on carbon. After concentration of the solution 67.5% yield of free acid was obtained. It melted with gradual decomposition beginning at 255° and boiled out of the tube at 264°.[13]

Anal. Calcd. for $C_7H_{13}NO_2$: C, 58.71; H, 9.15; N, 9.78. Found: C, 58.37; H, 9.49; N, 9.95.

Acknowledgment.—The author gives thanks to Mr. O. Kolsto and his group for the microanalyses. He is particularly indebted to Mr. F. E. Fischer for the preparation of amonium 4-pyridylacetate and β-(2-pyridyl)-acrylic acid.

(13) V. Prelog, D. Kohlbach, E. Cerkovnikov, A. Rezek, and M. Piantanida, *Ann.*, **532**, 69 (1937), give 237–238°. We found that, if samples were not thoroughly dried, the melting range was between 230–240°.

On the Preparation and Reactions of Dibenzyl Oximinomalonate and Its Sodium Complex[1]

J. R. Kuszewski and H. R. Snyder

William Albert Noyes Laboratory, University of Illinois, Urbana, Illinois

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Kissman and Withop[2] have prepared dibenzyl oximinomalonate (I) for use as an intermediate in amino acid synthesis. These authors did not isolate I but employed it in solution as an intermediate in the preparation of tryptophan. Pure, crystalline I has now been obtained by acid hydrolysis of its sodium complex, dibenzyl sodiooximinomalonate acid salt (II).

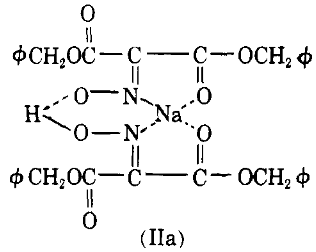
The sodium complex (II) was discovered accidentally in an attempted large-scale reduction of crude I to dibenzyl aminomalonate according to the method of Kissman and Withop.[2] The reaction mixture, which contained mostly unchanged I, was washed with 10% aqueous sodium carbonate, whereupon a light yellow precipitate appeared. Recrystallization of this precipitate from toluene or from acetone–petroleum ether gave II as a white powder.

Treatment of II with dilute acid, followed by recrystallization from chloroform–cyclohexane, gave I as white crystals which melted at 65.5–67°. The sodium complex (II) could be regenerated from the oxime (I) in dilute aqueous ammonium hydroxide by addition of one-half molar equivalent of sodium chloride and allowing the solution to stand. Precipitation of II was complete in about fifteen minutes.

$$\mathrm{NaCl} + \underset{\text{(I)}}{2\mathrm{HON{=}C(CO_2CH_2C_6H_5)_2}} \underset{\text{dil. HCl}}{\overset{\text{dil. NH}_4\text{OH}}{\rightleftharpoons}}$$

$$\underset{\text{(II)}}{\mathrm{NaON{=}C(CO_2CH_2C_6H_5)_2{\cdot}HON{=}C(CO_2CH_2C_6H_5)}}$$

The solubility of II in organic solvents suggests that II is a chelated complex of sodium. A probable structure for II is IIa. Nonpolar sodium complexes are well known. A similar complex of sodium with diethyl



(IIa)

oximinomalonate has been prepared, in nonaqueous medium, by Shaw and Nolan[3] and by Bouveault and Wahl.[4] However, under conditions similar to those used in the preparation of II, diethyl oximinomalonate does not give any precipitate. Evidently, the presence of benzyl groups in II is responsible for the low solubility of II in dilute ammonium hydroxide.

When II is shaken repeatedly with water, the water becomes weakly alkaline, and the insoluble residue reverts to I. Therefore, since II can be both formed and destroyed in aqueous medium, particular importance must be attached to the pH of the reaction medium. Determination of conditions for optimum yield of II was beyond the scope of this study.

Attempts to prepare complexes of I with ions other than sodium met with little success, under conditions similar to those which favored the formation of II from sodium chloride. Use of potassium chloride or lithium chloride in place of sodium chloride in dilute aqueous ammonia resulted in clear solutions from which no solid separated even after several hours. Cupric, cobaltous, and nickel salts gave highly colored oils which could be solidified but not purified. Magnesium and calcium salts gave gummy yellow precipitates which could not be purified.

Since, under the stated conditions, sodium gives a complex with I, and potassium does not, an attempt was made to precipitate sodium selectively from a mixture with potassium. When an equimolar mixture of sodium chloride and potassium chloride was added to I in dilute ammonium hydroxide and the mixture allowed to stand for four hours, essentially pure II precipitated in 74% yield. On longer standing, the precipitate changed to an oil, perhaps because of a change in *p*H caused by slow evaporation of ammonia.

Experimental[5]

Dibenzyl Sodio Oximinomalonate Acid Salt (II).—To a solution of 0.3133 g. (0.001 mole) of dibenzyl oximinomalonate in 3 ml. of 5 *N* ammonium hydroxide was added 0.0292 g. (0.0005 mole) of sodium chloride. The solution was diluted with water to 5 ml. and allowed to stand for 30 min. The white precipitate, after filtration and air drying, weighed 0.270 g. (83%); m.p. 156.0–156.1° dec. An analytical sample was prepared by threefold recrystallization from dry toluene.

Anal. Calcd. for $C_{31}H_{29}O_{10}N_2Na$: C, 62.96; H, 4.50; N, 4.32; Na, 3.55. Found: C, 62.93; H, 4.51; N, 4.41; Na, 3.47.

Dibenzyl Oximinomalonate (I).—A solution of 10.00 g. (0.0154 mole) of II in 200 ml. of 0.1 *N* hydrochloric acid was shaken with 200 ml. of ether. The ether layer was separated, washed with 100 ml. of water in two portions, dried over magnesium sulfate, and evaporated *in vacuo;* the yellow, crystalline residue weighed

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(1) This work was supported by a grant [AT(11-1)-314] from the Atomic Energy Commission.

(2) H. M. Kissman and B. Withop, *J. Am. Chem. Soc.*, **75**, 1967 (1953).

(3) K. N. F. Shaw and C. Nolan, *J. Org. Chem.*, **22**, 1668 (1957).

(4) L. Bouveault and A. Wahl, *Bull. soc. chim. France*, [3] **29**, 628, 960 (1903); *Compt. rend.*, **137**, 196 (1903).

(5) Analyses were performed by Mr. Josef Nemeth and associates.

9.44 g. (98%). An analytical sample was prepared by twofold recrystallization from chloroform–cyclohexane; m.p. 65.5–67°.

Anal. Calcd. for $C_{17}H_{15}O_5N$: C, 65.17; H, 4.83; N, 4.48. Found: C, 65.14; H, 4.87; N, 4.42.

Preparation of II in the Presence of Potassium Chloride.—To a solution of 0.3133 g. (0.001 mole) of I in 3 ml. of 5 *N* ammonium hydroxide were added 0.0292 g. (0.0005 mole) of sodium chloride plus 0.0328 g. (0.0005 mole) of potassium chloride. The solution was diluted with water to 5 ml., divided into two equal portions, and placed in cork-stoppered vessels. After 4 hr., the precipitate in the first vessel was filtered and air-dried; 0.1200 g. (74%) of II resulted. A flame test on II prepared in this manner revealed the presence of a small amount of potassium.

The precipitate in the second vessel gradually changed to an oil on standing for 2 days.

π-Allyl-π-Cyclopentadienylcobalt Halides

R. F. Heck

Research Center, Hercules Powder Company,
Wilmington, Delaware

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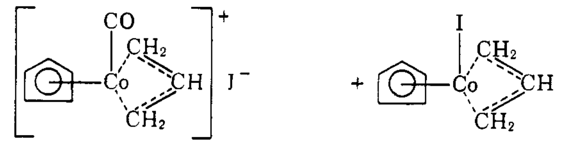
Fischer has reported the preparation of the ionic compound, π-allyl-π-cyclopentadienylcobalt carbonyl bromide by the reaction of allyl bromide with π-cyclopentadienylcobalt dicarbonyl.[1] We have found that allyl iodide reacts with π-cyclopentadienylcobalt dicarbonyl at 25° in tetrahydrofuran solution to give two products, a yellow-green insoluble, ionic material as the major product and about 10% of a soluble covalent compound. The ionic compound reacts with hexafluorophosphate ion to give an insoluble yellow product which is identical with the π-allyl-π-cyclopentadienylcobalt carbonyl hexafluorophosphate prepared by Fisher,[1] indicating that the original compound was probably π-allyl-π-cyclopentadienylcobalt carbonyl iodide. The covalent compound, obtained as very dark red needles by evaporation of the tetrahydrofuran solution and recrystallization, melted with decomposition at 95.5–97°. The compound is oxidized by air quite rapidly, particularly in solution. The compound sublimed in high vacuum at 50–60°. It is soluble in organic solvents but insoluble in water. The compound has no carbonyl bands in its infrared spectrum. Analyses and the nuclear magnetic resonance spectrum indicate that the compound is π-allyl-π-cyclopentadienylcobalt iodide. The n.m.r. spectrum at 60 Mc. in deuteriochloroform had four bands with an area ratio of 5:2:1:2 at 71, 88 (doublet), 112 (multiplet), and 198 (doublet) c.p.s., respectively, relative to an external benzene standard.

Under the same conditions, allyl bromide reacts with π-cyclopentadienylcobalt dicarbonyl to give only a few per cent of π-allyl-π-cyclopentadienylcobalt bromide, the major product being π-allyl-π-cyclopentadienylcobalt carbonyl bromide as observed by Fischer.[1] The covalent bromide is a dark red crystalline compound of m.p. 96–98° dec. The properties and spectra are very similar to those of the iodide. The n.m.r. spectrum in deuteriochloroform had four bands in the area ratios of 2:5:1:2 at 70, 80, 120, and 220 c.p.s., respectively, referred to an external benzene standard.

$$CH_2{=}CH{-}CH_2I + \pi{-}C_5H_5Co(CO)_2 \longrightarrow$$



Allyl chloride reacts with π-cyclopentadienylcobalt dicarbonyl to yield only a bright green salt which is probably π-allyl-π-cyclopentadienylcobalt carbonyl chloride, since it gives the same insoluble hexafluorophosphate as is obtained from the bromide.

Experimental

π-Allyl-π-Cyclopentadienylcobalt Iodide.—Cyclopentadienylcobalt dicarbonyl (3.0 ml.), 10 ml. of purified tetrahydrofuran and 2.0 ml. of allyl iodide were injected into a nitrogen-filled tube which had been closed with a self-sealing rubber cap. A yellow solid soon began to separate. After standing for 2 days the gas formed was allowed to escape and the solid was separated from the very dark solution by centrifuging. The solid was washed several times under nitrogen with tetrahydrofuran. The combined tetrahydrofuran solutions were evaporated *in vacuo* at room temperature to about 4 ml. The yellowish solid which separated was removed by centrifuging again. Addition of 10 ml. of pentane to the solution and cooling to −80° gave very dark red, nearly black crystals. Several recrystallizations from tetrahydrofuran and pentane gave 0.37 g. shiny black needles, m.p. 95.5–97° dec. The solid compound could be handled in the air for short periods but it oxidizes readily. In solution it decomposes very rapidly in air.

Anal. Calcd. for $C_8H_{10}ICo$: C, 32.90; H, 4.11; I, 43.5. Found: C, 32.86; H, 3.51; I, 43.3.

The infrared spectrum in carbon tetrachloride had bands at 3.25 μ (w), 3.33 (w), 4.70 (w), 5.50 (w), 5.80 (vw), 6.12 (vw), 6.38 (w), 7.01 (m), 7.12 (m), 7.23 (m), 7.41 (w), 8.20 (w), 8.30 (w), 8.99 (w), 9.50 (w), 9.81 (m), 9.90 (m), 10.10 (m), 10.85 (m), 11.10 (w), 11.50 (w), and 11.92 (m). There were additional bands in carbon bisulfide solution at 12.15 μ (s) and 13.10 (w).

The tetrahydrofuran-insoluble, yellow solid obtained in the above reaction was readily soluble in water. The aqueous solution gave a yellow precipitate with an aqueous solution of potassium hexafluorophosphate. The solid was recrystallized from aqueous acetone. The infrared spectrum of a Nujol mull of the product had a strong carbonyl band at 4.79 μ.

The reactions of allyl bromide and chloride with π-cyclopentadienylcobalt dicarbonyl were carried out as described for the allyl iodide reaction.

Acknowledgment.—The nuclear magnetic resonance spectra were measured by C. R. Boss.

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[1] E. O. Fischer and R. D. Fischer, *Z. Naturforsch.*, **16b**, 475 (1961).