

catalysts for the oxidation of aniline sulfate by sulfuric acid, mercury being the better. The effect is not strictly proportional to the amount of the catalyst.

2. Together the two catalysts give effects much greater than the additive value. This is,

accordingly, a case of coactivation. Mercury and copper in the ratio of two moles to one give the most pronounced effect.

3. The reaction is monomolecular or pseudo-monomolecular in the first stages.

COLLEGE PARK, MD. RECEIVED SEPTEMBER 17, 1936

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 148]

## Condensations by Sodium. VIII. Solvent Exchange Reactions, Preparation of Phenylmalonic Acid, and Comments on Some Mechanisms of Reactions which Employ Sodium

BY AVERY A. MORTON AND INGENUIN HECHENBLEIKNER

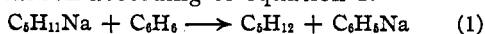
When benzene or a mixture of benzene and ligroin was used as the solvent for the preparation of amylsodium from amyl chloride and sodium by the recently described<sup>1</sup> synthesis of organo-metallic compounds, the product after carbonation was benzoic instead of caproic acid. Exchange of phenyl for the amyl radical was complete and the yield of benzoic acid, calculated on the basis of a molecule of acid for every one of amyl chloride used, was as high as 78%. Toluene, dimethylaniline, anisole, diphenylmethane and fluorene, when used similarly either as solvents or as diluents in a ligroin solution, shared this interesting property so that the monocarboxylic acids formed as products of carbonation were phenylacetic, N-dimethylantranilic, *o*-methoxybenzoic, diphenylacetic and diphenyleneacetic acids in yields of 40, 18, 20, 14 and 18.5%, respectively (see Table II). No attempt was made to obtain the maximum yields.

In order to illustrate the possibilities of extending this solvent exchange type of synthesis beyond the preparation of acids we have prepared phenylsodium by interaction of amyl chloride, sodium and benzene and then brought about its reaction with propyl chloride. Propylbenzene was found in substantial quantity. In a like manner phenylsodium was induced to react with ethylene oxide yielding  $\beta$ -phenylethyl alcohol as one of the products.

Syntheses of this type continued to show promise of use in the preparation of malonic acids. A notable example was the formation of phenylmalonic in addition to phenylacetic acid from the reaction in toluene solution. With amyl chlo-

ride in a mixture of toluene and ligroin a yield of 33% of phenylmalonic acid was obtained from the same run which yielded 40% of phenylacetic acid. With isobutyl chloride the yields were 20% of phenylmalonic and 11% of phenylacetic acid. When the addition of toluene was delayed until after all reactions between amyl chloride and sodium had ceased, the yields of phenylmalonic and phenylacetic acids were 28 and 5%, respectively. The method is therefore a far more convenient source of this compound than has hitherto been available. It is especially interesting to note that the yield of the malonic acid is often considerably in excess of that for the monocarboxylic acid.

**Mechanism of Exchange Reactions.**—Our work has now progressed to a point where we have assurance as to the manner in which some of the products are formed. The monosubstitution product, benzoic acid, arises from metathesis of the sodium compound with the hydrocarbon according to equation 1.

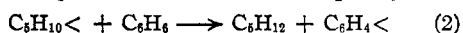


Important evidence of the correctness of this view was furnished by (a) reserving the addition of benzene in experiments 3 and 4 until after the free radicals had disappeared and the formation of amylsodium had been completed, a condition which resulted in the entire replacement of caproic by benzoic acid among the products of carbonation and (b) by carrying out, as in experiment 6, an exchange reaction in the presence of carbon dioxide to remove amylsodium as fast as it was formed and thereupon failing to find any benzoic acid. Neither was this acid found in six experiments made under pressure of carbon dioxide. We therefore conclude that the free radi-

(1) Morton and Hechenbleikner, *THIS JOURNAL*, **58**, 1697 (1936).

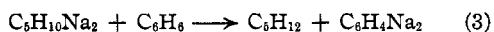
cal amyl did not react with benzene under the conditions of our experiments and that the occurrence of benzoic acid was due to the reaction of the monosodium compound with benzene according to equation 1. A mild form of acidity on the part of the hydrogen atom in benzene which permits the formation of a stable salt, sodium phenide, is thus suggested. The much higher yield of benzoic acid (78%) than was usually obtained for caproic acid in like experiments reported in the previous paper may be interpreted as indicating the greater stability of phenylsodium in a Wurtz synthesis.

Although the free radical amyl was without a role in the solvent exchange reactions, some evidence suggesting that the radical amyldiene was in part responsible for the formation of iso- and terephthalic acids was uncovered. In the aforementioned experiments on the interaction of benzene, amyl chloride and sodium, under pressure of carbon dioxide, a mixture of the two phthalic acids was obtained in each instance. On the reasonable assumption that carbon dioxide would remove the organo-dimetallic compound before it could react with benzene as effectively as it had in the case of amylsodium, we conclude that free amyldiene must have reacted with benzene according to equation 2, and that the phenylene so



formed then added two atoms of sodium yielding phenylene disodium which was promptly carbonated, producing the mixture of phthalic acids.

Iso- and terephthalic acids may also be formed because of a reaction of amyldiene disodium with benzene according to equation 3. Although the likelihood of benzene reacting with two molecules



of amylsodium (equation 4) appeared to be very

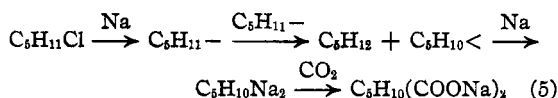


good, we have so far been unable to produce evidence which would point conclusively to such a chemical change. The facts bearing on this point can be stated briefly. (1) When benzene was present at a temperature below 5° during or after the reaction of amyl chloride with sodium the subsequent carbonation yielded benzoic and butylmalonic but no phthalic acids. Apparently amyldiene disodium reacted more sluggishly with benzene than did amylsodium so that at this temperature a solvent exchange reaction occurred with amylsodium only. (2) When benzene was al-

lowed to react at 65° with the products of the reaction between amyl chloride and sodium, phthalic acids appeared among the products and the amount of butylmalonic acid was decreased. These two facts suggested that under these conditions bimetalation of benzene may have occurred by reaction 3. With toluene, it is true, we did obtain evidence that disubstitution by means of amylsodium had taken place, for the yield of phenylmalonic acid in one experiment was 28% under conditions which had produced butylmalonic acid in yields no higher than 24% and usually near 17% (see previous paper).

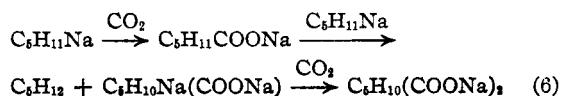
#### Mechanism of Malonic Acid Formation.—

As an explanation for the occurrence of butylmalonic acid we favor that which pictures an initial formation of the free radical amyl, its disproportionation to amyldiene and pentane, the addition of sodium to the former and the carbonation of the disodium product shown in sequence below.



Our opinion is founded on (a) the agreement of the experimental facts with all the results which would be predicted on the free radical basis, and (b) the inability to find any evidence to bolster up alternative mechanisms, *viz.*, one involving amylsodium and another the splitting out of hydrogen chloride.

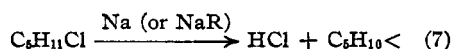
A full discussion of our efforts to connect amylsodium with the formation of butylmalonic acid was included in the previous paper. That evidence, coupled with additional information in this paper, is overwhelmingly against any such idea. To conserve space we are limiting our present discussion of this point to only one of the ways in which amylsodium could conceivably be responsible for the occurrence of the dicarboxylic acids. The following sequence assumes a certain lability of the hydrogen atom on the alpha carbon atom of sodium caproate so that it reacts with amylsodium.



Four points can be cited against this mechanism: (1) the failure as reported in the previous paper to get an increased yield of butylmalonic acid when sodium caproate, prepared *in situ* by partial

carbonation, was present during the addition of amyl chloride to sodium; (2) the destruction of most of the amylsodium, prior to carbonation by fourteen hours of heating at 80° while leaving the yield of butylmalonic acid unchanged, a fact which we interpreted in the previous paper as illustrating the surprising stability of amylidene disodium, obviously formed prior to carbonation; (3) the reaction in benzene solution recorded in this paper in which amylsodium was removed by complete reaction with benzene below 5° but from which butylmalonic acid was isolated among the carbonation products, thereby showing again that sodium amyl could not be a source of butylmalonic acid and that amylidene disodium must have been present before carbonation; (4) the unlikelihood that amylsodium would react with sodium caproate in the manner above indicated since Schorigin<sup>2</sup> has already shown in the case of phenylsodium and Gilman and Van Ess<sup>3</sup> have found with alkyl lithium that the secondary products in reactions with carboxyl containing compounds were ketones and tertiary carbinols. In short, organo-metallic compounds of this type, when they do react with alkali salts of carboxylic acid, show a tendency to react with the carboxyl group after the usual manner of an ester with the Grignard reagent rather than with a weakly acid hydrogen atom on the alpha carbon atom. The above facts confirm the view expressed in the previous paper that amylsodium is in nowise connected with the formation of butylmalonic acid.

Splitting out of hydrogen halide from an alkyl halide was initially proposed by Michael<sup>4</sup> as a first step in the Wurtz synthesis. Acree<sup>5</sup> in a study of the action of phenylsodium on ethyl bromide suggested a similar role for phenylsodium as a means of accounting for the presence of ethylene among the products of the reaction. Ethylidene was assumed to be the intermediate. These assumptions are adaptations of the well-known activity of sodium ethylate in double bond formation with the exception that hydrogen halide is taken from the same rather than from adjacent carbon atoms. The equation for the reaction is



The corresponding equation for the formation of

amylidene in the reaction of sodium on diamyl mercury would require the splitting out of  $\text{HHgC}_6\text{H}_{11}$  instead of HCl. Reference to the work in the fifth paper<sup>6</sup> on the formation of butylmalonic acid in the reactions under pressure of carbon dioxide is sufficient to dispose of the possibility that amylsodium had caused the eviction of hydrogen chloride in this manner, since carbon dioxide should remove the organometallic compound as fast as it was formed. Other agents commonly employed in forming ethylenic bonds are not available under all conditions in these reactions. Thus sodium ethylate or sodium hydroxide could not be present in the autoclave reactions<sup>6</sup> in the presence of an excess of carbon dioxide and sodium carbonate on the other hand was not present when the formation of organo-alkali compounds<sup>1</sup> was carried out in absence of carbon dioxide. Metallic sodium, therefore, remains as the sole agent which might function in this manner and be present in all cases. Such an opinion of the special activity of sodium would appear to require considerable tinkering in an endeavor to link the general mechanism of double bond formation with the Wurtz synthesis. We have thought it worth while, however, to make one more attempt under conditions which are ordinarily quite favorable for the splitting out of hydrogen halide. Since the formation of phenylmalonic acid occurred with considerable ease we elected to try the reaction of benzyl chloride with sodium in the presence of sodium alcoholate, formed *in situ* by the addition of a little alcohol. A vigorous reaction ensued and the product had the customary dark color but no phenylmalonic acid could be found upon carbonation. If a substituted methylene radical were formed under these conditions, as might be thought possible from the opinion of Bergmann and Hervey,<sup>7</sup> metallic sodium did not serve as an interceptor. Further investigations of this idea did not appear promising.

As stated before the favored explanation for the occurrence of malonic acids is that the free radical amyl undergoes disproportionation forming an idene radical which then adds two atoms of sodium. This view is in full accord with every fact which has been brought out by these studies. Thus the yields of carboxylic acids in all cases, whether in the autoclave reactions (fifth paper),<sup>6</sup>

(2) Schorigin, *Ber.*, **41**, 2723 (1908).

(3) Gilman and Van Ess, *THIS JOURNAL*, **55**, 1258 (1933).

(4) Michael, *Am. Chem. J.*, **25**, 419 (1901).

(5) Acree, *ibid.*, **29**, 588 (1903).

(6) Morton, LeFevre and Hechenbleikner, *THIS JOURNAL*, **58**, 754 (1936).

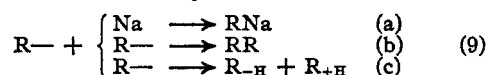
(7) Bergmann and Hervey, *Ber.*, **62**, 893 (1929).

the reactions with mercury diamyl (sixth paper),<sup>8</sup> the experiments in the isolation of the intermediate amylsodium (seventh paper),<sup>1</sup> or in the exchange reactions reported in this paper, have never been in excess of that which could be accounted for on this basis. Moreover, the amount of pentane recovered in the reaction of sodium with diamyl mercury<sup>9</sup> was close to that demanded by the theory. If we accept the view that the free radical mechanism pictures a correct outline of events, the isolation of butylmalonic acid means that in the disproportionation of free amyl an intermediate step is the formation of amylidene which then rearranges to amylene. Metallic sodium acted as an imperfect interceptor for the amylidene stage. The quantity of butylmalonic acid on this basis is actually a measure of the free radical known to have disproportionated.

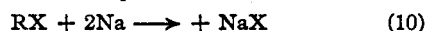
**Mechanism of the Wurtz Reaction.**—In applying our data to the mechanism of the Wurtz-Fittig reaction we shall show that (a) free radicals are formed either before or simultaneously with the formation of alkylsodium, and (b) the free radical amyl undergoes disproportionation instead of dimerization to at least 92% (the true value may be even higher) from which it follows that decane is probably formed by the reaction of amylsodium with amyl chloride. Schlubach and Goes<sup>10</sup> represented the first step of the Wurtz-Fittig reaction as the formation of a free radical by the action of sodium on an alkyl halide according to equation 8. Subsequently the radical added sodium, dimerized or underwent disproportionation.



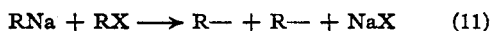
See equations 9. In the final step the alkylsodium reacted with alkyl halide.



Goldschmidt and Schön,<sup>11</sup> however, gave the first phase as shown in equation 10



and have outlined the possibility of the occurrence of free radicals from the reaction



Our experiments under pressure of carbon dioxide are equivalent to carrying out a Wurtz-Fittig re-

action in the presence of an agent, carbon dioxide, which would trap the alkyl sodium but not the free radical. Since butylmalonic acid continued to be formed under these conditions, even when the pressure was as high as 900 pounds (60 atm), we conclude that free radicals must have been formed either prior to or simultaneously with the formation of alkylsodium as given in equation 8.

That the tendency of the amyl radical under these conditions was overwhelmingly toward disproportionation (equation 9c) rather than toward dimerization (equation 9b) can be seen by reference to one<sup>12</sup> of the experiments in which we were particularly successful in finding conditions under which metallic sodium acted as a nearly perfect trap for the amylidene. In this instance only 2%, calculated on the basis of the sodium, went to products<sup>13</sup> which were other than acids. When recalculated in terms of the amyl chloride consumed we find that 45.5% appeared as amyl sodium (caproic acid), 50% as a free radical which underwent disproportionation (butylmalonic acid) and only 4.5% as unknown (decane, pentane and pentene). The combined amount of free radical which was present and could either disproportionate or dimerize was therefore 54.5% and of this amount 92% is known to have taken the former path. Because of this great tendency for disproportionation it seems likely that decane, when synthesized from the action of sodium on amyl chloride, is formed largely by way of the amylsodium plus amyl chloride path. Particularly is this view made likely by reference to the 45.5% yield of amylsodium in the same reaction. As regards the formation of amylsodium by equation (9a) or (10) our data do not permit a differentiation.

Our conclusions on the mechanism of the Wurtz reaction can be summarized briefly. This synthesis occurs because of the reaction between amylsodium and amyl chloride, a view confirmed by (a) our isolation of the organo-metallic compound in quantity and (b) the evidence showing that the free radical amyl had scarcely any tendency to combine with itself forming decane. Having shown that free radicals are present either prior to or simultaneously with the formation of amylsodium, it is an entirely reasonable supposi-

(12) See reaction number 6, Table II, *THIS JOURNAL*, **58**, 756 (1936).

(13) By the term Wurtz in the former paper we included all reactions possible in a Wurtz synthesis. The figure was arrived at by difference. Hence the column marked Wurtz referred to decane, pentane and pentene.

(8) Morton and Hechenbleikner, *THIS JOURNAL*, **58**, 1024 (1936).

(9) See reaction 20, Table I, ref. 8, p. 1026. By error the calculated amount of pentane was given as 1.08 instead of 0.79.

(10) Schlubach and Goes, *Ber.*, **55**, 2889 (1922).

(11) Goldschmidt and Schön, *ibid.*, **59**, 948 (1926).

tion that amylsodium is a consequence of the addition of an atom of sodium to the free radical.

### Experiments

**General Direction.**—The usual method of carrying out the reactions, unless otherwise specified, was the same as described in the previous paper,<sup>1</sup> *viz.*, addition of amyl chloride to fine sodium sand with gentle stirring in the desired solvent. Such changes as were made necessary by the use of a different solvent are indicated clearly. The separation of the products was in general made possible by the fact that the aliphatic monocarboxylic acids could be extracted with petroleum ether, the malonic acids were usually soluble in cold or hot water, but could be extracted with ether, the phthalic acids were insoluble in water or ligroin. The melting points of the products were compared with those in Beilstein. The sodium sand was made up in large batches so that the grade did not change through a series of experiments. This precaution was necessary because the yields of acids were affected by the fineness of the sand. The data for the experiments are given as far as possible in tables followed by supplementary notes on each reaction. In the paragraph immediately following that section attention is called to the significance of each experiment. The numbering is for convenience only. Yields are calculated on the basis of the sodium employed except in reaction 3 in which the value is referred to diamyl mercury.

TABLE I

#### EXCHANGE REACTIONS WITH BENZENE

Constant factors. Eastman Kodak Co. *n*-amyl chloride used in all experiments except in number 3, where diamyl mercury and in number 5 where isobutyl chloride were used. Mallinckrodt thiophene-free benzene used.

No.	Sodium, chloride,		Benzoic acid		Phthalic acids		Butylmalonic acid	
	g.	ml.	G.	%	G.	%	G.	%
1	15	30	6.4	21.4			3.5	17.5
2	15	20	15.7	78			0.43	3.2
3	4	10 <sup>a</sup>	2.2	32	0.2	4		
4	10	20	2.3	11.5	.9	6.5	1.1	8.2
5	10	15	5.3	32			Traces	
6	5	30	0.0					

<sup>a</sup> Quantity of diamyl mercury in grams instead of ml.

1. Sodium sand in 150 ml. of benzene with 50 ml. of pentane to keep the mixture from solidifying. Temperature below 5° during addition of the chloride which required two hours. Stirred for fifteen minutes after addition was completed.

2. Sodium in 80 ml. of benzene and 50 ml. of pentane. Amyl chloride in 50 ml. of benzene. Temperature below -2° during addition of amyl chloride solution which re-

quired one hour. Stirred for one hour longer at room temperature.

3. Diamyl mercury used in place of amyl chloride. Sodium sand in 100 ml. of pentane. Mixture stirred for two hours following mixing of reagents, after which 100 ml. of benzene was added.

4. Sodium sand in 50 ml. of ligroin; amyl chloride in 50 ml. of same solvent. Addition time one and one-half hours, temperature 18-22°. Stood one hour at room temperature. Benzene, 100 ml., then added and mixture heated to 65° for one hour. The phthalic acid mixture contained 0.054 g. of the iso- form which was separated by the solubility of the barium salt.

5. Isobutyl chloride dissolved in 50 ml. of benzene. Sodium sand in 50 ml. of benzene. Time of addition one and one-quarter hours; temperature 25-30°. Mixture allowed to stand for two hours before carbonation.

6. Sodium sand in 30 ml. of benzene; amyl chloride added undiluted; temperature 10-20°. Carbon dioxide passed in during the addition of the alkyl chloride; reaction time one hour. No benzoic acid was obtained. Caproic acid, 23%. No analysis was made for butylmalonic acid.

Special attention is directed to (a) the absence of phthalic acids in 1 and 2 where the temperature of the reaction was below 5° and the presence of these acids where the temperature was 65° (experiment 4); (b) the very high yield of benzoic acid in number 2 where the concentration of benzene was less and the rate of addition of amyl chloride was greater than in number 1; (c) the exchange reaction, experiment 5, with isobutyl chloride and the small quantity of dicarboxylic acids among the products; (d) the failure to find benzoic acid when carbon dioxide was bubbled through the reaction mixture (experiment 6) indicating the ease with which amylsodium could be removed from the reaction before the latter could react with benzene; (e) the combined yields of phthalic and butylmalonic acids in experiment 4 which amounted to 14.7%, a value within the range of 13-17% noted in the previous paper for the yield of butylmalonic acid under the same conditions and hence suggestive of the formation of phthalic acids at the expense of butylmalonic acid in the exchange reaction; (f) the delayed addition of benzene to the reaction mixture in experiments 3 and 4 which showed that an exchange reaction had occurred between benzene and the organo-metallic compound.

7. Sodium sand in 25 ml. of ligroin and 25 ml. of toluene. Amyl chloride dissolved in 25 ml. of ligroin and 25 ml. of toluene. Addition at 0-5° for two and one-half hours. Stirred three hours at 40-45° during which time 100 ml. more ligroin was added because the mixture became so thick it could not be stirred. At the end of this time the almost solid greenish-yellow mass was carbonated.

8. Solvent conditions the same as in experiment 7. Isobutyl chloride used instead of amyl chloride. Addition time three hours at 0-5°. Stirred two hours at 40-45°. Carbonated at 60°.

9. Sodium sand in 50 ml. of ligroin. Time of addition two hours at 0-10°. Stood at room temperature for three hours. 100 ml. of toluene added and the mixture heated to 50° for ten minutes.

TABLE II  
 EXCHANGE REACTION WITH COMPOUNDS OTHER THAN BENZENE

No.	Sodium, g.	Amyl chloride, ml.	Solvent or diluent	Ml.	Mono-acid G.	%	Di-acid G.	%	Butylmalonic acid G.	%
7	15	20	Toluene	50	9	40	5.0	33		
8	15	15	Toluene	50	2	11	2.4	20		
9	10	20	Toluene	100	1.2	5.2	4.15	28		
10	10	20	Anisole	50	5	20			Trace	
11	10	20	Diphenylmethane	20	4.8	14	None		Trace	
12	10	20	Dimethylaniline	50	5	18				
13	15	20	Fluorene	10 (g.)	6.5	18.5			1	7

10. Sodium sand in ligroin-anisole mixture, 25 ml. of each. Amyl chloride dissolved in the same mixture was added at 20–25° during one hour. *o*-Methoxybenzoic acid obtained. Melting point 99°. Recorded value in literature 98.5°.

11. Sodium sand and diphenylmethane in 50 ml. of ligroin. Amyl chloride in 50 ml. of ligroin added at 25–30° during one hour. Mixture stood twelve hours at room temperature before carbonation. Diphenylacetic acid m. p. 145–146° obtained. Recorded values in the literature vary from 144 to 149°. The corresponding malonic acid is unstable.

12. Sodium sand in a mixture of 50 ml. each of ligroin and dimethylaniline. Amyl chloride dissolved in 50 ml. of ligroin added at 0–10° during 1.25 hours. The mixture was allowed to stand for four hours before carbonation. *N*-Dimethylantranilic acid of m. p. 68–70° was found. Recorded value in the literature is 70°.

13. Sodium sand and amyl chloride separately contained in 50 ml. of ligroin. Addition time one hour at 0–15°. Stirred twenty minutes at room temperature. Fluorene, 10 g., in 100 ml. of ligroin then added. Diphenyleneacetic acid obtained. Melting point of ethyl ester 44–45°. Recorded value in literature 43–45°. The corresponding malonic acid is unstable.

Special attention is directed to (a) the formation of substituted malonic acids with an aromatic compound containing a methyl group illustrated in experiments 7, 8, 9 with toluene; (b) the addition of fluorene to the reaction mixture after the formation of the organo-alkali compounds from amyl chloride and sodium had been completed, a method found satisfactory after other attempts in which fluorene was present during the first stage of the reaction had failed to give products which could be isolated readily; (c) the occurrence of ortho substitution products with anisole and dimethylaniline.

**Reaction of Benzyl Chloride and Sodium Ethylate.**—To a mixture of 15 g. of sodium sand and 20 ml. of benzyl chloride in 100 ml. of ligroin was added slowly 5 ml. of anhydrous ethyl alcohol at room temperature. The reaction mixture evolved a gas and turned a dark red color characteristic of the color present in any of the reactions in the absence of alcohol. After carbonation, however, scarcely a trace of acid was found to be present.

**Propylbenzene from Amyl Chloride, Benzene, Sodium and Propyl Chloride.**—To 75 g. of sodium sand suspended with stirring in 350 ml. of benzene and contained in a three-necked flask protected by an atmosphere of nitrogen was added 180 ml. of technical *n*-amyl chloride at 18° over a period of three hours. The mixture was then al-

lowed to stand fourteen hours after which 100 g. of *n*-propyl chloride was added. The mixture was heated to 80° for two hours, after which it was decomposed and the hydrocarbon layer distilled. Propylbenzene, b. p. 159°, was obtained in a yield of 23% (30 g.). Higher boiling fractions were present which were not investigated.

**Phenylethyl Alcohol from Amyl Chloride, Benzene, Sodium and Ethylene Oxide.**—In a similar apparatus 20 g. of sodium sand was suspended in a mixture of 150 ml. of benzene and 50 ml. of ligroin. Amyl chloride, 40 ml., was added at 0° during two hours. The mixture was stirred for four hours after which 8 g. of ethylene oxide was passed in at 0°. The yield of phenylethyl alcohol obtained from the process was 12.5% (5 g.). About 3 g. of heptyl alcohol was also obtained. Higher alcohols insoluble in benzene were also present.

**Exchange Reactions with Benzene under Pressure of Carbon Dioxide.**—Six experiments were carried out in the autoclave described in a previous publication in this series. The amount of sodium sand was varied from 10 to 15 g. and the quantity of benzene varied from 100 to 120 ml. Amyl chloride, 120 ml. and carbon dioxide, 200 lb. (13 atm.) were present in each case. The temperatures varied from 80 to 132°. In no case was benzoic acid found to be present among the acids isolated from the reaction mixture, although caproic, 1 to 2.5 g. of phthalic (iso and tere mixture), and butylmalonic acids were readily obtainable.

### Summary

A yield as high as 78% of benzoic acid can be obtained in an exchange reaction between amyl chloride, sodium and benzene. In varying yields phenylacetic, *N*-dimethylantranilic, *o*-methoxybenzoic, diphenylacetic and diphenyleneacetic acids have been obtained in a similar manner from amyl chloride and sodium with toluene, dimethylaniline, anisole, diphenylmethane and fluorene.

Phenylsodium, prepared from amyl chloride and sodium has been treated with propyl chloride and ethylene oxide to yield propylbenzene and phenylethyl alcohol, respectively.

Phenylmalonic acid has been prepared by reaction of toluene with amyl chloride and sodium or with the products of the reaction of this chloride and the metal.

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.

CAMBRIDGE, MASS.

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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<sup>1,2</sup>

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).

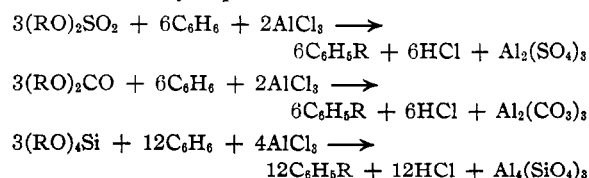
The use of esters other than the halides as alkylating agents also has been proposed. Among these esters are the alkyl chlorocarbonates,<sup>3</sup> ethyl toluene-*p*-sulfonate,<sup>4</sup> trialkyl or trialkyl borates<sup>5</sup> and the esters of aliphatic acids such as ethyl acetate or ethyl valerate.<sup>6</sup> 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.<sup>7</sup>

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<sup>8</sup> 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



### 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-

(1) Abstracted from a thesis presented by Howard L. Kane to the Graduate School in partial fulfillment 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.

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(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).