tivities. The excess nitrite was removed by treatment with sulfamic acid before reducing values were determined.

The data summarized in Table V fail to give any evidence by selective inactivation for the presence of a second carbohydrase in addition to amylase in the preparations of purified pancreatic amylase used here. The differences obtained in the inactivation studies of "glucosidase" activities were small and undue emphasis cannot be placed on comparisons of inactivation percentages when different activities, obtained by different types of measurements, are involved. However, the results as a whole give the same trend for the inactivation of "glucosidase" and of amylase activities and appear to justify the conclusion that the properties of pancreatic amylase observed in this investigation are not influenced to any important extent by the presence of contaminating carbohydrases.

Summary and Conclusions

A study of the action of highly purified pancreatic amylase shows that the extent of the hydrolysis of unfractionated potato starch, Lintner soluble starch and of the linear fraction from corn starch depends in each case upon the concentration of amylase. Relatively very high concentrations of the amylase gave no evidence of a limit in the hydrolysis of starch by pancreatic amylase such as is observed with β-amylase.

The reaction curves showed a rapid phase of reaction followed by a phase of very slow rate of change but the extent of the hydrolysis attained was dependent within wide limits upon the concentration of amylase. Under the conditions of these experiments the slowing down of the reactions was not due to any appreciable inactivation of the amylase nor to inter-reaction with or equilibrium between amylase and maltose, glucose or other readily dialyzable products of hydrolysis.

Evidence is presented which shows that the slowing down of the hydrolysis is due to relatively low concentrations of products which the amylase hydrolyzes slowly, for which it has low affinity.

Data are presented which show that the results obtained here are not influenced to any appreciable extent by the presence of maltase or of other carbohydrases.

NEW YORK 27, N. Y. RECEIVED[42] APRIL 21, 1948

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[42] Original manuscript received May 7, 1947.

[CONTRIBUTION FROM PHILLIPS PETROLEUM COMPANY, RESEARCH DEPARTMENT]

Butylation of Benzene during Propylation in the Presence of Isobutane. Ratio of Reactivities of Benzene and Isobutane

BY FRANCIS E. CONDON AND MARYAN P. MATUSZAK

In an experiment originally designed to determine the ratio of the rates of alkylation of benzene and isobutane, a mixture of these two hydrocarbons was subjected to alkylation with propylene in the presence of hydrofluoric acid as catalyst. It was found that, besides isopropylation of benzene, considerable *t*-butylation occurred. The formation of *t*-butylbenzene may be taken as an indication of the intermediate formation of *t*-butyl carbonium ions, which must have been derived from isobutane in accordance with the following considerations.

According to the ionic mechanism of catalytic alkylation of a hydrocarbon, the initial step is formation of a carbonium ion[1]; for example

$$\mathrm{H^+ + C_3H_6 \longrightarrow \mathit{i}\text{-}C_3H_7^+} \qquad (1)$$

When the alkylatable hydrocarbon is an isoparaffin like isobutane, the various subsequent steps may be generalized as reactions in which a carbonium ion, however formed, produces another carbonium ion, either by acquiring hydrogen with its bonding electrons from isobutane, thereby producing also a paraffin

$$\mathrm{\mathit{i}\text{-}C_3H_7^+ + \mathit{i}\text{-}C_4H_{10} \xrightarrow{k} \mathit{t}\text{-}C_4H_9^+ + C_3H_8} \qquad (2)$$

or by uniting with an olefin, which may have been introduced as such, or may have been formed by the reverse of a reaction like 1

$$\mathrm{\mathit{i}\text{-}C_3H_7^+ + \mathit{i}\text{-}C_4H_8 \longrightarrow C_7H_{15}^+} \qquad (3)$$

The new carbonium ions formed by such reactions undergo similar reactions; in addition, some of them undergo preliminary rearrangement, thereby accounting for the multiplicity of products from isoparaffin alkylation.[2]

In the aforementioned experiment, substantially no alkylation of isobutane occurred, in spite of a 50-fold molecular excess of isobutane over benzene. Consequently, it was not possible to deduce, from the composition of the alkylation product, a numerical value for the ratio of the rate of alkylation of benzene to the rate of alkylation of isobutane. There was deduced, however, an approximate numerical value for the ratio of the reactivity of benzene with isopropyl carbonium ion to the reactivity of isobutane with this ion. This deduction was possible because the isopropylation of benzene

$$\mathrm{\mathit{i}\text{-}C_3H_7^+ + C_6H_6 \xrightarrow{k'} \mathit{i}\text{-}C_3H_7C_6H_5 + H^+} \qquad (4)$$

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[1] Price and Ciskowski, THIS JOURNAL, **60**, 2499 (1938).

[2] (a) Bartlett, Condon and Schneider, *ibid.*, **66**, 1531 (1944); (b) see also Schmerling, *ibid.*, **68**, 275 (1946); Ciapetta, *Ind. Eng. Chem*, **37**, 1210 (1945).

was competitive with reaction 2, which must have been substantially the only precursor to the *t*-butylation of benzene, inasmuch as the benzene was reacting with all carbonium ions so rapidly that reaction 3 was negligible. On the assumption that all *t*-butyl carbonium ions reacted with benzene immediately after formation by reaction 2, the ratio of the rate of reaction 4 to the rate of reaction 2 must have equalled the ratio of the number of isopropyl groups, a, to the number of *t*-butyl groups, b; that is

$$\text{Rate 4/Rate 2} = k'(i\text{-}C_3H_7^+)(C_6H_6)/k(i\text{-}C_3H_7^+)(i\text{-}C_4H_{10}) = a/b$$

Consequently

$$k'/k = a(i\text{-}C_4H_{10})/b(C_6H_6)$$

The value of a/b, obtained from the composition of the product, was 7.1. The value of $(i\text{-}C_4H_{10})/(C_6H_6)$ was taken as 49, the mol ratio of isobutane to benzene in the feed, on the approximation that alkylated benzene is alkylated at the same rate as benzene. These values gave $k'/k = 350$. That is, benzene was approximately 350 times as reactive as isobutane.

TABLE I

BUTYLATION OF BENZENE DURING HYDROFLUORIC ACID-CATALYZED ALKYLATION OF 2 MOLE PER CENT. BENZENE IN ISOBUTANE WITH PROPYLENE

		Part 1	Part 2
Temperature, °C.		35–38	35–38
Average contact time, min.		8.0	9.3
HF initially charged, kg.		1.4	
HF added during run, kg.		0.3	0.3
Initial acidity, wt. % HF[a]		98.4	93.0
Final acidity, wt. % HF[a]		93.0	93.3
Feed composition, wt. % (mole %)	Propane	0.5	0.5 (0.6)
	Isobutane	95.17	93.48 (93.4)
	n-Butane	1.7	1.7 (1.7)
	Benzene	2.63	2.58 (1.9)
	Propylene	...	1.74 (2.4)
Hydrocarbon charged, kg.		23.7	23.8
Hydrocarbon effluent, kg.		22.4	21.6
Effluent composition, wt. %	Propane	0.4	0.6
	Isobutane	96.6	95.0
	n-Butane	0.9	0.9
	Alkylate[b]	2.10	3.50
Alkylate[b] composition, wt. % (mole %)			
Paraffins		0.4	1.4 (1.7)
Benzene		96.6	20.1 (31.7)
Isopropylbenzene		0.0	29.3 (29.9)
t-Butylbenzene		0.0	6.3 (5.8)
m-Diisopropylbenzene[c]		0.0	14.8 (11.2)
p-Diisopropylbenzene		0.0	12.5 (9.5)
m-*t*-Butylisopropylbenzene		0.0	3.6 (2.5)
p-*t*-Butylisopropylbenzene		0.0	3.4 (2.4)
Residue		3.0[d]	8.6 (5.3)

[a] By titration of 1 g. with 1 *N* potassium hydroxide (phenolphthalein). [b] Including unreacted benzene. [c] In view of recently reported findings of Melpolder, Woodbridge and Headington, THIS JOURNAL, **70**, 935 (1948), the *m*-diisopropylbenzene (b. p. 203.18°) may have included some *o*- (b. p. 203.75°). [d] B. p. above 270°.

Experimental Part

Materials.—The isobutane and the propylene were products of Phillips Petroleum Company. They were analyzed by fractionation in a Podbielniak Heligrid low-temperature column. C. P. benzene was used.

Anhydrous hydrofluoric acid from the Harshaw Chemical Company was used.

Equipment and Procedure.—The experiment was of the continuous type, with recycling of the acid. The hydrocarbon feed was blended in a 94-liter (25-gal.) steel cylinder, from which it was displaced by pumping water in through a tube which led to the bottom. From the cylinder the feed passed through a silica-gel drier into the reactor. Surging of the feed was minimized by an electrically heated surge tank attached to the feed line after the drier. The reactor[3] was a 1470-ml. steel vessel having a 6.3-cm. (2.5-in.) turbo-mixer, turning about 1725 r. p. m. The reactor was surrounded by a stirred water-bath. Temperature in the reactor was measured by a thermocouple. Acid-to-hydrocarbon volume ratio in the reactor was maintained near unity by occasional additions of fresh acid. This ratio was determined by withdrawing several ml. of the mixture through an eduction tube into a graduated test-tube immersed in a Dry Ice-bath and measuring the volumes of the hydrocarbon and acid layers. From the reactor the mixture passed to a 1440-ml. inclined separator, from which the acid layer was recycled to the reactor by gravity through a U-shaped trap which prevented passage of the reaction mixture into the acid-return line. The pressure in the system was maintained at 10 atm. by a Hanlon-Waters air-operated motor valve, controlled by a Taylor "Fulscope" controller, located on the effluent line from the settler. The hydrocarbon effluent was collected in tared 57-liter (15-gal.) steel cylinders.

The data for the experiment are in Table I. In part 1, half of an isobutane–benzene mixture was used, without propylene, to equilibrate the silica-gel drier and the catalyst and to test the isobutane for any possible presence

TABLE II

PROPERTIES OF FRACTIONS OF PRODUCT FROM HYDROFLUORIC ACID-CATALYZED ALKYLATION OF 2 MOLE PER CENT. OF BENZENE IN ISOBUTANE WITH PROPYLENE

Fraction	Wt., g.	Boiling range, °C. (740 mm.)	d^{20}_4	$n^{20}D$	Mol. wt.[a]
		Part 1			
11	79.8	80.0– 80.0	0.875	1.4977	...
12	360.1	80.0– 80.0	0.880	1.5006	...
13	5.4	80.0–270	....	....	...
Res.	13.3	Above 270	....	....	...
		Part 2			
21	80.9	73.3– 79.7	0.859	1.4874	...
22	78.7	79.7– 80.0	.881	1.4997	...
23	19.4	80.0–152.2	.8599	1.4882	...
24	195.3	152.2–152.9	.8616	1.4902	118
25	19.6	152.9–166.7	.8621	1.4905	121
26	42.4	166.7–176.3	.8662	1.4920	142
27	90.7	176.3–203.3	.8580	1.4890	159
28	42.1	203.3–210.5	.8580	1.4894	151
29	63.0	210.5–212.2	.8573	1.4890	158
30	19.3	212.2–214.1	.8581	1.4888	159
31	17.1	214.1–220.3	.8594	1.4891	171
32	25.8	220.3–230.1	.8618	1.4910	169
33	29.4	230.1–237.9	.8578	1.4890	198
34	35.3	Residue	....	....	...

[a] By lowering of the freezing point of benzene.

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(3) See "Hydrofluoric Acid Alkylation," Phillips Petroleum Co., Bartlesville, Oklahoma, 1946, p. 2, Fig. 1.

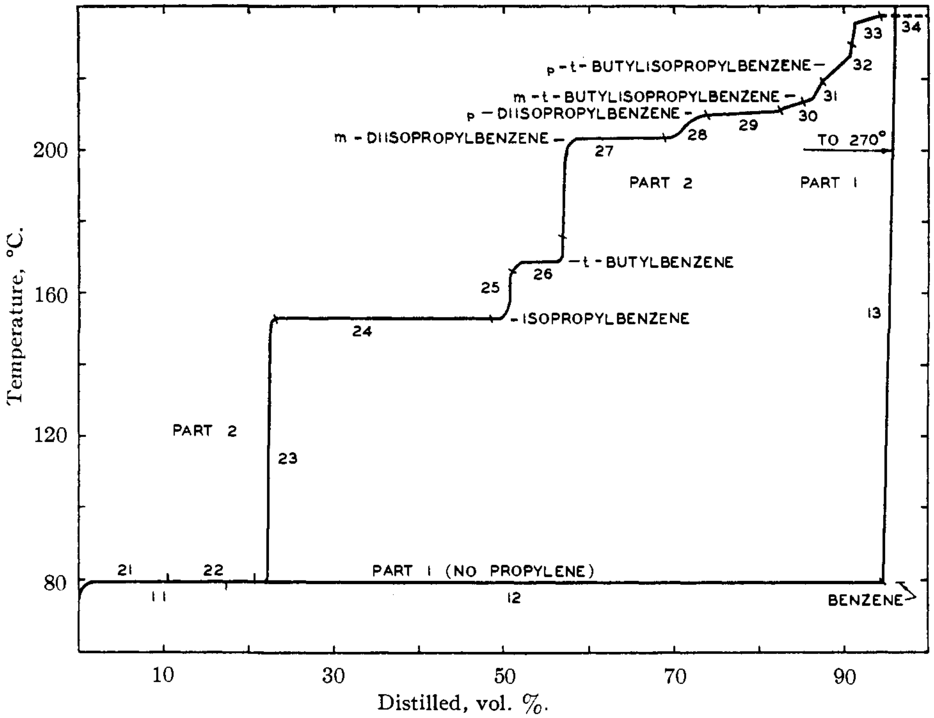

Fig. 1.—Fractionation of product from HF alkylation of 2 mole % benzene in isobutane with propylene (numbers designate fractions).

of isobutylene as an impurity. In part 2, the other half of the isobutane–benzene mixture, after being mixed with the propylene, was used; the first 0.5 kg. of hydrocarbon effluent was discarded, inasmuch as it represented flushing of the system.

The hydrocarbon effluent was partly debutanized in a 3-m. (10-ft.) Monel column, 3.17 cm. (1.25 in.) in diameter, packed with 6.35-mm. (0.25-in.) carbon Raschig rings. The debutanization was completed in a 1.5-m. (5-ft.) vacuum-jacketed glass column, 12.7 mm. (0.5 in.) in diameter, packed with 2.4-mm. ($^3/_{32}$-in.) wire helices. All overhead material was combined and was analyzed by low-temperature Podbielniak fractionation.

Product boiling above 25° was fractionated in a Podbielniak Heligrid vacuum-jacketed column. To a 20-g. residue from fractionation of the product from part 1, 18 g. of cetane (b. p. 290°) was added as a "chaser," and distillation was continued from an ordinary distilling flask.

From the fractionation curves shown in Fig. 1, from the properties of the fractions in Table II, and from the results of preparation of solid derivatives described in Table III, the product compositions reported in Table I were computed.

Preparation of Derivatives (Table III).—*p*-*t*-Butylacetanilide was prepared according to Ipatieff and Schmerling.[4] Benzoic acid and *m*- and *p*-*t*-butylbenzoic acids were obtained by oxidizing 1-cc. (0.85-g.) samples with 8.5 g. of chromium trioxide in 30 cc. of boiling glacial acetic acid for one hour. Iso- and terephthalic acids were obtained from fractions 27 and 29 by oxidizing 3-cc. (2.5-g.) samples with 200 cc. of boiling dilute nitric acid (1:3). They were esterified with methanol, in the presence of a little sulfuric acid.

TABLE III

DERIVATIVES OF FRACTIONS OF PRODUCT FROM HYDROFLUORIC ACID-CATALYZED ALKYLATION OF 2 MOLE PER CENT. BENZENE IN ISOBUTANE WITH PROPYLENE

Fraction	Derivative	Yield, %	Neut. equiv.	M. p., °C. Obsd. (uncorr.)	M. p., °C. Beilstein	Beilstein reference
26	*p*-*t*-Butylacetanilide	20	. . .	168.5–170	170	XII, 1167
24	Benzoic acid	30	. . .	121 –123	121	IX, 96
27	Dimethyl isophthalate	25	. . .	62 – 64	67–68	IX, 834
29	Dimethyl terephthalate	25	. . .	138 –139.5	140	IX, 843
30	*m*-*t*-Butylbenzoic acid	3	184	125 –128	127	IX, 560
31	*m*-*t*-Butylbenzoic acid	5	183	117 –123	127	IX, 560
32	*p*-*t*-Butylbenzoic acid	2	186	161.5–164	164	IX, 560

Acknowledgments.—Mr. G. T. Leatherman assisted with the experiment; Miss Alicia Perez determined molecular weights; and Phillips Petroleum Company kindly granted permission to publish the data.

Summary

A 2 mole per cent. mixture of benzene in isobutane was subjected to hydrofluoric acid-catalyzed alkylation with propylene. The principal

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[4] Ipatieff and Schmerling, THIS JOURNAL, 59, 1056 (1937).

reaction was isopropylation of benzene. Substantially no alkylation of isobutane occurred; however, isobutane reacted, yielding *t*-butylbenzene and *m*- and *p*-*t*-butylisopropylbenzenes. The composition of the product showed that benzene reacted approximately 350 times as readily as isobutane.

Bartlesville, Okla. Received July 19, 1947

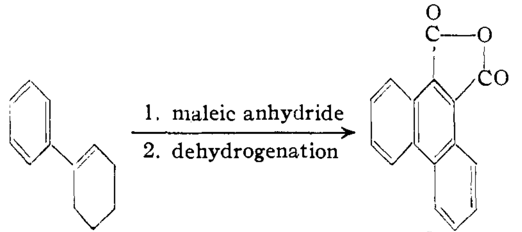
[Contribution from the Chemical Laboratory of Harvard University]

Condensation of Phenylcycloalkenes with Maleic Anhydride. I. Synthesis of 7-Methoxy-3,4-benzphenanthrene

By Jacob Szmuszkovicz[1] and Edward J. Modest

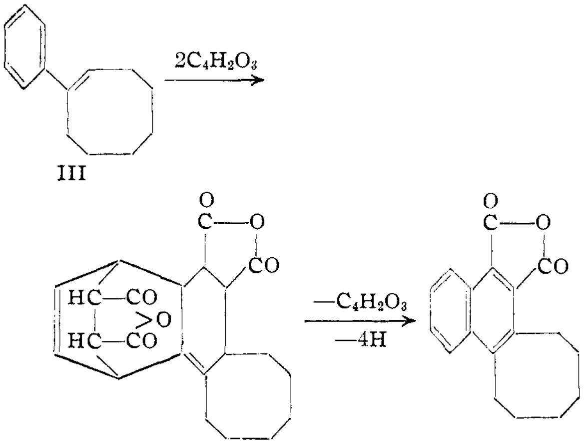
Additions to diene systems in which one double bond is in a benzene ring and the second in an alicyclic ring have not hitherto been reported.[2] The 1,2-double bond in naphthalene in conjugation with the double bond of an olefinic system,[3] with that in cyclopentene[4] or in cyclohexene,[5] is sufficiently reactive to participate in the Diels–Alder condensation. Styrene itself forms copolymers with dienophiles, but some derivatives of styrene form normal adducts.[6,7]

We now have found that 1-phenylcyclohexene-1 (I) adds maleic anhydride at 220° with formation of an amorphous adduct, which can be dehydrogenated to phenanthrene-9,10-dicarboxylic acid anhydride (II); the over-all yield is 25%. Other investigators have prepared this aromatic anhydride from bicyclohexenyl (17% yield)[8]; from phenanthrene, sodium, and carbon dioxide (25.7% yield)[9]; and from diphenyl-2-carboxylic acid (42% yield).[10]



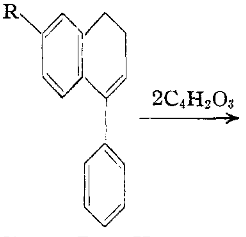
I II

1-Phenylcyclooöctene-1 (III) reacts with maleic anhydride at steam-bath temperature. The product, obtained in quantitative yield, is the bis-adduct (IV), which upon dehydrogenation with sulfur yields 1,2-cyclooöctanonaphthalene-3,4-dicarboxylic acid anhydride (V).

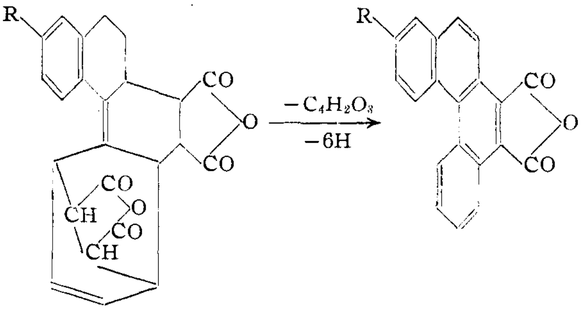


III IV V

1-Phenyl-3,4-dihydronaphthalene (VIa) and 1-phenyl-6-methoxy-3,4-dihydronaphthalene (VIb) react with maleic anhydride; the bis-adducts VIIa and VIIb are formed. The yields vary with the reaction temperature employed, from moderate at 95° to quantitative at 160°.



VI a, R = H
b, R = OCH$_3$



VII a, R = H
b, R = OCH$_3$

VIII a, R = H
b, R = OCH$_3$

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(1) On leave of absence from the Weizmann Institute of Science, Rehovoth, Palestine.

(2) Kloetzel, "Organic Reactions," Vol. IV, John Wiley and Sons, New York, N. Y., in press.

(3) Cohen and Warren, *J. Chem. Soc.*, 1315 (1937).

(4) Bachmann and Kloetzel, This Journal, **60**, 2204 (1938).

(5) F. Bergmann and Szmuszkovicz, *ibid.*, **69**, 1367 (1947).

(6) Hudson and Robinson, *J. Chem. Soc.*, 715 (1941).

(7) Wagner-Jauregg, *Ann.*, **491**, 1 (1931).

(8) C. Weizmann, E. Bergmann and Berlin, This Journal, **60**, 1331 (1938).

(9) Jeanes and Adams, *ibid.*, **59**, 2608 (1937); U. S. Patent 2,231,-787 [*C. A.*, **35**, 3268 (1941)].

(10) Schönberg and Warren, *J. Chem. Soc.*, 1838 (1939); compare Geissman and Tess, This Journal, **62**, 514 (1940).