If the amount of zinc chloride is reduced to one-tenth of that used in this experiment, the temperature has to be raised to about 200° in order that the reaction may proceed at a fairly rapid rate.

When *o*-chlorobenzotrichloride was used in place of benzotrichloride, the reaction products consisted, as was to be expected, of phthalyl and *o*-chlorobenzoyl chlorides.

4. **Butyryl Chloride from Phthalyl Chloride.**—A flask connected to a short fractionating column was charged with 340 g. of phthalyl chloride, heated at about 140° and treated slowly with 132 g. of *n*-butyric acid. Hydrogen chloride was evolved as the acid was added and part of the butyryl chloride distilled over. Finally, vacuum was applied and the remainder of the chloride recovered. Refractionation gave 146.5 g. of butyryl chloride which represents a 91.5% yield of the theoretical on butyric acid.

5. **Fumaryl Chloride from Maleic Anhydride.**—A mixture of 98 g. of maleic anhydride, 231 g. of 94% phthalyl chloride and about 0.5 g. of zinc chloride was heated overnight at about 140°. Vacuum was applied and the fumaryl chloride distilled until phthalic anhydride began to separate in the condenser. The distillate, amounting to 146 g., was found to contain 129 g. of fumaryl chloride and 15 g. of unreacted maleic anhydride. The yield, therefore, of the chloride on the anhydride which was consumed was nearly quantitative.

The writer is indebted to Messrs. M. N. Dvornikoff and O. J. Weinkauff for assistance in the experimental part of the investigation.

Summary

Phthalyl chloride can be made in good yields from thionyl chloride or benzotrichloride and phthalic anhydride at elevated temperatures using zinc chloride as catalyst and, reversibly, thionyl chloride is formed from the interaction of sulfur dioxide with phthalyl chloride under the same conditions.

Acid chlorides can be produced in excellent yields from the interaction of acids or their anhydrides with phthalyl chloride.

In the case of the anhydrides of acids, such as succinic and maleic acids, which do not react directly with phthalyl or thionyl chlorides, the reaction can be catalyzed with traces of zinc chloride to give good yields of the desired acid chlorides.

ST. LOUIS, MO. RECEIVED NOVEMBER 5, 1936

[CONTRIBUTION NO. 45 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Mellitic Acid from Coals, Cokes and Graphites

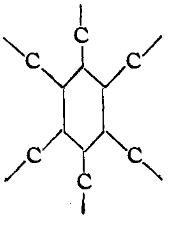
BY BERNARD JUETTNER

Carbonization of coal involves the loss of volatile decomposition products such as gas, tar and water, and the formation of a condensed, nonvolatile residue. The more important factors influencing the degree of condensation of the residue are: the final temperature, the rate of heating and the nature of the coal. Another factor may be the speed at which the decomposition products are removed, which in turn depends largely on the thermal variables mentioned above, on the pressure in the retort during the carbonization, and on the particle size of the coal.[1,2] The ash of the coal may also exert an influence due to catalytic effects.

The purpose of this work is to determine the degree of condensation of various carbonaceous materials, by conversion of these high molecular weight condensed bodies into small identifiable units of structural significance. The development of such a method permits the evaluation of the relative importance of such variables as maximum temperature, heating rate and specific nature of the material.

To accomplish the purpose in view the oxidation reagent employed must be powerful enough to penetrate to the last skeletal nuclei, but should not result in complete breakdown to carbon dioxide.

Mellitic acid, the benzene hexacarboxylic acid, is known as an oxidation product of various carbonaceous materials. It forms a relatively insoluble ammonium salt and hence can be determined nearly quantitatively; it is very resistant to further oxidation, and is of definite structural significance, since it can only be formed from such structures as



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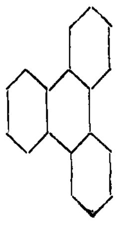

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(1) Lowry, *Ind. Eng. Chem.*, **26**, 321 (1934).

(2) Juettner and Howard, Coal Research Lab., Carnegie Inst. of Tech., Contrib. No. 8; Juettner and Howard, *Ind. Eng. Chem.*, **26**, 1115 (1934).

or more condensed bodies. It therefore appeared that a systematic study of the yields of this acid obtained from various condensed carbonaceous materials would contribute to the end in view.

There is wide disagreement in the literature as to the yield of mellitic acid obtainable by oxidation of carbonaceous materials. This is no doubt due to variation in the nature of the materials themselves, the oxidation reagent employed and to the technique used in isolating the acid. In many cases no mention of yields is made.[3] In the recent work of Meyer and Raudnitz,[4] carbons from various sources were oxidized by refluxing with nitric acid (sp. gr. 1.5–1.52) and 0.2% vanadic acid for eighty hours. If the solution was still dark after twenty hours, sulfuric acid was added and boiling continued. The crude mellitic acid was converted into the ammonium salt. This had to be purified through the copper salt. Their yields, which are the highest in the literature, are based on the crude ammonium salt. The yield of pure mellitic acid is not given.

The few references[5] in the literature to yields of mellitic acid obtained by the oxidation of coals and cokes report values of 1% or less, or do not make any quantitative statements. Nearly the same quantity, 0.6% of mellitic acid, was found in this Laboratory[6] by oxidizing Edenborn coal for thirty days with 1 *N* nitric acid. Even after two months of refluxing with the dilute nitric acid the oxidation was very incomplete, not reaching the skeletal nuclei. Therefore a search was made for a reagent that would attack the condensed structure and yet not destroy the mellitic acid formed. Under such conditions the maximum yield of this acid should be obtained. Mellitic acid is reported not to be oxidized by boiling concentrated nitric acid nor by alkaline permanganate. It therefore appeared that in this respect these reagents would meet our requirements.

Experimental

Characteristics of Coal, Cokes and Graphites.—In this work only one coal and the various cokes prepared from it were oxidized. This coal, a Pittsburgh seam coal from the Edenborn Mine, is described in detail in a Bureau of Mines publication.[7] The 500° coke was prepared in a rotating Fischer retort at a heating rate of 1.9° per minute. The temperature was held at 500° for one hour. All the other cokes were prepared in a small tube retort at varying heating rates.[8] The final temperature was maintained for one hour. The artificial graphite was an Acheson graphite electric furnace electrode. All these materials were ground to pass 200 mesh. Only the natural graphite was of smaller particle size. This graphite is known as "Dixon Micronized" No. 200–05.

Oxidation Procedures.—Since it was desirable that the oxidation method be applicable to a wide range of coals, cokes and other carbons, the 500° Edenborn coke was selected as a product of intermediate complexity suitable for evaluation of the various processes.

Alkaline Permanganate Oxidation.—Samples of 100 g. were oxidized with an excess of permanganate in three liters of water containing 200 g. of potassium hydroxide for one week. The oxidation was carried out in an iron vessel provided with water cooled lid and stirrer. Any excess permanganate still present at the end of the experiment was destroyed with formic acid. The manganese dioxide was filtered off and washed thoroughly.

The filtrate was concentrated and the following methods were used in an attempt to recover the free acids. (1) The concentrated filtrate was acidified with sulfuric acid and the salts recovered on evaporation were extracted with ether and acetone. This procedure was used by Bone.[9] The recovery was very poor. (2) The filtrate was acidified with hydrochloric acid and the solution poured into a large excess of methyl alcohol. The precipitate, potassium chloride, was filtered off and the filtrate evaporated to dryness. Again the recovery was incomplete and the acids high in inorganic residue. (3) The concentrated filtrate was placed in the middle cell of a three-compartment dialyzer with a parchment membrane on the acid and cellophane on the alkaline side. After electrolysis for four days with a current of 3–4 amp. the acids were found to have migrated completely to the anode compartment. Cathodic and anodic compartments were emptied and refilled with distilled water twice during twenty-four hours. No organic material was found in the cathode liquors, but in cases of incomplete oxidation the larger molecular weight compounds remained in the middle compartment. The combined anodic solutions were evaporated to dryness and the non-volatile acids weighed. The ash content of the free acids was usually less than 0.5% and never more than 1.0%.

The acids were dissolved in 300 cc. of warm water and poured into 1.5 liters of concentrated ammonium hydroxide. The ammonium hydroxide precipitate consisted, in the case of the alkaline permanganate oxidations, mainly of hydrated ammonium oxalate, which is only moderately soluble under these conditions. To obtain the free acids the ammonium hydroxide precipitate was electrolyzed.

The acids recovered by evaporation of the anodic solution to dryness were esterified with diazomethane. The

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(3) For a review see Treibs, *Ges. Abhandl. Kenntnis Kohle*, **5**, 580–587 (1920). Meyer and Jacobson, "Lehrbuch der organ. Chemie," Vol. II, pt. 1, p. 592.

(4) Meyer and Raudnitz, *Ber.*, **63B**, 2010–2018 (1930).

(5) Fischer and Schrader, *Ges. Abhandl. Kenntnis Kohle*, **5**, 200 (1920); Fischer, Schrader and Treibs, *ibid.*, **5**, 235, 319 (1920–21). Fuchs and Stengel, *ibid.*, **9**, 130 (1926–29); Bone and Quarendon, *Proc. Roy. Soc.* (London), **A110**, 537 (1926); Bone, Horton and Ward, *ibid.*, **A127**, 480 (1930); Bone, Parsons, Sapiro and Groocock, *ibid.*, **A148**, 492 (1935).

(6) Juettner, Smith and Howard, THIS JOURNAL, **57**, 2322 (1935).

(7) Bur. Mines Tech. Paper 525 (1932).

(8) Warren, *Ind. Eng. Chem.*, **27**, 72, 1350 (1935).

(9) Bone, Horton and Ward, *Proc. Roy. Soc.* (London), **A127**, 489 (1930).

esters were placed in a molecular fractionating still. When the heating bath temperature was 100° dimethyl oxalate distilled over (0.001 mm.). The residue in the still was purified by recrystallization from methyl alcohol and water and found to be the hexamethyl ester of mellitic acid. *Anal.* Calcd.: C, 50.71; H, 4.23. Found: C, 50.81; H, 4.21. M. p. of authentic sample 187°; mixed m. p. 186°.

The dimethyl oxalate was recrystallized from chilled ether. *Anal.* Calcd.: C, 40.66; H, 5.12. Found: C, 40.77; H, 5.12.

The ammonium oxalate was also determined by titration with 0.1 *N* permanganate in sulfuric acid solution, mellitic acid not being oxidized under these conditions.

Oxidation with Nitric Acid (Sp. Gr. 1.5).—One hundred grams of the 500° coke was refluxed for fourteen days with 1500 cc. of fuming nitric acid to which 0.24 g. of ammonium vanadate was added. The whole mixture was then evaporated to dryness on a steam-bath under vacuum. The solid residue was weighed, dissolved in water, made alkaline and electrolyzed in the usual manner. Ammonium mellitate was precipitated as before. The use of nitric acid alone resulted in the formation of a large amount of complex oxidation products which on electrolysis remained in the center compartment, even in the presence of excess alkali.

Nitric Acid Followed by Alkaline Permanganate (Standard Procedure).—After drying and weighing, the residue from the nitric acid treatment was further oxidized with an excess of alkaline permanganate for seven days, and the excess permanganate destroyed with formic acid. The manganese dioxide was filtered off and washed thoroughly. The filtrate was concentrated and electrolyzed. The acids from the anode compartment were recovered by evaporation. After first drying and weighing the acids were redissolved in 300 cc. of warm water, filtered and poured into 1500 cc. of ammonium hydroxide (sp. gr. 0.9). The mixture was chilled to 0° under constant stirring and held there for one-half hour. This procedure has been used throughout our work and was found much more satisfactory than saturation with ammonia gas from the standpoint of reproducibility and pure precipitation. However, it should be kept in mind that 4 g. of mellitic acid remains in solution under these conditions and is lost. By using nitric acid first and then alkaline permanganate the highest yields of mellitic acid were obtained. The ammonium hydroxide precipitate was found to be pure ammonium mellitate, shown to be free from oxalic acid by failure to reduce 0.1 *N* permanganate in acid solution. This procedure was later adopted as standard.

Nitric Acid Followed by Acid Permanganate and then by Alkaline Permanganate.—After refluxing in the same manner with nitric acid, the acid was diluted with an equal volume of water and a solution of 50 g. of potassium permanganate was run into the boiling acid. The whole was then evaporated to dryness in vacuum on the water-bath. When all nitric acid had been eliminated, the residue was treated with excess potassium hydroxide solution and further oxidized with permanganate. The acid permanganate appears to oxidize the mellitic acid to some extent under these conditions.

Examination of Ammonium Precipitates from the Various Procedures.—The ammonium precipitate from the procedure using alkaline permanganate alone consisted mainly of ammonium oxalate monohydrate. The corresponding precipitates from the three other procedures did not consume any 0.1 *N* permanganate when titrated for oxalic acid. All these precipitates were white. The weight was taken after drying for forty-eight hours over sulfuric acid under reduced pressure. Under these conditions the precipitate had the approximate composition of a hexahydrate. *Anal.* Calcd.: C, 26.09; H, 6.52; N, 15.22. Found: C, 26.22; H, 6.20; N, 15.80; ash, 0.05. Ammonium mellitate is reported[10] to form a nonahydrate, $C_6(COONH_4)_6 \cdot 9H_2O$.

A suitable mixture for electrolysis was found to be 10 g. of ammonium precipitate, 14 g. of potassium hydroxide, and about 4 cc. of 85% formic acid. In one experiment, for example, 136.6 g. of ammonium mellitate was dissolved in 2000 cc. of water containing 200 g. of potassium hydroxide and 55 cc. of formic acid. The whole was split in two equal portions and electrolyzed in two dialyzers. The current was not allowed to exceed 4 amp. at 110 volts. The evaporation residue from the anodes was dried for eighteen hours on the steam-bath and then for four days in high vacuum over phosphoric anhydride at room temperature. The weight of the residue after that time was 86.82 g. There was still a slight weight change after four days' drying. Recoveries on smaller samples from individual oxidations were of the same order.

Anal. Calcd. for $C_{12}H_6O_{12}$: C, 42.10; H, 1.75. Found: C, 41.94; H, 1.95; ash, 0.17.

Identification by Means of the Neutral Methyl Ester.—The acid recovered by electrolysis was esterified with diazomethane. Recrystallization from methyl alcohol, to which hot water was added, yielded, on cooling, the colorless needles of the hexamethyl ester: m. p. 187°, giving no depression when mixed with an authentic sample of the ester. Determinations of the yield of ester were made on individual specimens and also on a composite sample representing the greater number of the experiments. The yield of the pure ester averaged 84% of the theoretical.

Amounts of Reagents Used.—In all cases a large excess of reagents was used: 1500 cc. of nitric acid, sp. gr. 1.50, was used per 100 g. An excess of potassium permanganate was also used. For the original coal the amount was about 2.0 g. of permanganate per g., in a week's oxidation; for the cokes the quantity used decreased with increasing carbonization temperature, about 3.5, 1.5 and 1.0 g. per gram of coke being used for the 500, 700 and 1000° cokes, respectively, in a one-week oxidation period; for the graphites about 9.0 g. per gram was used in a two-week period.

Carbon Balance.—In all cases the carbon was oxidized to carbon dioxide, mellitic acid, and acids soluble in ammonium hydroxide. Tests showed that 4 g. of mellitic acid remained dissolved in ammonium hydroxide under our conditions. By evaporating the residual liquid in the center compartment of the dialyzer only silica was found.

To determine whether any organic material was lost when the manganese dioxide was filtered off, it was dissolved in hydrochloric acid and filtered. With the cokes small amounts of silica were found, but no organic matter.

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(10) Beilstein's "Handbuch der organ. Chemie."

With the artificial graphite, 9.0 g. of apparently unchanged graphite was obtained; with the natural graphite 7.6 g. No trace of graphitic acid or any other intermediate oxidation product was found.

Discussion

Effects of Reagents on Yields of Mellitic Acid.—Table I shows the yield of mellitic acid by the alkaline permanganate oxidation to be small and of little significance. From Table II it is evident that the oxidation procedure which gives the highest yield of mellitic acid from the 500° coke is nitric acid followed by alkaline permanganate, and that the yield is adversely affected by the use of the acid permanganate intermediate stage. This effect is much more marked in the case of the 1000° coke: when nitric acid and alkaline permanganate were used 22.5 g. of mellitic acid was recovered per 100 g. By the additional use of acid permanganate only 10.3 g. of mellitic acid was obtained. Nitric acid followed by alkaline permanganate was therefore chosen as the standard procedure.

TABLE I

OXIDATION OF COAL AND COKE WITH ALKALINE PERMANGANATE

Per 100 g.	Edenborn coal	500° Edenborn coke	500° Edenborn coke
C per 100 g.	78.27	80.17	80.17
Time of oxidation, hours	7	7	280
Non-volatile acids after electrolysis, g.	85.0	97	67.3
Oxalic acid, g. (calcd. from ammonium oxalate)	30	22	12.4
Mellitic acid, g. (calcd.)[a]	1.02	2.92	3.37
Hexamethyl ester of mellitic acid obtained, g.	0.61	0.81	1.78

[a] Calculated from yield of ammonium mellitate using an experimentally determined conversion factor of 0.636.

TABLE II

ACTION OF OTHER OXIDIZING AGENTS ON 500° EDENBORN COKE

100 g. coke	Mellitic acid recovered, g.
Alkaline permanganate for 280 hours	3.37[a]
Nitric acid	7.25
Nitric acid + alkaline permanganate	11.9
Nitric acid + acid permanganate + alkaline permanganate	10.9

[a] Calculated from ammonium mellitate.

Reproducibility and Losses of Standard Procedure.—In Table III the results of three parallel experiments with the 500° coke are given and show good agreement. The losses occurring, when mellitic acid was subjected to the standard procedure, are shown in the same table and probably can largely be attributed to manipulative losses rather than to oxidation of the mellitic acid itself.

TABLE III

REPRODUCIBILITY AND LOSSES IN STANDARD PROCEDURE

	Residue after nitric acid treatment, g.	Acids after alk. permanganate oxidation, g.	Mellitic acid recovered, g.
100 g. 500° Edenborn coke	95.5	29.7	11.9
	96.2	30.8	11.5
	96.3	28.8	11.5
100 g. mellitic acid	97.5	87.5	83.5

Effect of Carbonization Temperature on the Yield of Mellitic Acid.—From the data given in Table IV it is evident that condensation progresses rapidly up to 700°, where an apparent stability is reached. It should be emphasized that only up to a certain stage should the yield of mellitic acid be expected to increase as condensation takes place and that beyond this point a decrease would be expected, since in large C_6 ring structures a greater fraction of the carbon would necessarily appear as carbon dioxide. When it is taken into account that 4 g. of mellitic acid remained in the ammonium hydroxide during precipitation the ratio of the yields of mellitic acid from coal and coke is greatly increased over that calculated from the data in the table. To assist in the interpretation of the results on coal and coke, oxidations were also carried out, by the standardized procedure, on a natural and on an artificial graphite, where presumably a high degree of condensation is reached.

TABLE IV

EFFECT OF TEMPERATURE OF CARBONIZATION ON YIELD OF MELLITIC ACID

Edenborn 100 g.	Coal	500° Coke	540° Coke	700° Coke	1000° Coke
Heating rate, °C./min.	...	1.9	1.4	1.4	1.4
Carbon per 100 g.	78.27	80.17	79.47	79.80	86.74
Residue after nitric acid oxidation, g.	70.1	95.5	100.6	79.4	50.9
Acids after permanganate oxidation, g.	28.1	29.7	29.1	39.7	29.4
Mellitic acid recovered, g.	5.5	11.9	15.5	24.1	22.5

Oxidation of Artificial and Natural Graphites.—The standard procedure was applied, except that the oxidation period with alkaline permanganate was increased to two weeks. At the end of that time the permanganate was still being decolorized slowly. The material recovered after the nitric acid oxidation resembled ordinary graphite, in both cases, but when treated with alkaline permanganate the oxidizing agent was consumed at a rapid rate. In the case of the Acheson graphite the permanganate was reduced at a rate of about 9 g. per hour at first; after two weeks the rate fell to 1.7 g. per hour. A parallel experiment was made with the Acheson graphite not pre-oxidized with nitric acid. In this case the alkaline permanganate oxidation was very slow, the rate of reduction being 1–2 g. per hour at first and remaining constant for one week, when the experiment was discontinued. To study the effect of particle size, "Aquadag," a colloidal graphite, was also oxidized and unexpectedly gave a smaller yield of mellitic acid than the other graphites.

The data in Table V show that carbonic and mellitic acids are the principal oxidation products of natural and artificial graphite. From these figures we see that in the oxidation of a highly condensed cyclic substance, such as graphite, only a small portion of the carbon is utilized for mellitic acid formation; by far the largest part is converted to carbon dioxide, since large condensed structures have to be destroyed to get to the mellitic acid nucleus. This suggests that the structure which would give the optimum yield of mellitic acid would be one containing many small aromatic "islands," such "islands" being the results of a small crystal size in the case of certain graphites, or the interposition in the lattice of such atoms as oxygen, nitrogen or sulfur in the case of cokes. From a continuous cyclic system, such as graphite is generally believed to be, we had expected only carbon dioxide. For a better interpretation of highly condensed carbons by means of mellitic acid yields much more work is needed, especially the effect of the nature of the original carbon during carbonization and also the effect of particle size in the oxidation should be studied. Further work to that end is in progress.

TABLE V

OXIDATION OF GRAPHITES

100 g. samples	Acheson electrode graphite, −200 mesh	Natural graphite "Micronized Dixon Graphite"	"Aquadag" per 100 g. dry materia
Carbon per 100 g.	99.5	97.4	..
Residue after nitric acid oxidation, g.	71.0	78.5	21.5
Acids after permanganate oxidation, g.	23.7	26.9	14.5
Mellitic acid recovered, g.	19.1	21.7	8.3

Effect of Heating Rate on the Yield of Mellitic Acid from Cokes.—Cokes prepared at a maximum temperature of 540° but heated at a rate of 1.4°/minute and 21.8°/minute, and at maximum temperatures of 700 and 1000° with heating rates of 1.4, 5.5 and 21.8°/minute, respectively, were oxidized using the standard procedure. The yields of mellitic acid showed only slight variations for the cokes prepared at a given temperature, from which it follows that the final temperature of carbonization is the most important factor in determining the yields of mellitic acid obtained.

It should be mentioned that these yields of mellitic acid are the highest for any pure organic compound other than carbonic and oxalic acids obtained from coal or coke. The yields given in the tables are those actually recovered. Since it was shown that 4 g. is lost in the ammonia precipitation, the mellitic acid formed would be greater by this amount over the yields shown in the tables.

Acknowledgments.—The author wishes to thank H. C. Howard, F. C. Silbert and W. B. Warren of this Laboratory for assistance and cooperation in this work.

Summary

Alkaline permanganate, nitric acid, nitric acid followed by alkaline permanganate and nitric acid followed successively by acid permanganate and alkaline permanganate have been used in the oxidation of coal, cokes and graphites to mellitic acid. The action of nitric acid followed by alkaline permanganate is particularly effective in oxidizing a wide range of carbonaceous materials to mellitic acid. Neither reagent alone is satisfactory. With alkaline permanganate alone little mellitic acid is formed and large amounts of oxalic acid. With nitric acid alone mellitic acid is recovered and no oxalic acid, but the yield of mellitic acid is low due to the formation of intermediate oxidation products of high molecular weight. By subsequent alkaline permanganate treatment these intermediates are oxidized to mellitic acid. This is well illustrated by the behavior of graphite. Nitric acid or permanganate alone have no visible effect on graphite, but by oxidation with nitric acid first, followed by alkaline permanganate, 19.1 g. of mellitic acid was recovered per 100 g. of artificial graphite. This yield is of the same order as that from a natural

graphite and from the 700 and 1000° Edenborn cokes.

The effect of the carbonization temperature of the coke on the yield of mellitic acid was studied. From Edenborn coal, little mellitic acid was obtained. With increasing carbonization temperature the yield increased rapidly up to 700°. With the 1000° coke about the same quantity was recovered as with the 700° coke. With high temperature cokes the interpretation of our results becomes difficult. There is at present no satisfactory explanation for the uniformity of mellitic acid yields from such widely different carbons as 700 and 1000° cokes, artificial and natural graphites.

Cokes with the same final carbonization temperatures but widely different heating rates show small differences in the mellitic acid yield, which probably does not have important significance.

PITTSBURGH, PENNA. RECEIVED OCTOBER 12, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Some Ethers of 3-Butyn-1-ol[1]

BY P. A. MCCUSKER AND J. W. KROEGER

In view of the commercial availability of certain derivatives of ethylene glycol commonly known as Cellosolves and Carbitols, it was proposed to investigate the preparation and properties of acetylenic compounds derived from these starting materials. This group of compounds, the 1-alkoxy-3-butynes, provides not only a new type of acetylene for investigation but also furnishes a starting point for further syntheses since the terminal hydrogen of the chain is quite labile, being attached to a triply bonded carbon atom.

Various types of acetylenic ethers are reported in the literature[2] the majority of which are ethers of propargyl alcohol. Of the group of compounds described herein, all are new with the exception of 1-methoxy-3-butyne which was prepared by Lespieau[3] by dehydrohalogenation.

The technique of the preparation of acetylenic compounds as originally described by Picon,[4] who treated sodium acetylide in liquid ammonia with alkyl iodides, has been modified in this Laboratory to apply to alkyl bromides. The Cellosolves and Carbitols were converted to the corresponding bromides by the method of Palomaa and Kenetti.[5] Of these, 2,2′-dibromodiethyl ether and ethyl 2-bromoethyl glycol ether, the bromides derived from diethylene glycol and diethylene glycol monoethyl ether, respectively, are new compounds. The acetylenes were obtained from these various bromides in yields of 60 to 75% according to the type reaction

$$\mathrm{R{-}O{-}CH_2{-}CH_2Br + NaC{\equiv}CH \longrightarrow R{-}O{-}CH_2{-}CH_2{-}C{\equiv}CH + NaBr}$$

These acetylenes are quite stable to light and air. Carefully purified samples were water-white after standing for three months. The characteristic odor of the 1-alkynes is unusually powerful in these acetylenic ethers.

Sodium acetylide does not react appreciably with 2,2′-dichlorodiethyl ether, under the experimental conditions used. Ethylene bromohydrin when treated with sodium acetylide is converted to acetaldehyde, principally.

Experimental

Preparation of Bromides.—Commercial samples of the various glycol derivatives were treated with phosphorus tribromide in the presence of pyridine.[4] Redistillation of the glycol ethers was usually unnecessary. The physical constants for 2,2′-dibromodiethyl ether, which has not previously been reported, are: b. p. 115° (32 mm.); $n^{27}\mathrm{D}$ 1.5131; $d^{27}{}_4$ 1.8222. The constants for ethyl, 2-bromoethyl glycol ether are: b. p. 100–101° (33 mm.); $n^{24}\mathrm{D}$ 1.4580; $d^{24}{}_4$ 1.3340.

Preparation of Acetylenes.—One liter of liquid ammonia was placed in a 3-liter three-necked flask and stirred vigorously while a rapid stream of acetylene was bubbled through. To this, 1.2 moles (excess) of sodium dissolved in liquid ammonia was added slowly. When all the sodium had been converted to sodium acetylide, one mole of bromide was slowly dropped in and the mixture was stirred for two to four hours. Five hundred milliliters of water was then added and the organic layer which separated was washed with dilute hydrochloric acid, then with saturated

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[1] Eighteenth paper on the chemistry of the alkyl acetylenes and their addition products; previous paper, THIS JOURNAL, **58**, 1861 (1936).

[2] Lespieau, *Compt. rend.*, **194**, 287 (1932); Yvon, *ibid.*, **180**, 748 (1925); Grard, *Ann. chim.*, **13**, 336 (1930); Liebermann, *Ann.*, **135**, 266 (1865).

[3] Lespieau, *Compt. rend.*, **144**, 116 (1907).

[4] Picon, *ibid.*, **158**, 1346 (1914); **169**, 32 (1919).

[5] Palomaa and Kenetti, *Ber.*, **64B**, 797 (1931); Tallmann, THIS JOURNAL, **56**, 127 (1934).