repeated hydrogenation under mild conditions. The close agreement between the properties of corresponding products from the extract and residue indicates that these materials are very similar in their essential chemical structure. It is concluded that coal structure is made up of fundamental units with an average molecular weight of about 300, held together in larger aggregates by some relatively weak type of linkage, and that the extract differs from the residue mainly in the degree of this association.

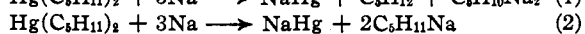PITTSBURGH, PENNA.   RECEIVED MARCH 9, 1936

Condensations by Sodium. VI. Malonic Acids from Mercury Dialkyls

BY AVERY A. MORTON AND INGENUIN HECHENBLEIKNER

The recent discovery[1] that malonic acids could be obtained by interaction of sodium, alkyl chlorides and carbon dioxide has directed our attention to the behavior of a possible intermediate, the sodium alkyl. Organo-metallic compounds of this class are conveniently prepared by action of sodium on mercury dialkyls. Analyses by Schlenk and Holtz[2] have shown close agreement with the theoretical value for a monosodium compound. Originally it was our purpose to prepare the alkyl sodium and study its decomposition products at different temperatures by carbonation. We accordingly varied the procedure from that employed by Schlenk and Holtz in order to obtain larger quantities of material. It was apparent, however, that it was unnecessary to heat the supposed amyl sodium in order to obtain other products besides caproic acid. Butylmalonic acid was always obtained in considerable amounts upon carbonating what was expected to be a monosodium compound only. This interesting result caused us to turn our attention to a study of the factors affecting the proportions of the several products from the reaction. Conditions were found whereby diamyl mercury was made to yield as high as 40–50% of butylmalonic acid. It is a reasonable inference that amylidene disodium was an intermediate product. When a similar reaction was carried out with diethyl mercury, methylmalonic acid was likewise formed although the factors needed for high yield in this case were not surveyed.

The over-all equations assumed to express the formation of the products before carbonation are

$$Hg(C_5H_{11})_2 + 3Na \longrightarrow NaHg + C_5H_{12} + C_5H_{10}Na_2 \quad (1)$$
$$Hg(C_5H_{11})_2 + 3Na \longrightarrow NaHg + 2C_5H_{11}Na \quad (2)$$

The above equations do not picture the mechanism by which the malonic acids were formed. A few possible paths are by disproportionation or decomposition (splitting out of sodium hydride[3] and addition of two sodium atoms to the amylidene so formed) of the monosodium compound, by disproportionation of the free radical, and by direct formation of amylidene (Michael's[4] mechanism) or amylidene disodium. Although it would be possible to reflect at some length on these possibilities we believe that a better opinion can be formed after more studies. A few inconclusive tests on the formation of sodium hydride are presented in the experimental portion of this paper.

Variations in the ratio of butylmalonic to caproic acid were interesting to observe because they afforded some knowledge of the conditions for increased yields of the malonic acid. Whether the total yield of acids was high or low seemed to have little bearing on this ratio but increasing the amount of solvent from 50 or 100 to 200 ml. changed the ratio from an average of 0.5 to 1.7 (see reactions 1 to 8 as compared with 11 to 14 in Table I). The cause of the variation is not clear. Possibly it is related to a change in the amount of mercury compound adsorbed on the surface of the sodium in the initial stage of the reaction. Higher ratios were also obtained when carbon dioxide was bubbled through the mixture during or immediately after the addition of diamyl mercury. (Reactions 15 to 17 and 9. Reaction 10 showed no increase.) This ratio change appears to be related chiefly to a decrease in the amount of caproic acid formed rather than to any substantial increase in the malonic acid. We were somewhat surprised that the quantity of caproic acid was so

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

(2) Schlenk and Holtz, Ber., **50**, 262 (1917).

(3) Carothers and Coffman, THIS JOURNAL, **51**, 588 (1929).

(4) Michael. Am. Chem. J., **25**, 429 (1901).

sharply reduced, and interested to note that the amount of butylmalonic acid was so little affected by this act.

The total yield of acids decreased as the temperature at which sodium acted upon the mercury dialkyl was increased. This fact suggested that the preparation of the mercury compound from sodium amalgam and the organic halide might be improved if it were carried out at as low a temperature as possible. Acting upon this idea we have succeeded in increasing the yield of mercury diethyl to 70% as contrasted with the small yield found by Jones and Werner.[5] The improvement brings this method, originally studied by Frankland and Duppa, to a level practically equal to that attained with the Grignard reagent.[6] A procedure for making diamyl mercury from amyl chloride and sodium amalgam also has been worked out. Although the yield is only 25%, a considerable saving in cost is effected by substitution of the chloride for the iodide.

Equally if not more interesting were the results in a solvent. When the reaction between mercury diamyl and sodium was carried out in benzene, phthalic (iso- and tere- mixture) and benzoic acids instead of butylmalonic and caproic acids were the products. In toluene phenylmalonic and phenylacetic acids were obtained. Reactions of this type, i. e., where the solvent participates in the reaction, have already been observed by Schorigin,[7] who obtained a 12% yield of benzoic with no phthalic acid by carbonating the product of the action of sodium on diethyl mercury in boiling benzene. Our higher yields (75% of benzoic and 24% of phthalic acid mixture) were probably due to the lower temperature at which the reaction was carried out as well as to the difference in the mercury compound used. Formation by this method of phenylmalonic acid, the principal product in a toluene medium, has never to our knowledge been recorded before.

These types of reactions, which we shall hereafter designate as "solvent exchange reactions," furnish an entirely new and interesting synthesis of malonic acids. Such reactions may also be employed to obtain both di- and mono-sodium compounds which can be used as intermediates for many products. The possibilities in this field are very numerous and we are engaged in their further study.

(5) Jones and Werner, THIS JOURNAL, **40**, 1270 (1918).

(6) Gilman and Brown, *ibid.*, **52**, 3314 (1930).

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

Experiments

Reactions with Diamyl Mercury.—The usual method of carrying out the reactions was to displace air in the vessel containing solvent and sodium sand (from a stock quantity) with dry oxygen-free nitrogen or hydrogen and then add the mercury compound. Pressure bottles were used for reactions which were carried out with standing or shaking. For stirring, the conventional three-necked flask with mercury seal as employed in Grignard reactions was used. A considerable excess of sodium was used in all cases in order to obtain a maximum decomposition of the mercury compound. Even under these conditions we were by no means successful in quantitatively recovering the mercury. In general we preferred to stir the mixture since less caking of the amalgam resulted. After carbonation a large excess of ice (not ice-water) was quickly dumped into the mixture. When the evolution of gas had subsided, the liquids were poured off and the separation of butylmalonic and caproic acids carried out as described in the previous paper. The amalgam remaining in the flask was decomposed with dilute acetic acid and the recovered mercury weighed. Unless otherwise stated all yields were based on this recovered mercury. In Table I some conditions and yields are summarized. The numbering of reactions is for convenience in reference and is without relation to the order of performing the experiments.

Preparation of Diethyl Mercury.—One per cent. of mercury amalgam was prepared by grasping pieces of sodium with tongs and plunging them under mercury contained with kerosene in a beaker. This amalgam, 2900 g. (1.25 g. atom), was stirred with 156 g. (1 mole) of ethyl iodide and 10 ml. of ethyl acetate in 1 liter of petroleum ether for twenty-four hours. Water was then added to the mixture which appeared black from the colloidal mercury present. After stirring for thirty minutes to decompose the amalgam the petroleum ether layer was separated by decantation, washed, dried and distilled. Yields of 60–70% based on the ethyl iodide used were regularly obtained.

Preparation of Diamyl Mercury.—Two per cent. sodium amalgam was prepared by the method given before. The semi-fluid amalgam, 1450 g. (1.25 g. atom), was then placed in a flask fitted with a reflux condenser and a stirrer sealed by having the glass bearing project into the liquid as described by Kamm and Marvel.[8] A liter of low boiling ligroin, 107 g. (1 mole) of Eastman technical amyl chloride, and 10 ml. of ethyl acetate were then added and the mixture refluxed and stirred for twenty-four hours. Decomposition was carried out as described above. A 25% yield of mercury diamyl of b. p. 95–96° at 3 mm. was usually obtained. The product could also be recovered by steam distillation.

Reactions with Diethyl Mercury.—After a number of trials in each of which traces of methylmalonic acid were found, the following method was employed: diethyl mercury, 11.4 g. was added to 3 g. of sodium sand under 50 ml. of pentane in a pressure bottle filled with nitrogen. After standing for twenty hours in a warm closet at 48° the mixture was carbonated by shaking with carbon dioxide under a pressure of 3 atmospheres. Decomposition was

(8) Kamm and Marvel, "Organic Syntheses," Vol. I, 1921, p. 4.

TABLE I

Re-action	Sodium g.	Diamyl mercury g.	Sol-vent[a]	L.	Time[b] hrs.	Treat-ment[c]	Temp., °C.	Gas present	Mercury recovered G.	%	Butyl malonic G.	%	Caproic G.	%	Ratio of % malonic to caproic
1	4	7.5	P	50	3	S[d]	R	N₂	3.1	71	0.68	27	1.87	52	0.52
2	4	7.5	P	50	3	Sh	R	N₂	2	46	.39	24	1.25	54	.44
3	4	7.5	P	50	3	S	R	N₂	3.1	71	.57	23	1.44	40	.58
4	4	7.5	P	50	3	S[e]	R	N₂	3.9	90	.89	28	2.13	47	.60
5	4	7.5	P	75	3	Sh	R	N₂	1.5	34	.35	29	0.75	43	.67
6	4	7.5	P	100	20	S	40	N₂	3.4	78	.44	16	1.68	43	.37
7	4	7.5	P	100	28	Sh[f]	R	N₂	2.6	60	.44	21	1.5	50	.42
8	3	10	L	100	0.5	Sr	100	H₂	4.4	76	.87	25	2	39	.64
9	3	10	L	100	0.16	Sr	R	H₂	2.1	36	.53	32	0.4	16	2.0
10	3	10	P	100	3	Sr	R	CO₂	1.7	29	.11	8	.29	15	0.53
11	4	7.5	P	200	3	Sr	R	N₂	1.7	39	.58	43	.50	25	1.76
12	10	7.5	P	200	1	Sr	R	N₂	2.4	55	.83	44	.67	24	1.83
13	3	10	P	200	2	Sr	R	N₂	5.4	93	2.24	51	1.6	26	1.96
14	4	7.5	P	200	2	Sr	35	N₂	3.5	60	1.33	47	1.4	35	1.34
15[g]	10	7.5	P	200	2	Sr	35	CO₂	4.1	94	1.62	49	0.91	19	2.6
16	10	7.5	P	200	2	Sr	R	CO₂	[h]	..	1.52	..	.5	..	4.45
17	10	7.5	P	200	1	Sr	R	CO₂	3.7	85	1.4	47	.93	22	2.13
18	10	7.5	P	300	1	Sr	R	N₂	3.7	71	1.3	44	1.28	35	1.25
19	5	15[i]	L	130	1	Sr	100	H₂	8.3	95	0.25	..	0	..	..
20[j]	10	30	N	150	1	Sr	100	N₂	15	86	1.53	13	Trace	..	..

[a] Solvents used were Eastman practical pentane (P), olefin-free ligroin (L), and Nujol (N).   [b] Time before carbonation.   [c] Abbreviations in this column have the following meanings: S—the container was allowed to stand with occasional shaking, Sh—it was put in a shaking machine for the designated time, Sr—the mixture was stirred.   [d] Stood in the dark.   [e] Stood in laboratory daylight.   [f] Shaken three hours, stood twenty-five hours.   [g] No trace of oxalic acid was found.   In other preliminary experiments not recorded in this paper we were unable to find any oxalic acid.   Compare with oxalic acid formation recorded in the previous paper.[1]   [h] Impossible to estimate because mercury spilled into the flask from the mercury sealed stirrer.   [i] Amyl mercuric chloride used instead of diamyl mercury.   [j] The pentene and pentane evolved were caught in a trap cooled with carbon dioxide snow.   One gram of material boiling at 37-39° was obtained.   Analyses for the unsaturates by the bromide–bromate method showed 11% of pentene.   The remainder, 0.89 g., agrees roughly with the quantity, 1.08 g., of pentane calculated if the reaction progressed according to equation 1. Another product obtained in this experiment was a mixture of tarry acids which precipitated upon acidification of the alkaline solution.

effected in the same manner employed for the products of the reaction with diamyl mercury. The mercury recovered amounted to 7.1 g. (80%). Methylmalonic acid was isolated by neutralizing exactly the alkaline solution with hydrochloric acid, evaporating to dryness, adding concentrated hydrochloric acid and extracting with ether. The ether was then evaporated and the neutralized aqueous solution of the residue was treated with lead acetate to precipitate the lead methylmalonate. A tenth of a gram of pure acid, m. p. 122° and decomposition point 130–135°, was obtained. Confirmation that it was the malonic acid was obtained by measurement of the acid equivalent. Samples of the reaction product were also tested for formic acid (from sodium hydride plus carbon dioxide) by steam distilling the acidified solution, treating the distillate with mercuric oxide to convert to the mercury salt, filtering, evaporating and heating. No reduction to mercury occurred. A blank test with formic acid alone under the same conditions gave a positive result. Moissan[9] has stated that sodium hydride will reduce carbon dioxide to carbon. We observed no carbon in the product after carbonation. These tests indicated that no decomposition of ethyl sodium to sodium hydride[3] and ethylene or ethylidene occurred under the conditions of our experiments.

(9) Moissan, Compt. rend., 134, 71 (1902).

Reactions with a Solvent.—The procedure for these reactions was in general the same as described before. In each experiment the sodium was stirred with diamyl mercury in 100 ml. of solvent under an atmosphere of nitrogen

TABLE II

Sodium, g.	3	5
Diamyl mercury, g.	10	5
Solvent	Benzene	Toluene
Time, hours	1	1.5
Mercury recovered { g.	5.3	[c]
{ %	93	..
Yield of carboxylic acids { Di-, g.	1.1[a]	1[d]
{ Mono-, g.	4.9[b]	0.5

[a] The dicarboxylic acids were a mixture of tere- and isophthalic acids; yield 24% based on the mercury recovered.
[b] Equivalent to 75% yield based on the mercury recovered.
[c] Value not recorded because mercury spilled in from seal on the stirrer.
[d] Although the yield could not be calculated on the amount of mercury recovered, it was equal to 45% based on the diamylmercury used. The yield of phenylacetic acid on this same basis was 13%. Phenylmalonic acid was identified by its decomposition temperature and acidity.

for the length of time given in Column 4, Table II, before carbonation. It was usually necessary to warm the mixture at the start in order to initiate the reaction. Conditions and yields are summarized in Table II.

Conclusions

When diamyl mercury was treated with sodium and the product of the reaction carbonated, yields as high as 40–50% of butylmalonic acid were obtained. Diethyl mercury by the same series of reactions yielded methylmalonic acid.

An improvement in Frankland and Duppa's method for the preparation of diethyl mercury

was realized. Diamyl mercury was prepared from amyl chloride by this same method.

Benzene and toluene were shown to participate in the reaction when they are used as solvents. Di- as well as monocarboxylic acids were obtained in each case. Substitution in the last solvent took place in the methyl group resulting in the formation of the corresponding malonic acid. Such participations of the solvent in the reaction have been designated as "solvent exchange reactions."
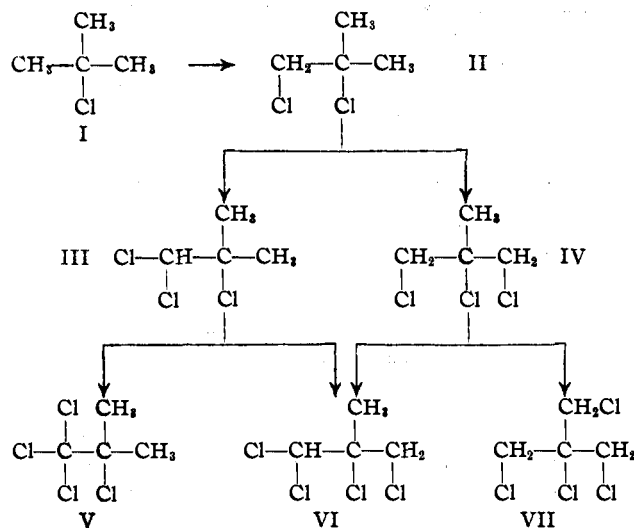
CAMBRIDGE, MASS.   RECEIVED APRIL 2, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Liquid-Phase Photochemical Chlorination of 2-Chloro-2-methylpropane and Some Related Compounds[1]

BY A. O. ROGERS AND R. E. NELSON

The chlorination of 2-chloro-2-methylpropane proceeds in a series of steps

Although the literature contains a number of references to 1,2-dichloro-2-methylpropane (II), the higher polychlorides have received very little attention. Pogorshelski[2] identified 1,2,3-trichloro-2-methylpropane (IV) among the products from the chlorination of 2-methylpropene. The properties of 1,1,2-trichloro-2-methylpropane (III), 1,1,1,2-tetrachloro-2-methylpropane (V) and 1,2,3-trichloro-2-chloromethylpropane (VII)
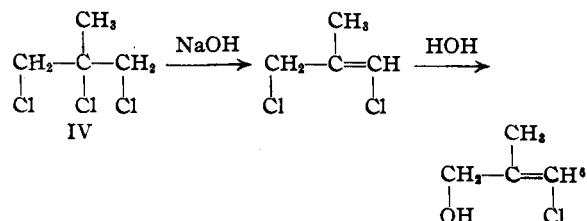
are not accurately described in the literature;[3,4,5] no mention of 1,1,2,3-tetrachloro-2-methylpropane (VI) has been found.

The identities of the various isomeric tri- and tetrachlorides may be deduced from the order of their boiling points, and are confirmed by the following facts.

(a) Compound IV agrees in physical properties with the compound to which Pogorshelski[2] assigned the same structure.

(b) The alkaline hydrolysis of compound IV yields an unsaturated chlorohydrin with a percentage of chlorine agreeing with the formula C_4H_7OCl (equation below).

(c) The pyrolysis of compound IV yields a mixture of unsaturated compounds whose composition agrees with the formula $C_4H_6Cl_2$. This mixture, on chlorination, yields compounds VI and VII; on hydrolysis, about 60% of the chlorine present is removed, with the

(1) Based upon a thesis submitted by A. O. Rogers to the Faculty of Purdue University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1935.

(2) Pogorshelski, J. Russ. Phys.-Chem. Soc., 36, 1129–1184 (1904); Chem. Zentr., 76, I, 668 (1905).

(3) Mouneyrat, Ann. chim. phys., [7] 20, 534 (1900); Chem. Zentr., 71, II, 721 (1900).

(4) Willgerodt and Dürr, Ber., 20, 540 (1887).

(5) Kleinfeller, ibid., 62, 1595 (1929).

(6) Rogers and Nelson, THIS JOURNAL, 58, 1029 (1936).