EXPERIMENTAL

Pyrolysis of perfluoropropionic acid. Perfluoropropionic acid (16.4 g., 0.10 mole) was passed through a quartz tube heated to 650° using nitrogen as carrier gas. The residence time in the tube was about 3 seconds. The products contained 85–90% tetrafluoroethylene, about 10% of pentafluoroethane, and traces of hexafluoropropylene and perfluorocyclobutane; all determined by mass spectrographic analysis. In other experiments, Monel tubes with either nitrogen or carbon dioxide as the carrier were used with similar results.

Pyrolysis of perfluorobutyric acid. Perfluorobutyric acid (21.4 g., 0.10 mole) was passed through a Monel tube under the same conditions as those used with perfluoropropionic acid. The product contained 86% hexafluoropropylene, about 10% hexafluoroethane, and 4% octafluoropropane.

Pyrolysis of ω-hydroperfluorononanoic acid. Dropping 20 g. ω-hydroperfluorononanoic acid through a Vycor tube at 586–613° produced 12 g. of nearly pure ω-hydroperfluorooctene-1 as well as an undetermined amount of unchanged acid.

Pyrolysis of perfluorooctanoic acid. Perfluorooctanoic acid (3.4 g., 0.0082 mole) was dropped through a Vycor tube at 620° with a residence time of about 5 seconds, using carbon dioxide as a carrier. The yield of olefin was 89%. Since the starting material was a mixture of isomers, no attempt was made to determine the isomeric purity of the products.

Acknowledgment. The authors wish to thank Dr. R. E. Brooks for his guidance in the early stages of the work.

POLYCHEMICALS DEPARTMENT
E. I. DU PONT DE NEMOURS & CO.
DU PONT EXPERIMENTAL STATION
WILMINGTON, DEL.

Inner Complexes. I. Copper and Beryllium Chelates of 4-Acetyl-5-ketohexanoic Esters

RUDOLPH W. KLUIBER, FREDERICK G. OBERENDER, AND CARL J. ROSSI

Received November 23, 1959

Although the properties of inner complexes depend largely on the nature of the ring system, such physical constants as solubility and melting point can be modified by varying the substituents attached to the chelate ring. In a study of these effects and potential commercial uses of inner complexes, we have prepared a series of metal derivatives of various esters of 4-acetyl-5-ketohexanoic acid (I). The ethyl and methyl esters and their copper derivatives have previously been reported by March[1] who prepared them by basic condensation of the corresponding β-chloropropionic ester and 2,4-pentanedione. Because of the availability of various acrylic esters, their monoaddition to 2,4-pentanedione presented a potentially more attractive synthesis. Analogous Michael reactions have been reported with malonic esters[2,3] and β-keto esters,[3,4] but no work has been reported on the monoaddition of acrylic esters to the active methylene of a β-diketone system.

$$CH_2 = CH\text{—}COOR + CH_3COCH_2COCH_3 \longrightarrow (CH_3CO)_2CHCH_2CH_2COOR$$

I

Ethyl 4-acetyl-5-ketohexanoate has now been prepared in 83% yield from ethyl acrylate and an excess of 2,4-pentanedione using a stoichiometric amount of sodium ethoxide in ethanol. This was converted to the copper chelate using ammoniacal copper sulfate and to the beryllium chelate using a sodium acetate–buffered beryllium nitrate solution. The use of a buffered solution eliminates the neutralization step and decreases the contamination of the product with beryllium oxide. In preparing the metal derivatives from the other esters, the distillation of the intermediate ester diketone was omitted and only the yields for the over-all conversion to the pure chelate were recorded. The solubility of these chelates in aliphatic and aromatic hydrocarbons increases with increasing chain branching. For the straight chain ester copper chelates the solubility rises to a maximum and decreases as the chain length increases. The solubility of *bis*(2,4-pentanediono) copper II in benzene was found to be 1.0 mg./ml. at 27°, whereas for the copper chelates of the *n*-alkyl 5-keto-4-acetyl hexanoates, the solubility was: ethyl, 2.0 mg./ml.; butyl, >7 mg./ml.; lauryl, 2.3 mg./ml. These are given in Table I along with other characterization data.

In three cases, the *n*-decyl, lauryl, and isoamyl esters, about 10% of a crystalline *bis*-adduct separated from the crude Michael addition product. These 4,4-diacetylpimelic esters are characterized in Table II.

EXPERIMENTAL

Alkyl 4-acetyl-5-keto-hexanoate. The following preparation of the ethyl ester illustrates the general procedure used in the preparation of the other alkyl esters. However, except for the ethyl ester, the crude residual product was converted directly to the metal derivatives. Metallic sodium (12 g., 0.52 mole) was dissolved in approximately 250 ml. of commercial absolute ethanol in a 500 ml. three necked flask equipped with a stirrer and a dropping funnel. 2,4-Pentanedione (100 g., 1.0 mole) was added to the stirred sodium ethoxide solution cooled by an ice bath. Ethyl acrylate 50 g. (0.5 mole) was added dropwise with stirring to the cooled reaction mixture, and the stirring was continued approximately 16 hr. at room temperature. The reaction was quenched with an excess of glacial acetic acid and the clear solution (*p*H 4–5) was evaporated under reduced pressure. The semisolid residue was treated with 20 ml. of water and extracted with four 100-ml. portions of ether. After drying the extracts over anhydrous magnesium sulfate, the ether was removed under reduced pressure and the residual product distilled, yielding 83 g. (83%) of a light yellow liquid, b.p. 124–128° (3 mm.) (reported[1] 154–155°, 15 mm.).

---

(1) F. March, *Ann. Chim. Phys.*, **726**, 331 (1902).

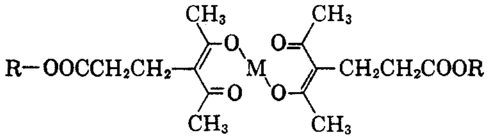
(2) C. S. Marvel and M. P. Stoddard, *J. Org. Chem.*, **3**, 198 (1938).

(3) E. H. Riddle, *Monomeric Acrylic Esters*, Reinhold Publishing Corp., New York, 1954, pp. 172–185.

(4) L. Ruzicka, *Helv. Chim. Acta*, **2**, 144 (1919).

TABLE I[5]

CHARACTERIZATION OF



R	M	Empirical Formula	% Yield, Over-all	M.P., °	% Calculated C	% Calculated H	% Found C	% Found H
Methyl	Cu	$C_{18}H_{26}O_8Cu$	35	200 dec.[a]	—	—	—	—
Ethyl	Cu	$C_{20}H_{30}O_8Cu$	60	205 dec.[b]	—	—	—	—
Ethyl	Be	$C_{20}H_{30}O_8Be$	62	113–114	58.94	7.42	58.65	7.67
Allyl	Cu	$C_{22}H_{30}O_8Cu$	20	174–175	54.35	6.22	54.18	6.31
Allyl	Be	$C_{22}H_{30}O_8Be$	25	88.1–88.8	61.22	7.01	61.39	7.09
Butyl	Cu	$C_{24}H_{38}O_8Cu$	32	157–159	55.66	7.39	55.69	7.74
n-Amyl	Cu	$C_{26}H_{42}O_8Cu$	20	148.5–152	57.18	7.75	57.51	7.90
i-Amyl	Cu	$C_{26}H_{42}O_8Cu$	25	151.5–152	57.18	7.75	57.45	7.63
2-Octyl	Cu	$C_{32}H_{54}O_8Cu$	27	121.5–122.5	60.97	8.64	60.41	8.86
n-Decyl	Cu	$C_{36}H_{62}O_8Cu$	24	123–124	62.99	9.11	62.99	8.96
Lauryl	Cu	$C_{40}H_{70}O_8Cu$	33	122–123.5	64.70	9.50	64.45	9.58
Lauryl	Be	$C_{40}H_{70}O_8Be$	20	50–52	69.92	10.25	70.04	10.16

[a] Reported m.p. 220.[1] [b] Reported m.p. 209.[1]

TABLE II[5]

CHARACTERIZATION OF $(CH_3CO)_2C(CH_2CH_2COOR)_2$

R	M.P., °	Empirical Formula	% Calculated C	% Calculated H	% Found C	% Found H
i-Amyl	54–54.5	$C_{21}H_{36}O_6$	65.59	9.44	65.85	9.62
n-Decyl	56.5–57	$C_{31}H_{56}O_6$	70.95	10.76	71.21	10.81
Lauryl	65–65.5	$C_{35}H_{64}O_6$	72.37	11.11	72.13	10.91

Bis*[3-(2'-carbethoxyethyl)-2,4-pentanediono]beryllium* (II). Beryllium nitrate trihydrate (20 g., 0.1 mole) was dissolved in a minimum amount of water in a 500 ml. three necked flask equipped with an efficient stirrer. This solution was buffered to approximately *p*H 5 by the addition of 150 ml. of saturated sodium acetate. Ethyl 5-keto-4-acetylhexanoate (40 g., 0.2 mole) was added and the resultant reaction mixture was stirred vigorously for 2 hr. (precipitation of the product began after 10 min.). The reaction mixture was cooled in an ice bath, and the white product collected by suction filtration, yielding, after being washed with 150 ml. of ice water and dried overnight in vacuo at 50°, 35 g. (87%) of crude beryllium chelate of ethyl 5-keto-4-acetylhexanoate, m.p. 115–118°. Recrystallization from benzene–petroleum ether yielded 31 g. (76%) of white crystalline product, m.p. 113–114°. The infrared spectrum of the compound pressed in potassium bromide contained only a single peak at 6.30 in the 6.25–6.75 μ region, confirming the absence of a hydrogen attached directly to the ring.[6]

The other beryllium compounds were analogously prepared.

Bis*[3-(2'-carbalkoxyethyl)-2,4-pentanediono]copper* (II). The crude diketo ester (0.2 mole) was shaken overnight with 100 ml. of aqueous ammoniacal copper sulfate (0.1 mole). The precipitated solid was removed by filtration and crystallized from benzene–petroleum ether. In the 6.25–6.75 μ region of the infrared, these compounds absorbed strongly only at 6.34 μ.

RESEARCH DEPARTMENT
UNION CARBIDE PLASTICS CO.
A DIVISION OF UNION CARBIDE CORP.
BOUND BROOK, N. J.

---

(5) All melting points are corrected. Analyses by the laboratory of Drs. Weiler and Strauss, Oxford, England.

(6) R. P. Dryden and A. Winston, *J. Phys. Chem.*, **62**, 635 (1958).