methylaminobenzaldehyde was reduced readily, but attempts to distil the reduction product resulted in the formation of a gum.

Aside from these cases the method here described appears to be quite general in its applicability.

Summary

The discovery made by the writers of the promoting effect of iron salts on the catalytic reduction of aldehydes using platinum black as a catalyst has been applied to a number of aldehydes with the view (1) to determining how general this effect is and (2) to working out a satisfactory general method for the reduction of aldehydes. A standard procedure is described, the advantages and limitations of this method are set forth, and detailed directions are presented for the preparation of various primary alcohols.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE PREPARATION OF PALLADOUS OXIDE AND ITS USE AS A CATALYST IN THE REDUCTION OF ORGANIC COMPOUNDS.[1] VI

BY R. L. SHRINER[2] WITH ROGER ADAMS

RECEIVED APRIL 2, 1924 PUBLISHED JULY 7, 1924

In previous papers, a convenient method for the preparation of platinum dioxide and its successful use as a catalyst in the hydrogenation of organic compounds has been reported.[3] Since the method of preparing an oxide by fusion of chloroplatinic acid with sodium nitrate gave an excellent catalyst in the case of platinum, a study of the preparation of oxides from other noble metals by the same procedure has been undertaken. This communication reports on the preparation of palladous oxide and preliminary experiments on its use as a catalyst.

Palladium has been widely used as a reduction catalyst as palladium black and as a colloid[4] and, in many cases, appears superior to platinum. This investigation has been undertaken in the hope of finding a more active and conveniently prepared palladium catalyst than has been produced

---

[1] Part of the palladium used in this investigation was purchased with the aid of a grant from the Bache Fund of the National Academy of Sciences. For this aid the authors are greatly indebted.

[2] This communication is an abstract of a thesis submitted by R. L. Shriner in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] (a) Voorhees and Adams, THIS JOURNAL, **44,** 1397 (1922). (b) Carothers and Adams, *ibid.*, **45,** 1071 (1923). (c) Adams and Shriner, *ibid.*, **45,** 2171 (1923). (d) Kaufmann and Adams, *ibid.*, **45,** 3029 (1923).

[4] For a good review of the use of palladium black and colloidal palladium, see "Catalysis in Organic Chemistry," by Sabatier, translated by E. E. Reid, D. Van Nostrand Co., 1922.

by other methods. Very few quantitative data are available on the time required for reduction with palladium catalyst, and none on the comparison of palladium catalysts of various purities.

Three oxides of palladium are known, those corresponding to the formulas PdO, Pd_2O_3 and PdO_2, and hydrates of these oxides. An oxide of the formula Pd_5O_6 has also been reported by Schneider[5] but Wöhler[6] who has made a study of the above oxides showed that this compound was really the monoxide and that the formula Pd_5O_6 was based on a faulty analytical method. A suboxide,[7] Pd_2O, was likewise shown to be a mixture of palladium and palladous oxide. Since the oxide obtained by the fusion of chloroplatinic acid and sodium nitrate was a hydrated platinum dioxide, an analogous palladium oxide might be expected at least as a natural reaction product. Most palladic compounds, however, are unstable even at room temperature, especially in the presence of water. Palladic dioxide decomposes at ordinary temperatures into palladous oxide and oxygen. When the palladium chloride and sodium nitrate are fused, the dioxide, if formed, would be immediately decomposed either by the high temperature or by the later treatment with water. On the addition of water no liberation of oxygen was observed, so that the palladous oxide either formed directly, or the dioxide formed and decomposed during the fusion. The following reaction may represent what occurs.

$$2PdCl_2 + 4NaNO_3 \longrightarrow 4NaCl + 2PdO + 4NO_2 + O_2$$

Palladous oxide has been prepared by Berzelius[8] by heating palladium amalgam, by heating the metal with alkali or precipitation with alkali from a solution of a palladous salt.[9] It has also been obtained by gentle ignition of the nitrate[10] at 120–130°.

Since Schneider's Pd_5O_6 was actually palladous oxide and was prepared by the fusion of a palladous salt with an excess of potassium nitrate and potassium hydroxide, a sample of the oxide was prepared by this method. When prepared in this manner and used as a catalyst, it proved much inferior to the oxide prepared by the use of sodium nitrate alone. The reduction of maleic acid was only half as fast, and that of benzaldehyde only one-sixth as rapid as when the catalyst prepared by the method following was used.

Preparation of Palladous Oxide

The same general procedure was used in the preparation of this oxide that has been previously described[3c] for the preparation of the platinum oxide

---

[5] Schneider, *Pogg. Ann.*, **141,** 519 (1870).

[6] Wöhler and König, *Z. anorg. Chem.*, **46,** 323 (1905); **48,** 203 (1906); **57,** 398 (1908).

[7] *Phil. Trans.*, **132,** 276 (1842). *Monatsh.*, **12,** 40 (1892).

[8] Berzelius, *Schweigg. J.*, **7,** 66 (1813).

[9] *Pogg. Ann.*, **13,** 454 (1828).

[10] Fischer, *ibid.*, **71,** 431 (1847).

catalyst, except that it was found desirable to heat the melt to a higher temperature in order to obtain the greatest activity of the catalyst and also to complete the precipitation. The method for obtaining the best results may be summarized as follows.

In a 150cc. casserole, 50 g. of C. P. sodium nitrate and a solution of palladous chloride, corresponding to 2 g. of palladium, are thoroughly mixed, evaporated to dryness, and then further heated until fused. The mixture fuses at 270–280°, and when the temperature reaches 350–370° a vigorous evolution of oxides of nitrogen occurs with considerable foaming. After this evolution of gas which lasts for 3 to 5 minutes, the temperature is raised rapidly and maintained between 575° and 600° for 5 minutes. The melt is then permitted to cool, dissolved in 200cc. of distilled water, and the palladous oxide filtered off. It was found impossible to wash this oxide with pure water since it showed a great tendency to become colloidal. It was, therefore, thoroughly washed with 1% sodium nitrate solution[11] and dried in a vacuum desiccator over sulfuric acid.

The temperatures recorded above and in the following experiments were obtained by stirring the melt with a thermocouple encased in a Pyrex tube. It is, however, not necessary to use a thermocouple, since the temperature may be followed by the evolution of gases, and the final degree of heating is readily obtained with a single Meker burner. The total time required for preparation of the catalyst, including filtration and washing, is about 45 minutes.

The filtrates from the fusions should be clear and colorless. Palladous nitrate and chloride give a deep brown color in concentrated solutions which becomes light yellow on dilution, and this color can be used as an index for the completeness of precipitation. If the filtrate possesses a yellowish-orange opalescence, some of the oxide has become colloidal. In order to recover palladium from the filtrate, it can either be evaporated to dryness and re-fused or rendered slightly alkaline with sodium carbonate and precipitated by heating with formaldehyde.

A small amount of the oxide always adheres to the casserole and cannot be removed by ordinary means, but is readily dissolved by boiling hydrobromic acid.

Two other tests for palladium may be mentioned: one, the formation of an orange-to-yellow color with stannous chloride which changes to green in concentrated solution (differing thus from platinum) or remains yellow in a dilute solution. A more characteristic test, one which differentiates palladium from platinum is that with dimethylglyoxime,[12] which precipitates palladium from a slightly acid solution as a yellow, flocculent precipitate. These tests are convenient in order to avoid confusion when working with the two metals.

---

[11] Carothers and Adams have found that addition of sodium nitrate to the catalyst in no way affects the activity of platinum as a catalyst in the reduction of aldehydes.

[12] Wunder and Thuringer, *Z. anal. Chem.*, **52,** 101, 660 (1913). Davis, *Bur. Mines Repts., Invest.*, **1922,** No. 2351.

Quantitative Analysis

The catalyst was analyzed for moisture, metallic palladium and alkali salts by the same method used for platinum.[3c] In order to make the analysis more complete, however, oxygen was also determined directly by heating a separate sample of the oxide in a current of hydrogen in a short electric combustion furnace and the water so formed, collected and weighed. The difference between this weight and the weight of moisture gave the weight of water corresponding to the oxygen in the oxide. In calculating the formula for the oxide, the amounts of moisture and alkali salts were treated as impurities, and subtracted from the weight of the sample. The percentages of palladium and oxygen are thus based on the true weight of metal oxide.

Moisture determination			Other Constituents							
Sample	Wt. H_2O	% H_2O	Sample	Wt. Pd.	H_2O + moisture	Moisture	Alkali salts	% Alkali salts	% Pd	% O
0.4371	0.0068	1.55	0.5344	0.4445	0.0918	0.0078	0.0129	2.42	86.53	13.78
.4838	.0067	1.38	.5221	.4342	.0839	.0076	.0133	2.55	86.63	13.55
	Av.	1.46					Av.	2.48	86.58	13.66

Calcd. for PdO; Pd, 86.96%; O, 13.04%.

The results show that the oxide is palladous oxide, PdO, with small amounts of water and alkali salts.

Properties

Palladous oxide prepared in this manner is a black powder. Microscopically it differs from the platinum dioxide which is amorphous in that it is crystalline in appearance although no definite form could be detected. Its insolubility in acids, slight solubility in aqua regia and decomposition of hydrogen peroxide have been described by Wöhler.[6] To these properties may be added its ready solubility in constant-boiling hydrobromic acid.

Effect of Temperature on the Yield and on the Activity of the Oxide as a Catalyst

In order to determine the best temperature for the formation of the most active catalyst and also for the complete conversion of the palladous chloride into the oxide, fusions were made at five different temperatures. The oxide obtained in each case was tested for catalytic activity by using it for the reduction of maleic acid. This was chosen as a standard test substance because it can be readily obtained pure, the reduction is clean-cut with no side reactions, and the reduced product, succinic acid, can be readily isolated in practically quantitative yield. The reductions were carried out by dissolving 0.1 mole (11.6 g.) of maleic acid in 150 cc. of alcohol, adding 0.23 g. of catalyst and shaking the mixture in the apparatus previously described.[3a] The general method was the same as in the case of platinum except that three successive portions of maleic acid were reduced without reactivation of the catalyst in order to test the durability of the oxide as a catalyst. The results are shown in Table I.

Table I

Comparison of Activities of Catalyst Prepared at Different Temperatures

Sample No.	Maximum temperature of fusion °C.	% Pd precipitated	Lag Min.	Time for reduction First 0.1 mole Min.	Second 0.1 mole Min.	Third 0.1 mole Min.
1	400	91	3	21	300	. . .
2	450	90	3	15	53	75
3	500	100	5	14	25	31
4	600	100	1.5	8	15	26
5	650	100	6	14	66	330

Complete precipitation of the palladium was obtained only at 500° and above, and the most active sample was No. 4. Moreover, this catalyst prepared at 600° was reduced to the black more rapidly than any of the other samples, and hence this temperature was chosen for the preparation of the catalyst.

In all of the reductions described above, a peculiar phenomenon occurred. During the reduction the catalyst remained suspended in the liquid, but as soon as the reduction was complete, that is, when the calculated amount of hydrogen had been absorbed, the catalyst coagulated in large spongy masses that readily settled out and could easily be filtered off.

An experiment was made to determine whether the order, (1) reduction of the oxide (2) addition of maleic acid, had any effect on the rate of reduction. When this was done, 15 minutes was required for the reduction of 11.6 g. maleic acid, and the catalyst instead of being suspended throughout the liquid was more or less agglomerated.

The Reduction of Aromatic Aldehydes

When benzaldehyde was reduced with platinum, it was found that the reaction did not go to completion with spectroscopically pure platinum, unless reactivated several times with oxygen. Platinum which has been used and reworked several times, however, functioned as an excellent catalyst, due to the accumulation of small amounts of impurity. It was shown that the addition of a very small amount of ferrous chloride (0.0001 mole) to the catalyst before it was used caused the reduction to proceed to completion smoothly and rapidly.[3b]

The reduction of other aldehydes with platinum in the presence of ferrous chloride was also successful. In order to obtain data that would give information on the relative values of platinum and palladium as catalysts, a series of aldehydes were reduced with pure palladium alone, and with pure palladium in the presence of ferrous chloride. To this end, 0.2 mole of each of the following aldehydes dissolved in 150 cc. of 95% alcohol was reduced in the presence of 0.23 g. of catalyst. In one series of reductions, pure palladium was used. This was prepared by reducing spectroscopically pure ammonium chloropalladate, obtained from the Bureau of Standards, in a stream of hydrogen at 450°, dissolving the metallic palladium in aqua regia, evaporating, dissolving the residue in dil. hydrochloric acid and fusing with sodium nitrate the solution thus obtained. In the second series of reductions, the catalyst prepared as described above was used, but 1 cc. of a solution containing 0.0001 mole of ferrous chloride was added. Because the results obtained were unexpected and contrary to the experience with platinum the whole series of reductions was then repeated with another lot of catalyst prepared in the same manner. For purposes of comparison the times for reduction with platinum[13] are also included in the data which are summarized in Table II.

TABLE II
TIME FOR REDUCTION TO ALCOHOL

Catalyst	Benzaldehyde Min.	Salicyl aldehyde Min.	Anisaldehyde Min.	Vanillin Min.	Piperonal Min.
Pure Pd					
1	21	44	33	71	42
2	21	42	39	66	44
Pure Pd + 0.0001 mole of $FeCl_2$					
1	24	34	38	45	52
2	26	35	45	45	50
Pure Pt + 0.0001 mole of $FeCl_2$					
1	23	60	22	50	15

The reduction of aldehydes with palladium differs markedly from the reduction with platinum in three respects. First, the reduction is readily carried to completion with pure palladium, and the presence of iron is not essential. Second, the ferrous salt caused no acceleration in the case of benzaldehyde, anisaldehyde and piperonal, but instead caused a slight increase in the time required. Paal[14] noticed that iron salts decrease the catalytic activity of palladium in the reduction of unsaturated oils. On the other hand, the reduction of salicyl aldehyde is accelerated about 20% and that of vanillin about 30%. It is remarkable that only those aldehydes were accelerated which contained a free hydroxyl group, and that the ethers derived from them are not so affected. It is well known that phenols form complexes with iron salts, so it may be that such a combination prevents the iron from poisoning the catalyst. While this might explain why the reduction of salicyl aldehyde is accelerated but that with anisaldehyde is not, it does not explain why the reduction of salicyl aldehyde is slower with pure palladium than in the presence of iron.

Although the reduction of salicyl and vanillyl aldehydes is hastened by the presence of iron, this substance must not be added, if pure white prod-

---

[13] Carothers and Adams, THIS JOURNAL, **46**, 1675 (1924).

[14] Paal, *Ber.*, **46**, 3069 (1913).

ucts are desired. During the process of isolation, the ferrous chloride becomes oxidized, giving colored products and several recrystallizations from benzene in the presence of Norite are necessary to get a white product. These recrystallizations also reduce the yield of alcohol.

In order to determine whether the amount of iron was the optimum, and to see whether the amount of iron had any effect on the results, three reductions of 0.2 mole of benzaldehyde were carried out in the presence of 0.0004, 0.0001, and 0.00001 mole of ferrous chloride. The time required for reduction was 28, 24 and 26 minutes, respectively, showing that only a very small amount was necessary to poison the catalyst and that the time of reduction in the experiments described above was not appreciably influenced by the amount of iron.

When salicyl aldehyde was reduced in the presence of increasing amounts of ferrous chloride, the time for the reduction was at first shortened and then as the amount of iron was still further increased, the time also increased. The results shown in Table III were obtained by reducing 22.4 g. of salicyl aldehyde in 150 cc. of alcohol with 0.23 g. of catalyst and the addition of proper amounts of a solution of 4.0 *M* ferrous chloride.

Table III

Effect of Amount of Ferrous Chloride on the Reduction of Salicyl Aldehyde[a]

Amount of ferrous chloride Mole	Time before reduction started Min.	Time for reduction to saligenin Min.	Total time Min.
None	4	44	48
0.00005	10	38	48
.00010	11	34	45
.00015	12	36	45
.00020	14	41	55
.0010	14	51	65

[a] Much more striking results were obtained on another sample of aldehyde which, although purified in the same manner, was colorless while all other samples still retained a slight straw coloring matter. The acceleration in a run of 0.2 mole of aldehyde when 0.002 mole of ferrous chloride was added was 70%.

The first point to be noted in Table III is the continual increase in the lag with increasing amounts of ferrous chloride. This indicates that the presence of the iron salt inhibits the formation of palladium black, as has previously been noted with platinum dioxide, benzaldehyde, and ferric chloride.[3b] That ferric chloride is produced by oxidation of the ferrous chloride by the palladous oxide is shown by the deep red color which the solution of salicyl aldehyde assumes at first, but which disappears before active reduction starts.

In the second place, the actual time required for the reduction decreases with increasing amounts of ferrous chloride up to a certain concentration, after which the addition of more ferrous chloride causes an increase in the time necessary. This is not due to the formation of a more easily reduced complex of ferrous chloride and the phenolic aldehyde since the amount of ferrous chloride giving the maximum activating effect is so small. It requires only 0.00015 mole of ferrous chloride to start poisoning the reduction of 0.2 mole of aldehyde. It seems much more probable that the ferrous chloride functions as a promoter, a matter which will be considered in more detail in a later paper. It is obvious that the most economical condition from the point of view of the total time consumed is the third reduction above, in which only 0.0001 mole of ferrous chloride was present.

Thirdly, the reduction with palladium differs from that with platinum in that the reduction does not stop at the alcohol, but continues until the aldehyde group has been converted to a methyl group. This fact has been noted by previous workers[15] using colloidal palladium or palladium black, but by stopping the reaction when two atoms of hydrogen have been absorbed, the alcohol can be isolated.

When the reduction of benzaldehyde is permitted to go to completion, the formation of the alcohol takes place rapidly, as indicated above, but the reduction of the benzyl alcohol to toluene takes place very slowly. When 0.2 mole of benzaldehyde is reduced to toluene with 0.23 g. of pure palladium catalyst, 5.5 hours is required. The presence of iron chloride inhibits the reduction of benzyl alcohol to toluene, as shown by the fact that 8.9 hours was required when 0.0001 mole of ferrous chloride was added.

A reduction of benzaldehyde with a sample of oxide made from commercial palladous chloride was complete in only 2.2 hours. This extremely rapid reduction is in marked contrast with the results obtained with pure palladium. Since iron[16] is known to be a common impurity in commercial palladium, it was thought that the addition of iron to the pure palladium would accelerate the reduction, as was the case with platinum, but no such acceleration occurred except with hydroxyaldehydes. This result with a commercial sample of palladous chloride again emphasizes the necessity of specifying the kind and source of the metal used as a catalyst and explains why some investigators cannot duplicate the work of others. The nature of this activating impurity has not yet been determined.

Effect of Amount of Catalyst on Rate of Reduction

In Table IV is shown the effect of increasing amounts of catalyst on the rate of reduction.

It will be noted that the rate of reduction was approximately proportional to the amount of catalyst. The most rapid reduction obtained was that with 0.49 g. (0.4 mole of palladium) of catalyst, and in this experiment

---

[15] Skita and Bruner, *Ber.*, **48**, 1685 (1915). Rosenmund, Zetzsche and Heise, *Ber.*, **54**, 425, 638, 2038 (1921).

[16] Keeler and Smith, *Am. Chem. J.*, **14**, 423 (1892).

TABLE IV

EFFECT OF AMOUNT OF CATALYST ON RATE OF REDUCTION

Palladium			Platinum[3b]		
Amount of catalyst		Time for reduction of 0.2 mole of benzaldehyde	Amount of catalyst		Time for reduction of 0.2 mole of benzaldehyde
G.	Moles of Pd	Min.	G.	Moles of Pt	Min.
0.490	0.004	11	0.230	0.0010	23
.245	.002	21	.115	.0005	34
.122	.001	40	.0575	.00025	60
.061	.0005	63	.0288	.000125	330

the bottle became very warm, the temperature rising to 55°. Very little difference in the activities of platinum and palladium was found when a comparison is made between the same weights of each used and the time required for reduction. (See Table V.)

Activation of the Catalyst by Oxygen

The necessity for the presence of oxygen in the reduction of aldehydes and the marked saving in time resulting from shaking with oxygen have already been shown in the case of platinum. In order to determine the effect of shaking palladium with oxygen, 0.1 mole of benzaldehyde was reduced to the alcohol and then another 0.1 mole of aldehyde added and the reduction permitted to go to completion. This series of reductions was then repeated with activation with oxygen for 10 minutes before the addition of each 0.1 mole of aldehyde.

Four successive 0.1 *M* quantities of maleic acid were also reduced with and without reactivation of the catalyst. The reductions, in each case, were performed with catalyst from a single sample. The results, shown in Table V, demonstrate clearly that oxygen accelerates the reduction of benzaldehyde and that the time necessary for the reduction of a given quantity can be more than halved by activating with oxygen at intervals.

Quite the reverse is the effect of oxygen in the reduction of maleic acid. Here it actually lengthened the time required for reduction.

TABLE V

EFFECT OF ACTIVATION WITH OXYGEN

	Benzaldehyde		Maleic acid	
0.1 Mole portion	No activation Min.	Activation Min.	No activation Min.	Activation Min.
First	10	9	10	10
Second	28	11	16	28
Third	144	42	19	32
Fourth	248	123	20	37
Total time	435	185	65	107

A similar poisoning effect was noted with platinum. When 0.1 mole of maleic acid was reduced with 0.23 g. of platinum dioxide, 8 minutes was required for the first portion, and 374 minutes for the second. When the catalyst was shaken with oxygen before the second portion of maleic acid was introduced, only one-tenth of the calculated amount of hydrogen was absorbed in 9 hours, after which time no further reduction took place.

In all the data reported on the use of platinum oxide as a catalyst in the reduction of aldehydes, oxygen has not only accelerated the reduction but its presence seems to be one of the essential factors. The rapid fatigue of pure platinum in the reduction of benzaldehyde, the continuation of reduction on shaking the fatigued catalyst with oxygen and the effect of the addition of a very small quantity of ferrous chloride are certainly strong indications of the necessity for oxygen in platinum when used in the reduction of aldehydes.

In the reduction of benzaldehyde using palladium, oxygen is also an accelerator. On the other hand, palladium differs from platinum in that the reduction of the aldehydes with palladium may be completed without activation, and in that ferrous chloride acts as a poison with certain aldehydes but hastens the reduction of others. The observation of the poisoning effect of oxygen in the reduction of maleic acid with both platinum and palladium leads to the conclusion that the question of the need for oxygen cannot be answered in a manner that will apply in all cases. Oxygen may be placed with ferrous chloride in the class of promoters; each exerts its own specific selective action which depends not only on the nature of the catalyst but on the type of compound undergoing reduction. This latter fact is very important and has been overlooked by the investigators who have taken up the problem of determining whether oxygen is necessary for the activity of catalysts such as platinum, palladium, or even the base metals such as nickel. They have disregarded the nature of the compounds to be reduced. The influence[17] of the carrier frequently used in catalytic work is probably, in effect, similar to that of the addition of ferrous chloride upon platinum or palladium in the reduction of aldehydes.

Iridium chloride when fused with sodium nitrate at various temperatures yielded a bluish-black powder, undoubtedly the sesquioxide Ir_2O_3. The oxide thus formed contains a large amount of alkali salts. These are not all removed by treatment with dil. sulfuric acid. The oxide was not a catalyst in the reduction of aldehydes. It was obvious that metallic iridium was not formed. This agrees with the reports in the literature that iridium oxides are reduced to iridium only at high temperatures. Even after reducing this oxide at a high temperature to metallic iridium, the latter was only a very poor catalyst in the reduction of aldehydes.

Summary

1. Palladous oxide was prepared by the fusion of palladous chloride with sodium nitrate. It has been shown to be an effective catalyst in

---

[17] Rosenmund, *Ber.*, **56**, 2262 (1923).

hydrogenation, the most active form being produced when the fusion temperature is 600°.

2. The importance of knowing the exact purity of the catalyst used for the reductions has been demonstrated. Ferrous chloride accelerates the reduction of aromatic aldehydes which contain a free hydroxyl group but not those which do not have this group.
3. The importance of considering the nature of the substances to be reduced when studying promoters has been demonstrated. The reduction of successive portions of benzaldehyde is accelerated by shaking with oxygen. On the other hand, the reduction of maleic acid is not so accelerated but is actually slowed.
4. Comparison of platinum and palladium oxides as catalysts in the reduction of various aromatic aldehydes and maleic acid shows that they have approximately the same activity.

Urbana, Illinois

[Contribution from the Department of Chemistry, Yale University]

RESEARCHES ON AMINES. IX. SOME CHEMICAL PROPERTIES OF AMINO-ACETO-PHENYLANILIDE

By Erwin B. Kelsey

Received April 10, 1924 Published July 7, 1924

In previous publications,[1] the writer, with A. J. Hill, described the preparation of isothiocyano-acetanilide and certain of its nucleus substituted derivatives. It has been shown that such mustard oils are unstable and rearrange at once into substituted normal thiohydantoins.

$$\mathrm{RNHCOCH_2NCS} \longrightarrow \mathrm{R}\overline{\mathrm{N{-}CS{-}NHCH_2CO}}.$$

This paper deals with the attempts to synthesize isothiocyano-aceto-ethylanilide, $C_6H_5N(C_2H_5)COCH_2NCS$, and isothiocyano-aceto-phenylanilide, $(C_6H_5)_2NCOCH_2NCS$, since in mustard oils of this type, normal thiohydantoin formation through intramolecular change is rendered impossible.

The methods of synthesis described in the previous papers[2] were again employed, and the chloro-anilides successively converted into the corresponding primary amine, dithiocarbamate, and carbo-ethoxy-dithiocarbamate. Although the writer was unable to obtain either of the isothiocyanates named above, certain unusual and interesting facts have been brought to light, as follows.

1. Chloro-aceto-ethylanilide reacts rapidly with aqueous or alcoholic

---

[1] Johnson, Hill and Kelsey, This Journal, **42,** 1711 (1920). Hill and Kelsey, *ibid.*, **44,** 2357 (1922).

[2] Hill and Kelsey, *ibid.*, **42,** 1704 (1920).