the methods employed. A critical discussion of the bromination method is given, and certain errors pointed out.

5. Wynne-Jones' attempt to determine the ratio of proton to deuteron transfer by progressive exchange of H for D in nitroparaffins is inapplicable to nitroethane and nitroisopropane because of the instability of the substrate at certain stages in the process.

6. Equations for rate constants as functions of temperature are given, and energies and entropies of activation calculated. It is shown that the differences in rates observed cannot be explained in terms of changes in the activation energy alone; the differences in the observed rates are caused by an interplay of variations in both energy and entropy of activation.

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Reactions of Trialkyl Phosphates, Alkyl Acetates, and Tertiary Butyl Hypochlorite in the Friedel-Crafts Syntheses[1]

BY NATHAN BERMAN AND ALEXANDER LOWY

The synthesis of alkylated substances by means of the Friedel-Crafts reaction has been extended widely from the original use of alkyl chlorides with aromatic hydrocarbons. An important advance in the alkylation reaction was the application of esters to the synthesis. Among the esters used were: alkyl borates, alkyl acetates, alkyl formates, *n*-butyl oxalate, tetraethyl silicate, and diethyl carbonate. The trialkyl phosphates gave phenol ethers with phenol.

The purpose of this investigation was to observe whether the use of esters might be extended to the alkyl esters of phosphoric acid, acetic acid, and tertiary butyl hypochlorite. These substances proved to be efficient alkylating agents. The conditions which influenced the yield of alkylated benzenes were observed, such as concentration of reagents, duration of heating, and reaction time.

Experimental

The apparatus employed for the alkylations was the usual one-liter three-necked Pyrex flask, into one neck of which extended a dropping funnel and thermometer. The central neck was fitted with a glass stopper and mercury seal, through which extended a motor-driven glass stirrer. The third neck was connected to a modified Hopkins-type reflux condenser. Fractionations were conducted with a seventeen-inch (43-cm.) Vigreux column, which was wrapped in asbestos paper.

The aluminum chloride used throughout was of 99.5% purity. The benzene was dried over sodium and distilled at 80–81°. The various esters were purified by distillation or by vacuum distillation before use.

Typical Experiment. Triethyl Phosphate.—Benzene (435 g.) was stirred with 68.5 g. (0.515 mole) of aluminum chloride in the Pyrex flask, surrounded by an ice-water bath; 25 g. (0.137 mole) of triethyl phosphate was added dropwise through a separatory funnel over a two-hour period. The mixture was then stirred for eight hours at room temperature (20–25°). Throughout this time there was a vigorous evolution of hydrogen chloride. The mixture was poured over cracked ice and allowed to hydrolyze overnight. The benzene layer was washed with aqueous sodium bicarbonate and water, dried over calcium chloride, filtered, and fractionally distilled. There was obtained 27 g. of ethylbenzene boiling at 134–137°; n^{20}_D 1.4951. There was also obtained 8 g. of a higher boiling fraction.

Preparation of Triisopropyl Phosphate.—The procedure analogous to that described in "Organic Syntheses" for the preparation of *n*-butyl phosphate[2] was followed. In the four-necked flask fitted with (a) a mercury-sealed stirrer, (b) a Hopkins-Cole type condenser, (c) a thermometer, and (d) a separatory funnel, there was mixed three moles (180 g.) of isopropyl alcohol with 3.3 moles of pyridine and 275 ml. of benzene as solvent. This mixture was stirred and cooled in an ice-salt bath to −5°. Through the separatory funnel, 153 g. of phosphorus oxychloride was added dropwise over six hours at such a rate that the temperature never exceeded 10°. The mixture was refluxed for two hours at 80°; 500 ml. of water was added to dissolve the pyridine hydrochloride; the benzene layer was washed with 100 ml. of water and dried over anhydrous sodium sulfate. On vacuum distillation, 100 g. of triisopropyl phosphate was collected, which represents a 44.7% yield. Its boiling point was 122–125°, at 15–16 mm. pressure.

The accompanying Table I gives the results of the experiments conducted with the various esters as alkylating agents. The experimental procedure was analogous to that followed in the experiment with triethyl phosphate, except as indicated below.

I. Alkylating agent = triethyl phosphate (b. p. 96–101° at 3–5 mm.). Product = ethylbenzene (b. p. 134–137°; n^{20}_D 1.4951).

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[1] Abstracted from a thesis presented by Nathan Berman to the Graduate School in partial fulfilment of the requirements for the Ph.D. degree.

[2] *Org. Syntheses*, **16**, pp. 9–12 (1936).

II. Alkylating agent = triisopropyl phosphate. Product = isopropylbenzene (b. p. 151–154°; $n^{20}\text{D}$ 1.4917; *d* 0.859 (20°)).

III. Alkylating agent = tributyl phosphate (b. p. 157–160° at 4 mm.). Product = *s*-butylbenzene (b. p. 171–175°; $n^{20}\text{D}$ 1.4884).

IV. Alkylating agent = isopropyl acetate. Product = isopropylbenzene.

V. Alkylating agent = *s*-butyl acetate. Product = *s*-butylbenzene (b. p. 173–177°; $n^{20}\text{D}$ 1.4889).

VI. Alkylating agent = methylamyl acetate (b. p. 143–146°). Product = isohexylbenzene.

VII. Alkylating agent = tertiary butyl hypochlorite. Product = *t*-butylbenzene (b. p. 165–170°; $n^{20}\text{D}$ 1.4963).

TABLE I

	Alkylating agent		$AlCl_3$				Alkylated benzene		High boiler
Expt.	G.	Mole	G.	Mole	Temp., °C.	Time, hrs.	G.	%	g.
I-A	50	0.274	130	0.977	20–25	28	24	27.5	15
I-B	25	.137	68.5	.515	20–25	10	27	61.5	8
II	25	.112	48.9	.368	10–15	4	21	52.1	8
					20–25	20			
III	25	.094	46.9	.353	20–25	2	27	71.5	4
					80	14			
IV-A	50	.49	71.7	.538	80	1	8	13.6	3.5
					20–25	9			
IV-B	50	.49	71.7	.538	80	20	6	10.2	3
IV-C	25	.245	71.7	.538	20–25	23	17	57.8	6
V-A	50	.431	126	.945	80	10	9	15.6	19
V-B	50	.431	36	.472	80	20	31	53.7	7
V-C	50	.431	4.7	.0428	80	10	None		..
VI-A	50	.347	102	.765	80	10	None[a]		..
VI-B	50	.347	25.5	.191	80	10	None[a]		..
VI-C	50	.347	51	.383	80	10	27[b]	48.0	9
VI-D	25	.174	25.5	.191	80	10	17[c]	60.4	4
VII-A	30	.277	33.7	.253	20–25	25	16	43.1	6
VII-B	25	.231	None		15	3	None		..
					80	48			

[a] No mercury. [b] Amount of mercury unknown. [c] 10 g. of mercury.

In the experiments conducted with *s*-butyl acetate, the 19-g. high boiling fraction (experiment V-A) showed the usual effect of a high concentration of aluminum chloride. The molar ratio of aluminum chloride to ester of approximately one to one (experiment V-B) was more favorable to the production of *s*-butylbenzene. Experiment V-C showed that the relatively small amount of aluminum chloride did not promote the reaction, from which it was assumed that the aluminum chloride plays an integral part in the reaction, and its role is not purely catalytic.

The formula given to methyl amyl acetate by the Carbon and Carbide Co. was: $CH_3COOCH(CH_3)CH_2CH(CH_3)_2$(2,4-dimethylbutyl acetate). It has been established that under the conditions of the experiments mercury is a necessary catalyst for the alkylation of benzene with methyl amyl acetate. The physical constants of the alkylated benzene were: b. p. 195–200°; $n^{15}\text{D}$ 1.4930; *d* = 0.866 (15°), which corresponds with *β*-methyl-*δ*-phenylpentane (b. p. 197°; $n^{15}\text{D}$ 1.4876; *d* 0.863 (15°)).

t-Butyl hypochlorite was supplied by the Pennsylvania Salt Manufacturing Co. The question was considered as to whether it would condense the alkyl or alkoxy group on to benzene. Under the conditions of experiment VII-B, aluminum chloride was found to be a necessary catalyst for the alkylation of benzene by tertiary butyl hypochlorite. Since no ether but *t*-butylbenzene was obtained exclusively, it was apparent that the alkyl–oxygen bond in the hypochlorite was split in the reaction.

Aluminum Chloride with Isopropyl Acetate.—For the elucidation of the mechanism of these syntheses, it is important to determine the behavior of the esters when treated with aluminum chloride. In the following experiment an attempt was made to isolate any isopropyl chloride which might be evolved in the reaction of isopropyl acetate with aluminum chloride. Twenty-five grams of isopropyl acetate was added dropwise to 71.8 g. of aluminum chloride at 15° in the reaction flask. The mixture was stirred for five and one-half hours at 15° and then for two hours at 50°. Some reaction was apparent due to the mixture becoming thick and dark with an evolution of hydrogen chloride. No isopropyl chloride (b. p. 39°) was obtained.

Under the conditions of the experiment, any alkyl halide which might be formed could react further at once and hence was not isolated.

Summary

1. It has been shown that the trialkylphosphates (ethyl, isopropyl and butyl), the alkyl acetates (isopropyl, *s*-butyl, and methyl amyl) and *t*-butyl hypochlorite will condense with benzene in the presence of aluminum chloride to give the corresponding alkylated benzene. These reactions may be summarized by the equations

$$(RO)_3PO + 3C_6H_6 + AlCl_3 \longrightarrow 3RC_6H_5 + AlPO_4 + 3HCl$$

$$CH_3COOR + C_6H_6 + AlCl_3 \longrightarrow RC_6H_5 + HCl + CH_3COOAlCl_2$$[3]

$$t\text{-}C_4H_9OCl + C_6H_6 + (AlCl_3) \longrightarrow t\text{-}C_4H_9C_6H_5 + HOCl$$

2. The preparation of triisopropyl phosphate has been described.

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(3) Groggins, *Ind. Eng. Chem.*, **23**, 152 (1931).