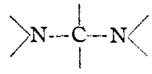
for the high nitrogen content of the solid is that a considerable quantity of nitrogen is introduced by the reaction of active nitrogen with the solid on the walls of the vessel. The similar results secured by the employment of either a condensed or uncondensed discharge for the activation of nitrogen are in accord with the present concept that active nitrogen consists principally of atomic nitrogen, which most probably is the form taking part in the above reaction.

Comparison of the results of this work with those obtained by Kroepelin and Vogel[15] in the study of the action of atomic hydrogen on oleic acid and paraffin oil reveals a striking similarity in the course of the two reactions. (1) In both cases the initial reaction involves combination with the active element and the probable simultaneous formation of free radicals. (2) The active intermediates formed are subsequently stabilized and yield, to a certain extent, brown polymerization products. (3) The introduction of oxygen into the products can be avoided only by using an atmosphere absolutely free from oxygen.

**Acknowledgment.**—We are indebted to Drs. Wulf, Jones and Melvin for numerous experimental suggestions, to Dr. Wulf for the aid received in discussions on the theoretical aspects of this work and to Mr. Testa for the difficult and clever job of glass blowing on the apparatus.

## Summary

Nitrogen activated by a condensed or uncondensed discharge reacts with diphenylacetylene to form a brown nitrogenous high-melting solid, hydrogen cyanide, excited cyanogen (CN*) and probably traces of benzonitrile and an isonitrile. From its physical and chemical properties, the brown solid, which is the major product of the reaction, appears to be a complex material of high molecular weight. It contains about 16–18% nitrogen, is resistant to acid hydrolysis, liberates ammonia on alkaline hydrolysis, yields benzoic acid and an unidentified, crystalline acid possessing nitrogen on nitric acid oxidation and seems to contain  $>N{-}\overset{|}{\underset{|}{C}}{-}N<$ group. Tetrahydronaphthalene and benzonitrile also react with atomic nitrogen to form amorphous solids having physical properties similar to the product from the acetylene derivative. The ratios of fixed nitrogen to organic material in the solid products from the three compounds decrease in the order diphenylacetylene, tetrahydronaphthalene, benzonitrile. In accordance with this, the ratios of nitrogen fixed as hydrogen cyanide to nitrogen fixed as solid decrease in the reverse order. In contrast to the behavior of the aromatic compounds, isoprene with active nitrogen gives instead of a polymerized solid a low-boiling nitrogenous liquid. The results are discussed with reference to the general mechanism of the reaction.

WASHINGTON, D. C.

RECEIVED APRIL 16, 1938

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[15] Kroepelin and Vogel, *Ber.*, **68**, 684 (1935); see also v. Bogdandy, Polanyi and Veszi, *Z. angew. Chem.*, **46**, 15 (1933).

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 172]

# Condensations by Sodium. XIV. The Phthalic Acids and Some Factors Influencing Yields of Butyl- and Dimethylmalonic Acids

BY AVERY A. MORTON AND FRANKLIN FALLWELL, JR.

This paper describes the formation of all the phthalic acids in these reactions employing sodium and shows that they arise from two distinct sources. When phenylsodium, prepared by refluxing benzene with amylsodium, is carbonated, a third to a fifth of the total acids formed is a mixture of iso- and terephthalic acids, the remainder being benzoic acid. On the other hand preparing the same reagent, phenylsodium, in the presence of sodium benzoate, refluxing and treating the product with carbon dioxide gives the ortho isomer as the sole phthalic acid present. These results demonstrate clearly that there are two types of organosodium intermediates present. According to our common conventions one would be a *m*- or *p*-phenylenedisodium compound and the other sodium *o*-sodiobenzoate. The non-identity of their carbonation products provides a sharp distinction, the lack of which made tracking to the possible sources of butylmalonic acid[1] very difficult.

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[1] Morton, Fallwell and Palmer, THIS JOURNAL, **60**, 1426 (1938).

Phenylenedisodiums, sources of the iso- and terephthalic acids, do not come from dimetalation of benzene by amylidenedisodium, a conclusion reached after a series of experiments with increasing ratios of benzene to amylsodium failed to show formation of these acids at the expense of butylmalonic acid (Fig. 1). This careful study was necessary because a chance agreement[2] in the yields of butylmalonic acid and these phthalic acids before and after addition of 150 ml. of benzene as well as the non-formation of the latter in a low temperature exchange had suggested such a possibility. The complete curve shows these products quite unrelated to each other. An earlier experiment[1] already has indicated that disproportionation of phenylsodium in boiling benzene does not occur appreciably, thus eliminating this possible source of phenylenedisodium. The plotted results of the present work show a slight maximum at 55 ml. of benzene which falls off somewhat as the quantity of benzene is increased. The mechanism field is therefore narrowed and includes the possibility that benzene has been attacked simultaneously or successively by two molecules of amylsodium. In addition this study had revealed a pronounced minimum for the combined yields of caproic and benzoic acids which corresponds with a slight maximum in the yield of phthalic acids. A molal ratio for benzene to amylsodium of two to one was present at this point, an interesting circumstance which together with the peculiarity for the existence of a minimum in the total acids and the failure to get more than 15% of the benzene converted into phenylsodium even under the most favorable circumstances, promises to make an interesting field for further study.

Abnormal reactivity and orienting influences prevail in this series. The sodium carboxyl group, for example, acts in the same manner as do the dimethylamino and methoxyl[3] groups in directing an entering sodium atom to the ortho position. Dimethylaniline and anisole have labile hydrogen atoms in the ortho rather than in the para position. Isophthalic acid predominates by four to one over terephthalic acid, a result calling for *m*-phenylenedisodium as the chief product of the double metalation of benzene. Such results emphasize the novelty in the behavior of these organosodium reagents. One characteristic difference marks these reactions from those in which the ordinary rules of orientation have been derived. In general chemical changes here occur on solid surfaces rather than in homogeneous solutions, a circumstance suggesting that the normal orienting influences may be shelved in the presence of a powerful reagent which operates through an initial adsorption of the molecule. The unpredicted nature of our results may be judged in the light of an observation of Gilman and Kirby[4] that a mixture of benzene, diethylmercury and potassium acted normally, giving phthalic and terephthalic acids after carbonation.

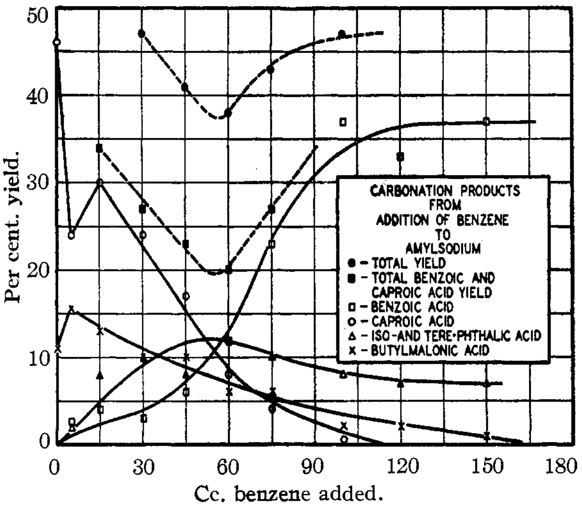

Fig. 1.

Another unusual feature in this work is the difference in the type of reaction which occurs on sodium benzoate when it is added before or after preparation of phenylsodium. The product in the former instance is largely phthalic acid and in the latter is chiefly triphenylcarbinol. Here also we believe the result is influenced by variations in the types of adsorption possible for we have observed that sodium benzoate is readily adsorbed on sodium, so much so in fact that it will completely block the reaction between sodium and amyl chloride if allowed to stand in contact with the metal for a few hours before addition of the chloride.

On the general principle that active nickel will labilize the hydrogen atom we attempted to improve the yield of phthalic acid by carrying out a reaction in the presence of this catalyst. A slight improvement only was realized. A similar experiment on sodium caproate, however, more than

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(2) Morton and Hechenbleikner, THIS JOURNAL, **58**, 2599 (1936).

(3) Morton and Hechenbleikner, *ibid.*, **58**, 2599 (1936); see also Niederl, Roth and Plentl, *ibid.*, **59**, 1901 (1937).

(4) Gilman and Kirby, *ibid.*, **58**, 2074 (1936).

doubled the yield of butylmalonic acid. Preparation of dimethylmalonic acid from sodium isobutyrate was not influenced by the use of nickel.

## Experiments

**Procedure.**—The usual quantities consisting of 35 g. of fine sodium sand and 75 ml. of technical amyl chloride (Eastman Kodak Co.) were employed. The apparatus was the same as described in an earlier paper.[1] Unless otherwise noted the sand was activated prior to reaction by addition of about 5 ml. of *n*-amyl alcohol. This change in manipulation eliminated entirely a short induction period usually observed, changed the yields of caproic and butylmalonic acids to 35 g. (46%) and 5.5 g. (11%), respectively, and increased the ratio of mono- to dicarboxylic acid considerably. The usual amounts obtained without activated sand are around 30 and 16% for the two acids concerned. Two and one-half hours are required for addition of amyl chloride to the metal, one hour for stirring at 25–30° after addition, and one hour for carbonating at 35–40°. The solvent was petroleum ether except in those cases where benzene was used to provide phenylsodium as the organometallic reagent. Here also the use of activated sodium caused a small increase in the yield of benzoic acid.

**Iso- and Terephthalic Acids.**—Following the preparation of amylsodium as before described, 5, 15, 30, 45, 60, 75, 100, 120 and 150 ml. of thiophene-free benzene were added in separate experiments, the mixture in each case heated to 80° for two hours, and then cooled to below 40° for carbonation. Separation of the mixture of caproic and benzoic acids was accomplished first by petroleum ether and then by benzene extraction accompanied by distillation, that of the insoluble phthalic acids by filtration, and that of butylmalonic acids by extraction with ether. Corresponding yields for the amounts of benzene mentioned above are: for caproic acid, 17, 22, 17, 13, 6, 3, trace, 0, 0 g. (24, 30, 24, 17, 8, 4, trace, 0, 0%); for butylmalonic acid 7.7, 6.5, 5, 5, 3, 3, 1, 1, trace, g. (16, 13, 10, 10, 6, 6, 2, 2, trace, %); for benzoic acid, 2, 3, 2.5, 4.5, 9, 17, 28, 25, 28 g. (3, 4, 3, 6, 12, 23, 37, 33, 37, %); for phthalic acid, 1.2, 4, 5, 4, 6, 5, 4, 3.5, 3.5, g. (2, 8, 10, 8, 12, 10, 8, 7, 7%). For a graph of these results see Fig. 1. A single run in which 15 ml. of the benzene was present in the mixture before addition of amyl chloride produced 14 g. (19%) of caproic acid, 7.5 g. (15%) of butylmalonic acid, 3 g. (4%) of benzoic acid and 3 g. (6%) of the phthalic acid mixture.

Separation of the phthalic acid through the barium salts[5] is incomplete. On converting to the *p*-bromophenacyl[6] esters for identification, the insolubility of the tere- isomer in chloroform was noted. By one such separation the melting point of the crude iso- ester was 174–178° as compared with 179° for the pure material; that of the crude tere- isomer was 215–222° (pure compound is 225°). Products separated by means of the barium salts could be further purified by this method. The approximate composition was 80% iso- and 20% tere-.

**Phthalic Acid.**—Benzoic acid, 20 g., was added to 45 g. of sodium sand in benzene solution. Immediately after formation of sodium benzoate, 5 ml. of *n*-amyl alcohol was added and the mixture stirred for ten minutes. Amyl chloride, 15 ml., was next added to form the phenylsodium after the usual manner. The mixture was then heated for two hours at 80°. Upon cooling to about 30°, carbonating and decomposing, there was found 2.5 g. (6% referred to benzoic acid) of phthalic acid, decomposing at 160–180° followed by subliming as the anhydride in long white needles, m. p. 110–123 in the crude state (pure 128°). Neutralization equivalent of the crude product was 86 (pure 83). From the same reaction 1.5 g. (3%) of triphenylcarbinol was recovered. Repetition of the experiment using amylsodium instead of phenylsodium yielded 0.3 g. (1.0%) only of phthalic acid probably because the mixture could not be refluxed at so high a temperature.

**Triphenylcarbinol.**—Sodium benzoate was prepared in a separate container and then added to phenylsodium prepared in the customary manner in benzene as a solvent. After two hours of heating at 75°, carbonating and separating the products, 10.0 g. (24%) of triphenylcarbinol and 0.5 g. (1%) only of phthalic acid were obtained. Yields are calculated on the basis of the sodium benzoate added. Another method of introducing sodium benzoate after formation of phenylsodium was to pass carbon dioxide very slowly (two hours) into the organosodium reagent while the mixture was kept near 50°. Triphenylcarbinol, 7.5 g. (14%), calculated on the amyl chloride originally added was recovered. The amount of phthalic acid obtained was 0.8 g.

**Catalytic Action of Nickel.**—Raney nickel catalyst from 4 g. of the alloy was added in a benzene suspension to the mixture of sodium caproate and phenylsodium obtained by addition of 75 ml. of amyl chloride to sodium and sodium caproate (20 g. of the acid and 45 g. of metal) in benzene solution. After two hours of heating at 75° and subsequent carbonating, 10 g. (36% calculated on the caproic acid used) of butylmalonic acid, in addition to benzoic and recovered caproic acid, was obtained together with 0.8 g. of triphenylcarbinol. Use of double the amount of nickel (from 8 g. of the alloy) caused little change (9 g. or 33%) in the butylmalonic acid yield. The usual yield of this malonic acid in absence of nickel is 16.5%.

When sodium benzoate mixed with nickel was added to phenylsodium under the same conditions used for preparation of triphenylcarbinol above, the yield of ortho phthalic acid was 1 g. (2%). The yield of dimethylmalonic acid from sodium isobutyrate as described below was unaffected (28%) by addition of nickel.

**Dimethylmalonic Acid.**—A fine suspension of sodium isobutyrate, from isobutyric acid (20 g.) and sodium (10 g.) in benzene as a solvent, was added to phenylsodium prepared as before stated. After two hours of stirring at 75° the mixture was carbonated. Dimethylmalonic acid, identified by neutralization equivalent and decomposition point, was recovered along with a mixture of benzoic and unreacted isobutyric acid. The yield was 8.0 g. or 27% calculated on the basis of the isobutyric acid. Preparation of the sodium isobutyrate in a separate vessel was necessary in this case because its formation prior to addition of amyl chloride inhibited the latter reaction.

## Summary

Iso- and terephthalic acids apparently are formed from phenylenedisodiums, which in turn

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[5] Smith, THIS JOURNAL, **43**, 1920 (1921).

[6] Kelly and Kleff, *ibid.*, **54**, 4444 (1932).

arise from sodium exchange reactions between benzene and two amylsodium molecules.

Phthalic acid is formed in these processes as a result of sodium benzoate being present during addition of amyl chloride to sodium in benzene solution.

If sodium benzoate is added after formation of phenylsodium the yield of phthalic acid is suppressed and that of triphenylcarbinol is increased.

Nickel as a catalyst causes a considerable increase in yield of butylmalonic acid, a slight increase for phthalic acid and no change in the quantity of dimethylmalonic acid.

The sodium metal can be activated by addition of a small amount of amyl alcohol. The total yield of acids and the proportion of caproic acid is thereby increased.

CAMBRIDGE, MASS. RECEIVED JUNE 3, 1938

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

# Bromo Ethers Derived from Hydantoins Having Terminal Ethylene Double Bonds in the C-5-Position

BY DOROTHY A. HAHN, MARGARET J. MCLEAN AND HELEN T. MURPHY[1]

The addition of bromine to each of two geometric isomers of ethyl N-3-methyl-C-5-benzalhydantoin-N-1-acetate, m. p. 50.5–51.5° and 121–122°, respectively, has been reported.[2] It was stated at that time that a molar quantity of bromine was decolorized as rapidly as added to a solution of either unsaturated hydantoin in carbon tetrachloride and that no evolution of hydrobromic acid took place until after the solution had been heated. In separating the product the carbon tetrachloride was replaced gradually by absolute alcohol and under these conditions a white crystalline compound, m. p. 113–113.5°, was precipitated which on analysis was found to contain one molecule of alcohol. The latter was obviously not present in the form of alcohol of crystallization since it could not be removed even by heating in a high vacuum. The formation of this compound was assumed tentatively to take place in the following way

$$C_2H_5OOCCH_2\overline{NCON(CH_3)COC}{=}CHC_6H_5 \xrightarrow{Br_2}$$

$$C_2H_5OOCCH_2\overline{NCON(CH_3)COC}BrCHBrC_6H_5$$

the latter compound then losing hydrobromic acid and adding ethanol to form

$$C_2H_5OOCCH_2\overline{NCON(CH_3)COC}{=}CBrC_6H_5C_2H_5OH$$

This interpretation of the reaction was based not only upon the results of analysis and the fact that dense fumes of hydrobromic acid had been evolved during the process of heating, but also upon references in the literature which established the formation of unsaturated monobromo derivatives following the addition of bromine to unsaturated hydantoins possessing analogous configurations.[3]

In repeating this experiment it was discovered that although both modifications of ethyl N-3-methyl-C-5-benzalhydantoin-N-1-acetate when treated in this way gave the same compound, m. p. 113–113.5°, a second and more soluble product, m. p. 92–94°, isomeric with the first was also formed in both cases. On the assumption that this represented a geometric modification of the higher melting compound, it was examined spectrographically since it was known that different types of unsaturated hydantoins could be identified readily, and that even isomers could be distinguished one from the other by means of their absorption curves.[4] The results of this investigation were very surprising since while the absorption curves of the two products indicated isomers, they also showed clearly that both belonged to the class of *saturated* and not unsaturated hydantoin derivatives.[5] This discovery led to a consideration of possible molecular configurations for compounds having the above composition that would account for the existence of isomeric saturated hydantoins. And since, due to the presence of two asymmetric carbon atoms, stereo

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(1) The preparation of N-1,N-3-dimethyl-C-5-benzalhydantoin and its derivatives together with the investigation of their respective absorption spectra must be credited to Miss Helen T. Murphy, an honor student at Mount Holyoke College. The spectrographic work was carried out under the direction of Dr. Hildegard Stücklen, Assistant Professor of Physical Chemistry, to whom grateful acknowledgment is due.

(2) Litzinger, THIS JOURNAL, **56**, 676 (1934).

(3) Wheeler, Hoffman and Johnson, *J. Biol. Chem.*, **10**, 154 (1911); Wheeler and Hoffman, *Am. Chem. J.*, **45**, 375–6 (1911); Johnson and Hoffman, *ibid.*, **47**, 20 (1912).

(4) Seikel, THIS JOURNAL, **59**, 436 (1937).

(5) (a) Hahn and Evans, *ibid.*, **50**, 809 (1928); (b) Hahn and Dyer, *ibid.*, **52**, 2505 (1930); Seikel, unpublished work.