

check with the supposed existence of two hydroxyl groups.

Further evidence for the existence of at least two hydroxyl groups is based upon the observation that the physiological activity of pantothenic acid was 98% destroyed by allowing it to stand in the presence of acetaldehyde-hydrochloric acid (1%) solution for sixteen hours at room temperature. This activity was in part recovered (50%) by acidic hydrolysis. Similar destruction and recovery was effected by using acetone or benzaldehyde in place of acetaldehyde. This strongly suggests that condensation products similar to the well-known acetone glucose were formed. This type of condensation can take place with α , β -, α , γ - or α , δ -glycols.¹²

The basic property of pantothenic acid is so low that the argument previously presented¹³ still holds. Pantothenic acid is not strong enough as an acid to be an alpha hydroxy acid. Furthermore, the ferric chloride test for α -hydroxy

(12) Hibbert, *et al.*, *THIS JOURNAL*, **46**, 1286, (1924).

(13) Williams and Moser, *ibid.*, **56**, 169 (1934).

acids^{14,15} was applied to purified calcium pantothenate with negative results.

We gratefully acknowledge the generous financial assistance of Standard Brands, Inc., of New York, of the National Research Council, and finally of the Rockefeller Foundation, whose substantial grant made the intensive study possible.

Summary

Oxidation equivalent analysis data and combustion analysis data agree with the formula $(C_8H_{14}O_5N)_2Ca$ for the calcium salt of pantothenic acid. Studies directed toward the determination of constituent groups indicate the presence in the molecule of one carboxyl group, two hydroxyl groups and probably a substituted amide group. The absence of amino, imino, tertiary amine, simple amide, methoxyl, methyl imino, olefinic, aldehydic, ketonic and aromatic groups is likewise indicated.

(14) Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1910, Vol. I, p. 78.

(15) Berg, *Bull. soc. chim.*, [3] **11**, 883 (1894).

CORVALLIS, OREGON

RECEIVED DECEMBER 3, 1938

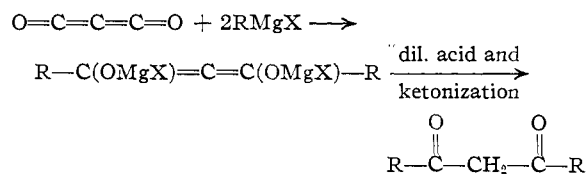
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reaction of Carbon Suboxide with Methylmagnesium Iodide

BY JOHN H. BILLMAN AND CARL M. SMITH

A survey of the reactions of carbon suboxide¹ shows that on treatment with water, alcohols, thiols, ammonia, amines, hydroxylamine, hydrazines, and halogens, the expected derivatives of malonic acid are formed in each case. However, its reaction with organomagnesium halides, where its dual ketene nature should lead to interesting products, has not been investigated previously.

It might be expected that carbon suboxide would react with two moles of Grignard reagent to give an intermediate addition product which on hydrolysis would produce a 1,3-diketone.



However, actually on treating an ether solution of methylmagnesium iodide with carbon suboxide

in dry ether, no acetylacetone could be obtained from the addition product even though the Grignard reagent was present in excess throughout the major portion of the reaction. The only crystalline solid that was isolated melted at 155°. Analysis and molecular weight gave an empirical formula of $C_{12}H_{12}O_6$. The chemical properties of this compound suggested that it might be triacetophloroglucinol. Accordingly a sample of the compound described by Heller² and by Gösche and Tambor³ as triacetophloroglucinol was synthesized. A comparison of the synthetic and the isolated compound was made and they were found to be identical.

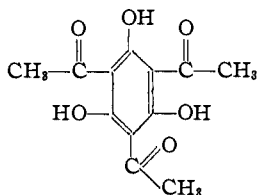
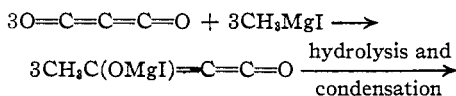
It was noted that during the reaction a precipitate formed. This addition compound upon hydrolysis was converted to triacetophloroglucinol. Because of the formation of this latter compound it is obvious that only one mole of methylmagnesium iodide reacted with each mole

(1) Reyerson and Kobe, *Chem. Rev.*, **7**, 479 (1930).

(2) Heller, *Ber.*, **45**, 418 (1912).

(3) Gösche and Tambor, *ibid.*, **45**, 1237 (1912).

of carbon suboxide even in the presence of an excess of the Grignard reagent.



The preparation of the substituted phloroglucinol is another example of the formation of an aromatic compound from simple aliphatic molecules.

An extension of this reaction, the identification of the other compounds found and a study of its mechanism are in progress.⁴

Experimental

An ether solution of carbon suboxide was prepared by heating malonic acid with phosphorus pentoxide, using the apparatus and procedure of Stock and Stoltzenberg.⁵ The solution was kept in a large test-tube in a Dewar containing acetone and dry ice. To an ether solution of methylmagnesium iodide prepared in the ordinary way from 0.195 mole (27.5 g.) of methyl iodide and 0.195 mole (4.7 g.) of magnesium in a total of 200 cc. of ether the carbon suboxide solution was added in small portions at such a rate that the temperature in the reaction flask did not rise above 7°. Cooling was maintained with an ice-salt bath. A brilliant orange-yellow precipitate formed immediately; it grew darker to a bright vermilion as more carbon suboxide was added. When a negative test for the Grignard reagent⁶ was obtained, the ice-salt bath was removed and stirring continued for ten minutes. The addition product was then decomposed with 50 cc. of water followed by a solution of 25 cc. of sulfuric acid in 150 cc. of water. The ice-bath was replaced during the hydrolysis. The ether layer was separated and the water layer extracted six times with 25-cc. portions of ether. The combined ether layer and extracts were then shaken first with dilute thiosulfate to remove the free iodine and finally with dilute sodium bicarbonate solution. The ether was

(4) After submitting this paper, we were informed that Dr. L. H. Reyerson and Dr. K. M. Kobe had run a phenyl Grignard on carbon suboxide and had obtained a white solid which they did not identify.

(5) Stock and Stoltzenberg, *Ber.*, **50**, 498 (1917).

(6) Gilman and Schulze, *This Journal*, **47**, 2002 (1925).

then dried over anhydrous sodium sulfate. A portion of the ether extract failed to form a copper salt when shaken with saturated cupric acetate solution. The whole ether solution was evaporated to dryness under reduced pressure using water at room temperature as a source of heat. Four and one-tenth grams of fine brown crystals, melting at 146–147°, was obtained, corresponding to 24% of the theoretical yield. Solution in a slight excess of cold dilute alkali, followed by fractional precipitation by acid and recrystallization of the amorphous precipitate from methyl alcohol gave a white solid, melting at 152° (I). The product in this form gives excellent analytical results, but recrystallization from benzene raises the melting point to 155°. The melting point of C-triacetophloroglucinol according to Göschke and Tambor³ and Heller² is 156°. Triacetophloroglucinol prepared in 64% yield by the method of Göschke and Tambor,³ after recrystallization from benzene, melted at 155°. A mixed melting point with I and the above authentic specimen melted at 155°.

Anal. Calcd. for C₁₂H₁₂O₆: C, 57.14; H, 4.76; mol. wt., 252. Found: C, 57.26; H, 4.76; mol. wt., 259.

Three-tenths of a gram of I dissolved in 20 cc. of 1 N sodium hydroxide was warmed for five minutes at 40–50°. One drop of 2 N sulfuric acid in excess of the amount needed to cause the solution to become cloudy was added and the solution filtered. The dark brown precipitate melted at 146–147°; after recrystallization from benzene a mixed melting point showed it to be unchanged (I). Excess 2 N acid was then added to the solution and the precipitate filtered off. It was very soluble in methyl alcohol; water was added to the methyl alcohol solution and the more volatile solvent was boiled off, giving 0.21 g. of fine white needles, melting at 166–168°. Recrystallization from carbon tetrachloride raised the melting point to 169.5–170°. The mixed melting point of this compound with authentic diacetophloroglucinol, produced by following the above procedure for alkaline splitting, was 169–170°. Heller² gives the melting point of diacetophloroglucinol as 168°.

Anal. Calcd. for C₁₀H₁₀O₆: C, 57.14; H, 4.76. Found: C, 57.12; H, 4.78.

Summary

1. It has been shown that in the presence of an excess of methylmagnesium iodide only one mole has reacted with one mole of carbon suboxide.
2. Triacetophloroglucinol has been isolated from a reaction mixture of methylmagnesium iodide and carbon suboxide.

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RECEIVED DECEMBER 2, 1938