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PREPARATION OF MODIFIED BETA-DIKETONES AND THE EFFECTS OF STRUCTURE UPON PROPERTIES

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Abstract—Acetylacetone represents but the first of a potential homologous series if one terminal methyl group is considered as a substitution site. Modification by substitution of various hydrocarbon moieties was investigated with the expectation that changes in the properties of the metal chelates of these substituted acetonates should result. Among the objectives of this investigation was to obtain increased solubility of the chelates in hydrocarbon solvents. This paper reports success in achieving this objective.

ALTHOUGH other methods of synthesis are known such as conversion of ketone enol esters by thermal rearrangement(1) and by intermolecular acylations using boron fluoride,(1,2) the method of preparation chosen was selected because of the ease with which the substituent group could be modified and the ready availability of methylacetylene. Metallation of methylacetylene with sodium in liquid ammonia, reaction of the sodium propyne with the acid chloride of the desired substituent, and hydration of the triple bond resulted in the terminally substituted beta-diketone. Thus the only restriction upon the final product was the availability of the acid chloride or the acid.

EXPERIMENTAL

Preparation of sodium propyne

A flask was maintained in a dry ice–acetone bath at −50 to −60° under a continuous blanket of dry nitrogen. Ammonia was liquified as it was metered into the flask. Freshly cut sodium was added in small pieces through the N_2-purged outlet and the familiar blue solution was obtained. The methylacetylene was metered as a gas into the chilled flask and dripped into the blue solution. Final disappearance of the blue colour indicated the complete reaction of Na. The NH_3, sodium propyne slurry was filtered, the solid propyne of 96 per cent purity (analysis by titration of alkalinity) was dried and stored in nitrogen flushed, sealed bottles.

Acid chloride

Acetyl, benzoyl, butyryl, crotonyl and octanoyl chlorides were purchased from Eastman Kodak and were used without further purification. For oleoyl, phenyl acetyl and stearoyl chlorides, the literature method(3) of PCl_3 or $SOCl_2$ plus the acid was used. Excess chlorinating agent was removed by warming under reduced pressure to yield 95 per cent or higher purity product.

Sodium propyne-acid chloride reaction

Nitrogen was used to blanket the usual 3-necked, stirred, round bottom flask fitted with additional funnel and reflux condenser. All outlets were protected with $CaSO_4$ drying tubes. After flushing the system with N_2, a high boiling ether, such as di-isopropyl ether, dioxane, or bis-2-ethoxy-diethyl

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(1) A. B. BOESE and F. G. YOUNG, U.S. Patent 2,395,800; F. G. YOUNG, F. C. FROSTWICK, J. J. SANDERSON and C. R. HAUSER, *J. Am. chem. Soc.* **72**, 3635 (1950).

(2) C. R. HAUSER and J. T. ADAMS, *J. Am. chem. Soc.* **66**, 345 (1944); M. KASTNER: *Newer Methods of Preparative Organic Chemistry*, p. 289 Interscience Publishers, New York (1948).

(3) A. W. RALSTON and W. M. SELLEY, *J. Am. chem. Soc.* **61**, 1019 (1939).

ether was added, the acid chloride was added and the temperature of the thermostatted bath increased to a reaction temperature of 70–100°. The sodium methylacetylide maintained as a slurry in ether in the additional funnel, was dripped in slowly as heating and stirring was continued for 30–90 min after all the acetylide had been added. *Safety note:* This order of addition was necessary since the intermediate acetylenic ketone reacts exothermally and almost instantaneously with the sodium methylacetylide. In addition, very low yields of desired product are obtained because of the side reactions.

After the acetylide reaction was completed, the intermediate acetylenic ketone was hydrolysed to the 1,3-diketone by the method of Moureu.(4) The reaction mixture was cooled to 40°C and a 1–2 per cent excess of piperidine (mole/mole basis) was added. Addition to the triple bond was monitored by i.r. spectra until reaction was completed, when a 50 per cent excess (based on piperidine) of 10% HCl was then added. The water–ether mixture was stirred for 2–4 hr to convert the piperidine adduct to the beta-diketone.

Since several of the 1,3-diketones have been previously prepared,(1) no attempt was made to isolate any of these except oleoyl and the mixed oleoyl–linoyl acetone. The Cu chelates were obtained from the reaction mixture and analysis for Cu content was taken as sufficient proof of identification.

Separation of the product was accomplished either by shaking the ether layer with a saturated water solution of copper acetate to obtain the Cu chelate or by a series of distillations. The solvent water and ether were removed by distillation at 20–60 mm in a one-plate column. The residue was then distilled at 3–5 mm using a wiping film column (A. O. Smith Co.). Several passes were required to strip the product from the higher boiling by-products.

Preparation of copper oleoylacetonate

Into a 12-l., round bottom flask equipped with a reflux condenser, stirrer, and additional funnel and N_2 purge was added 1530 g of oleic acid chloride distilled using wiping film still (A. O. Smith Co.) $b_{1-5\,mm}$ 210–25° found 11·4 per cent Cl, 0·1–0·05 per cent P; theory 11·8 per cent Cl. Dioxane (3000 ml) and the stirred mixture was heated to 100°C. A slurry of 315 g sodium methylacetylide in 2500 ml of dioxane was added in small increments over a period of 3–4 hr. Heating and stirring was continued 30 min after all the acetylide was added. The mixture was cooled to 40° and 380 g piperidine were added during about a 1-hr period. The stirred mixture was cooled to room temperature, the solids removed by centrifugation and the mother liquor distilled at 20 mm to remove the dioxane. To the residue was added 3 l. of di-isopropyl-ether and the solution was treated with aqueous 10% HCl to form oleoylacetone (ref. index 25° 1·4784, sp. gr. 0·895). The water–acid layer was separated by means of a separating funnel and the organic layer was water washed to pH 7. A saturated cupric acetate solution was shaken with the organic layer and copper oleoyl acetonate was isolated in 19 per cent yield. Recrystallized three times from diethyl ether, found 9·58 per cent Cu, theory 8·96 per cent.

Synthesis tests of the procedure

Using the procedure outlined, phenylacetyl chloride, octanoyl chloride, stearoyl chloride and oleoylchloride were converted to their corresponding copper chelates. The first three were nicely crystalline, light blue materials. The chelate of oleoylacetone was a rather waxy, greasy material, m.p. 85–88°C.

Solubility tests were simply conducted by saturating the chosen solvent with the Cu-chelate, an aliquot of the solution ashed and the copper oxide weighed. Check runs using tagged Cu and counting methods confirmed these results. Further compounds were prepared to test the effect of unsaturation and chain length of the substituent group on chelate solubility in hydrocarbons. The data are summarized in Table 1.

The potential utility of these hydrocarbon soluble metal chelates was tested. Thus oleoylacetone as a 2% solution in iso-octane was used at a rate of 5 lb of oleoylacetone per ton of NaOH to treat an aqueous 50% NaOH solution which contained 26 ppm Fe. The distribution coefficient in this extraction was 1·610 with one-half of the Fe removed in a single stage.

A similar test was made with the 2% solution in iso-octane at a rate of 160 lb of oleoylacetone per ton of Ni tailings solution. The distribution coefficient for Ni was 228 and for Co was 0·25. The original 0·0142 g Cu/l was completely removed.

(4) C. Moureu and I. Lazennee, *Bull. Soc. chim. Fr.* **35**, 1190 (1906).

TABLE 1.—EFFECT OF CHAIN LENGTH AND DEGREE OF UNSATURATION UPON CHELATE SOLUBILITIES

Substituent group	Solubility of Cu chelate in grams Cu/l solution Benzene	$HCCl_3$	n-Hexane
Acetyl	0·364	—	0·0534
Butyryl	2·950	26·4	<0·4
Crotonyl	2·410	45·4	<0·4
Octanoyl	6·080	4·3	1·04
Stearoyl	0·880	3·6	0·56
Oleoyl	26·280	41·8	4·240
Mixed {50% oleoyl 50% linoleoyl*	37·100	49·5	9·830

* Ref. index 25° 1·4770, sp. gr. 0·875.

Among the various metal chelates of oleoylacetone prepared, those of Fe III and of thorium remained liquids despite all attempts to obtain crystalline products. The thorium chelate with a slight excess of the oleoyl-acetone appeared to be miscible with n-hexane in all proportions.

DISCUSSION

We can note that in comparing the C_4 acids, butyryl and crotonyl, unsaturation of a short chain is not sufficient to impart any significant degree of solubility. Simple increase in chain length up to C_8 shows a consistent increase in solubility, but with a C_{18}, as stearoyl, the hydrocarbon moiety has effected a decrease in solubility. Oleoyl shows the outstanding and unexpected increase in solubility one double bond is able to impart. The additional unsaturation of linoleoyl shows the consistent increase in solubility which might be expected to be valid with a proper chain length. Indeed, a substituent of about C_8 might show similar results. We would thus suggest on the basis of our results* that solubility is dependent upon both the length of chain and the amount of unsaturation. The existence of literature(5) previously unknown to us was brought to our attention during the course of this work and further planned work was terminated.

* Table 2 overleaf.

(5) C. C. TOWNE, U.S. Patent 2,223,932.

TABLE 2.—PHYSICAL PROPERTIES OF VARIOUS COMPOUNDS

Compound	B.p.	Piperidine adduct	Diketone	m.p. Cu chelate Lit.	m.p. Cu chelate Found	Recrystallization solvent for chelate	% Cu in chelate Theory	% Cu in chelate Found
$\mathrm{Me\overset{\overset{O}{/\!/}}{C}{-}C{\equiv}C{-}Me}$	71·5–71·75 at 97–8 mm	—	—	—	—	—	—	—
$\mathrm{C_3H_7\overset{\overset{O}{/\!/}}{C}{-}C{\equiv}CMe}$		—	—	—	—	Et_2O	20·0	17·0
$\mathrm{MeCHCHCO{-}C{\equiv}CMe}$	—	—	—	—	—	Et_2O	20·3	16·8
$\mathrm{\phi\overset{\overset{O}{/\!/}}{C}{-}C{\equiv}CMe}$	73° at 0·4 mm	m. 98–8·5°	m. 59·5–61°	—	—	—	—	—
$\mathrm{C_{17}H_{33}\overset{\overset{O}{/\!/}}{C}{-}C{\equiv}CMe}$	—	—	—	U.K.	83·5–6·5°	EtOH, then Et_2O	8·96	9·20
$\mathrm{C_7H_{15}\overset{\overset{O}{/\!/}}{C}{-}C{\equiv}CMe}$	94–9° at 5 mm	—	—	118°	120·5°	EtOH	14·43	14·4
$\mathrm{\phi CH_2\overset{\overset{O}{/\!/}}{C}{-}C{\equiv}CMe}$	805–2° at 0·4 mm	—	87–8 at 0·6 mm	—	—	EtOH	15·3	14·8
$\mathrm{C_{17}H_{35}\overset{\overset{O}{/\!/}}{C}{-}C{\equiv}CMe}$	—	—	50°	113°	118·4–120·2	EtOH or *iso*-octane	8·94	8·9