.027	.023	.92
94.9% D$_2$SO$_4$	70	18[a]	...	.0005	..
94.9% D$_2$SO$_4$	70	24[a]	...	.0006	..
95.3% H$_2$SO$_4$	60	35[c,d]	.521	.....	..
94.9% D$_2$SO$_4$	60	17[c]	.143	.103	.86
94.9% D$_2$SO$_4$	60	65[d,e]	.589	.436	..
95.6% D$_2$SO$_4$	60	28[a,d,e]	...	.0027	..
95.6% D$_2$SO$_4$	60	23[b,e]	...	.341	..
95.6% D$_2$SO$_4$	60	23[e]	.434	.259	.82

[a] Used n-octane.　[b] Used 2-methylheptane.　[c] Stirring more vigorous than in preceding runs; 4.2 cc. acid. [d] Acid changed for fresh halfway through the run or daily. [e] Stirring as in note c; 4.2 cc. of acid, 3.0 cc. of hydrocarbon.

(11) Randall and Longtin, *Ind. Eng. Chem., Anal. Ed.*, **11**, 44 (1939).

(12) A. P. I. Research Project 44, Infrared Absorption Spectrogram, serial numbers 173 and 174, dated February 28, 1945.

It appeared in earlier work that the activity of the catalyst declined with time. Higher temperatures did not prevent this. This effect may arise from products of the oxidative side reactions. In certain runs, as shown in the table, each day the hydrocarbon was distilled off, the acid replaced, the hydrocarbon distilled back, and the run continued. In the runs at slower stirring speed 5.0 cc. of hydrocarbon and 2.1 cc. of acid were used; at the higher speed, 5.0 cc. of hydrocarbon and 4.2 cc. of acid or 3.0 cc. of hydrocarbon and 4.2 cc. of acid.

A run with light sulfuric acid was protracted to a 52.1% loss in rotation so that the infrared spectrum might be examined without interference of carbon–deuterium bands. The spectrum was changed slightly by this treatment but as mentioned earlier this method is not suitable for the determination of 2-methylheptane in 3-methylheptane. There would appear to be some of the 2-methyl compound present but its upper limit can be set at 20%.

Discussion

In brief, these results show that (+)3-methylheptane is converted into *dl*-3-methylheptane and isomerized by the action of sulfuric acid. With sulfuric acid-d_2 the gross rate of exchange of hydrogen atoms is about 14 to 15 times as fast as that of racemization. Increased stirring increases the rate of racemization and exchange but does not affect their ratio.

Exchange.—Ingold, Raisin and Wilson[6] agitated 77 mole % sulfuric acid containing some deuterium with several hydrocarbons at room temperatures for a number of days. Their results were not very consistent, but the rates of exchange of cyclohexane and methylcyclohexane indicated that hydrocarbons containing a tertiary hydrogen atom reacted more rapidly and that the number of exchangeable hydrogen atoms exceeded one. Stewart and Harman[13] showed that all of the hydrogen atoms of 2-butene exchanged rapidly with those of tritium sulfuric acid and that there was considerable exchange even upon bubbling the butene through the acid.

In the present experiments, it is shown that the rates of exchange of 3-methylheptane and of 2-methylheptane are more than 100 times faster than that of *n*-octane. The acid layer becomes colored with the first two but not with the third.[14] Sulfur dioxide is evolved in the first case but not the second.

Racemization and Isomerization.—(+)3-Methylheptane is racemized by treatment with sulfuric acid. The degree of racemization has been carried beyond 50% as shown in Table I. Only a small change in infrared absorption spectrum occurs during this process. However, since the spectrum of 3-methylheptane is insensitive to

the presence of small quantities of 2-methylheptane, one can say only that some, but not more than 20%, of the latter seems to have been present. 2-Methylheptane is more stable[15] than 3-methylheptane and would appear to be the most likely first isomerization product. Thus, there is a genuine racemization the rate of which exceeds that of any isomerization.

The rather slow rate of isomerization is not wholly unexpected in view of previous literature.[14,16,17] However, the relative rates of isomerization and exchange contrast with those reported for aluminum halide plus isotopic hydrogen halide[18,19] in which cases ordinarily the rate of isomerization exceeded or roughly equaled the rate of exchange.

Pines and Wackher[20] have shown that the isomerization of hydrocarbons by the aluminum halide–hydrogen halide complex is slow in the absence of small quantities of olefins, oxygen or other activators. In such cases, the exchange reaction is also slower but still much faster than the isomerization.

Although sulfuric acid has not been shown to require such activators, the present experiments have employed highly purified material and a vacuum line technique. In view of the oxidizing capacity of sulfuric acid, it is questionable whether such precautions are necessary. This point has not been investigated.

Mechanism.—Alkylation of butylenes by isobutane with concentrated sulfuric acid as a catalyst proceeds at about 10° with a contact time of about one-half hour.[21] The lack of any effect of such treatment on the optically active hydrocarbon alone, is incompatible with those theories of alkylation which involve the initial interaction of the alkane and sulfuric acid.[22] On the contrary, these experiments support those theories which involve initial interaction of sulfuric acid and olefin.[23] We would not care at this stage, however, to apply our results directly to the case of the aluminum chloride type of catalyst.

Any mechanism of the racemization–exchange reaction must be consistent with several facts: (1) the hydrogen atom at the tertiary position is by no means the only one which exchanges; rather the number of exchangeable hydrogen atoms exceeds 8; (2) branched chain octanes exchange far faster than normal octane; (3) for ev-

(13) Stewart and Harman, THIS JOURNAL, 68, 1135 (1946).

(14) See also Birch and Dunstan, *Trans. Faraday Soc.*, **35**, 1013 (1939).

(15) American Petroleum Institute Project 44, Table 3x.

(16) Caesar and Francis, *Ind. Eng. Chem.*, **33**, 1426 (1941).

(17) McCulloch, U. S. Patent 2,404,080; *C. A.*, **40**, 6493⁴ (1946).

(18) Powell and Reid, THIS JOURNAL, **67**, 1020 (1945).

(19) Pines and Wackher, *ibid.*, **68**, 2518 (1946).

(20) Pines and Wackher, *ibid.*, **68**, 595 (1946).

(21) Egloff and Hulla, *Chem. Rev.*, **37**, 323 (1945).

(22) For example, Ciapetta, *Ind. Eng. Chem.*, **37**, 1210 (1945), who employs as an intermediate a carbonium ion derived from the initial interaction of the isoalkane and the catalyst, or McAllister, Anderson, Ballard and Ross, *J. Org. Chem.*, **6**, 647 (1941), who employ as intermediates methyl and isopropyl fragments obtained from the initial interaction of catalyst and isobutane.

(23) For example, Schmerling, THIS JOURNAL, **68**, 275 (1946), and Gorin, Kuhn and Miles, *Ind. Eng. Chem.*, **38**, 795 (1946).

ery molecule racemized about 15 atoms of hydrogen are exchanged. A method whereby the chain branching activates hydrogen atoms rather far removed from the branching point is essential.

If one assumes that all hydrogen atoms exchange with equal rates and that no changes in sulfuric acid composition nor in extent of hydrocarbon–acid interface occur during reaction

$$- \, d\alpha/dt \, = \, k\alpha$$

and

$$\ln \, \alpha/\alpha_0 \, = \, -kt \qquad (4)$$

where α is the rotation of the hydrocarbon. Also

$$r \, = \, k' \qquad (5)$$

where r is the fraction of hydrogen atoms on the hydrocarbon which are exchanged in unit time by hydrogen atoms in the sulfuric acid (the term hydrogen atom includes both protons and deuterons). The increase in the fraction of deuterium in the total hydrogen of the octane, $X_{oct.}$, is then

$$dX_{oct.}/dt \, = \, k'[X_{H_2SO_4} \, (1 \, - \, X_{oct.}) \, - \, X_{oct.} \, (1 \, - \, X_{H_2SO_4})]$$
$$= \, k'(X_{H_2SO_4} \, - \, X_{oct.}) \qquad (6)$$

since exchange of H for H or D for D is without effect and the net rate is that of D for H less H for D. $X_{H_2SO_4}$ is the fraction of deuterium in the total hydrogen of the sulfuric acid.

If a = moles of octane and b = moles of acid, the total number of moles of hydrogen atoms is $18a + 2b$. Thence, starting with light octane and heavy sulfuric acid

$$X_{oct.} \, = \, 2b(1 \, - \, X_{H_2SO_4})/18a \qquad (7)$$

Thence, by equation (6)

$$dX_{oct.}/dt \, = \, k'(1 \, - \, 9(a/b)X_{oct.} \, - \, X_{oct.}) \qquad (8)$$

and if $(9a/b + 1) \, = \, q$, then

$$\ln(1 \, - \, qX_{oct.}) \, = \, - \, qk't \qquad (9)$$

and

$$\frac{\log \, (1 \, - \, qX_{oct.})}{q \, \log \, (\alpha/\alpha_0)} \, = \, \frac{k'}{k} \qquad (10)$$

If for every molecule of hydrocarbon which is racemized, all the hydrogens are exchanged (some exchanges may not change $X_{oct.}$, i. e., H for H), then the value of the ratio in equation (10) should be unity. In general if k' and k are proportional, the restrictions on composition of acid and extent of interface may be dropped.

In Table I, the ratio of equation (10) is tabulated for appropriate runs. It is seen to be nearly constant in spite of considerable variation in extent of reaction, degree of stirring, and in ratio of acid to hydrocarbon. Its average value, about 0.85, is, however, somewhat below unity.

A possible reaction sequence is
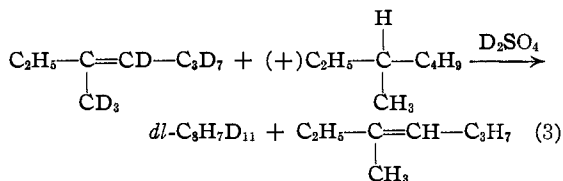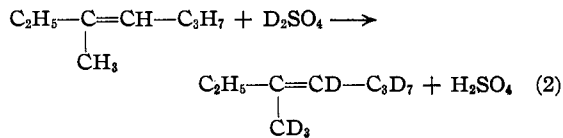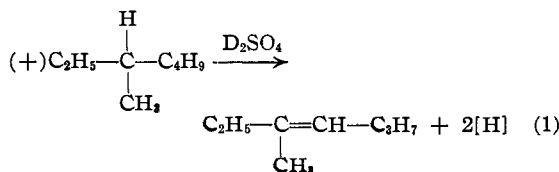
In the first step, the hydrocarbon is oxidized to form an olefin or its equivalent (an alkyl hydrogen sulfate, for example). Exchange of olefin with the heavy sulfuric acid would be rapid and lead nearly to complete exchange.[13] In the third step hydrogen is transferred from octane to produce heavily deuterated racemic octane and octylene. There is considerable evidence for such hydrogen transfer reactions in alkylation reactions. Thus McAllister, et al.,[22] have shown that a large fraction of the product resulting from the treatment of isobutane and sulfuric acid with the octylenes obtained by dehydrating 2-ethyl-1-hexanol is 3-methylheptane. The isomerization might involve the same intermediate. If reaction (3) occurs on the average before reaction (2) is complete, the ratio of equation (10) would fall below unity.

One might reconcile the facts with a theory which involves sulfuric acid as a strong proton donor displacing hydrogen atoms from hydrocarbons with accompanying inversion of configuration. One would be forced to assume that displacement of hydrogen atoms from ordinary primary and secondary positions is very slow (as in n-octane) but that displacement is relatively fast from primary and secondary positions adjoining a tertiary carbon atom. Since each substitution at a tertiary position would produce an octane of opposite configuration, the rate of substitution at the tertiary position would be about one-thirtieth of the total rate of exchange and the rate of exchange of the hydrogen at the tertiary position would be one-fourth that of the average exchangeable hydrogen since the number of exchangeable hydrogens on this basis would be 8. It is difficult to reconcile our results with a number so low. The first mechanism in addition to giving close to the proper number of exchangeable hydrogens is also correlated with the relative ease of oxidation of the hydrocarbons.

Since the net amount of material oxidized did not exceed a few per cent., the first mechanism constitutes a chain reaction. Equations (1), (2) and (3) may be expressed by conventional carbonium ion mechanisms but the probability of skeletal isomerization of any carbonium ions so formed must be assumed rather small. Alternatively, reaction (2) may be expressed by the mechanism proposed by Turkevich.[24]

(24) Turkevich and Smith, *Nature*, **157**, 874 (1946).

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.

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

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	E.	soluble[c] in C.	B.	insol.[d] in solvents
1	Me₂CHOH	80	11 d	R[e]	60	10	Trace	..
2	EtOH	100	49 h	0.4	60	10	..	7
3	Me₂CHOH	100	46 h	1–50	60	7	20	..
4	Me₂CHOH	100	72 h	1.503.0	20	33	..	4
5	Et₂CHOH	100	45 h	1–50	40	27	13	..
6	EtMe₂COH	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	Me₂COH	150	24 h	0.7–1.5	13	13	7	53

[a] In this column Me = CH₃, Et = C₂H₅. [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.

readily to conjugated bonds[8] than does the third but obviously is a weaker metalating agent.

(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).

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-

(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).