Evidence is presented to show that the formation of phenylsodium occurs from the action of amylsodium, but not the free radical amyl, with benzene.

The formation of iso- and terephthalic acids in the interaction of benzene, amyl chloride and sodium has been shown to be due probably to reactions of either amylidene or amylidene disodium with benzene.

Further discussion of the mechanism of the formation of butylmalonic acid from the reaction of amyl chloride and sodium has been made and the probable path has been judged to be by disproportionation of the free radical amyl.

In the disproportionation of this free radical to pentane and pentene, the presence of the intermediate state, amylidene, which rearranges to pentene has been indicated.

Application of these studies to the mechanism of the Wurtz–Fittig reaction has shown that it proceeds by means of the reaction of an alkylsodium with the alkyl chloride and that free radicals are present during the early stages.

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[CONTRIBUTION NO. 323 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Reactions of Alkyl Sulfates, Tetraethyl Orthosilicate and Diethyl Carbonate in Friedel–Crafts Syntheses[1,2]

BY HOWARD L. KANE AND ALEXANDER LOWY

Alkylations by the method of Friedel and Crafts are generally carried out using the halides or olefins. Nevertheless, certain disadvantages, especially among the lower members, are inherent in both these methods (particularly the necessity for pressure apparatus or very high stirring speeds).

The use of esters other than the halides as alkylating agents also has been proposed. Among these esters are the alkyl chlorocarbonates,[3] ethyl toluene-*p*-sulfonate,[4] trialkyl or triaralkyl borates[5] and the esters of aliphatic acids such as ethyl acetate or ethyl valerate.[6] An apparent exception to this mode of behavior exists in the case of ethyl nitrate, which acts as a nitrating agent rather than an alkylating agent.[7]

The purpose of this investigation was to observe whether the alkyl esters of sulfuric, orthosilicic and carbonic acids were active in this type of synthesis. As was anticipated, these substances proved to be efficient alkylating agents. The conditions which influenced the yield of mono-alkylated benzenes were also observed, such as concentrations of reagents, duration of heating and reaction time.

It is probable that many other esters (such as the sulfites, phosphates, acid sulfates, etc.) can undergo this type of condensation. The exceptional case of the nitrate may likewise become normal under different experimental conditions. This generalization is in harmony with the observation of Slanina, Sowa and Nieuwland[8] that acidic substances promote the olefin–benzene condensation in the presence of boron fluoride, this probably occurring through the formation of alkyl esters.

In the present investigation it has been shown that dimethyl, diethyl, diisopropyl and dibutyl sulfates, tetraethyl orthosilicate and diethyl carbonate will condense with benzene in the presence of aluminum chloride. These reactions may be summarized by equations

$$3(RO)_2SO_2 + 6C_6H_6 + 2AlCl_3 \longrightarrow 6C_6H_5R + 6HCl + Al_2(SO_4)_3$$

$$3(RO)_2CO + 6C_6H_6 + 2AlCl_3 \longrightarrow 6C_6H_5R + 6HCl + Al_2(CO_3)_3$$

$$3(RO)_4Si + 12C_6H_6 + 4AlCl_3 \longrightarrow 12C_6H_5R + 12HCl + Al_4(SiO_4)_3$$

Experimental

The apparatus employed for the alkylations was the usual one-liter three-necked flask, into one neck of which extended a dropping funnel and thermometer. The cen-

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

[2] Presented before the Division of Organic Chemistry of the American Chemical Society, September, 1936, in Pittsburgh, Pa.

[3] (a) Rennie, *J. Chem. Soc.*, **41**, 33 (1882); (b) Kunckell and Ulex, *J. prakt. Chem.*, (ii) **86**, 518 (1912).

[4] Clemo and Walton, *J. Chem. Soc.*, 723 (1928).

[5] Kaufmann, German Patent 555,403; French Patent 720,034.

[6] Kashtanov, *J. Gen. Chem.* (*U. S. S. R.*), **2**, 515 (1932).

[7] (a) Boedtker, *Bull. soc. chim.*, (iv) **3**, 726 (1908); (b) Tronov and Sibgatullin, *J. Russ. Phys.-Chem. Soc.*, **62**, 2267 (1930).

[8] (a) Slanina, Sowa and Nieuwland, THIS JOURNAL, **57**, 1547 (1935); (b) Wunderly, Sowa and Nieuwland, *ibid.*, **58**, 1007 (1936); (c) Ipatieff, Corson and Pines, *ibid.*, **58**, 919 (1936).

tral 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. This condenser could be cooled by water in the usual way, or it could be packed with solid carbon dioxide. This latter procedure was employed when methyl or ethyl esters were the reactants.

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 vacuum distillation before use.

Diethyl Sulfate.—The experiment which gave the highest yield of ethylbenzene from diethyl sulfate is described below (IIA).

Benzene (574 g.) was stirred (1000 r. p. m.) with aluminum chloride (96 g., 0.72 mole), and cooled in an ice-bath. Diethyl sulfate (77 g., 0.5 mole) mixed with 50 g. of benzene (making a total of eight moles) was then added during four hours. The ice-bath was removed an hour later, and the mixture warmed slowly. After five and one-half hours the temperature had reached 70°, where it was maintained for two more hours. After cooling for one-half hour the product was poured over cracked ice. The total reaction time was thus thirteen hours, during the whole of which the reflux condenser was cooled by packing with solid carbon dioxide.

The benzene layer, when hydrolysis of the aluminum chloride was complete, was washed with dilute sulfuric acid, aqueous sodium bicarbonate and water. It was then dried over calcium chloride for one day.

The dried benzene layer was then fractionally distilled, and yielded 75.7 g. of ethylbenzene, boiling at 133–137°. Three and one-half grams of a product boiling in the diethylbenzene range (175–185°), and four grams of residue were also obtained. Calculation of the theoretical yields was made on the assumption that all alkyl groups in the various esters were active. On this basis 0.5 mole of diethyl sulfate should form 1.0 mole of ethylbenzene (106 g.). The above yield of 75.7 g. is thus 71.4% of the theoretical.

The effects of variation in aluminum chloride concentration are summarized in Table I. Comparison of IA with IB shows that low concentrations of aluminum chloride result in incomplete reaction. Comparison of IIA with IIB, on the other hand, shows that excessive amounts of aluminum chloride also cause a reduction in yield of ethylbenzene; the yield of higher-boiling products is correspondingly increased. The amount of aluminum chloride employed in IB and IIA is 2.2 times the stoichiometrical quantity required by the above equation.

TABLE I

DIETHYL SULFATE—EFFECT OF $AlCl_3$ CONCENTRATION

No.	Diethyl sulfate, g.	$AlCl_3$, g.	Benzene, g.	Molar ratio of $AlCl_3$ to diethyl sulfate	Ethylbenzene (133–137°) % yield	Diethylbenzenes (175–185°) % yield	Residue, g.
IA	38.5	24	312	0.72	36.5	21	3.5
IB	38.5	48	312	1.44	62.5	21	1.5
IIA	77	96	624	1.44	71.4	5	4.0
IIB	77	146	624	2.20	31.6	12	12.0

The effects of variation in temperature were studied in a series of experiments summarized in Table II. Best yields were obtained by conducting the reaction for the first few hours at low temperatures, and then heating for a short time (IIIA). Heating at 50 or 70° for the entire experiment gave much reduced yields of ethylbenzene (IIIB, IIIC).

TABLE II

DIETHYL SULFATE—EFFECT OF HEATING

Diethyl sulfate, 38.5 g.; $AlCl_3$, 48 g.; benzene, 312 g.

No.	Time at 10°, hours	Time at higher temp., hours	Higher temp., °C.	Ethylbenzene (133–137°) % yield	Diethylbenzenes (175–185°) % yield	Residue, g.
IIIA	5	1	70	66.5	18	2.5
IIIB	0	5.5	50	40.5	6	3.0
IIIC	0	5.5	70	36.7	6	4.5

The addition of calcium carbonate to react with hydrochloric acid had very little effect on the reaction. When 100 g. of calcium carbonate, 96 g. of aluminum chloride, 77 g. of diethyl sulfate and 624 g. of benzene reacted under the usual conditions (similar to IIIA, Table II), the yield of ethylbenzene was still 63.7%. Even when 1 g. of water and 1 g. of concentrated ammonium hydroxide were also added, the yield was 64.2%. This is surprising in view of the usual sensitivity of Friedel–Crafts reactions to moisture.

Dimethyl Sulfate.—Benzene (624 g., 8 moles) was stirred (1000 r. p. m.) with $AlCl_3$ (48 g., 0.36 mole) for one hour. Dimethyl sulfate (31.5 g., 0.25 mole) was then added during a two-hour period. The flask was kept at 25° during this addition, and for three hours longer. The temperature was raised to 70° during the course of one hour and maintained at that temperature for another hour. During the entire experiment the reflux condenser was cooled with solid carbon dioxide. The mixture was hydrolyzed with cracked ice. The benzene layer was separated, washed with aqueous sodium bicarbonate and water and then dried over calcium chloride for twelve hours. Fractional distillation of the product through a 66-cm. Young column gave 27.5 g. of toluene (108–113°), 3 g. in the xylene range (135–145°) and 1.5 g. of residue. The yield of toluene was thus 59.8%, based on both methyl groups of dimethyl sulfate.

Other reactions in which dimethyl sulfate was employed confirmed the result of the diethyl sulfate reactions where aluminum chloride concentration was concerned. The best yields were obtained with a ratio of aluminum chloride to ester of 1.44 to 1. Small variations in the neighborhood of this value were not attempted.

Dimethyl sulfate was very slowly reactive below 20°.

Diisopropyl Sulfate.—This ester was prepared by the reaction of isopropyl alcohol with sulfuryl chloride.[9] Levaillant reports 34% yield by this method, but by allowing the crude carbon tetrachloride solution to stand for two to three days (until the cloudiness disappeared) a yield of 48.6% was obtained. The product distilling at 74–80° under 3–4 mm. was employed.

The usual procedure as described above was effective except that it was necessary to reflux the crude product with aqueous sodium bicarbonate before washing. The ester reacted freely at 0°. The reaction between 91 g. (0.5 mole) of diisopropyl sulfate, 96 g. (0.72 mole) of alu-

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(9) Levaillant, *Compt. rend.*, **188**, 261 (1929).

minum chloride and 624 g. (8.0 moles) of benzene, gave 53.0 g. of isopropylbenzene (44.2%) boiling at 148–152°. Twenty-five grams of higher-boiling products was obtained.

Dibutyl Sulfate.—This ester was prepared by the method of Barkenbus and Owen[10] in 64% yield (b. p. 110–118° at 4–6 mm.).

Thirty-five grams (0.17 mole) of the dibutyl sulfate so prepared was treated in the usual way with 208 g. (2.67 moles) of benzene and 32 g. (0.24 mole) of aluminum chloride, except that heating was omitted. The reaction was conducted for six hours in an ice-bath, and then for fifteen hours at 30°. Stirring was continued at 1000 r. p. m. The product contained a bright cherry-red lower layer. After hydrolysis, refluxing with sodium bicarbonate, washing and drying, the entire mixture was fractionally distilled, yielding the following products: 165–175°, 19.5 g. (43.6% calculated as isomeric butylbenzenes); 175–185°, 5.5 g.; higher boiling products, 2.0 g.

Tetraethyl Orthosilicate.—Best yields of ethylbenzene were obtained when the ratio of aluminum chloride to tetraethyl orthosilicate was 2.88 moles to one. When 52 g. (0.25 mole) of the ester was treated with 624 g. of benzene and 96 g. of aluminum chloride, 56.5 g. of ethylbenzene (133–137°) was obtained (53.3% based on all ethyl groups of tetraethyl orthosilicate). The reaction was conducted for sixteen hours at 25° (reaction being slow at lower temperatures); the temperature was raised during five and one-half hours to 70°, and maintained there for four hours. Hydrolysis and fractionation were accomplished in the usual way, as with diethyl sulfate.

Diethyl Carbonate.—Fifty-nine grams of diethyl carbonate (0.5 mole), 96 g. of aluminum chloride (0.72 mole) and 624 g. of benzene (8.0 moles) were treated as described above for twenty-six hours at 25° and three hours at 70° (four hours were consumed in gradually raising the temperature from 25 to 70°). The reaction was slow at temperatures below 25°. After hydrolysis, washing, drying and fractionation as with diethyl sulfate, 59.8 g. of ethylbenzene (133–137°) or 56.4%, and 19.5 g. of higher boiling products were obtained.

Naphthalene.—Several experiments in which naphthalene reacted with diethyl sulfate in the presence of aluminum chloride and a solvent gave a product boiling in the ethylnaphthalene range, from which no pure compound could be isolated. The solvents used were carbon disulfide and *o*-dichlorobenzene.

In one experiment 128 g. of naphthalene (1.0 mole), 441 g. of *o*-dichlorobenzene (3.0 moles) and 77 g. of diethyl sulfate (0.5 mole) were stirred at 1000 r. p. m. for one hour. Then 147 g. of aluminum chloride (1.1 moles) was added in small portions during twenty-five and one-half hours. The temperature of an ice and salt bath was maintained at 0 ± 2° for the first fourteen and the last three hours, being permitted to warm up to 25° for the intervening time. Stirring was continued throughout the experiment. The black product was hydrolyzed and washed in the way described in the benzene experiments, and was then steam-distilled. The oil layer was separated, dried and fractionally distilled. Thirty-five grams of a hydrocarbon oil boiling at 240–270° was obtained along with 10 g. of higher boiling products. Redistillation of the 240–270° fraction gave 25 g. of a product boiling at 245–255°. β-Ethylnaphthalene boils at 251°, α-ethylnaphthalene at 258–259° corrected.

Flow Method.—An apparatus was devised in which the liquid reactants (benzene and diethyl sulfate, for example) could be made to flow over the aluminum chloride, contained in a long, narrow, inclined tube. The best yield obtained by this method was 25.7% of ethylbenzene.

Action of Aluminum Chloride on Alkyl Esters.—Aluminum chloride has been shown to react with tetraethyl orthosilicate in the absence of a solvent, the products being ethyl chloride and ether.[11] Dimethyl sulfate reacts with stannic chloride, forming methyl chloride and other products, also in the absence of a solvent.[12] To determine whether the course of these reactions would be altered at the dilutions employed in the alkylations described above, the following experiments were conducted.

38.5 g. of diethyl sulfate was treated with 48 g. of aluminum chloride in 300 g. of 90–100° olefin-free ligroin. The temperature was kept at 10–50°. The volatile products were condensed with solid carbon dioxide. Five grams of a product not ethyl chloride was obtained. Repetition of this experiment using 29.5 g. of diethyl carbonate in place of the sulfate, at temperatures below 50°, also gave 3 g. of a product, but no ethyl chloride.

That reaction of some kind did occur was evident from the fact that the aluminum chloride became gelatinous as the addition of ester proceeded. It is possible that the ligroin was not inactive, as had been supposed. Recent evidence shows that paraffin hydrocarbons are not inert in the presence of aluminum chloride, zirconium chloride and boron fluoride.[13]

Summary

1. The use of esters as alkylating agents in the Friedel–Crafts syntheses has been extended to include a number of new examples.

2. The best yields of mono-alkylated benzene obtained with the following esters were: dimethyl sulfate, 59.8%; diethyl sulfate, 71.4%; diisopropyl sulfate, 44.2%; dibutyl sulfate, 43.6%; tetraethyl orthosilicate, 53.3%; and diethyl carbonate, 56.4%.

3. The general conditions affecting the yield, such as reaction time, temperature and proportions of reagents have been studied. The best ratio of aluminum chloride to ester was 1.44 moles to one, except in the case of the silicate, where it was 2.88 to one.

4. Attempts to alkylate naphthalene with diethyl sulfate led to hydrocarbon oils which could not be fractionated into separate ethylated naphthalenes.

5. Attempts to use a flow method with diethyl sulfate gave much reduced yields.

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[10] Barkenbus and Owen, THIS JOURNAL, **56**, 1204 (1934).

[11] Stokes, *Am. Chem. J.*, **14**, 444 (1892).

[12] Boulin and Simon, *Compt. rend.*, **169**, 618 (1919).

[13] (a) Grosse and Ipatieff, THIS JOURNAL, **57**, 2415 (1935); (b) Ipatieff and Grosse, *ibid.*, **57**, 1616 (1935).

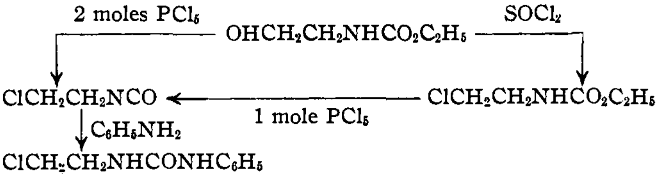
6. No ethyl chloride could be obtained by the action of diethyl sulfate or carbonate on aluminum chloride in ligroin.

PITTSBURGH, PENNA. RECEIVED OCTOBER 28, 1936

Syntheses from Ethanolamine. III. Synthesis of N-β-Chloroethyl Urethan and of β-Chloroethyl Isocyanate

BY HENRY WENKER

In extending a study of syntheses from enthanolamine, it has been found that N-β-oxyethyl urethan reacts with thionyl chloride to form N-β-chloroethyl urethan. Under the influence of phosphorus pentachloride, the latter compound yields β-chloroethyl isocyanate, which can also be prepared directly from the oxyurethan by using 2 moles of phosphorus pentachloride. The constitution of the isocyanate was confirmed by the preparation of the respective α-aryl-β-(β-chloroethyl) ureas from aniline and from *p*-phenetidine. The reactions involved are expressed by the formulas



Both compounds have not been described hitherto; their use for further syntheses is now being investigated.

Experimental

N-β-Chloroethyl Urethan.—One hundred and forty-three grams of thionyl chloride is added gradually to 133 g. of N-β-oxyethyl urethan. The reaction is finished by short heating on the water-bath and the product distilled *in vacuo*. With the exception of a small residue, all distilled from 128–130° at 13 mm. The yield was 138 g. or 91%.

Anal. Calcd. for $C_5H_{10}O_2NCl$: N, 9.3; Cl, 23.4. Found: N, 9.1; Cl, 23.2.

N-β-Chloroethyl urethan is a colorless, fairly mobile liquid possessing a slightly pungent odor. It dissolves readily in ethanol and ether, but not in water.

β-Chloroethyl Isocyanate.—Preparation from N-β-oxyethyl urethan: 133 g. of the urethan is dropped, under external cooling, on 420 g. of phosphorus pentachloride contained in a 2-liter flask. About one-half of the pentachloride remains undissolved, but heating on the water-bath soon produces a clear homogeneous solution. The product is then distilled very slowly, using an efficient fractionating column. Even so, there is a considerable intermediate fraction, until finally the pure isocyanate distils at 135°. The yield was 52 g. or 49%.

Anal. Calcd. for C_3H_4ONCl: N, 13.3; Cl, 33.6. Found: N, 13.0; Cl, 33.4.

The preparation from N-β-chloroethyl urethan is identical, except that for one mole of the urethan, or 151 g., one mole of pentachloride or 210 g. is used. The yield is the same as above.

β-Chloroethyl isocyanate is a colorless, mobile liquid, heavier than water and rapidly decomposed by it under evolution of carbon dioxide. The resulting solution is clear with silver nitrate, but on standing becomes cloudy. The isocyanate has an unpleasant odor and its vapor is very irritating on the eyes.

Ten and one-half grams of isocyanate was added to 9.3 g. of aniline dissolved in 50 ml. of ether. The solution boiled up spontaneously and a sludge of white crystals was formed. Crystallized from dilute ethanol, the product melted at 124°; the literature[1] gives 124° for α-phenyl-β-(β-chloroethyl) urea.

The isocyanate reacts similarly with *p*-phenetidine; the urea melts at 149°. It forms fine white crystals of silky luster.

Anal. Calcd. for $C_{11}H_{15}O_2N_2Cl$: N, 11.5; Cl, 17.9. Found: N, 11.2; Cl, 17.9.

Phosphorus pentoxide, which has been used successfully[2] for the preparation of phenyl isocyanate from phenyl urethan instead of the pentachloride,[3] was found to be unsuitable for the purpose of converting N-β-chloroethyl urethan into the isocyanate; upon heating decomposition with evolution of hydrogen chloride occurred.

Summary

N-β-Oxyethyl urethan reacts with thionyl chloride to form N-β-chloroethyl urethan; both urethans, the former with 2 moles, the latter with 1 mole of phosphorus pentachloride, yield β-chloroethyl isocyanate.

ELIZABETH, N. J. RECEIVED OCTOBER 26, 1936

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(1) Gabriel and Stelzner, *Ber.*, **28**, 2937 (1895).

(2) Hofmann, *ibid.*, **3**, 655 (1870).

(3) Lengfeld and Stieglitz, *Am. Chem. J.*, **16**, 71 (1894).