233. *The Reaction of Benzoic Anhydride with Aromatic Compounds Catalysed by Boron Trifluoride.*

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Boron trifluoride catalyses the interaction in nitrobenzene solution of benzoic anhydride with aromatic compounds to give ketones. Phenyl 1-naphthyl ketone, phenyl 2-hydroxy-1-naphthyl ketone, and phenyl 2-thienyl ketone are formed by reaction of the acid anhydride with naphthalene, 2-naphthyl methyl ether, and thiophen respectively. The same catalyst is effective in the Fries rearrangement of 2-naphthyl benzoate.

In 1939—1940 we initiated a programme of work on the acylation of aromatic compounds with benzoic and other anhydrides in the presence of boron trifluoride, but were unable to complete it. We therefore record here the results of the work as far as we were able to carry it.

Meerwein and Vossen have reported (*J. pr. Chem.*, 1934, **141**, 149) the interaction of acetic anhydride with benzene and other aromatic compounds in the presence of boron trifluoride to give aryl methyl ketones, but do not mention the use of any other acid anhydrides. Their experimental procedure involved the saturation of the mixed reactants at 0° with the catalyst, followed by warming till all the fluoride was given off again. The yield of some ketones was decreased by intermolecular condensations of the acetic anhydride to give β-diketones. Bowlus and Nieuwland (*J. Amer. Chem. Soc.*, 1931, **53**, 3835) state that benzoic and phthalic anhydrides (in an unspecified solvent) do not absorb boron trifluoride, but that benzoic acid in chloroform takes up the gas, forming an insoluble complex.

We have found that benzoic and phthalic anhydrides in nitrobenzene, and the former in carbon tetrachloride and in tetrachloroethane, react with boron trifluoride, depositing solid complexes. The weight of gas taken up, after allowing for its solubility in the solvent, was approximately equivalent to 2 moles of BF_3 per mole of anhydride.

For our acylation experiments we chose nitrobenzene as solvent, on the grounds that the reaction presumably resembles the Friedel–Crafts reaction in being ionic in nature (see Linstead, *Ann. Reports*, 1937, 251; Price and Ciskowski, *J. Amer. Chem. Soc.*, 1938, **60**, 2499), and therefore should proceed most readily in a solvent of high dielectric constant.

By reaction of benzoic anhydride with thiophen we obtained a 40% yield of phenyl 2-thienyl ketone; a dirty residue, non-volatile in steam, was also formed. 2-Naphthyl methyl ether gave 55% of phenyl 2-hydroxy-1-naphthyl ketone; complete demethylation occurred.

Phenyl naphthyl ketone (77% crude product) was obtained by reaction of benzoic anhydride with naphthalene; after three crystallisations, substantially pure phenyl 1-naphthyl ketone was obtained (about 60%). Price and Ciskowski (*loc. cit.*) in the reaction of benzyl alcohol with naphthalene in the presence of boron trifluoride, also found the 1-isomer to predominate.

It was found that (under the conditions used in the benzoylations) boron trifluoride catalysed the Fries rearrangement of 2-naphthyl benzoate; a 34% yield of pure phenyl 2-hydroxy-1-naphthyl ketone was obtained.

In order to confirm the reasoning which led to the choice of nitrobenzene as solvent for the reaction mixture, an attempt was made to acylate naphthalene with benzoic anhydride in carbon tetrachloride solution. Under the same conditions as were used in the reaction in nitrobenzene only 4% of crude phenyl naphthyl ketone was obtained. Benzoic acid in reaction with naphthalene and boron trifluoride in nitrobenzene solution gave no phenyl naphthyl ketone.

The procedure used here appears to be unnecessarily vigorous for the benzoylation of reactive substances such as thiophen, as is shown by the formation of tarry by-products. The benzoylation of naphthalene by this method gives a rather higher yield of phenyl 1-naphthyl ketone, and the product is less contaminated with the 2-isomer than that of the Friedel–Crafts reaction of benzoyl chloride with naphthalene, catalysed by aluminium chloride (see, for example, Caille, *Compt. rend.*, 1911, **153**, 393); the necessary time of reaction is less (24 hours as against 3 days).

EXPERIMENTAL.

(Melting points are corrected.)

Materials.—Naphthalene, benzoic acid, and benzoic anhydride were dried in a vacuum desiccator before use. Solvents were dried with calcium chloride and redistilled. Boron trifluoride was prepared by the method of Krause and Nitsche (*Ber.*, 1921, **54**, 2786). A mixture of boric oxide, potassium borofluoride, and concentrated sulphuric acid was heated slowly from 135° to 250°. The gas was passed through a spray trap, but was not purified in any other way.

Absorption of Boron Trifluoride by the Reactants.—Experiments were carried out in test tubes fitted with side tubes. These, with inlet tube, rubber connections and clips were weighed empty and with the liquid before and after absorption. The liquid was cooled in ice during absorption. Absorption was allowed to proceed to constant weight. These experiments were made primarily to determine whether the acid anhydrides did or did not absorb boron trifluoride, and high accuracy is not claimed.

The data are presented in the Table. In column 4 the solubility of the gas in the solvent or solution is given in g. per 100 g. of solvent. In column 5 the molar ratio, boron trifluoride to benzoic acid or anhydride, is given.

Absorption of Boron Trifluoride.

Solute.	Solvent.	Wt. of solute per 100 g. of solvent.	Solubility, g./100 g.	Ratio, moles BF_3/ moles acid or anhydride.
None	Nitrobenzene	—	17·6	—
None	Tetrachloroethane	—	9·8	—
Benzoic anhydride	Nitrobenzene	12·6	24·4	1·8
Benzoic anhydride	Tetrachloroethane	7·87	15·0	2·2
Phthalic anhydride	Nitrobenzene	10	26·3	1·9

Benzoylation Experiments.—The reactants and solvent were placed in a three-necked flask, which was fitted with an inlet tube, mechanical stirrer, and calcium chloride tube. The stirrer was of the glass link type, and was run very fast so as to break up the surface of the liquid. A mercury-sealed stirrer was used in some experiments, but a simple well-fitting glass sleeve was found quite satisfactory. The inlet tube was bent so that the gas was delivered in the liquid, directly under the stirrer. An excess of boron trifluoride (3—5 moles per mole of benzoic anhydride) was passed in the course of 1—2 hours according to the scale of experiment. During absorption of boron trifluoride the flask was cooled in ice. After absorption, the reaction mixture was stirred and kept at 0° for 3—4 hours, and then left, while slowly warming to room temperature, for a further 18 hours. It was then shaken with dilute sodium hydroxide solution, and the solvent and any excess reactants were removed in steam. The product was obtained either from the steam distillate or from the residue by extraction.

Phenyl 2-*thienyl ketone*. Benzoic anhydride (2 g.) and thiophen (1 c.c.) in nitrobenzene (12 g.) were treated with excess of boron trifluoride, and the product was worked up as above. The ketone distilled in steam after the solvent had been removed; it was extracted from the distillate with ether and dried, and the ether was removed; 0·7 g. of brownish crystals was obtained. After 2 crystallisations from light petroleum (b. p. 60—80°) the compound had m. p. 52°.

Phenyl 2-*hydroxy*-1-*naphthyl ketone from* 2-*naphthyl methyl ether*. Benzoic anhydride (4 g.) and 2-naphthyl methyl ether (2·5 g.) in nitrobenzene (18 g.) were treated with excess of boron trifluoride as above. From the residue of the steam distillation, 2·5 g.(70%) of crude ketone were obtained, completely soluble in warm sodium hydroxide solution. Crystallised from ligroin and twice from 60% alcohol, it gave fine yellow needles, m. p. 140—140·5°.

Phenyl 1-*naphthyl ketone*. (*a*) Benzoic anhydride (22·6 g.), naphthalene (12·8 g.), and nitrobenzene (140 c.c.) were treated with about 23 g. of boron trifluoride (*i.e.*, about 3 moles per mole of benzoic anhydride). From an ether extract of the residue from the steam distillation, 19 g. (77%) of crude phenyl naphthyl ketone were obtained. A solution of 0·3 g. in 1 c.c. of benzene gave no precipitate after being boiled for 2 minutes and kept for 15 hours with 0·2 g. of picric acid in 1 c.c. of benzene (the 2-isomer gives an insoluble picrate in benzene, the 1-isomer none, and a mixture can be separated by virtue of this fact; see Perrier and Caille, *Compt. rend.*, 1908, **146**, 769). The remainder of the crude product was crystallised 3 times from dilute alcohol, with charcoal; m. p. 73—74° (Perrier and Caille, *loc. cit.*, give 76°).

(*b*) Naphthalene (4·3 g.) and benzoic anhydride (7·5 g.) in carbon tetrachloride (75 c.c.) were treated with excess of boron trifluoride; a copious white precipitate was thrown down. About 2·8 g. of unchanged naphthalene were found in the steam distillate. From the residue 0·3 g. (about 4%) of crude phenyl naphthyl ketone was obtained.

Attempted reaction of benzoic acid with naphthalene. Benzoic acid (5 g.) and naphthalene (5 g.) in nitrobenzene (65 c.c.) were treated with boron trifluoride as above. The materials were recovered substantially unchanged, and no phenyl naphthyl ketone was detected.

Fries Rearrangement of 2-Naphthyl Benzoate.—Naphthyl benzoate (7 g.) in nitrobenzene (65 c.c.) was treated with a large excess (about 15 g.) of boron trifluoride as above. The residue from the steam distillate was made strongly alkaline, and filtered hot from some black solid. The filtrate was made acid and filtered again. The residue on the filter was crystallised twice from dilute alcohol with the addition of charcoal. The product was phenyl 2-hydroxy-1-naphthyl ketone (2·4 g., 34%), m. p. 140·5—141°.

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