ter known gas reactions and point out three effects which are of importance in the former. (1) There is a certain time lag between the absorption of light and the decomposition of the molecule. The large number of collisions with solvent molecules makes deactivation possible during this interval. (2) Similarly, since all collisions of reaction products would be triple collisions, secondary recombination would be enhanced. (3) If the decomposition yields atoms or radicals these would lose their excess kinetic energy by collision before going much more than the length of a molecular diameter and if they were still close together they would undergo primary recombination. All of these effects would decrease the quantum yield but the third would be of greatest importance. Hence, they conclude that for all reactions involving atoms or radicals the primary quantum yield should be definitely less than one. Furthermore, light of shorter wave length should cause the decomposition products to leave with greater kinetic energy; they should travel further before losing their kinetic energy and primary recombination would be decreased. Thus light of shorter wave length should produce a greater quantum yield. The photodecomposition of ethylene iodide would seem to proceed by atoms and radicals. If the low yield at the beginning of an experiment is not due to inhibition, then the present results would tend to substantiate the theory of Franck and Rabinowitsch.

Without citing any evidence, Emschwiller[15] states that when solutions of ethylene iodide are exposed to polychromatic ultraviolet light the primary decomposition products are ethylene and iodine. Such a simple mechanism cannot account for the retardation of the reaction rate observed in our experiments, since union of ethylene and iodine proceeds too slowly at room temperatures. The mechanism suggested here follows from related studies on the decomposition of ethylene iodide. With polychromatic light the ethylene iodide photodecomposition is quite likely complicated by the iodine photosensitized decomposition, which would increase the difficulty of interpreting the results.

The study of the photodecomposition of the halogen addition products of ethylene is being continued in this Laboratory. It is also planned to extend the investigations to the gaseous reactions.

Summary

The apparent quantum yield for the photodecomposition of ethylene iodide in carbon tetrachloride solutions by light of wave lengths 303 and 313 mμ was found to be 0.76. This includes both the photo- and any subsequent thermal reactions. A mechanism involving a primary dissociation into C_2H_4I and atomic iodine has been suggested. The rate equation based on this mechanism is in agreement with the data obtained. A further study of this reaction should be of interest in connection with the Franck and Rabinowitsch theory of photochemical reactions in solution.

ROCHESTER, NEW YORK RECEIVED AUGUST 12, 1935

[15] Emschwiller, *Compt. rend.*, **199**, 854 (1934).

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

Reaction of Paraffins with Aromatic Hydrocarbons (Destructive Alkylation)[1]

BY ARISTID V. GROSSE AND V. N. IPATIEFF

We have recently described the catalytic reaction of saturated hydrocarbons with olefins.[2] We have also found that paraffins can react with aromatic hydrocarbons in the presence of catalysts under mild conditions. The reaction consists in the splitting of the paraffin into a lower molecular weight paraffin and an olefin "in statu nascendi," which immediately alkylates the aromatic hydrocarbon. The general reaction proceeds according to the equation

$$\underset{\text{Paraffin}}{C_{(m+n)}H_{2(m+n)+2}} + \underset{\text{Aromatic hydrocarbon}}{C_xH_{2x-6}} \xrightarrow{\text{Catalyst}} \underset{\text{Lower molecular paraffin}}{C_nH_{2n+2}} + \underset{\text{Alkyl-aromatic hydrocarbon}}{C_xH_{2x-5}\cdot C_mH_{2m+}}$$

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[1] Presented before the Organic Division of the 90th meeting of the American Chemical Society at San Francisco on August 21, 1935.

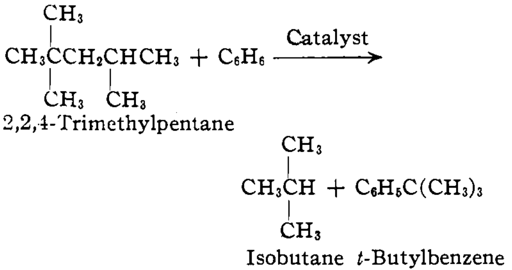
[2] V. N. Ipatieff and A. V. Grosse, THIS JOURNAL, **57**, 1616 (1935).

This reaction may be appropriately termed destructive alkylation.

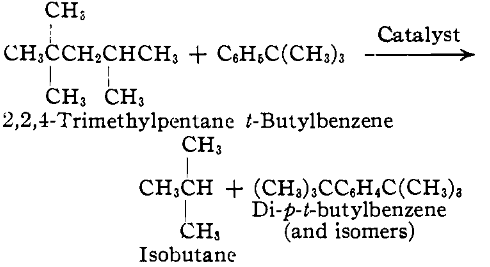
The reaction was first discovered in the case of an octane (2,2,4-trimethylpentane) and benzene, and will be described in detail here. The same reaction takes place with *other aromatic* hydrocarbons, for instance, with toluene and the xylenes, and with *other paraffins*, for instance, *n*-heptane, hexanes and pentanes.

The reaction between 2,2,4-trimethylpentane and benzene was studied in the presence of aluminum chloride, zirconium chloride, boron fluoride and magnesium chloride. In the last two cases there is no reaction, and both hydrocarbons remain unchanged.

In the presence of aluminum chloride and zirconium chloride, the following reactions take place



$$\underset{\text{2,2,4-Trimethylpentane}}{CH_3C(CH_3)_2CH_2CH(CH_3)CH_3} + C_6H_6 \xrightarrow{\text{Catalyst}} \underset{\text{Isobutane}}{CH_3CH(CH_3)CH_3} + \underset{t\text{-Butylbenzene}}{C_6H_5C(CH_3)_3} \qquad (1)$$



$$\underset{\text{2,2,4-Trimethylpentane}}{CH_3C(CH_3)_2CH_2CH(CH_3)CH_3} + \underset{t\text{-Butylbenzene}}{C_6H_5C(CH_3)_3} \xrightarrow{\text{Catalyst}} \underset{\text{Isobutane}}{CH_3CH(CH_3)CH_3} + \underset{\text{Di-}p\text{-}t\text{-butylbenzene (and isomers)}}{(CH_3)_3CC_6H_4C(CH_3)_3} \qquad (2)$$

The octane can be *practically completely* converted into isobutane and the *t*-butylbenzenes. With aluminum chloride, the reaction takes place at 25–50° and ordinary pressure during about four hours; with zirconium chloride, at a temperature of 50–75° during about four hours. These chlorides act as real catalysts, since one molecule of each of them can convert at least twenty molecules of the octane. Hydrogen chloride is added in each case to promote the action of the chlorides. The aluminum chloride and also zirconium chloride partly combine with the aromatic hydrocarbons forming the well-known pasty or liquid brown-red addition compounds of Gustavson.[3]

Experimental Part

(1) Reaction of 2,2,4-Trimethylpentane with Benzene in the Presence of Aluminum Chloride

The reaction was carried out at atmospheric pressure in a three-necked glass flask fitted with (a) a stirrer, (b) a separatory funnel, (c) a reflux condenser with an outlet tube and (d) a gas inlet tube for nitrogen and dry hydrogen chloride from a cylinder.

The gas from the outlet tube of the condenser passed through two dry ice receivers, Nos. 1 and 2, at −78°, a mercury manometer, a safety bottle and a graduated gas holder. A known quantity of the aluminum chloride was placed in the flask. Before starting the reaction, the whole apparatus was flushed out with oxygen-free nitrogen and then the benzene and octane were poured in through the separatory funnel.

From the start of the experiment, dry hydrogen chloride gas was bubbled through the liquid reagents until saturation, a few bubbles being added from time to time during the course of the reaction. The reaction proceeded at room temperature (20°) with evolution of condensable gas and the formation of a dark brown lower layer which quite rapidly increased in quantity. After about one hour the temperature of the reaction vessel was slowly increased to 50° by placing it in a water-bath. After a total reaction time of four and one-half hours, the reaction was stopped.

The Products of the Reaction and their Identification.—The reaction products consisted of (a) gases (condensable and uncondensable at −78°), (b) a clear, water-white upper layer and (c) a dark brown lower layer.

In one typical experiment, the amounts of reagents used and the products obtained after the completion of the reaction, were as follows:

BEFORE REACTION

		Grams
Aluminum chloride (9.4 g. or 0.0705 mole reacted, 8.8 g. recovered unchanged)		18.2
Hydrogen chloride		≃ 0.3
2,2,4-Trimethylpentane (very pure, n^{20}_{D} 1.3922), 1.40 moles		160.1
Benzene (very pure), 1.63 moles		127.3
Total		305.9

AFTER REACTION

Uncondensable gas (at −78°) = 800 cc.		
Condensable gas (at −78°):		
Receiver 1		69.77
Receiver 2		0.0
Upper layer		202.5
Lower layer:		
Unreacted $AlCl_3$,	8.8	32.6
Reacted $AlCl_3$,	9.4	
Hydrocarbons,	14.4	
Losses		1.0
Total		305.9

(a) **Gases.**—The condensable gas at −78° (dry ice) was analyzed by low-temperature Podbielniak distillation and contained 64.7 g. of isobutane, 4.7 g. of pure benzene and only traces (≃0.3 g.) of propane and pentanes. The

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(3) Gustavson, *J. prakt. Chem.*, [2] **34**, 161–177 (1883), [2] **68**, 209–234 (1903); [2] **72**, 57–79 (1905); *Compt. rend.*, **136**. 1065 (1903); **140**, 940 (1905).

TABLE I

UPPER LAYER

(Octane + Benzene + Aluminum Chloride)

Charge = 241 cc. = 192 g.; d^{20}_4 = 0.796; n^{20}_D = 1.4663

Frac.	B. range at 752 mm.	Vol., cc.	Wt., g.	% of total	Density g./cc. at °C.	n^{20}_D	% Paraffins[a]	Remarks
1	71.0- 80.0	13.0	10.7		0.8198 at 22.5	1.4659	18.5	Index of residual paraffins n^{20}_D 1.3966
2	80.0- 81.5	78.5	64.9		0.8275 at 22.5	1.4711	17.9	n^{20}_D 1.3920; odor of isooctane; boiling at 99°
3	81.5-168.0	27.5	21.0		0.7635 at 22.4	1.4332	Ab. 45.0	n^{20}_D 1.3938; odor of isooctane
4	168.0-169.0	73.0	63.1	34.0	0.8644 at 22.7	1.4916	None	
5	169.0-192.0	less 0.5	≃0.2		....	....	..	
6	192.0-216.0	34.5	30.2		0.8751 at 22.6	1.4949	Less than 2.0	These 2% had n^{20}_D 1.4879 and reacted with nitrating mixture
Bottoms	> 216.0	≃3.0	≃2.5			1.5267	Less than 2.0	
Losses			≃0.0					
Total			192.0					

[a] The paraffins remained after the aromatics were absorbed by shaking (in a volume ratio of 1:1) first with 100% sulfuric acid, second with 7% or 15% free SO_3–H_2SO_4, until the residual hydrocarbon gave no reaction with nitrating mixture.

isobutane was very pure; it had a constant boiling point of −10.2° at 760 mm. pressure and the theoretical molecular weight when determined by Stock's gas balance.

The uncondensable gas (800 cc.) was nitrogen, displaced by isobutane from the reaction flask.

(b) **Upper Layer.**—After washing with water and drying, the upper layer was subjected to a high temperature Podbielniak distillation. The distillation curve is shown on Diagram 1; the properties of the fractions are given in Table I. All fractions were water-white and stable to potassium permanganate solution and therefore free from olefins; all reacted with nitrating mixture and therefore contained aromatic hydrocarbons. The principal products of the reaction are present in fractions 4 and 6, since fractions 1, 2 and 3 contain pure unreacted benzene and isooctane.

From the data of Table I it can be seen that fraction 4 consists of a very pure aromatic hydrocarbon (or mixture of closely boiling isomers), and fraction 6 is also practically free from paraffins.

TABLE II

	Bromide from fraction 4	Bromo-*t*-butylbenzene[4]
Boiling point at 740 mm., °C.	230–231	230
Melting point, °C.	+19	+14
Bromine, %	36.8 (Parr bomb)	37.5
Index of refraction, n^{20}_D	1.5290	..
Density, d^{15}_4	1.2519	1.2572
Appearance	White needles	White needles

Investigation of Fraction 4.—The composition of this fraction corresponds to an alkyl-benzene of the formula $C_{10}H_{14}$. *Anal.* Calcd.: C, 89.48; H, 10.52. Found: C, 89.39, 89.49; H, 10.60, 10.59.

By bromination in the presence of iron powder, it was practically quantitatively converted into a monobromine derivative which proved to be identical with bromo-*t*-butylbenzene described by Schramm[4] as seen from the data of Table II.

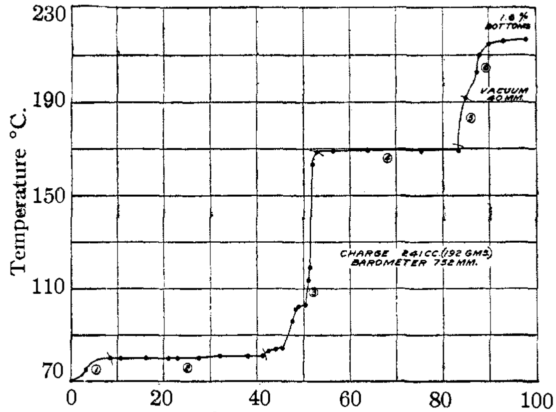

Fig. 1.—High temperature Podbielniak distillation.

For further identification this hydrocarbon was sulfonated and the sulfonic acid, obtained quantitatively, converted into a phenol. The barium salt of the acid (proved later to be *p*-*t*-butylbenzene sulfonic acid) was fractionally crystallized; all fractions were identical proving the homogeneity of our hydrocarbon.

The potassium salt (obtained through double decomposition with potassium sulfate) was melted with potassium hydroxide at 280–350° in a copper dish. The phenol, ob-

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(4) Schramm, *Monatsh.*, **9**, 846 (1888).

tained in nearly quantitative yields, proved to be identical with *p*-*t*-butylphenol by comparing the data of Table III.

TABLE III

	Phenol from fraction 4	*p*-*t*-Butylbenzene[5]
Melting point, °C.	98.5 (sharp)	98.5
Sublimation point	About 100°	Around 100°
Appearance	White long silky needles	White long needles
Mixed melting point	No depression	

These results, together with its physical properties as shown in the following table, leave no doubt but that our hydrocarbon is *t*-butylbenzene.

	Hydrocarbon from fraction 4	*t*-Butylbenzene
Boiling point at 760 mm., °C.	169	169
Melting point, °C.	Below −50	
Density, d^{20}_4	0.8665	0.8671
Index of refraction, n^{20}_D	1.4910	1.4925
% C	89.49	89.48
% H	10.59	10.52
Monobromide from	Identical (see Table II)	
Phenol from	Identical (see Table III)	

Investigation of Fraction 6.—On cooling well-developed spears or needles appeared, which when recrystallized from methanol melted at 76°, and on mixing with pure di-*p*-*t*-butylbenzene (1:1) showed no depression and can be therefore identified with it. Its quantity corresponded to ≃40% of the fraction, the remainder being composed in all probability of the *o*- and *m*-isomers.

(c) **Investigation of the Lower Layer.**—This layer represents a deep red liquid which is much more mobile than the lower layer in ethylene polymerization.[6] It contained, besides unreacted aluminum chloride, addition compounds of aluminum chloride with hydrocarbons and hydrogen chloride. Water easily decomposed these compounds into a water-white hydrocarbon layer and an acid solution of aluminum chloride.

The hydrocarbons were fractionated; fractions below 200° (about 60% of the layer) contained only benzene and mono-*t*-butylbenzene. Fractions from 200–300° (E. P.) decolorized permanganate solution rapidly and contained unsaturated hydrocarbons, which in all probability retarded the continued activity of aluminum chloride.

(2) Reaction of 2,2,4-Trimethylpentane with Benzene in the Presence of Zirconium Chloride

This reaction was carried out in a rotating autoclave (volume, 750 cc.), the chemicals being placed in a glass liner, at a temperature of 50° for one and one-half hours and at 75° for two hours, the maximum pressure increasing to 7 kg./sq. cm. The balance of reagents used and the products obtained are given below.

BALANCE OF PRODUCTS

Bomb evacuated to 4 mm. before HCl addition; reaction products collected in same apparatus as with $AlCl_3$.

BEFORE REACTION

	Grams
Benzene (c. p., Na dry)	63.01
2,2,4-Trimethylpentane (purest, n^{20}_D 1.3922)	78.52
$ZrCl_4$	16.73
HCl	≃ 8.00
Total	166.0

AFTER REACTION

Uncondensable gas = 0.0 cc.	0.00
HCl (in NaOH scrubbers)	4.00
Condensable gas at −78°	41.63
Upper layer	82.50
Lower layer: hydrocarbon part and HCl	21.28
Lower layer: $ZrCl_4$	16.73
Total	166.0

The liquefied gas contained 40.4 g. of isobutane and 1.2 g. of benzene. The isobutane was absolutely pure.

The water-white upper layer was fractionated with a high temperature Podbielniak column, the results obtained being given in Table IV.

There was obtained, just as in the case of aluminum chloride, mono-*t*-butylbenzene and di-*t*-butylbenzenes (only the para compound was isolated in the pure state), and some unreacted benzene and octane.

TABLE IV

Charge = 89 cc. = 72.5 g.

Frac.	B. range, °C., at 750 mm.	Vol., cc.	Wt., g.	n^{20}_D	d^{20}_4	% Aromatics	Remarks
1	79–84	27.5	23.4	1.4790	0.8495	86, balance is octane	Benzene and 14% octane (n^{20}_D 1.3945)
2	84–169	9.0	7.7	1.4790	0.8526	≃90	
3	169–170	28.5	24.7	1.4930	0.8673	100	Pure *t*-butylbenzene
4	170–224	11.0	9.6	1.4944	0.8735		Some di-*p*-*t*-butylbenzene
5	224–256	5.5	4.9	1.5025	....		About 50% of fraction-pure di-*p*-*t*-butylbenzene (m. p. 76°)
Bottoms	>256	2.0	1.7	....	....		
Losses			0.5				
Total			72.5				

All fractions were stable to permanganate solution.

The lower layer is very mobile, dark brown in color and very similar to the aluminum chloride layer. Dilute cold

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[5] Senkowski, *Ber.*, **23**, 2417 (1890).

[6] V. N. Ipatieff and A. V. Grosse unpublished results.

hydrochloric acid decomposes it rapidly, giving liquid hydrocarbons and a zirconium oxychloride solution. These hydrocarbons consisted of benzene, *t*-butylbenzene and some partly unsaturated, in all probability polynuclear, hydrocarbons.

(3) **Reaction of 2,2,4-Trimethylpentane with Benzene in the Presence of (a) Magnesium Chloride ($MgCl_2$) and** (b) Boron Fluoride (BF_3)

There was no reaction in the presence of magnesium chloride and hydrogen chloride at 200° and a pressure of 20 atmospheres during twenty hours. Boron fluoride, promoted by nickel and water, effected no reaction at 55° during four hours in a nickel-lined autoclave.

Summary

A new reaction between paraffins and aromatic hydrocarbons in the presence of catalysts has been described. It consists in the formation of a lower molecular weight paraffin and an alkylated aromatic hydrocarbon, for instance, 2,2,4-trimethylpentane reacts with benzene, giving isobutane and mono- and di-*t*-butylbenzenes.

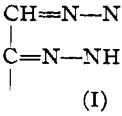
RIVERSIDE, ILL. RECEIVED AUGUST 19, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLUMBIA UNIVERSITY]

The Constitution of Osazones[1]

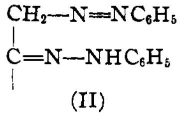
BY LEWIS L. ENGEL[2]

The first suggestion that the Fischer formula for the osazones[3] does not give an adequate explanation of their behavior was made by Zerner and Waltuch,[4] who observed a small but unmistakable mutarotation of the phenylosazones of *l*-arabinose and *l*-xylose in alcoholic pyridine solution. Later, Levene and LaForge[5] confirmed these findings and extended them to the phenylosazones of *d*-glucose, *d*-altrose, *d*-galactose and *d*-gulose. The first observation of the mutarotation of an osazone formed from a secondary hydrazine was made by Votoček and Valentin,[6] who reported that the methylphenylosazone of fructose shows a large mutarotation in methyl alcoholic solution. As an explanation for mutarotation, Zerner and Waltuch suggested that the classical osazone structure (I) was present in equilibrium with the isomeric azo-form (II). The finding of Votoček and Valentin, however, seems to exclude this explanation, since fructose methylphenylosazone possesses no hydrogen capable of migrating in this manner. The present author has been unable to confirm this result of Votoček and Valentin, but has found other evidence which conflicts with the hypothesis of Zerner and Waltuch.



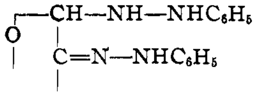
$$\begin{array}{l} CH{=}N{-}NHC_6H_5 \\ | \\ C{=}N{-}NHC_6H_5 \\ | \end{array}$$

(I)



$$\begin{array}{l} CH_2{-}N{=}NC_6H_5 \\ | \\ C{=}N{-}NHC_6H_5 \\ | \end{array}$$

(II)



$$\begin{array}{ll} \ulcorner & CH{-}NH{-}NHC_6H_5 \\ O & | \\ | & C{=}N{-}NHC_6H_5 \\ & | \end{array}$$

(III)

Haworth[7] has suggested that if one of the phenylhydrazine groups in an osazone be assumed to exist as a phenylhydrazino group attached to a cyclic sugar (III), mutarotation could be explained as being due to a shift from the α-form to the β-form. It is also possible that the mutarotation of osazones may be due to partial hydrolysis in solution. In order to test these views it is necessary to ascertain, first, whether the osazones are cyclic compounds; second, whether the nature of the attachment of the sugar to phenylhydrazine is such that hydrolysis will take place under the conditions of the mutarotation experiments; and third, whether the mutarotation is affected by factors which should affect the equilibrium.

It was hoped that the question of the ring could be settled by a study of the methylation products of glucose phenylosazone, but unexpected difficulties were encountered. Methylation by a number of methods was attempted but in no case was it possible to obtain homogeneous crystalline products. Methylation in dioxane with dimethyl sulfate and alkali yielded sirupy products with methoxyl contents ranging from 16.3

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(1) This work was aided by a grant from The Chemical Foundation, Inc.

(2) William J. Gies Fellow, 1933–34; Columbia University Fellow, 1934–35. This report is from a thesis submitted by L. L. Engel in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

(3) Fischer, *Ber.*, **20**, 821 (1887).

(4) Zerner and Waltuch, *Monatsh.*, **35**, 1025 (1914).

(5) Levene and LaForge, *J. Biol. Chem.*, 20, 429 (1915).

(6) Votoček and Valentin, *Coll. Czech. Chem. Comm.*, **3**, 432 (1931).

(7) Haworth, "Constitution of Sugars," Edward Arnold, London, 1929, p. 7