

in a solution of 2.3 g. of aluminum bromide¹¹ in 47 ml. of dry benzene. The aluminum complex was hydrolyzed by pouring the reaction mixture into a slush of 400 g. of crushed ice and 50 ml. of concentrated hydrochloric acid. The mixture was washed on the steam-bath for 20–30 minutes, cooled, and ether added until two phases separated. The benzene-ether phase was separated and the aqueous phase extracted twice with 25-ml. portions of ether. The benzene-ether phase and the ethereal extracts were combined, washed with water, and dried over anhydrous sodium sulfate. The ether was removed by warming on the steam-bath, and then the remaining benzene solution was concentrated to a small volume. Upon diluting with low-boiling petroleum ether, sandy pink crystals of the lactone (II) crystallized. The yield was 0.37 g., m.p. 192–193°; after two crystallizations (charcoal) from benzene-petroleum ether, m.p. 192.5–193.5°.

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.45; H, 4.67. Found: C, 79.75; H, 4.84.

Diphenyl-*o*-hydroxyphenoxyacetic Acid Lactone (III).—In a 250-ml. round-bottomed flask fitted with a reflux condenser and calcium chloride drying tube were placed 19.0 g. (0.072 mole) of diphenylchloroacetyl chloride, 7.9 g. (0.072 mole) of catechol and 60 ml. of dry acetone. To this solution was added, in small portions, 9.9 g. (0.072 mole) of freshly ignited, finely powdered potassium carbonate. After the mixture ceased evolving carbon dioxide, it was boiled under reflux for 6 hours. The light yellow reaction mixture, which contained some insoluble material, was cooled and enough water (100 ml.) added to dissolve the water-soluble salts present. On further dilution with cold water, a yellow precipitate settled out which was collected on a buchner funnel. A semi-solid yellowish-brown oil was removed from the solid material by working with a spatula.

(11) C. Weygand, "Organic Preparations," Interscience Publishers, Inc., New York, N. Y., 1945, p. 196.

The oil and the filtrate, which also contained oily material, were combined, extracted with a total of 125 ml. of ether, and the ethereal extract washed with four 50-ml. portions of 5% sodium carbonate solution followed by four 50-ml. portions of water. The solid material was similarly treated. All ethereal extracts were combined, dried over anhydrous sodium sulfate and the ether evaporated to a small volume. On cooling the solution, large six-sided prisms separated. These were recrystallized from ether to yield 5.5 g. (25%) of the ether-lactone (III), m.p. 136–137.5°. No depression of the melting point was observed on admixture with the substance obtained from the reaction of diphenylketene with *o*-benzoquinone, or with the product obtained from catechol and benzoic acid.

The action of hydriodic acid on III yielded diphenylacetic acid and catechol. One gram of III was boiled 2.5 hours with 30 ml. of hydriodic acid and 30 ml. of glacial acetic acid. The solution was cooled and saturated sodium bisulfite solution added to remove iodine. The precipitate which formed upon addition of water was collected and dried overnight. There was obtained 0.61 g. of diphenylacetic acid, m.p. 146–148°, m.m.p. 146–147.5°. The filtrate was extracted five times with 25-ml. portions of ether and the ethereal extract shaken with a globule of mercury. After removal of the ether, there remained a sirupy yellow liquid which was dissolved in 5 ml. of water and treated dropwise with 10% potassium hydroxide solution until a slight excess was present. Ice was added to the alkaline solution and then 0.7 ml. of acetic anhydride poured in as quickly as possible. The mixture was shaken vigorously until the catechol diacetate precipitated. It was collected, washed thoroughly with water, dried and crystallized twice from a small quantity of 70% alcohol. The yield of catechol diacetate was 0.21 g., fine white needles, m.p. 62–63°, m.m.p. 62–62.5°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Chemistry of Carbon Suboxide. I. Reaction with Phenylmagnesium Bromide

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When phenylmagnesium bromide reacts with carbon suboxide in equal molar proportions, there is formed upon decomposition of the complex, acetophenone, 3-benzoyl-6-phenyl-1,2-pyran-2,4(3H)-dione (II) and 2,4,6-trihydroxytrimesophenone (III). All three compounds probably have benzoylketene or an analogously constituted Grignard complex as a common precursor, II being a dimer and III a trimer of this ketene. When phenylmagnesium bromide and carbon suboxide react in a two-to-one molar proportion, respectively, and the resulting complex is decomposed, there results benzophenone, triphenylcarbinol and β,β -diphenylhydracrylic acid. Five other unidentified compounds were isolated from the reaction mixture and characterized: $C_{15}H_{10}O_2$, $C_{18}H_{12}O_2$, $C_{27}H_{18}O_3$, $C_{36}H_{14}O_2$ and $C_{18}H_{18}O_4$.

The reaction of carbon suboxide with methylmagnesium iodide was studied by Billman¹ who reported the isolation of triacetylphloroglucinol as a product of the union of three moles of each of the two reactants. The current investigation was undertaken to explore further the reaction of the Grignard reagent with this oxide of carbon.

The addition of carbon suboxide to phenylmagnesium bromide produced a complex, decomposition of which gave a mixture from which were isolated acetophenone, β,β -diphenylhydracrylic acid (I), benzophenone, triphenylcarbinol, 3-benzoyl-6-phenyl-1,2-pyran-2,4(3H)-dione (II), 2,4,6-trihydroxytrimesophenone (III), diphenyl and five unidentified compounds: $C_{15}H_{10}O_2$, $C_{18}H_{12}O_2$, $C_{27}H_{18}O_3$, $C_{36}H_{14}O_2$ and $C_{18}H_{18}O_4$. The unidentified compounds have been characterized. Although the balance of products appeared to differ when the proportion of oxide to Grignard reagent was varied,

the nature of the products did not change markedly.

The course of the reaction becomes apparent from the compounds that were isolated and identified. The first mole of Grignard reagent added to carbon suboxide to produce an ion-pair of indeterminate geometry, the anion being a resonance hybrid. Decomposition of this complex with acid probably produced benzoylactic acid which decarboxylated under the conditions of the reaction to give acetophenone. The presence of I among the products indicates that when two moles of Grignard reagent become involved with one mole of carbon suboxide, one mole must have added one-two and the other added one-four² to the oxide molecule. Apparently the complex formed from two moles of Grignard reagent was unstable and partially decomposed in the dry ether solution to benzophenone, which

(2) The two negative charges would tend to become distributed as far as possible from one another in the anion of the double complex that was formed.

(1) J. H. Billman and C. Smith, *THIS JOURNAL*, **61**, 457 (1939).

under nitrogen in 300 ml. of dry ether and cooled to 0° in an ice-bath. A Dry Ice condenser was substituted for the water condenser, and 24 ml. of carbon suboxide (0.358 mole) in 100 ml. of ether was added slowly from a pressure-equalizing dropping funnel. A yellow precipitate formed immediately and gradually darkened, becoming dark red and gummy by the end of the 45-minute time of addition. The mixture was stirred for 18 hours at room temperature and then decomposed with 350 ml. of water saturated with ammonium chloride. The first few drops produced vigorous refluxing even with an ice-bath, and slow refluxing continued throughout the addition. After the resulting mixture had been stirred for several hours at room temperature, the dark red ether solution was decanted and the viscous magnesium salts were washed with ether. The combined extracts were concentrated to 500 ml., extracted four times with 50-ml. portions of a 5% sodium bicarbonate solution (combined extracts, fraction 1a), and similarly extracted with a 5% sodium carbonate solution (fraction 1b) and a 10% sodium hydroxide solution (fraction 1c). The remaining ether solution was dried and evaporated.

The magnesium salts from the decomposed Grignard reaction were dissolved in 1.5 liters of 4% sulfuric acid solution, and this solution was extracted three times with 200-ml. portions of methylene chloride. The combined methylene chloride extracts were treated analogously to the ether extracts to give four fractions, 2a, 2b, 2c and 2d. Basic fractions 1a, 1b, 1c and 2a, 2b, and 2c were acidified, and the non-soluble materials that separated were crystallized from organic solvents. Fractions 1d and 2d were evaporated to give 35 g. and 22 g. of red oil, respectively.

From fractions 1a, 1b, 2a and 2b was isolated 0.45 g. of recrystallized (ether) β,β -diphenylhydracrylic acid, m.p. 210.5–212°, undepressed by admixture with an authentic sample.⁷ From fractions 1c, 2a and 2b was isolated by crystallization from ethanol, 0.28 g. of 3-benzoyl-6-phenyl-1,2-pyran-2,4(3H)-dione, m.p. 169–170°, undepressed by admixture with an authentic sample.⁸ Fraction 2b gave 0.1 g. of 2,4,6-trihydroxytrimesophenone, isolated by fractional crystallization from ethanol, m.p. 183–184°, undepressed by admixture with an authentic sample.⁹

The oils from fractions 1d and 2d were combined and half of the total weight was submitted to chromatographic absorption on an acid-washed alumina column (pH 5) made up in benzene. Benzene, ether and alcohol were successively used as eluants, and the column filtrates were collected as fractions and evaporated. From the first benzene fractions was crystallized 3.9 g. of biphenyl, m.p. 68–69°, undepressed by admixture with an authentic sample. From the second benzene fraction was isolated 14.1 g. of an oil from which crystallized 0.20 g. of purple needles, m.p. 304–307°, recrystallized from glacial acetic acid, m.p. 305–307°.

Anal. Calcd. for $C_{18}H_{12}O_2$: C, 83.08; H, 4.65; mol. wt., 260. Found: C, 83.12; H, 4.75; mol. wt., 240 (Rast).

The remainder of the oil was distilled at 1 mm. pressure, and from the distillate was obtained 0.6 g. of biphenyl, 9.2 g. of benzophenone (m.p. 46–48°) and 0.29 g. of acetophenone. The benzophenone was identified through preparation of its oxime, m.p. 143°, undepressed by admixture with an authentic sample. The acetophenone was identified by preparation of its 2,4-dinitrophenylhydrazone, m.p. 243–

245°, not depressed by admixture with an authentic sample.

From the first ether eluants was isolated by crystallization from alcohol 170 mg. of yellow prisms, m.p. 186–187°.

Anal. Calcd. for $C_{18}H_{12}O_2$: C, 87.80; H, 5.96; mol. wt., 492. Found: C, 87.84; H, 5.71; mol. wt., 378 (Rast, with slight decomposition). This compound gave a negative ferric chloride test and no precipitate with 2,4-dinitrophenylhydrazine solution.

From the middle ether eluants was crystallized a yellow solid which on recrystallization from ethyl acetate gave yellow needles, weight 0.12 g., m.p. 163–164°. This substance produced a bright yellow color with concentrated sulfuric acid, gave no ferric chloride test and no precipitate with 2,4-dinitrophenylhydrazine.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.08; H, 4.78; mol. wt., 222. Found: C, 81.47; H, 4.51; mol. wt., 221, 261 (Rast).

From the final ether eluants was crystallized 0.50 g. of triphenylcarbinol, m.p. 162–163°, not depressed by admixture with an authentic sample.

From the alcohol eluants of the chromatograph was crystallized (from ether) 0.26 g. of white plates, m.p. 126–127°. This substance gave no ferric chloride test and no precipitate with 2,4-dinitrophenylhydrazine reagent. It was insoluble in both dilute acid and dilute base but was soluble in both concentrated hydrochloric and sulfuric acid, in neither case imparting a color to the solution. The compound gave an orange color with aluminum chloride and azoxybenzene, and did not discolor permanganate solution.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 70.06; H, 6.61; mol. wt., 274. Found: C, 70.27, 70.11; H, 6.31, 6.30; mol. wt., 138 (Rast).

With respect to the lack of agreement between the calculated and experimental molecular weights, it seems probable that the compound dissociated during the molecular weight determination; $C_8H_6O_2$ is a theoretically impossible molecular formula for the compound.

When one mole of phenylmagnesium bromide was added to one mole of carbon suboxide and the reaction mixture resolved into its component parts by the above procedures, 3-benzoyl-6-phenyl-1,2-pyran-2,4(3H)-dione (~ 1% yield), 2,4,6-trihydroxytrimesophenone (10% yield), biphenyl (~ 5% yield) and small amounts of benzophenone were isolated. However, an additional compound was isolated by crystallization from the original ether extracts of the decomposed Grignard mixtures. Recrystallization of the substance from a mixture of methylene chloride and alcohol produced a 5% yield of orange needles, m.p. 245–247°.

Anal. Calcd. for $C_{27}H_{18}O_8$: C, 83.08; H, 4.65; mol. wt., 390. Found: C, 82.83, 82.86; H, 4.79, 4.62; mol. wt., 373, 433 (Rast).

This compound gave a negative ferric chloride test and no precipitate with 2,4-dinitrophenylhydrazine. It decolorized permanganate solution, but the substance could not be reduced with sodium hydrosulfite. When 0.1 g. of the compound was shaken with 2 ml. of acetic anhydride and 0.05 g. of zinc, the color vanished, and a yellow oil was produced from which was crystallized (from an ethanol solution) a trace of a white compound, a hexahydro-derivative of the starting material.

Anal. Calcd. for $C_{27}H_{24}O_8$: C, 81.80; H, 6.06. Found: C, 81.76; H, 6.05.

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(7) H. Rupe and E. Busolt, *ibid.*, **40**, 4538 (1907).

(8) A. Beyer and W. H. Perkins, *ibid.*, **17**, 64 (1884).

(9) E. Ott and K. Schmidt, *ibid.*, **47**, 2391 (1914).