for one hour in an oil-bath at 140°. The substance melted with strong foaming. The clear melt was cooled, dissolved in ether and extracted several times with a 2% potassium hydroxide in water solution. Emulsions were broken up by the addition of isopropyl alcohol and gentle shaking of the separatory funnel. The combined alkaline layers were washed with ether, then freed from the remaining ether by heating. The cooled alkaline solution was acidified with a 10% hydrochloric acid. The precipitate formed upon acidification was filtered off, washed with water and dried in the vacuum desiccator. The dry substance weighed 24.3 g. and was dissolved by heating in 300 cc. of methanol. The methanol solution was refluxed with charcoal, then filtered hot and left for twenty-four hours at 5°. Crystals were formed which were filtered off and recrystallized from methanol. One and three-tenths grams of crystalline material was obtained, m. p. 212–213°. Melting point depression was not observed with cholesterylacetic acid prepared previously from low melting Acid A. Additional crystalline material could not be isolated from the mother liquor.

Summary

Condensation of cholesteryl *p*-toluenesulfonate and sodium malonic ester in xylene solution yielded cholesterylmalonic ester. From the cholesterylmalonic ester cholesterylmalonic acid was prepared, which was separated into a petroleum ether soluble fraction and a petroleum ether insoluble fraction. The two fractions were identified as isomeric cholesterylmalonic acids.

The petroleum ether insoluble cholesterylmalonic acid was crystallized and from it were prepared: di-adrenalin salt, dimethyl ester, cholesterylacetic acid and cholesterylacetic acid methyl ester.

The petroleum ether soluble cholesterylmalonic acid was obtained in impure form only. The di-adrenalin salt and dimethyl ester thereof were prepared.

The petroleum ether insoluble cholesterylmalonic acid was found to be levorotatory and the petroleum ether soluble acid dextrorotatory. From the difference in the direction of the optical rotation and differences in the consumption of oxygen of the dimethyl esters in the perbenzoic acid titration it was concluded that the petroleum ether insoluble cholesterylmalonic acid is cholesteryl-3-malonic acid and the petroleum ether soluble cholesterylmalonic acid has the structure of *i*-cholesterylmalonic acid.

CHICAGO 9, ILLINOIS RECEIVED MARCH 29, 1945

[CONTRIBUTION FROM MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

Vapor Phase Methylation of Aromatic Hydrocarbons over Solid Catalysts

BY WALTER M. KUTZ AND B. B. CORSON

Friedel and Crafts[1] in 1877 demonstrated the methylation of aromatic hydrocarbons in the liquid phase by methyl halides under the catalytic influence of anhydrous aluminum halides. Although many methylation studies have been subsequently published, this reaction has never been accomplished in the vapor phase over solid catalysts, although it has been attempted.[2]

Thinking that vapor phase methylation of aromatic hydrocarbons over solid catalysts might offer certain advantages, we studied this mode of operation and obtained satisfactory yields of methylated aromatics from benzene, toluene, and naphthalene, using methyl chloride and methyl bromide as methylating agents, and alumina, alumina–silica, activated clay, and aluminum chloride adsorbed on activated carbon as catalysts. Methyl iodide was ineffective as methylating agent under the conditions tried.

Contrary to expectation, certain dehydrohalogenation catalysts (barium chloride and ferric chloride) were ineffective. It was thought that the methylation reaction might go via the methylene group and that a dehydrohalogenation catalyst might catalyze the methylation reaction by removing hydrogen halide from methyl halide to form methylene. "Solid" phosphoric acid catalyst also was ineffective for the catalysis of the methylation reaction.

Experimental

Materials.—The methyl halides were commercial products which were used without further purification. The benzene and toluene were of nitration grade and the naphthalene was of chemical grade.

Catalysts.—Alumina catalyst was made from dried alumina gel which had been precipitated from dilute aqueous aluminum chloride by freshly distilled aqueous ammonia and dried at 110°. The dried gel was crushed and screened to 20–30 mesh and then molded in the form of $^1/_8'' \times {}^1/_8''$ pellets with 4% of aluminum stearate as die-lubricant. These pellets were heated in a stream of air at 600° to remove carbon before being used as catalyst.

Silica gel was precipitated from diluted water glass by hydrochloric acid and washed six times with distilled water (filtering by suction after each wash and slurrying the filter cake in each subsequent wash) until the sodium content of the silica gel was lowered to 0.1%. The washed silica gel cake (about 12% silicon dioxide) was dried at 110° and used in granular form (6–10 mesh).

Alumina–silica catalysts were made by dispersing freshly-prepared, washed silica gel in dilute aqueous aluminum chloride and adding aqueous ammonia to the vigorously stirred mixture to precipitate aluminum hydroxide intimately with the silica gel. The precipitate was washed about five times with distilled water (until the filtrate showed only a faint test for chloride ion) and dried at 110°; the dried material was crushed, screened, pelleted, and burned at 600°, as described above.

Barium chloride catalyst was prepared by soaking granular pumice (6–10 mesh) in a concentrated aqueous solution of the salt and drying the impregnated pumice

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(1) Friedel and Crafts, *Compt. rend.*, **84**, 1392 (1877).

(2) Schwartz and Pflugmacher, *J. prakt. Chem.*, **156**, 205 (1940).

TABLE I

METHYLATION OF BENZENE, TOLUENE AND NAPHTHALENE OVER ALUMINA CATALYST

Expt.[a]	Temp., °C.	C. T., sec.[b]	Feed: Benzene, g./hr.	Feed: Mole ratio, C_6H_6/CH_3Cl	Product: Mono-alkylated, g./hr.	Product: Poly-alkylated, g./hr.	Product: Wt. ratio, mono/poly	Methyl chloride, % conversion to alkylaromatics
1	450	8	25	2.9	4.1	1.7	2.4	73
2-A	400	10	21	2.5	4.4	2.6	1.7	95
2-B	400	9	23	2.7	5.3	1.0	5.3	71
2-C	400	9	24	2.7	3.8	0.9	4.2	55
3	400	10	26	6.1	5.1	0.8	6.4	100
4	400	7	25	1.4	2.1	1.7	1.2	27
5	400	9	25	3.3	4.5	2.1	2.1	86
6	400	1	217	2.8	20.8	4.8	4.4	33
7	400	5	47	2.8	7.5	3.0	2.5	80
8	400	13	16	2.4	3.5	2.1	2.5	91
9	350	10	23	2.7	3.8	1.0	3.8	56
10	300	10	24	2.8	2.5	1.0	2.5	44
11	250	7	25	2.9	0.3	...[d]	...[d]	3
12[c]	250	6	25	2.9	0.7	...[d]	...[d]	7
13	400	9	Toluene, 29	3.0	6.6	2.4	2.8	93
14[e]	400	8	Naphthalene, 6	1.2	0.8	0.6	1.3	36

[a] All experiments were eight hours long except 14, which was twenty-four hours long. [b] The free space was assumed to be 60% of the apparent volume. [c] Dry hydrogen chloride was added to give a HCl/CH_3Cl mole ratio of 1:3. [d] The amount of product was too small to give a signficant figure. [e] The liquid feed was an 18% solution of naphthalene in cyclohexane.

at 300° in a current of dry hydrogen chloride. Analysis showed 6.2% of $BaCl_2$.

The "solid" phosphoric acid catalyst was the regular Universal Oil Products Company polymerization catalyst.

The aluminum chloride–activated carbon catalyst was prepared by heating a mixture of equal weights of aluminum chloride and activated carbon in a glass-lined, rotating autoclave at 250° for three hours under an atmosphere (375 p. s. i., gage) of hydrogen and hydrogen chloride (the weight of the latter being 5% of the weight of the original chloride–carbon mixture.[3]) The final catalyst contained 40% of aluminum chloride.

Attempts to prepare a ferric chloride–activated carbon catalyst in a similar manner were unsuccessful. A mixture of equal weights of ferric chloride (anhydrous, sublimed) and activated carbon (Columbia brand, 45 × A, 6–8 mesh, previously dried for three hours at 300°, in a stream of dry nitrogen) was sealed into a glass tube and heated at 300° in an autoclave for one hour. Analysis showed that about 95% of the iron had been reduced to the ferrous state. The catalyst contained 29.1% of ferrous chloride and 1.5% of ferric chloride (based on the Fe^{+++}/Fe^{++} ratio).

Eventually, ferric chloride was adsorbed on Filtrol and silica gel by the above technique. When the sealed tubes were opened, chlorine could be smelled, but analysis showed that at least 95% of the iron was in the ferric state. The amount of adsorbed ferric chloride was 28.7% in the case of the Filtrol catalyst and 21.3% in the case of the silica catalyst.

Apparatus and Procedure.—Figure 1 presents a flow diagram of the process. The furnace consisted of a vertical 4" × 24" insulated, stainless steel block, electrically heated and thermostatically controlled to within ±3° of the desired temperature and containing a central longitudinal hole (1" dia.) for the catalyst tube and a parallel hole ($^3/_{16}$" dia.) for the thermocouple. The catalyst tube was of Pyrex (22 mm. o.d. × 100 cm. long) and the 100-cc. catalyst bed (±30 cm. long) was held in place in the middle of the heated zone by plugs of glass wool, the upper volume of the catalyst tube being packed with broken quartz for preheating.

The liquid feed (hydrocarbon or hydrocarbon plus methyl iodide) was pumped[4] into the top of the catalyst tube. The addition of methyl chloride, methyl bromide, and anhydrous hydrogen chloride was controlled by capillary flowmeters. Liquid product was collected in two ice-cooled traps. Gas samples were obtained by scrubbing the uncondensed exit gas from the liquid receivers with cold, methyl chloride-saturated 20% sodium hydroxide solution to remove hydrogen chloride (it was shown that methyl chloride was not hydrolyzed under these conditions) and collecting the gas in an evacuated receiver. To the gas receiver was also added the gas which was removed from the liquid product by stabilization. Gas samples

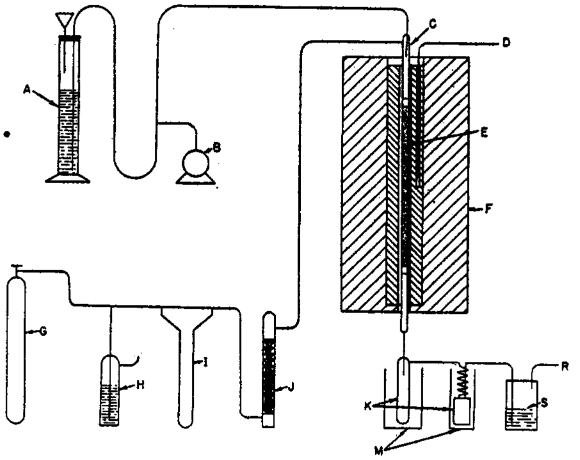

Fig. 1.—A. Liquid Charge; B. Bellows Pump; C. Catalyst Tube; D. Thermocouple; E. Catalyst; F. Furnace; G. Alkyl Halide; H. Safety Tube; I. Capillary Flow Meter; J. Drying Tower; K. Receivers for Product; M. Ice Baths; R. Line for Exit Gas; S. Gas Washing Bottle.

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(3) Ipatieff and Pines, U. S. Patent 2,169,494 (1939).

(4) Corson and Cerveny, *Ind. Eng. Chem., Anal. Ed.*, **14**, 899 (1942).

TABLE II

METHYLATION OF BENZENE OVER ALUMINA-SILICA AND OTHER CATALYSTS

				Feed		Product			
Expt.[a]	Catalyst	Temp., °C.	C. T., sec.[b]	Benzene, g./hr.	Mole ratio, C_6H_6/CH_3X	Mono-alkylated, g./hr.	Poly-alkylated, g./hr.	Wt. ratio, mono/poly	Methyl halide, % conversion to alkyl-aromatics
15	75 Al_2O_3–25 SiO_2[e]	450	9	24	3.5	2.6	1.5	1.7	70
16	75 Al_2O_3–25 SiO_2	400	10	20	2.7	3.1	2.2	1.4	79
17	75 Al_2O_3–25 SiO_2	350	11	20	2.7	1.4	0.6	2.3	29
18	75 Al_2O_3–25 SiO_2	300	9	28	3.1	0.7	0.4	1.7	16
19	75 Al_2O_3–25 SiO_2[c]	300	9	27	3.1	0.7	0.6	1.2	19
20	50 Al_2O_3–50 SiO_2	400	8	25	3.1	3.2	1.1	2.9	55
21	25 Al_2O_3–75 SiO_2	400	10	21	2.9	2.9	1.4	2.1	65
22	5 Al_2O_3–95 SiO_2	400	11	20	2.8	2.4	1.2	2.0	56
23	0 Al_2O_3–100 SiO_2	400	9	26	3.1	0.5	...[d]	...[d]	5
24	Filtrol[f]	400	9	22	2.4	1.0	0.4	2.5	14
25	Commercial Al_2O_3[g]	400	10	22	2.4	1.8	0.4	4.7	20
26	$BaCl_2$[c]	400	8	23	2.5	0	0	...	0
27	$BaCl_2$[c]	500	8	19	2.0	0	0	...	0
28	$FeCl_3$–Filtrol	200	12	27	2.9	0	0	...	0
29	$FeCl_3$–Filtrol	300	8	32	3.4	0	0	...	0
30	$FeCl_2$–Carbon	300	8	29	3.1	0	0	...	0
31	$FeCl_2$–Carbon	400	9	27	2.7	0	0	...	0
32	H_3PO_4[h]	300	12	20	2.1	0	0	...	0
33	H_3PO_4	350	11	19	2.1	0	0	...	0
34	H_3PO_4	400	9	23	2.4	0	0	...	0
35	H_3PO_4	450	9	21	2.2	0	0	...	0
36-A	$AlCl_3$–Carbon	150	16	17	1.8	2.3	1.4	1.6	42
36-B	$AlCl_3$–Carbon	150	15	18	1.9	0.7	1.1	0.6	26
36-C	$AlCl_3$–Carbon	150	15	19	2.0	0.7	...	...	7
37	75 Al_2O_3–25 SiO_2	400	9	MeBr 25	3.4	4.0	2.0	2	92
38	75 Al_2O_3–25 SiO_2	400	9	MeI 25	3	0	0	...	0
39	75 Al_2O_3–25 SiO_2	300	11	MeI 24	3	0	0	...	0
40	75 Al_2O_3–25 SiO_2	200	13	MeI 24	3	0	0	...	0

[a,b,c,d] Same as for Table I. [e] Weight per cent. [f] Filtrol (X-143) crushed and screened to 6–10 mesh. [g] Harshaw Chemical Company activated alumina, $^1/_8'' \times {}^1/_8''$ pellets. [h] Universal Oil Products Company polymerization catalyst.

for analysis were taken from the receiver by means of a mercury-filled buret. All alkylation runs were made at ordinary pressure.

Analytical Methods.—Liquid condensate was stabilized under a column to remove dissolved gas and 100 cc. of stabilized liquid product was distilled through a micro column.[5] The distillation cuts were identified by boiling point and refractive index. In the yield calculations on the methylation of benzene, it was assumed that 55% of the material boiling higher than toluene was xylene and that 45% of it was trimethylated benzene (fractionation of a 300-cc. composite of product boiling above toluene having shown 55% of xylene and 45% of higher boiling material). In the yield calculations for the methylation of toluene and naphthalene it was assumed that the material boiling higher than the monoalkylated product was dialkylated.

Discussion of Results

Effect of Temperature.—The optimum temperature for the methylation of benzene by methyl chloride was 400° (expts. 1, 2-A, 9, 10, 11, 12). At 250°, there was practically no conversion (expt. 11) and the addition of hydrogen chloride did not activate the catalyst at this temperature (expt. 12).

Catalyst Life.—According to expts. 2-A, 2-B, and 2-C, the production of toluene was fairly constant through three consecutive eight-hour periods, the production of polymethylbenzenes being greatest during the first period.

Effect of Contact Time.—The contact time was varied from 1 to 13 seconds. With a constant molecular ratio of benzene to methyl chloride in the feed, the effect of decreasing the contact time was to increase the ratio of mono- to polyalkylation (expts. 6, 7, 8, 2-A).

Catalyst Regeneration.—The catalyst which had been used for twenty-four consecutive hours in expts. 2-A, 2-B, and 2-C, was burned in a stream of air at 600° for four hours and re-tested in expt. 5. Its activity was restored, as was also the polyalkylating tendency which is characteristic of fresh catalysts.

Relative Activities of Alumina and Alumina–Silica Catalysts.—All the alumina–silica catalysts tested were less active than the laboratory-prepared alumina catalyst, but they were more active than silica alone (expt. 23), the activity being raised seven-fold by the addition of 5% of alumina (expt. 22). All the alumina–silica catalysts, however, were more active than the activated clay (Filtrol X-143) and the commercial alumina tested.

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(5) Glowacki, "The Determination and Examination of Light Oil in Gas," Am. Gas Assoc., New York, 1941.

Inasmuch as microscopic and X-ray examinations of the alumina catalyst showed that the laboratory-prepared alumina was more crystalline than the commercial alumina tested, it may be that the greater catalytic activity of the former is connected with its higher degree of crystallinity.

The ferric chloride–Filtrol catalyst was tested at 200° (expt. 28) and at 300° (expt. 29). Hydrogen chloride was evolved initially at both temperatures but no toluene was produced. The iron in the used catalysts was at least 95% in the ferrous state. Reduction of ferric chloride catalyst in the Friedel–Crafts reaction has been previously observed.[6] The ferrous chloride–activated carbon catalyst was tested at 300° (expt. 30) and at 400° (expt. 31). Toluene was not produced at either temperature. Hydrogen chloride was absent in the exit gas from the 300° experiment, but it was present in the 400° experiment.

The "solid" phosphoric acid catalyst showed no activity at approximately ten seconds contact time at 300, 350, 400 and 450°. Aluminum chloride adsorbed on activated carbon was active as would be expected, but three consecutive eight-hour periods (expts. 36-A, 36-B, 36-C) at 150° showed that the activity dropped off rapidly. The higher temperatures used with the other catalysts could not be employed with the aluminum chloride–activated carbon catalyst because of the sublimation of aluminum chloride.

By-products of Methyl Chloride.—The exit gas from expt. 2-A (after removal of hydrogen chloride) showed the following composition: 85% of paraffin (index 1.2), 4% of hydrogen, 11% of olefin (ethylene being less than 10% of the total olefin). The gas production accounted for 5% of the methyl chloride fed to the reactor, the remaining 95% of the methyl chloride being accounted for as methylated benzenes.

Methylation of Naphthalene with Methyl Chloride.—The monomethylated portion of the methylated naphthalene product showed constants (b. p. 240–246° (760 mm.); f. p., 4° (cooling curve); $n^{20}\text{D}$ 1.6135) which corresponded to a mixture of approximately 15% of the α-isomer and 85% of the β-isomer.[7]

Acknowledgment.—The authors express their thanks to Mrs. M. M. Goettman for assistance in the experimental work.

Summary

Benzene, toluene and naphthalene were methylated in vapor phase over solid catalysts. The methylating agents were methyl chloride and methyl bromide (methyl iodide was not effective), and the catalysts were alumina, alumina–silica, and aluminum chloride–activated carbon. Barium chloride–pumice, ferric chloride–Filtrol, ferrous chloride–activated carbon, and "solid" phosphoric acid did not catalyze the reaction.

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[6] Ipatieff and Corson, THIS JOURNAL, **59**, 1417 (1937).

[7] Coulson, *J. Soc. Chem. Ind.*, **60**, 123 (1941).

PITTSBURGH, PENNSYLVANIA RECEIVED MARCH 15, 1945

CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF POLAROID CORPORATION

Absorption Spectra. II. Some Aldehyde Condensation Products of Methyl Pyridines

BY ELKAN R. BLOUT AND VIRGINIA W. EAGER

Although there has been great interest in the light absorbing properties of compounds, only recently have there been any concerted attempts to correlate the structure of molecules with their light absorption.[1] A previous paper from this Laboratory has discussed the relation between the electronic nature and the absorption spectra of certain aldazines.[2] The ultraviolet absorption spectra of some substituted pyridines are discussed herein.

It is evident that the simplest aromatic hydrocarbon, benzene, and its nitrogen analog, pyridine, show many gross similarities. For example, they have approximately the same resonance energy[3]; they both absorb at approximately the same wave length (maximum at 255 mμ); and both compounds show anionoid and cationoid reactions.[4] We propose to illustrate some differences between the electronic natures of carbon and nitrogen by a comparison of the absorption spectra of some pyridine derivatives and their hydrocarbon analogs.

4-Styrylpyridine has a single absorption maximum at 307 mμ, and the shape of its spectrum is almost identical with that of stilbene where the maximum is at 294 mμ[5] (Fig. 1). The fact that

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[1] Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939); Bury, THIS JOURNAL, **57**, 2115 (1935); Pauling, *Proc. Nat. Acad. Sci.*, **25**, 577 (1939); Mulliken, *J. Chem. Phys.*, **7**, 121, 364, 570 (1939); Pauling, "Organic Chemistry," H. Gilman, Editor, 2nd ed., Vol. II, pp. 1944 ff. (1943).

[2] Blout and Gofstein, THIS JOURNAL, **67**, 13 (1945).

[3] Pauling in "Nature of the Chemical Bond" gives 39 kcal./mole for benzene and 43 kcal./mole for pyridine.

[4] Bowen, *Chem. Soc. Lond., Ann. Rep.*, **40**, 25 (1943), states that the replacement of carbon by nitrogen in aromatic organic compounds does not greatly alter the energy value of the π orbitals and hence there is little change in the absorption spectra.

[5] Arends, *Ber.*, **64**, 1936 (1931). A reëxamination of the spectrum of stilbene gives results in good agreement with these data (Table I).