pared with α-naphthol. The hydrochloride crystallized in the presence of a trace of stannous chloride as quite colorless needles; yield, 66%.

Anal. Calcd. for C_8H_8ONSCl: S, 15.90. Found: S, 15.76.

4,7-Thionaphthenequinone (XIII).—A solution of 10.8 g. of the amine hydrochloride in 300 cc. of water was treated with 51 cc. of concentrated sulfuric acid, heated to 95°, and poured rapidly with shaking into a solution of 10.5 g. of potassium dichromate in 150 cc. of water at 25°. The quinone separated at once as a mass of brown-yellow needles, m. p. 126–129° (7.9 g.). Crystallized from ether with the liberal use of Norite, it formed clear yellow needles, m. p. 130–131°; yield, 6.4 g. (73%). The quinone volatilizes easily and has an odor similar to that of *p*-benzoquinone. It is very sparingly soluble in water and readily soluble in alcohol or ether. The solution in concentrated sulfuric acid has a wine-red color which rapidly darkens.

Anal. Calcd. for $C_8H_4O_2S$: S, 19.54. Found: S, 19.40.

4,5,7-Trihydroxythionaphthene Triacetate (XIV).—4,7-Thionaphthenequinone (1.9 g.) was stirred into 3.5 cc. of acetic anhydride containing five drops of concentrated sulfuric acid at 40°. The triacetate soon separated on cooling to give a thick paste. It was collected and washed free of the dark-colored mother liquor with alcohol and ether, giving a nearly white powder melting at 147–150°; yield, 1.2 g. (33%). The substance crystallizes from alcohol as colorless plates, m. p. 151–153°.

Anal. Calcd. for $C_{14}H_{12}O_6S$: S, 10.40. Found: S, 10.37.

The triacetate was hydrolyzed with alcoholic alkali under nitrogen, the solution was diluted with water, acidified and treated with ferric chloride. 5-Hydroxy-4,7-thionaphthenequinone separated as small crystals on cooling the solution, and it was identified by conversion to the methyl ether with methyl alcohol and sulfuric acid. Yellow needles, m. p. 204–205°, were obtained on crystallization, and the substance (VIII) was identical with that described above.

4,7-Thionaphthenequinone monosemicarbazone was obtained from the quinone and semicarbazide hydrochloride in boiling alcohol. Brown-yellow crystals separated in a few minutes in 74% yield. Crystallized from alcohol (sparingly soluble), the substance forms yellow needles melting with decomposition at about 235°.

Anal. Calcd. for $C_9H_7O_2N_3S$: S, 14.50. Found: S, 14.56.

In the hope of determining which carbonyl group is involved in the semicarbazone formation, the substance was heated with sodium ethylate in alcohol in a sealed tube for five hours at 140°, following the method of cleavage of Thiele and Barlow[23] and of Wolff.[24] The material was largely converted into a black tar, but there was isolated a small quantity of a phenolic substance which, after purification with alkali, distillation, and crystallization from water, formed colorless plates melting at 70–70.5°. The substance has the composition and properties of an hydroxythionaphthene (calcd. for C_8H_6OS: S, 21.36. Found: S, 20.98). A mixture with an equal part of 4-hydroxythionaphthene (m. p. 80–81°) melted at 69–70°. The carboxymethyl ether melted at 158–159°, and a mixture with the 4-derivative (m. p. 152–153°) melted at 151–152°. Although these results are not decisive, we are inclined to regard the hydroxythionaphthene obtained in this way as a mixture of the 4 and 7 derivatives. Semicarbazide probably attacks both of the carbonyl groups of the quinone to some extent.

Summary

Quinones having a thiophene ring in place of the benzene ring of ortho and para naphthoquinones are about 75 mv. higher in reduction potential than the naphthoquinones of corresponding structure. This indicates a lower degree of aromaticity for thiophene as compared with benzene.

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[23] Thiele and Barlow, *Ann.*, **302**, 311 (1898).

[24] Wolff, *ibid.*, **394**, 86 (1912).

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.

RECEIVED JULY 1, 1935

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Reaction of Paraffins with Olefins[1]

BY VLADIMIR N. IPATIEFF AND ARISTID V. GROSSE

We have found that different classes of hydrocarbons, *i. e.*, paraffins, naphthenes, aromatics and olefins, in the presence of specific catalysts, react among themselves with much greater ease than has been considered possible heretofore. As catalysts metallic halides (of Al, B, Be, Ti, Zr, Hf, Th, Cb and Ta) proved effective in these reactions.

So far practically the only known reaction between hydrocarbons, which went smoothly and quantitatively, was M. Balsohn's[2] alkylation of aromatic hydrocarbons with olefins, with aluminum chloride as a catalyst. We started to investigate this reaction some time ago and in so doing have discovered the above-mentioned reactions which will be described in a series of papers. This paper will deal only with the reaction of paraffins with olefins.

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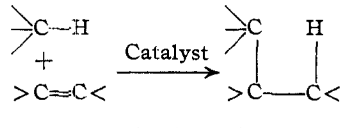
[1] Presented before the Organic Division, American Chemical Society, New York meeting, April 22–23, 1935.

[2] M. Balsohn, *Bull. soc. chim.*, [2] **31**, 539 (1879).

The general reaction consists in the direct addition of an olefin to a paraffin, according to the equation

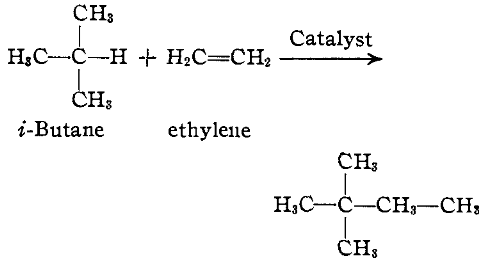
$$C_mH_{2m+2} + C_nH_{2n} \xrightarrow{\text{Catalyst}} C_{m+n}\,H_{2(m+n)+2}$$

or structurally



As a practical example the following case may be cited

(1)



i-Butane ethylene

The hexane, 2,2-dimethylbutane

Only with certain paraffins and under specific conditions, such as carefully controlled temperature and separation of the reaction product immediately after its formation, can the reactions be made to proceed as smoothly and quantitatively as expressed by these equations. In most cases the further alkylation of the paraffin formed takes place, for instance, the alkylation of the hexane into octane, octane into decane, etc. Furthermore, isomerization and the so-called reaction of "auto-destructive alkylation"[3] can occur simultaneously. Still other side reactions, some leading to products combining with the inorganic compounds present, may eventually occur. Aluminum chloride and boron fluoride were the most extensively studied agents for paraffin alkylation.

The elucidation of this reaction was achieved step by step through the investigation of the action of aluminum chloride on paraffins and olefins alone and their mixtures. Since the reactions with aluminum chloride are complicated and sometimes completely distorted by side reactions we will report in this paper only the alkylation of paraffins with boron fluoride as a catalyst. Before doing so, the action of boron fluoride on olefins and paraffins *alone* will be described.

Experimental Part

The Action of Boron Fluoride on Olefins.[4]—The olefins above ethylene are easily polymerized by boron fluoride[5,6] at room temperature and atmospheric or higher pressures in glass vessels. Ethylene is polymerized only if finely divided metals, especially nickel,[7] are present.

The olefins are polymerized into higher molecular weight *mono-olefins* in successive steps in marked contrast to aluminum chloride.[8] This is proved in the case of ethylene by the data of Table I. The polymerization was effected in a rotating autoclave containing a glass liner. One hundred parts by weight of ethylene was polymerized in the presence of 4.5 parts of BF_3 and 1.5 parts of Ni powder at 20–25° and 50 kg./sq. cm. total pressure during 150 hours.

The Action of Boron Fluoride on Paraffins.—Boron fluoride has no effect on paraffins, at least up to 50°, in marked contrast to aluminum chloride. The following two experiments show this to be true.

(1) C_8H_{18}.—100 g. of pure 2,2,4-trimethylpentane (b. p. at 760 mm. 99.3°, n^{25}D 1.3893) was heated with 10 g. of BF_3, 2.0 g. of water and 5.0 g. of nickel powder at 50° for three hours. The reaction product was fractionally distilled; all fractions went over at 99°, and had the same index of refraction n^{25}D 1.3891 to 1.3893 and were stable toward nitrating mixture. Under the same conditions, aluminum chloride in the presence of hydrogen chloride will completely convert this paraffin into a mixture of paraffins boiling from −10 to over 300°.

(2) C_4H_{10}.—60 g. of pure *i*-butane was left in contact with 20 g. of BF_3, 2.0 g. of water and 5.0 g. of nickel power at 50–55° for twenty-four hours. Less than 1%, if any, paraffins boiling below and above butanes were formed and the *i*-butane recovered was over 98% pure.

The Alkylation of Paraffins with Olefins.—The alkylation of paraffins takes place at temperatures as high as about 200°, although it is preferably conducted at room temperature, *i. e.*, 10–30°. Slight pressures, of from 5–20 atm., are preferably used.

As catalyst boron fluoride gas, finely divided metallic nickel and small quantities of water was used. Boron fluoride alone will not effect the

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[3] *I. e.*, splitting of the paraffin and subsequent alkylation of another paraffin molecule by the olefin formed. To be described in detail in a separate publication.

[4] A detailed description will appear separately.

[5] A. Butlerov and Goriainow, *Ber.*, **6**, 561 (1873); *Ann.*, **169**, 147 (1873); A. Butlerov, *Ber.*, **9**, 1605 (1876); *Ann.*, **189**, 44 (1877).

[6] F. Hofmann and M. Otto, German Patent 505,265, 512,959, 513,862; U. S. Patent 1,811,130; M. Otto, *Brennstoff-Chemie*, **8**, 321 (1927); F. Hofmann, *Petroleum Times*, **23**, 508 (1930).

[7] The accelerating action of nickel was first noticed by Hofmann and Otto (*loc. cit.*) but they did not realize it was a *conditio sine qua non* of the polymerization.

[8] It will be shown in a separate publication that using aluminum chloride no true polymerization takes place and that paraffins and highly unsaturated hydrocarbons are formed.

TABLE 1

PRODUCT FROM POLYMERIZATION OF ETHYLENE[a]

High Temperature Podbielniak Distillation, charge of 368 cc.

Fraction	Boiling range °C. at 754 mm.	Vol., cc.	Color[c]	n^{25}_D	$KMnO_4$ test	Nitrating test	Density d^{20}_4	Bromine no. (Francis' method)	Number of double bonds per mol.	Mol. wt. (in benzene freezing point method)	(Calcd. for mono-olefins: C, 85, 62; H, 14, 38) Analyses, % C	H
0	Gas, 6500 cc.; 20 cc. liq.[a,b]											
1	28–62	2.8	W. W.	1.3815	Oxidizes							
2	62–98	7.5	W. W.	1.3927	imme-							
3	98–168	15.3	W. W.	1.4190	diately	Reacts	0.7409	100	0.80	128	85.47	14.53
4	168–197	21.7	W. W.	1.4319	As above	violently	.7648					
5	197–218	42.8	W. W.	1.4376	As above	at once		86	.95	176		
6	218–248	29.0	W. W.	1.4423	As above		.7870					
7	248–258	30.4	W. W.	1.4452	In 45 sec.			68	.92	216	85.35	14.35
8	258–270	33.9	W. W.	1.4472	In 45 sec.		.7978	60	.85	226		
9	270–284	33.8	W. W.	1.4492	In 60 sec.	Reacts						
10	284–310	41.5	Sl. yel.	1.4536	In 60 sec.		.8133					
11	310–316	57.1	Sl. yel.	1.4572	In 60 sec.			42	.83	315	85.38	14.29
Botts.	>316	25.0	Yel.	1.4663			.8425					
Total		361										
Losses		≃7										

[a] Distillation rate was from 0.5–1.0 cc./min. [b] Ethylene and butylenes. [c] W. W. = water white.

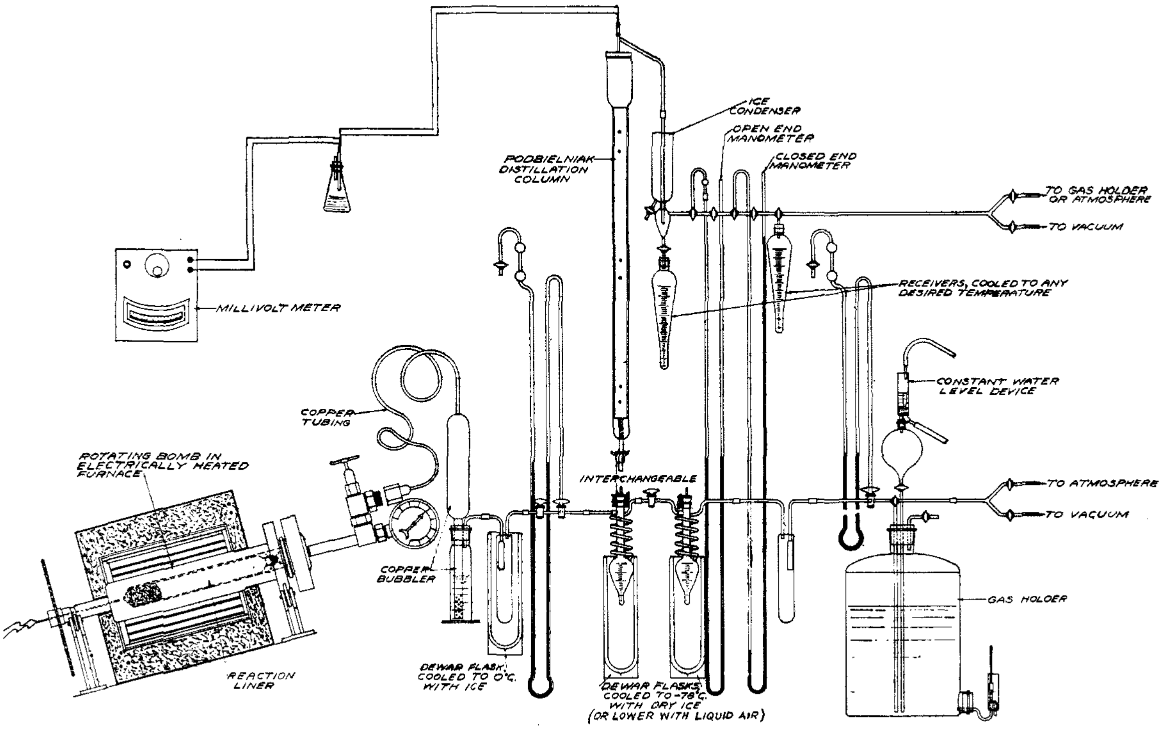

Fig. 1.

alkylation and the addition of the metal and water are necessary. The water can be substituted by anhydrous hydrogen fluoride.

In the following paragraphs the alkylation of (1) *i*-butane with ethylene, (2) *i*-butane with *i*-butylene, (3) *i*-pentane with ethylene, (4) 2,2,4-trimethylpentane with ethylene, and (5) the chemistry of the boron fluoride catalyst will be described.

Experimental Procedure

The reaction was generally carried out in high pressure Ipatieff rotating autoclaves of 800 cc. capacity (30 r. p. m.) (see Fig. 1). Special liners[9] of different material were

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(9) To be described in a separate publication.

TABLE II

Experiment[a]		1	2	3	4	5	6
i-Butane, g.	Charged	160	90	90	90	90	220
	Reacted	24	88	88	89	88	180
Ethylene, g.	Charged	81	130	115	110	90	104
	Reacted	61	130	115	109	85	104
BF_3 used, g.		2	8	8	14	14	30
Ni used, g.		5.0	5.0	5.0	10.0	10.0	5.0
H_2O used, g.		0.50	2.0	2.0	4.0	4.0	25g.HF
Time of reaction, hours		32	28	26	21	22	40
Temperature, °C.		20–25	20–30	20–30	20–25	20–25	20–25
Ratio of reacted C_2H_4 to reacted i-C_4H_{10} molecules		5.9:1	3.1:1	2.7:1	2.5:1	2.0:1	1.2:1
$n^{20}{}_D$ of total reaction prod.		1.4188	1.4126	1.4064	1.3998	1.3984	1.3819
Gasoline content of prod. (437°F. end-point) %		37	60	82	85	>90	97

[a] In experiments 1–5 Pyrex glass liners, in Expt. 6 a nickel liner were used.

inserted into the autoclaves, glass being used in many cases when both boron fluoride and water were present. In the hydrogen fluoride experiments, nickel liners were employed.

After the reaction, the high pressure release valve of the autoclave was connected to a high vacuum apparatus, shown in Fig. 1, for collecting and separating the different products obtained. Details can be seen from the drawing. W. Podbielniak low and high temperature fractionation columns[10] were extensively used throughout the investigations and found to be extremely useful.

The gaseous reagents such as ethylene or boron fluoride, were weighed in small duraluminum autoclaves (the hydrogen fluoride in copper), and the quantity used established by difference in weight. Sometimes gaseous reagents like butane were condensed in the bomb liner, cooled to −78° (dry ice), quickly weighed and inserted into the reaction bomb.

All the *hydrocarbons* used were 97% pure or better. The boron fluoride was purified by condensation and fractionation and stored in duraluminum autoclaves. The anhydrous hydrogen fluoride was prepared from dry KHF_2 and purified by redistillation, discarding the first and last fractions.

1. Alkylation of *i*-Butane with Ethylene.—In Table II the quantities of reagents, conditions and results of six experiments are given.

The reaction was effected in a rotating autoclave containing *i*-butane and the catalyst. The ethylene was introduced up to a pressure of 20 kg./sq. cm., and as the pressure dropped, fresh ethylene was added. The rate of absorption was fairly rapid, the pressure drop amounting to about 10–15 kg./sq. cm. per hour. As the data of the table show, both gases can be made to react practically to completion. It is remarkable to see a paraffin react thus at room temperature.

An increase in the ratio of BF_3 to available paraffin increases the rate of alkylation (compare Expts. 4 and 5 with Expt. 1). The nature of the product naturally depends on the number of molecules of ethylene absorbed by a molecule of *i*-butane.

A matter of greatest interest is the chemical nature of the reaction product. It consists, after removing the gaseous BF_3, principally, of a water-white mobile liquid and a few cc. of a *semi-solid semi-liquid* mixture of compounds containing boron fluoride and nickel salts of borofluoric acids, combined with organic substances, and representing the real catalyst (described further on p. 1621).

The water-white liquid was washed with water, dilute sodium hydroxide and water (3 times), and dried over calcium chloride.

Complete information on the product can be obtained from the following table (No. 3) containing the results of H. T. Podbielniak fractionations of the combined product from Experiments 3, 4 and 5, and the properties of the fractions obtained. All fractions were stable to the permanganate test, indicating the *absence of olefins:* the test consisted in adding 2–3 drops of a 4% potassium permanganate solution to a solution of 2–3 drops of the substance in 2–4 cc. of ethyl alcohol (96–100%); olefins rapidly decolorize the solution. All fractions were also stable toward nitrating mixture (2 vols. 96% H_2SO_4 and 1 vol. 70% HNO_3) proving the *absence of aromatics and olefins*. All fractions were water white in color.

These chemical tests with the chemical analyses in Table III, molecular weight determinations, indices of refraction and densities all prove consistently that alkylation of *i*-butane with ethylene has taken place, and that paraffins have formed from *i*-butane; in other words the product is quite different from that obtained in the polymerization of ethylene which gives olefins (see Table I, p. 1618).

An important fact is noticed in evaluating the Podbielniak distillation curve, namely, that the quantity of even C-number paraffins is much larger than odd C-number paraffins, as one has to expect from our equations (p. 1617): the amount of pentanes (boiling range 5–45°) 2 vol. %, hexanes (45–75°) 19 vol. %, heptanes (75–100°) 6 vol. %, octanes (100–125°) 22 vol. % of the total reaction product.[11] This is in marked contrast to

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[10] W. J. Podbielniak, *Ind. Eng. Chem.*, *Anal. Ed.*, **5**, 119, 135 (1933).

[11] The small quantities of odd C-number paraffins may be due to small quantities of *i*-pentane present as an impurity in our butane or to the inefficiency of separation by distillation, besides "autodestructive alkylation."

TABLE III

ALKYLATION OF *i*-BUTANE WITH ETHYLENE

Products from Experiments 3, 4 and 5: Charge, 339.0 g. or 482 cc. (H. T. Podbielniak Fractionation)[a]

Fraction	Boiling range °C. at 760 mm.	Volume, cc.	Wt., g.	n^{25}D	Density d^{20}	Remarks	Analyses, % C	Analyses, % H	Mol. wt.
0	Below 0	35.1	21.80			*i*-Butane			
1	0–45	7.6	4.76	1.3535 at 15°					
2	45–68	55.0	35.77	1.3700	0.6574		83.61	16.18	90
						Calcd. for hexanes	83.61	16.38	86
2A	68–75	39.0	25.98	1.3780					
3	75–100	25.2	17.08	1.3870					
4	100–114	50.3	34.80	1.3925	.6994		84.16	15.95	120
						Calcd. for octanes	84.11	15.89	114
4A	114–125	47.7	33.30	1.3970	.7085				
5	125–150	45.0	32.01	1.4032					
6	150–175	54.3	39.33	1.4110					
7	175–200	43.0	31.98	1.4187					
8	200–208	15.3	11.46	1.4221					
Botts.	>208	64.5	50.70	1.4400					
Total			339						

[a] Rate of distillation, 0.5–1.0 cc./min.

the action of aluminum chloride, where the reaction of "autodestructive alkylation"[3] takes place to such an extent that the original result of catalytic ethylation is completely masked.

It is probable that splitting of paraffins in the presence of BF_3 takes place, if it takes place at all, only *at the moment of their formation*, since it could be shown that BF_3 is without action on paraffins under our experimental condition (see p. 1617).

2. **Alkylation of *i*-Butane with *i*-Butylene.**—This was also effected in a rotating bomb at 25°. In one experiment 90 g. of *i*-butane, in the presence of 12 g. of BF_3, 5.0 g. of nickel powder and 2.0 g. of water (in a glass liner) reacted with about 85 g. of *i*-butylene, which was added in small portions during a period of twenty hours. After the reaction 20 g. of *i*-butane was recovered. After separating the BF_3 the water-white reaction product was distilled and the fractions obtained had the properties listed in Table V.

TABLE IV

BUTYLATION OF *i*-BUTANE

Charge, 69.4 g. or 94.5 cc. (H. T. Podbielniak distillation)[a]

Fraction	Boiling range, °C.	Vol., cc.	Wt., g.	n^{25}D	Remarks
0	−10–0	≃11	≃7		*i*-Butane
1	→22–77	5.0	≃3.3	1.3662	
2	77–95	2.6	1.75	1.3837	
3	95–125	30.3	20.9	1.3943	Octanes (boiling range 98–125°) d^{20}_4 0.6993
4	125–150	5.1	3.55	1.4027	
5	150–175	5.6	4.1	1.4122	
6	175–200	9.6	7.1	1.4194	Dodecanes[b] $C_{12}H_{26}$ (boiling range 185–220°)
7	200–225	6.0	4.5	1.4276	
8 & 8-A	225–250	5.3	4.1	1.4392	
9	250–275	5.6	4.4	1.4452	
Botts.	>275	9.6	7.5	1.4612	
Total		95	68		

Fraction 3 gave on analysis C, 84.16; H, 15.84; mol. wt., 120. Calcd. for octanes C, 84.11; H, 15.89; mol. wt., 114.

Fraction 8 gave on analysis C, 84.69; H, 15.33; mol. wt., 191, corresponding to tridecanes. Calcd. for $C_{13}H_{28}$: C, 84.68; H, 15.32; mol. wt., 184.

[a] Rate of distillation, 0.5–1.0 cc./min.

[b] Fractions 6 and 7 combined had n^{25}D 1.4228 and d^{25}_4 0.7553.

All fractions were water white and absolutely stable toward potassium permanganate solution and nitrating mixture except fraction 9. Here again we have a clearcut alkylation of *i*-butane to higher molecular weight paraffins. The reaction proceeds smoothly disregarding the extreme ease of polymerization of *i*-butylene with the same catalyst.

The products of the reaction are mostly octanes and dodecanes, corresponding to 32 and about 15 vol. % of the total product, respectively. The amounts of intermediate paraffins are between 2–5 vol. % each. These facts again support very nicely the formulation of the alkylation reaction as given on p. 1617.

3. **Alkylation of *i*-Pentane with Ethylene.**—*i*-Pentane was alkylated with ethylene at 25 and 150°. In an experiment at 150°, 75 g. of *i*-pentane was treated with ethylene for twenty-two hours in the presence of 15 g. of BF_3, 7.5 g. of HF + 5.0 g. of nickel powder, at a maximum pressure of 50 atm.

About 40% of the *i*-pentane was alkylated and the rest recovered. The water-white mixture of paraffins obtained was fractionated with the following results (Table V).

4. **Alkylation of 2,2,4-Trimethylpentane with Ethylene.**—This paraffin is alkylated much less readily than *i*-butane. Preliminary experiments show that 5–10% of the paraffin was alkylated at 25° during forty hours with BF_3, Ni-H_2O as catalyst. At the same time polymerization of ethylene to high boiling unsaturated hydrocarbons took place. However, paraffins were present in fractions of the product boiling below 250°, for instance, fraction 150–200°, stable to nitrating mixture, with an n^{20}D 1.4198, gave on chemical analysis: C, 84.64; H, 15.36, and mol.

TABLE V

CHARGE 100 CC. (H. T. PODBIELNIAK DISTILLATION)

Fraction	Boiling range °C. at 740 mm.	Volume, cc.	n^{20}D	Remarks	Analyses, %		Mol. wt., %
					C	H	
1	25–35	14.0	1.3576	*i*-Pentane			
2	→ 55–75	14.2	1.3723				
3	75–100	12.5	1.3878		83.88	16.12	99
				Calcd. for heptanes	83.89	16.12	100.1
4	100–125	12.6	1.4000		84.20	15.80	116
				Calcd. for octanes	84.11	15.89	114.1
5	125–150	8.2	1.4138				
6	150–175	7.0	1.4246				
Botts.	>175	31.5	1.4889				
Total		100.0					

Rate = 0.5-4.0 cc. min. All fractions were stable toward nitrating mixture. The presence of even C-number paraffins indicates that some auto-destructive alkylation is taking place at this temperature.

wt., 172; whereas the theoretical values for a paraffin of identical molecular weight are C, 84.61; H, 15.39.

The Chemistry of the Boron Fluoride Catalyst.—The study of the chemistry of our catalyst is only in its initial stages. Its catalytic nature is proved by the fact that one molecule of boron fluoride can convert about 75 molecules of ethylene (see Table II, Expt. 1). In most experiments a large portion of the boron fluoride can be recovered as such. Part of the boron fluoride reacts with a very small fraction (about 2%) of the olefin hydrocarbons, water (or hydrogen fluoride) and metallic nickel forming a complex of different compounds, fuming with BF_3. This complex ranges in consistency from a liquid to quite a solid mass. In Experiment 4, Table I, the complex was a heavy dark green-brown liquid of d^{20} 1.44, the total volume, 22 cc. In Experiment 6 (of the same table) it was practically a solid mass. Water decomposes these complexes and produces an oily layer of highly unsaturated hydrocarbons and a water solution of nickel salts of hydroborofluoric acids containing also some organic substances. In some cases, as for instance in Experiment 6, the action with water is violent, and takes place with a hissing sound similar to that observed when quenching iron.

The catalyst is also active in the presence of sulfur.

Further investigations will be necessary to elucidate the exact nature of the catalyst and these are planned for the future.

Conclusions

The data presented prove definitely that a catalytic reaction between paraffins and olefins can take place under very mild conditions. This reaction consists in the alkylation of the paraffin to higher weight paraffins through the addition of one, two or more molecules of olefin.

It will be noted that all paraffins alkylated so far, with the catalyst described, contain a tertiary carbon atom. Attempts to alkylate *n*-paraffins, for instance *n*-pentane, propane and methane with BF_3 catalysts, so far have not been successful. *n*-Paraffins, perhaps with the exception of ethane and methane, can be alkylated in the presence of aluminum, zirconium and other metal halides.

It is planned to publish the results of our other investigations on the reactions between hydrocarbons in the near future.

Acknowledgments.—We take this opportunity to express our thanks to Dr. Gustav Egloff for his interest in this problem.

Acknowledgment is also due to R. C. Wackher for combustion analyses and molecular weight determinations, to M. J. Stross and W. K. Simpson for Podbielniak distillation analyses.

Summary

A new catalytic reaction consisting in the direct addition of olefins to paraffins under very mild conditions has been described.

RIVERSIDE, ILLINOIS RECEIVED MARCH 18, 1935