

trum had maxima at 4250 and at 4000 Å. He also noted that his product was apparently identical with a pigment isolated by van Stolk, Guilbert, and Penau in 1932. In the spectrum of this compound as separated in this Laboratory, there was no trace of a shelf or maximum at 4500 Å. The spectrum was quite similar to that of unnamed carotene 1 as shown in Fig. 1, except for the absence of the maximum at 4500 Å. This maximum is not due to contamination of unnamed carotene 1 by  $\beta$ -carotene since absorption at 4800 Å. is too low. No preparation of unnamed carotene 1 from corn failed to show a maximum at 4500 Å. Since Fraps and Kemmerer's<sup>4</sup> curve for K carotene shows neither the 3790 Å. maximum nor the 3600 Å. shelf, it is possible that K carotene and un-named carotene 1 may not be identical.

Fraps and Kemmerer also stated that  $\alpha$ -carotene was found in all but one of twenty-two corn varieties. The authors have never observed  $\alpha$ -carotene in corn (six inbreds, several sweet corn varieties, and two hybrids were studied). The adsorbent used by Fraps and Kemmerer was capable of separating cryptoxanthol from neo-cryptoxanthol and might be expected to separate  $\beta$ -carotene from neo- $\beta$ -carotene. However, they did not report neo- $\beta$ -carotene in their corn extracts. They identified their  $\alpha$ -carotene spectrophotometrically and by mixed chromatography. In this connection, it should be pointed out that

Gillam and El Ridi<sup>5</sup> were unable to distinguish spectroscopically between  $\alpha$ -carotene and neo- $\beta$ -carotene. They found that  $\alpha$ -carotene and neo- $\beta$ -carotene formed a single zone when adsorbed on alumina from the carotene fraction of butter.<sup>19</sup> Examination of the spectra of  $\alpha$ -carotene and neo- $\beta$ -carotene by a very sensitive photoelectric spectrophotometer<sup>10,11</sup> shows that they can be differentiated spectroscopically with an instrument of sufficient accuracy. The experience of Gillam and El Ridi illustrates that failure of a mixture of two compounds to form two zones on a given adsorbent does not necessarily indicate that the compounds are identical. The writers consider it possible that the pigment identified by Fraps and Kemmerer as  $\alpha$ -carotene might have been neo- $\beta$ -carotene.

### Summary

1. Luteol,  $\gamma$ -carotene and a compound tentatively identified as a hydroxy- $\alpha$ -carotene were found in yellow corn grain for the first time.
2. A compound having some properties like Fraps and Kemmerer's K carotene was also separated from yellow corn grain.
3. Preliminary quantitative absorption spectra of neocryptoxanthol and two neozeaxanthol isomers are presented.

(19) A. E. Gillam and M. S. El Ridi. *Nature*, **136**, 914 (1935).

LAFAYETTE, INDIANA

RECEIVED JUNE 24, 1942

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

## The Malonic Ester Synthesis and Walden Inversion

BY WILLIAM E. GRIGSBY,<sup>1</sup> JOHN HIND, JACOB CHANLEY AND F. H. WESTHEIMER

It has been suggested recently that the reaction of alkyl halides and olefin oxides with the sodium salt of malonic ester is an example of the normal displacement reaction.<sup>2,3</sup> If this is the case, the reaction should proceed with Walden inversion about the carbon atom to which the halogen (or oxygen) atom is attached. An experimental demonstration of this inversion has now been established for the reaction of cyclopentene oxide with sodium malonic ester.

In all the previously known reactions of sodium

malonic ester with an oxide—ethylene oxide,<sup>4</sup> epichlorhydrin,<sup>4</sup> cyclohexene oxide<sup>5</sup> and others<sup>6</sup>—the reaction product is a lactone. With ethylene oxide, for example, the product is  $\alpha$ -carbethoxy- $\gamma$ -butyrolactone. If the reaction with cyclopentene oxide had proceeded without inversion, the product would have been the lactone of the mono-

(4) Traube and Lehmann, *Ber.*, **34**, 1971 (1901).

(5) Coffey, *Rec. trav. chim.*, **42**, 387 (1923).

(6) Kötze and Hoffman, *J. prakt. Chem.*, **110**, 101 (1925); Rothstein, *Bull. soc. chim.*, [5] **2**, 1936 (1935); Haller and Blanc, *Compt. rend.*, **142**, 1471 (1906). The reactions recorded in the literature were carried out between equimolar quantities of oxide, malonic ester, and sodium ethylate. However, repetition of the work of Traube and Lehmann, using two moles of malonic ester for each mole of sodium ethylate, showed that, in this case, excess malonic ester is without effect on the composition of the product obtained.

(1) Du Pont Fellow, 1941-1942.

(2) Hind, Dissertation, Chicago, 1939.

(3) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chap. VI, see also p. 143.

ethyl ester of *cis*-cyclopentanol-2-malonic acid (VI). In actual fact, inversion occurred and the product proved to be the diethyl ester of *trans*-cyclopentanol-2-malonic acid (II). Lactone formation in this case was precluded, since it would involve fusing two five-membered rings together in the *trans*-positions. Such a configuration involves a great deal of strain, and has been accomplished only once, and then with a carbocyclic compound.<sup>7</sup>

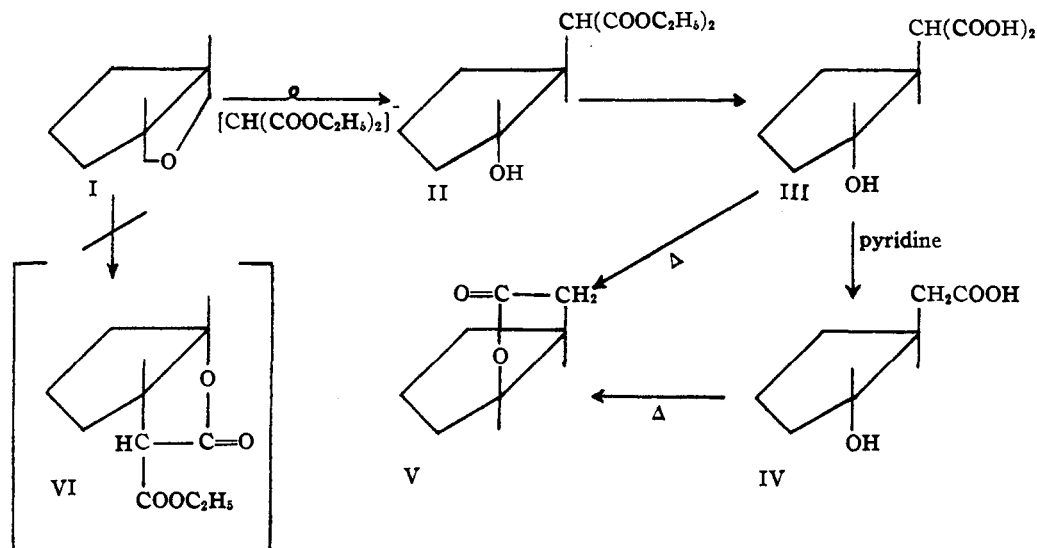
It is interesting to contrast the behavior of cyclopentene oxide with that of cyclohexene oxide. When cyclohexene oxide reacts with equivalent quantities of malonic ester and sodium ethylate, a lactone is formed.<sup>8</sup> No stereochemical conclusion can, however, be drawn from this fact. Many examples are known in which a six and a five membered ring are fused together in the *trans* positions.<sup>8</sup> As a matter of fact, lactones of both the *cis*- and the *trans*-cyclohexanol-2-acetic acids are known.<sup>9</sup>

Under favorable experimental conditions, the reaction between cyclopentene oxide and sodium malonic ester gave a 70–75% yield of the *trans*-diester. The ester was a liquid which could be purified by molecular distillation; saponification equivalent, and carbon, hydrogen and ethoxyl analyses all clearly showed that the compound was the *trans*-diester, II, not the *cis*-lactone, VI.

ture and configuration of which are known. On refluxing with dilute alkali, the ester was converted into the salt of a diacid. The acid was obtained in 80–90% yield as a crystalline solid which evidently did not contain water of crystallization. The analytical data agree with those calculated for *trans*-cyclopentanol-2-malonic acid (III), but are not in agreement with those for the corresponding *cis*-lactone. It seems improbable that the saponification altered the configuration of the molecule, since there was no asymmetric carbon atom in a position alpha to a carbonyl group; inversion by enolization is therefore ruled out.<sup>10</sup>

The *trans*-diacid was decarboxylated by refluxing for ten minutes in pyridine solution; carbon dioxide and *trans*-cyclopentanol-2-acetic acid (IV) were obtained in excellent yields. By neutral equivalent, melting point, solubility behavior and analysis, the compound was shown to be identical with that previously prepared by an entirely independent method by Hückel and Gelmroth.<sup>11</sup> The configuration of this acid is not in doubt; the corresponding *cis*-compound exists only in the form of a lactone (V), melting at  $-14^{\circ}$ .<sup>12</sup>

Evidence that the decarboxylation does not involve a change in configuration is offered by the fact that the lactone (V) of *cis*-cyclopentanol-2-acetic acid can be heated with pyridine and subsequently recovered unchanged.



The fact that the liquid ester was *trans* was confirmed by transforming it to a derivative the struc-

While the reactions outlined above almost cer-

(7) Linstead and Meade, *J. Chem. Soc.*, 935 (1934).

(8) Baeyer, *Ann.*, **268**, 145 (1890); Windaus, Hückel and Reverey, *Ber.*, **56**, 91 (1923); Cook and Linstead, *J. Chem. Soc.*, 956 (1934); Hückel and Friedrich, *Ann.*, **451**, 132 (1927).

(9) M. Newman, private communication.

(10) Hammett, *op. cit.*, Chap. VIII.

(11) Hückel and Gelmroth, *Ann.*, **514**, 233 (1934).

(12) Only in the case of a beta lactone has ring opening accompanied by Walden inversion been observed; Olson and Miller, *This Journal*, **60**, 2687 (1938); see also Day and Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941).

tainly did not involve a change in configuration, it is possible by more drastic means to rearrange the *trans*-compounds to the *cis*. Prolonged pyrolysis of the *trans*-diacid (fifty hours at 160°) was necessary to cause decarboxylation in the absence of pyridine and the product obtained was V, the lactone of *cis*-cyclopentanol-2-acetic acid. Under similar conditions, *trans*-cyclopentanol-2-acetic acid (IV) rearranged to the *cis*-lactone (V). The mechanism of this rearrangement may involve the acid-catalyzed dehydration of an hydroxy acid, followed by lactonization of the olefinic acid; it is possible, however, that the isomerization occurred without the actual formation of the unsaturated compound.

The series of reactions outlined above clearly shows that the reaction between cyclopentene oxide and sodium malonic ester occurs with Walden inversion. The facts are, therefore, consistent with the hypothesis that the reaction is a nucleophilic displacement on carbon involving the malonic ester anion  $(C_2H_5O_2CCHCO_2C_2H_5)^-$ . This general theory is also supported by the older observation of Wislicenus<sup>13</sup> that sodium malonic ester reacts much more readily with primary than with secondary halides.<sup>14</sup>

While the results of the present investigation were quite satisfactory, some experimental difficulties encountered during the research are worth discussing.

An interesting phenomenon was noticed regarding the saponification of the diester, II. The saponification took place more readily with dilute than with concentrated alkali, although of course complete saponification always led to the formation of the *trans*-diacid (III). Michael<sup>15</sup> noted a similar peculiarity in the saponification of some other mono substituted malonic esters, and Goldschmidt and Oslan<sup>16</sup> successfully explained why the rate of saponification of acetoacetic ester is independent of the alkali concentration.

It is also necessary to call attention to the fact that, in the reaction between sodium malonic ester and cyclopentene oxide, good yields were obtained only in alcoholic solution and in the presence of excess malonic ester. When benzene was used as a solvent, the yield fell to 30%. Furthermore, unless two molar equivalents of malonic ester were used, none of the pure *trans*-

diester could be isolated, and neither the configuration nor the structure of the products obtained has yet been established.

It is a fact, however, that reactions of sodium malonic ester are frequently improved by the addition of malonic ester. In the condensations with either halides or oxides, excess malonic ester greatly increases the yield of monosubstitution product,<sup>17</sup> while the abnormal Michael<sup>18</sup> reaction occurs only when the amount of sodium present is equivalent to the malonic ester used. It seems probable that the malonic ester functions as an acid, and removes the reactive anion of the substituted malonic ester from solution. This explanation seems reasonable in the present case, since experiments showed that the anion of *trans*-cyclopentanol-2-malonic ester decomposed on refluxing in alcohol. Although its decomposition did not give the same products as were obtained from the cyclopentene oxide reaction without excess malonic ester, the instability of the anion was evident.

### Experimental

**Reaction of Sodium Malonic Ester with Cyclopentene Oxide.**—About 125 cc. of absolute ethanol and 2.3 g. (0.1 mole) of sodium were placed in a 500-cc. three-necked flask, to which were attached a dropping funnel and a reflux condenser fitted with a calcium chloride tube. When all the metal had reacted, 31.5 g. (0.2 mole) of malonic ester was added. The solution was refluxed, 8.4 g. (0.1 mole) of cyclopentene oxide<sup>19</sup> was added over a period of an hour, and the solution refluxed for an additional three hours. The ethanol was removed by distillation, and a quantity of 10% sulfuric acid was added which was equivalent to the sodium used. The sodium sulfate was filtered and washed with ether, and the filtrate was extracted three times with ether. The combined ether extracts were washed, the ether distilled, and the excess malonic ester removed by vacuum distillation. The residue of pale yellow, crude *trans*-cyclopentanol-2-malonic ester corresponded to a yield of 70–75% and had a saponification equivalent of 110–115.<sup>20</sup> For identification and characterization, it was purified by molecular distillation in a Hickman still. At a pressure of  $10^{-4}$  mm., a colorless oil came over at 75°; if the pressure rose to  $10^{-2}$  mm., the product passed over at 150–160° with slight decomposition.

*Anal.* Calcd. for  $C_{12}H_{20}O_5$ (II): C, 58.98; H, 8.20;  $C_2H_5O$ , 36.86; sap. eq., 122. (Calcd. for  $C_{10}H_{14}O_4$ (V): C, 60.58; H, 7.12;  $C_2H_5O$ , 22.72; sap. eq., 99.) Found: C, 59.01, 59.43; H, 7.93, 8.00;  $C_2H_5O$ , 37.01; sap. eq.,

(17) Leuchs, *ibid.*, **44**, 1507 (1911); see also Cohen, Marshall and Woodman, *J. Chem. Soc.*, **107**, 887 (1915); and Brigl, *Z. physiol. Chem.*, **95**, 161 (1915).

(18) Michael and Ross, *THIS JOURNAL*, **52**, 4598 (1930).

(19) Verkade, Coops, Maan and Verkade-Sandbergen, *Ann.*, **467**, 217 (1928).

(20) Mulliken, "The Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1904, Vol. I, p. 111.

(13) Wislicenus, *Ann.*, **212**, 239 (1882).

(14) Hammett, *op. cit.*, pp. 152–154.

(15) Michael, *J. prakt. Chem.*, [2] **72**, 537 (1905).

(16) Goldschmidt and Oslan, *Ber.*, **32**, 3309 (1899).

120, 122;  $n_D^{20}$  1.4564;  $d_{21.5}^{40}$ , 1.109. The micro Zeisel analysis was performed by Dr. J. A. Alicino, Fordham University, New York, N. Y.

A similar reaction, carried out with benzene as solvent, gave a 27% yield of diester (II), identified by saponification, and isolation of the diacid, (III).

**Saponification of the Diester, II.**—The diester was saponified by refluxing the crude, undistilled ester for four hours with twice the calculated amount of 1.0 *N* sodium hydroxide. An amount of hydrochloric acid exactly equivalent to the sodium hydroxide was then added to this solution. Since it was impossible to extract the acid, because of its great solubility in water, the solution was evaporated to dryness *in vacuo* at room temperature. Unless solutions of the free acid were kept cool, they showed a marked tendency to precipitate out an insoluble polymer. The dry salt-cake was extracted with acetone and the acetone evaporated *in vacuo* at room temperature, leaving a 95% yield of a colorless oil. On stirring with benzene, this oil solidified (yields of 90% were obtained using only 1 g. of ester). The crude powder melted 20–30° lower than the best material finally obtained. The compound was difficult to recrystallize because it was extremely soluble in water, methanol, ethanol, acetone, ether and dioxane, was insoluble in benzene, chloroform, and ligroin, and precipitated as an oil from mixed solvents. However, it was possible to effect a purification by dissolving the compound in the minimum quantity of ethyl acetate or amyl alcohol, centrifuging to remove insoluble matter, and then removing most of the solvent with a stream of dry air. After a few days, the crystals were centrifuged, rapidly washed several times with ethyl acetate, and dried *in vacuo*. The melting point, after several recrystallizations from ethyl acetate, was 118.4–118.7° (with dec., cor.). Before analysis, the purified crystals were dried for a week in a vacuum desiccator over phosphorus pentoxide or over sulfuric acid. In no case did drying affect the melting point or neutral equivalent.

The yield on the recrystallization of the crude diacid was only about 50%; it seems reasonable to assume, however, that the crude material was essentially pure. The crude acid had a neutral equivalent which did not change on recrystallization and which was close to the theoretical value. Furthermore, subsequent decarboxylation gave yields of 80% of pure *trans*-cyclopentanol-2-acetic acid.

*Anal.* Calcd. for  $C_8H_{12}O_5$  (III): C, 51.04; H, 6.39; neut. eq., 94.0. Found: C, 51.27; H, 6.49; neut. eq. (semi-micro), 94.9, 95.0.

**Saponification with Concentrated Alkali.**—About 1.2 g. of *trans*-cyclopentanol-2-malonic ester (II) was refluxed for nine hours with twice the calculated amount of 5.5 *N* sodium hydroxide. The acid recovered from this treatment had a neutral equivalent of 136, and a saponification equivalent of 99. Further saponification with 1.0 *N* alkali gave an 85% yield of solid *trans*-diacid, (III).

**Decarboxylation.**—One gram of crude diacid was dissolved in 10 cc. of pyridine, refluxed for ten minutes, and then poured into slightly more 1 *N* sodium hydroxide than the amount calculated for the neutralization of the resulting acid. The pyridine and water were removed at room temperature, and the residue acidified with an amount of

1 *N* hydrochloric acid which was exactly equivalent to the alkali previously added. The water was removed *in vacuo*, and the residue extracted with acetone. The extract was filtered, and the acetone removed at reduced pressure, to avoid polymerization of the acid.<sup>11</sup> This gave an 80% yield of an oil which solidified on scratching. The reported melting point for the *trans*-acid (IV) is 52.5–53.5°. The observed melting point of the recrystallized acid was 53.3–54.3° (cor.).

*Anal.* Calcd. for  $C_7H_{12}O_3$  (IV): C, 58.29; H, 8.40; neut. eq., 144.1 (calcd. for  $C_7H_{10}O_3$  (VI): C, 66.67; H, 7.94; neut. eq., 126). Found: C, 58.30; H, 8.00; neut. eq. (semi-micro), 145.9, 145.6.

**Treatment of *cis*-Cyclopentanol-2-acetic Acid Lactone with Pyridine.**—A solution of 0.5 g. of the lactone in several cc. of pyridine was refluxed for fifteen minutes. Five cc. of 1 *N* sodium hydroxide was added, and the refluxing continued for another fifteen minutes. After evaporation to dryness, acid was added and the lactone recovered unchanged.

**Thermal *trans*-*cis* Isomerization.**—Two grams of crude *trans*-cyclopentanol-2-malonic acid was heated for fifty hours at 160°. After two vacuum distillations, 0.6 g. of *cis*-cyclopentanol-2-acetic acid lactone was obtained. The material melted at –14°, while Hückel and Gelmroth<sup>11</sup> reported –17°. When 1.5 g. of *trans*-cyclopentanol-2-acetic acid was heated in a similar fashion and distilled twice, the resulting product, in 40% yield, was the same lactone. These samples of lactone were further identified by boiling point, saponification equivalent, analysis, and by determining the melting point of a mixture of the compound with a sample prepared according to Hückel and Gelmroth.<sup>11</sup>

**Reaction without Excess Malonic Ester.**—The reaction was carried out as previously described, except that two molar proportions of sodium and malonic ester were used for one of cyclopentene oxide, or else equal proportions of all reactants were used. The product in this case was obtained in only 20–40% yields, and had a saponification equivalent of 165. After prolonged saponification, the resulting acid was partitioned between benzene and water. The water layer contained an acid of neutral equivalent 120–140, while the benzene soluble portion of the mixture had a neutral equivalent of about 200. Clearly, the saponification product was a mixture. The products obtained here have not yet been identified.

**Stability of the Anion of the Diester (II).**—A gram of *trans*-cyclopentanol-2-malonic ester was dissolved in absolute alcohol, 0.1 g. of sodium added, and the solution refluxed for two hours. At the end of this period of time, only 25% of the *trans* diester could be recovered; the rest had been converted into water soluble compounds. If the solution was refluxed for seven hours, the recovery was only 8%.

## Summary

1. A stereochemical study of the reaction of sodium malonic ester with cyclopentene oxide in the presence of excess malonic ester has shown that the reaction involves Walden inversion about one of the carbon atoms of the oxide ring.

2. This is the result which would be anticipated if the reaction proceeded by the usual mechanism for displacement reactions.

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RECEIVED JULY 23, 1942

[CONTRIBUTION FROM THE SANDERS LABORATORY OF CHEMISTRY, VASSAR COLLEGE]

## The Sorption of Carbon Monoxide by Metals. Temperature Variation Experiments

BY CARROLL W. GRIFFIN

### Introduction

The identification of two types of adsorption, namely, physical and activated, has been definitely established for gases on many solids. The existence of a third sorptive force has long been suspected and that this might be solution was mentioned by the author in the case of hydrogen and massive copper.<sup>1</sup> Further evidence to support this belief was obtained in studies of the sorption of hydrogen on supported copper,<sup>2</sup> on massive nickel,<sup>3</sup> on supported nickel,<sup>4</sup> and particularly by the "experiments with temperature variation."<sup>5</sup> In the last two studies the attack has consisted of bringing the gas into sorptive equilibrium with the metal at  $-78.5^{\circ}$ , raising the temperature to  $0^{\circ}$  and, after measuring the equilibrium conditions, returning the temperature to  $-78.5^{\circ}$ . In this manner it was revealed that the sorption at  $-78.5^{\circ}$  is followed first by a rapid desorption at  $0^{\circ}$  and then by a slower process (solution) at  $0^{\circ}$ . Upon cooling again to  $-78.5^{\circ}$  the sorption is found to be greater than the original sorption at this temperature to an extent equal to the volume slowly taken up at  $0^{\circ}$ .

The success of this method of study of course depends upon selecting two temperatures, one at which the secondary sorptive force, thought to be solution, is absent or is at a minimum, and the other at which it manifests itself distinctly. The amount of solution, and not simply its rate, will be greater at the higher temperature and also at higher pressures. These facts hold for the studies already cited.

It is obvious that  $-78.5$  and  $0^{\circ}$  might not always be the temperature at which the two sorptive forces would distinguish themselves best. Thus, although Benton and White do not specifically so label the experiment immediately under their

Table IV,<sup>6</sup> this is really a run "with temperature variation," the variation here being from  $110$  to  $210^{\circ}$ . In connection with their study of carbon monoxide on massive copper it might be emphasized that the authors did not find, after noting the desorption coming with the elevated temperature, any resorption (solution) as evidenced by a drop in pressure. Yet, when the temperature was again brought to  $110^{\circ}$ , the sorption of carbon monoxide amounted to  $15.00$  ml. as compared with an original  $14.43$  ml. It therefore seems, in the writer's opinion, since  $0.57$  ml. is more than ten times their experimental error, that actually solution of over half a milliliter did take place at  $210^{\circ}$ , in excess of any dissolved at  $110^{\circ}$ , but it occurred simultaneously with the desorption of the activated carbon monoxide molecules and *was overshadowed by the desorption*. For as long as both processes are taking place and the rate of desorption exceeds the rate of solution there can be no observable evidence of the latter, save the greater total sorption when return is made to the lower temperature. Only when the desorption at the higher temperature is completed quickly or is relatively small may one observe the pressure reversal which indicates that solution is taking place.

Sorption studies with temperature variation have been confined to hydrogen on metals with the exception that Benton and White have shown the general behavior of carbon monoxide on massive copper. Therefore, the present work was undertaken to learn whether or not the effects observed with hydrogen are common also to other gases. Platinum and copper were the metals selected and, since little or no solution can be expected with supported metals, both forms have been employed with platinum. With copper only the supported metal was used. Since it has already been shown that solution of carbon monoxide in massive copper becomes appreciable only above  $0^{\circ}$ , the temperatures selected for the supported copper

(1) Griffin, *THIS JOURNAL*, **49**, 2136 (1927).

(2) Griffin, *ibid.*, **57**, 1206 (1935).

(3) White and Benton, *J. Phys. Chem.*, **35**, 1784 (1931).

(4) Griffin, *THIS JOURNAL*, **61**, 270 (1939).

(5) Benton and White, *ibid.*, **54**, 1373 (1932); Griffin, *ibid.*, **63**, 2957 (1941).

(6) Benton and White, *ibid.*, **54**, 1373 (1932).