Sodium 2,3-dibromo-5-toluenesulfonate was obtained from the above amine in 71% yield by the Sandmeyer procedure.[7] The addition of excess ammonia to a small sample of 2,3-dibromo-5-toluenesulfonyl chloride gave 2,3-dibromo-5-toluenesulfonamide,[6] m.p. 219.2–219.5°. *Anal.* Calcd. for $C_7H_7O_2BrNS$: N, 4.26. Found: N, 4.3.

Hydrolysis of the sulfonic acid to 2,3-dibromotoluene was only partly successful with sulfuric or phosphoric acid at 265° in a glass-lined bomb, but was effected at 275–290° with phosphoric acid and superheated steam in a steam distillation apparatus. The yield was poor (15–20%); b.p. 120.5° at 18 mm.

2,4-Dibromotoluene.—The reduction of 2-bromo-4-nitrotoluene,[8] m.p. 76.4–76.8°, with tin and hydrochloric acid gave 2-bromo-4-aminotoluene,[8] m.p. 23° (after distillation at 130–132° at 20 mm.), in 70% yield. The Sandmeyer procedure gave 64% of 2,4-dibromotoluene after one distillation at 102–105° at 11 mm.

3,4-Dibromotoluene.—The bromination of 385 g. (2.25 moles) of 4-bromotoluene with 240 g. (1.50 moles) of bromine was carried out in the presence of iron catalyst over 4 days at 25–40°.[9] Excess bromine was then destroyed with sodium bisulfite. In addition to 156 g. (42%) of 3,4-dibromotoluene (b.p. 122–124° at 19 mm.), there was recovered 203 g. of 4-bromotoluene, 23 g. (6%) of 2,4-dibromotoluene (b.p. 126–130° at 19 mm.) and 45 g. (18%) of 2,4,5-tribromotoluene,[8] m.p. 110.6–111.2°.

Purification of Dibromotoluenes.—The samples of dibromotoluene from above and a sample of Eastman Kodak Co. 2,5-dibromotoluene were purified to constant freezing point by two, or three, alternate fractional distillations and crystallizations. The physical constants are summarized in Table III.

TABLE III

PHYSICAL CONSTANTS OF DIBROMOTOLUENES

Dibromotoluene	B. p. °C.	Mm.	F. p., °C.	$n^{25.0}_D$	d^{25}_4
2,3-	126–128	19	28.10	1.59835	1.8234
2,4-	103–104	11	− 9.70	1.59637	1.8176
2,5-	135–136	35	5.62	1.59984	1.8154
3,4-	123–124	19	−10.00	1.59787	1.8197

Reaction of Magnesium with Dibromotoluenes.—A solution of equimolar quantities (0.10–0.30 mole) of dibromotoluene and ethyl bromide[10] in 300–400 cc. of absolute ether was added with stirring over 2 hours to magnesium turnings equivalent to the total moles of organic bromides while the system was maintained under a stream of dry, oxygen-free nitrogen. The mixture was then refluxed for 2 hours longer, at which time nearly all of the magnesium had disappeared. The mixture was hydrolyzed in the cold with dilute sulfuric acid and the ether solution washed until neutral. The ether was removed and the product distilled to separate the toluene, monobromotoluene and dibromotoluene components.

The product obtained from 2,3- and 3,4-dibromotoluene contained a very much greater amount of high-boiling side-reaction product than was observed with the other two dibromotoluenes. Most of this distilled at 165–170° at 2 mm. Calculated as dibromobitolyl, this represented 19–21% of the starting material.

The monobromotoluene fractions thus obtained were washed with sulfuric acid and redistilled at 19 mm. (74–75°). Solutions of the several samples in 95% ethyl alcohol (approx. 2×10^{-3} *M*), were prepared and optical densities were measured at several wave lengths in the ultraviolet region using a Beckman ultraviolet spectrophotometer.

The precision of this determination was greatly improved by measuring simultaneously, at the same wave length and slit-width (0.5–1.0 mm.) setting of the instrument, the optical density of both of the pure monobromotoluene solutions and the unknown.[3] The molar extinction coefficients (ϵ) of the monobromotoluene samples were found to be as follows: from 2,3-dibromotoluene, 536 ± 2 and 447 ± 2 at 235 and 236 mμ, respectively; from 2,4-dibromotoluene, 318 ± 2 and 261 ± 2 at 240 and 270 mμ; from 2,5-dibromotoluene, 563 ± 2 and 466 ± 2 at 235 and 236 mμ; from 3,4-dibromotoluene, 282 ± 3 and 247 ± 2 at 240 and 270 mμ. These correspond to 91 ± 2% 2-bromotoluene, 70 ± 2% 2-bromotoluene, 70 ± 2% 2-bromotoluene and 90 ± 2% 3-bromotoluene, respectively.

Summary

The monomagnesium derivatives of four unsymmetrical dibromotoluenes have been found to be mixtures of both possible isomers. The relative amount of each isomer has been determined by hydrolysis and analysis of the resulting monobromotoluene mixture by ultraviolet absorption.

The physical constants of highly purified samples of 2-, 3- and 4-bromotoluene and 2,3-, 2,4-, 2,5- and 3,4-dibromotoluene are given.

EVANSTON, ILLINOIS RECEIVED JULY 5, 1950

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[7] "Org. Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 282.

[8] Nevile and Winther, *Ber.*, **14**, 418 (1881).

[9] Miller, *J. Chem. Soc.*, **61**, 1023 (1892).

[10] Grignard, *Compt. rend.*, **198**, 625 (1934).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE STANDARD OIL CO. (INDIANA)]

Reaction of Isoalkanes and Olefin Precursors Catalyzed by Sulfuric Acid[1]

BY ROBERT F. MARSCHNER AND D. R. CARMODY

An electronic interpretation of the alkylation of alkanes is attractive,[2] and the electronic mechanism advanced by Schmerling[3] and Bartlett, Condon and Schneider[4] is quite acceptable when aluminum chloride is the alkylation catalyst. A consequence of this mechanism[3c] is the formation of alkylate by a *combination* of two isoalkane molecules

$$2C_n \text{ isoalkane} + C_m \text{ alkene} \longrightarrow C_{2n} \text{ alkane} + C_m \text{ alkane} \quad (1)$$

as well as by *addition* of isoalkane and alkene

$$C_n \text{ isoalkane} + C_m \text{ alkene} \longrightarrow C_{(n+m)} \text{ alkane} \quad (2)$$

in which *n* and *m* are the number of carbons in the reagents. Although there is some evidence that eq. 1 occurs with sulfuric acid,[5–10] no studies with this catalyst as pertinent and convincing as those with aluminum chloride[3,4] have yet been reported. It will be observed, however, that equations 1 and 2

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[1] Presented in part before the Petroleum Division at the 109th Meeting of the American Chemical Society, Atlantic City, April, 1946.

[2] Whitmore, (a) THIS JOURNAL, **54**, 3274 (1932); (b) *Ind. Eng. Chem.*, **26**, 94 (1934); (c) *Chem. Eng. News*, **26**, 668 (1948).

[3] Schmerling, (a) THIS JOURNAL, **66**, 1422 (1944); (b) *ibid.*, **67**, 1778 (1945); (c) *ibid.*, **68**, 275 (1946).

[4] Bartlett, Condon and Schneider, *ibid.*, **66**, 1531 (1944).

[5] Birch, Dunstan, Fidler, Pim and Tait, *Ind. Eng. Chem.*, **31**, 1079 (1939).

[6] Waterman, Leendertse and Hesselink, *Rec. trav. chim.*, **58**, 1040 (1939).

[7] Birch and Dunstan, *Trans. Faraday Soc.*, **35**, 1013 (1939).

[8] McAllister, Anderson, Ballard and Ross, *J. Org. Chem.*, **6**, 649 (1941).

[9] Pines and Ipatieff, THIS JOURNAL, **67**, 1631 (1945).

[10] Gibson, Cole and Matuszak, *ibid.*, **68**, 2728 (1946).

TABLE I

REACTION OF ISOALKANES AND ALKENE PRECURSORS USING SULFURIC ACID

Run	1	2	3	4	5	6	7	8	9	10	11
Isoalkane	Isobutane		Isopentane								
Alkene precursor	*t*-AmOH		*i*-PrOH	C_8H_{18}	*t*-BuOH	*t*-BuCl	*s*-BuOH	*s*-BuCl	*n*-BuOH	*t*-AmOH	224MP
Sulfuric acid concn., wt. %	98.6	99.0	96.0	98.7	99.0	98.6	98.6	100.6	96.0	96.0	100.6
Reactants, g.: Isoalkane	298	280	333	318	319	316	314	316	317	289	328
Alkene precursor	82	101	60	56	75	90	74	91	74	135	116
Sulfuric acid	423	423	401	512	580	422	424	408	445	421	420
Total	803[a]	804[c]	794	886	974	828	812	815	836	845	864
Products, g.: Acid layer	457	444	442	512	599	453[f]	443	452[f]	478	454	427
Recovered isoalkane	198	164	297	132	128	164	159	186	271	115	220
Synthetic isoalkane	32	31	2[e]	59	65	49	42	27[g]	11	47	53
Alkylate above isopentane	129	129	50	173	172	142	144	132	58	225	153
Total	816	768	791	878	964	808	788	979	818	841	853
Weight balance, %	102	96	100	99	99	98	97	98	98	99	99
Hydrocarbon balance, %	104	87	99	97	97	95	94	95[g]	95	99	98
Alkylate compn., vol. %:											
Hexanes (44–71°)	13	10	5	31	23	17	19	24	22	21	25
Heptanes (71–95°)	[b]	3	2	6	5	15	4	2	2	8	1
Octanes (95–117°)	57	50	57	18	7	8	12	4	7	6	54
Nonanes (117–138°)	12	15	3	14	27	23	39	52	38	20	7
Decanes (138–159°)	4	6	5	18	24	26	17	15	14	19	11
Residue (above 159°)	15	16	28	13	14	11	9	3	17	26	2
Comparable literature data	—(5),*d*—		(5)	(5)	(10)	...	—(5)(8)—		...	(6),*h*	[i]

[a] 250 ml. cyclohexane diluent not included. [b] Value finite but not determined because of presence of diluent. [c] 250 ml. *n*-heptane diluent not included. [d] Glasgow, Strieff, Willingham and Rossini, *J. Research Natl. Bur. Standards*, **38**, 537 (1947). [e] Isobutane, not propane. [f] Includes 28 g. (run 6) and 32 g. (run 8) hydrogen chloride collected outside the reactor. [g] Loss known to include isobutane. [h] Steenis and Waterman, *Rec. trav. chim.*, **67**, 638 (1948). [i] Morton and Richards, *J. Inst. Petroleum Tech.*, **34**, 133 (1948).

should be distinguishable when, and only when, *n* is numerically different from *m*. This paper presents the results obtained by such a reaction of C_n isoalkanes and C_m alkene precursors in the presence of sulfuric acid.

Experimental

The purchased materials employed were of purity known to be adequate from previous examination and experience. The dibutylene consisted primarily of trimethylpentenes obtained by polymerizing mixed butylenes with boron trifluoride.

All runs were carried out in the same manner at 24 ± 5° (except run 1 at 2° and run 6 at 13°) using sulfuric acid of 96 to 101 weight per cent. concentration as indicated in Table I. The equipment consisted of a three-necked, round-bottomed flask surrounded by an appropriate cooling bath and fitted with a dropping funnel, a Dry Ice reflux condenser, and a stirrer[11] operated at full motor speed (1750 r.p.m.) to give thorough dispersion of the entire flask contents. Over a period of 3 to 5 hours, approximately one mole of the alkene precursor was added to five moles of isoalkane dispersed by the stirrer in five moles of sulfuric acid. Stirring of the orange-yellow reaction mixture was continued until the total reaction time was approximately 6 hours. When isobutane was charged, cyclohexane or *n*-heptane was employed to reduce the vapor pressure of the mixture.

The settled reaction layers were separated and weighed. Isobutane and isopentane were successively fractionated from the hydrocarbon layer through a vacuum-jacketed low-temperature fractionating column. The increase in weight of the sulfuric acid layer during the run included the water from the alcohols; some solution of alkene precursor in this layer usually occurred. The concentration of the sulfuric acid at the termination of the runs employing alcohols was about 93%.

The stabilized alkylate was fractionated carefully through a column equivalent to 30 theoretical plates; 6-, 7-, 8-, 9- and 10-carbon fractions were taken, corresponding approximately to the temperature intervals indicated in Table I; 10 to 15% of higher-boiling residue remained. All overhead cuts tested were saturated to bromine. The residues consisted of hendecanes and dodecanes, which could be neither separated cleanly nor recognized, and very little higher-boiling material. Individual fractionation curves closely resembled those for the same alkene–isoalkane pairs presented in the literature indicated at the bottom of Table I. Refractionation of the major products through other columns permitted better recognition of the most abundant isomers present; these data are summarized in Table II. In several instances, determination of octane number served to confirm recognition.

Several paraffins were treated with sulfuric acid, but in the absence of olefin precursor. The same conditions were employed as in the precursor studies, and the results are presented in Table III. The decane fraction was that obtained from the described isopentane reaction products. The 2,2,4-trimethylpentane simulated the octane fraction of the described isobutane reaction products. The results show that 2,2,4-trimethylpentane and the decane fraction were particularly subject to degeneration.

Results

An alkene precursor (alkanol, alkyl halide or alkene dimer) was slowly added to an isoalkane dispersed in cold, concentrated sulfuric acid. In the experiments summarized in Table IV, the alkene contained one carbon more than the isoalkane; in those of Table V, it contained one carbon less. The entire reaction mixtures were investigated. Confirmation of Equation 1 was found in the following facts:

(A) Consumption of isobutane during reaction with *t*-amyl alcohol (Table IV), determined by difference from the amount recovered, was approximately twice that of the olefin precursor added to the reaction. Likewise, consumption of isopentane during reaction with several butene precursors (Table V) was usually even more than twice the amount of precursor. Equation 2 requires the consumption of only one equivalent of isoalkane.

(B) Reaction of butene precursors and excess isopentane (Table V) led to an almost stoichiometric amount of isobutane. Somewhat less isopentane was produced from *t*-amyl alcohol and isobutane (Table IV). Equation 2 accounts for neither of these synthetic isoalkanes.

(C) Octanes were abundant products of the reactions involving isobutane (Table IV). Decanes

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(11) Huntress and Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).

TABLE II

PROPERTIES OF PREDOMINANT REACTION PRODUCTS

Fraction distilled C	Run	Distillate Vol. %	B.p., °C. 760 mm.	$n^{20}D$	Oct. no. CFR-F-2	Indicated hydrocarbons[a]	Reference properties B.p., °C. 760 mm.[b]	$n^{20}D$[b]	Oct. no. CFR-F-2[c]
4	5^d	98	−(11–9)	....	..	Isobutane (<1% *n*-butane)	−11.7	....	...
	7^d	84	−(11–10)	....	..	Isobutane (<5% *n*-butane)			
5	1^d	100	26–31	....	..	Isopentane (no *n*-pentane)	27.9	1.3537	...
6	1, 2	60	58–59	1.3723	..	2,3-Dimethylbutane(23MB)	58.0	1.3750	95
	4, 5^d	80	60–61	1.3725	..	2MP (+ 3MP or 23MB)			
	6, 7	80	60–61	1.3720	77.4	2MP (+ 23MB)	60.3	1.3715	73
	8	70	60–64	1.3729	..	2MP + 3MP			
	9^d	50	60–61	1.3715	..	2-Methylpentane (2MP)			
		30	61–63	1.3745	..	3MP (+ 2MP)	63.3	1.3765	74
	10	90	60–62	....					
	11	80	60–61	1.3730	..	2MP + 3MP			
7	6^d	20	79–80	1.3830	..	2,3-Dimethylpentane(23MP)	80.5	1.3815	...
		40	89–90	1.3873	..	23MP (+ Methylhexanes)	89.8	1.3920	...
8	2	100	95–106	....	21.9	22% 224MP + 78% *n*-Heptane			
	1	30	99–100	1.3911	..	2,2,4-Trimethylpentane(224MP)	99.2	1.3915	100
		30	113–114	1.4046	..	2,3,4-Trimethylpentane	113.5	1.4042	...
	3	30	108	1.3941	..	Dimethylhexanes			
		20	115	1.4004	..	Dimethylhexanes			
	11	90	98–100	1.3910	..	2,2,4-Trimethylpentane			
9	6	40	121–123	....					
	8	80	122–124	1.3997	90.3	2,2,5-Trimethylhexane	124.0	1.3996	...
	9	60	122–123	1.3991	..	2,2,5-Trimethylhexane			
	10	70	121–124	1.3994	..	2,2,5-Trimethylhexane			
10	8	50	147	1.409	..	2,2,6-Trimethylheptane(?)[e]	148.9[f]	1.4077[f]	...
	10^d	55	147–149	1.4093		2,2,6-Trimethylheptane(?)			
	11	50	148–149	1.4090	..	2,2,6-Trimethylheptane(?)			
	4, 11^d	41	147–149	1.4088	..	2,2,6-Trimethylheptane(?)			

[a] Abbreviations defined in parentheses. [b] Rossini, *et al.*, "Selected Values of Properties of Hydrocarbons" (Circular Natl. Bur. Standards C461), U. S. Gov. Printing Office, Washington, D. C., November, 1947. [c] Lovell, *Ind. Eng. Chem.*, **40**, 2388 (1948). [d] Entire fraction refractionated. [e] Reference (7). [f] Brooks, Cleaton and Carter, *J. Research Natl. Bur. Standards*, **19**, 319 (1937).

TABLE III

TREATMENT OF INDIVIDUAL ALKANES WITH SULFURIC ACID

Alkane treated	H_2SO_4 concn., wt. %	Conversion, %	Vol. % yields, based on converted alkane only Carbons 4[a]	5[b]	6	7	8	9	10	Residue
n-Pentane	96.0	1	0	..	..	0	..	..	..	..
2,3-Dimethylbutane	96.0	10[c]	..	45	5	30	..	..	..	20
n-Heptane	98.6	1	..	..	0	..	..	..	..	..
2,2,3-Trimethylbutane	96.0	8[c,d]	——2——		0	95	..	..	..	3
2,2,4-Trimethylpentane	100.6	78	23	8	4	1	13[e]	22	10	19
2,6-Dimethylheptane	96.0	15[c,d]	..	..	..	..	..	98	..	..
Decane fraction	96.0	52	——26——		19	7	1	21	[f]	26

[a] Isobutane. [b] Isopentane. [c] Maximum. [d] Mainly isomerization estimated from small changes in refractive index. [e] Higher-boiling isomers of 2,2,4-trimethylpentane. Compare with Morton and Richards, *J. Inst. Petroleum*, **34**, 133 (1948). [f] Recovered decane had b.p. 145–147 and $n^{20}D$ 1.4080; assumed to be unchanged.

TABLE IV

SULFURIC ACID CATALYZED REACTION OF ISOBUTANE AND *t*-AMYL ALCOHOL

	Moles	
t-Amyl alcohol charged	1.00	1.00
Isobutane charged	5.53	4.20
recovered	3.67	2.46
consumed	1.86	1.74
Isopentane synthesized	0.49	0.38
Octanes produced (combination)	.70	.50
Nonanes isolated (addition)	.13	.13

and hexanes[12] were prominent in the isopentane alkylates (Table V). Nonanes which from equation 2 would be the sole product of both reactions, were produced in only small to moderate amounts.

Supplementary evidence for equation 1 was obtained by a comparison of the behavior of other olefin precursors with isopentane; this is summarized in Table VI. Some combination occurred in the presence of *n*-butyl alcohol,[13] but very little when isopropyl alcohol was used; perhaps the olefin precursor must contain at least four carbon atoms if much combination is to occur. The alkylates from the precursors *t*-amyl alcohol and even 2,2,4-trimethylpentane resembled those of Table V. The course of combination must therefore depend primarily upon the isoalkane employed.

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[12] The hexanes are related in amount to both the isopentane consumed and the isobutane synthesized; this suggests that they were derived with isobutane *via* the decanes from isopentane: $2C_5 \rightleftarrows C_{10} \rightleftarrows C_6 + C_4$.

[13] Isopentane and 1-bromobutane failed to react.

TABLE V

SULFURIC ACID CATALYZED REACTION OF ISOPENTANE AND BUTYLENE PRECURSORS

Run	4	5	6	7	8
Butylene precursor	C_8H_{16}	*t*-BuOH	*t*-BuCl	*s*-BuOH	*s*-BuCl
	Moles				
Precursor charged	0.50	1.00	1.00	1.00	1.00
Isopentane charged	4.41	4.50	4.69	4.49	4.47
recovered	1.83	1.81	2.41	2.07	2.63
consumed	2.58	2.69	2.28	2.42	1.84
Isobutane isolated from	1.02	1.11	0.87	0.72	0.48
decanes[a]	0.58	0.43	.28	.31	.34
synthesized	.44	0.68	.59	.41	.14
Decanes isolated to	.23	.30	.28	.18	.15
hexanes[a]	.58	.43	.28	.31	.34
produced (combination)	.81	.73	.54	.49	.49
Nonanes isolated (addition)	.19	.36	.27	.44	.56

[a] Equal to hexanes isolated.

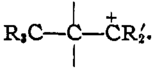
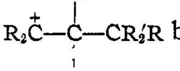
TABLE VI

SULFURIC ACID CATALYZED REACTION OF ISOPENTANE AND VARIOUS OLEFIN PRECURSORS

Run	3	9	10	11
Olefin precursor	*i*-PrOH	*n*-BuOH	*t*-AmOH	224 MP
	Moles			
Precursor charged	1.00	1.00	1.00	1.00
Isopentane charged	4.61	4.40	2.62	4.46
recovered	4.12	3.76	1.00	2.99
consumed	0.49	0.64	1.58	1.47
Isobutane isolated	.03	.19	0.53	0.89
from decanes[a]	.03	.14	.33	.41
synthesized	.00	.05	.20	.48
Decanes isolated	.02	.06	.20	.12
to hexanes[a]	.03	.14	.33	.41
produced (combination)	.05	.20	.53	.53
Nonanes isolated (addition)	.25[b]	.17	.23	.09

[a] Equal to hexanes isolated. [b] Isoöctanes, not nonanes.

Interpretation

Our results can be accounted for by applying the Schmerling[3c] mechanism in the following manner: (1) **Initiation.** Removal of an anion from the olefin precursor by the acid results in the formation of a carbonium ion. This ion can revert to the olefin, transfer, add to another olefin molecule, or rearrange. (2) **Transfer.** If the carbonium ion contains four or more carbons, it either has or can rearrange[14] to the tertiary structure, and the tertiary carbonium ion rapidly withdraws the tertiary hydrogen from the reagent isoalkane.[15] Thus the isoalkane is first brought into the reaction, and the synthetic isoalkane found among the products is simultaneously formed. (3) **Addition.** Because of the rapid transfer reaction, the reacting species—olefin as well as carbonium ion—have been derived predominantly from reagent isoalkane, which is always present in large excess. What we have called *combination* is simply *addition* following transfer; the doubled isoalkane consumption and the formation of octanes or decanes (rather than nonanes) are consequences of transfer. Part of the product is formed by addition of carbonium ion from the isoalkane with olefin from the precursor, of course. (4) **Rearrangement.** Addition of a tertiary carbonium ion and a tertiary olefin give carbonium ions of the form:  $R_3C{-}\overset{|}{\underset{|}{C}}{-}\overset{+}{C}R'_2$. These not only rearrange rapidly to  $R_2\overset{+}{C}{-}\overset{|}{\underset{|}{C}}{-}CR'_2R$ but also undergo cleavage which is exactly the reverse of addition.[16] The formation of hexanes (and additional isobutane) in the reactions involving isopentane is thus readily accounted for.[17] Other rearrangements of products of addition occur, but these are probably both slower and few; if so, the structures of all products isolated must be closely related to those initially formed.

Once the reaction of isoalkanes and olefins is initiated, all subsequent steps seem both reversible and rapid. Consequently, these experiments, and probably isoalkane alkylations generally, are better regarded as involving a state of dynamic equilibrium than as a sequence of successive steps. The extent of the combination reaction in the presence of sulfuric acid may be dependent upon the rate of isomerization of the initial alkene carbonium ion to the tertiary structure.

Summary

Isobutane and isopentane, and the various butene and other olefin precursors, reacted in the presence of sulfuric acid; (a) approximately twice as much isoalkane was consumed as required by simple addition of alkene, (b) isoalkane was synthesized in amounts almost equivalent to alkene consumed, and (c) alkanes with twice the carbon content of the initial isoalkane were produced.

These observations can be explained by the Whitmore carbonium-ion hypothesis, employing hydrogen transfer concepts advanced by Schmerling, supplemented by the principles that: (a) the essential reactions are rapid and reversible, and (b) the system reaches a state of dynamic equilibrium.

WHITING, INDIANA RECEIVED[18] MAY 29, 1950

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[14] Calkins and Stewart, THIS JOURNAL, **71**, 4144 (1949).

[15] Beeck, Otvos, Stevenson and Wagner, *J. Chem. Phys.*, **17**, 418 (1949).

[16] Whitmore and Mosher, THIS JOURNAL, **63**, 1120 (1941); **68**, 281 (1946).

[17] Cleavage of the related addition products from other tertiary species gives isoalkanes indistinguishable from the reagents. This can be made clear by writing out structural formulas, too space-consuming to include here. Just as transfer was revealed only by using reagents of different carbon content, isolation of hexanes provided the only likely clue to cleavage.

[18] Original manuscript submitted January, 1946.