complex of $C_6H_5AlH_2$ (III) was considerably less stable than the $(C_2H_5)_3N$ compound (I), decomposing slowly even at room temperature and rapidly above 50°. When III was allowed to stand at room temperature, a white solid began to deposit after 1 day, the quantity of the solid slowly increasing with time. The solid had an Al:N:active H ratio of 1:0.77:1.36, which approaches the ratios for the sesquialane, $(C_6H_5)_3Al_2H_3\cdot N(CH_3)_3$, or for a mixture of $(C_6H_5)_2AlH$ and $C_6H_5AlH_2\cdot N(CH_3)_3$ (1:0.5:1.5). Such a product, or mixture of products, could result from a disproportionation of $C_6H_5AlH_2\cdot N(CH_3)_3$. The observed instability of III may arise from the greater volatility of $(CH_3)_3N$ which shifts the equilibrium of eq. 2 to the right and results in disproportionation of the uncomplexed $C_6H_5AlH_2$.

$$C_6H_5AlH_2\cdot NR_3 \rightleftharpoons C_6H_5AlH_2 + NR_3 \qquad (2)$$

Experimental

All reagents were handled and all filtrations were performed in a nitrogen-atmosphere vacuum drybox, and all reactions were conducted under dry nitrogen. The trialkylamine chloroalane derivatives were prepared by the method of Ruff.[6] Benzene was purified and dried by refluxing over $LiAlH_4$, distilling, and storing over $LiAlH_4$. Commercially available organolithium compounds were used as received. Quantitative hydrolyses were performed on a Toepler pump system, and both condensable and noncondensable products were collected. The former were separated and identified by standard v.p.c. methods and the latter were identified by their mass spectra. Molecular weights were determined cryoscopically in benzene at 0.05 *M* concentrations. Results are accurate to approximately ±1%.

Preparation of $C_6H_5AlH_2\cdot N(C_2H_5)_3$ (I).—To a solution of 0.10 mole of $ClAlH_2\cdot N(C_2H_5)_3$ in 100 ml. of benzene was added, dropwise at room temperature, 0.10 mole of C_6H_5Li in benzene–ether solution. The precipitation of LiCl was immediate and the chloride-free filtrate was freeze dried to produce 20.1 g. (97.1% of theory) of a pale yellow, slightly viscous liquid. It decomposed without boiling below 80° at 0.01 mm. pressure.

Anal. Calcd. for $C_{12}H_{22}AlN$: C, 69.53; H, 10.70; Al, 13.02; N, 6.75; active H, 0.97; mol. wt., 207; Al:N:active H, 1:1:2; $C_6H_6:N(C_2H_5)_3$, 1:1. Found: C, 69.67; H, 9.95; Al, 12.72; N, 6.40; active H, 0.92; mol. wt., 241; Al:N:active H, 1:1.05:1.90; $C_6H_6:N(C_2H_5)_3$, 1:1.1.

Preparation of $(C_6H_5)_2AlH\cdot N(C_2H_5)_3$ (II).—To a solution of 0.10 mole of $Cl_2AlH\cdot N(C_2H_5)_3$ in 100 ml. of benzene was added 0.20 mole of C_6H_5Li as in the preparation of I. The yield of pale yellow, slightly viscous liquid was 27.2 g. (96.1% of theory). It decomposed without boiling below 80° at 0.1 μ pressure.

Anal. Calcd. for $C_{18}H_{26}AlN$: C, 76.28; H, 9.26; Al, 9.52; N, 4.95; active H, 0.36; mol. wt., 283, Al:N:active H, 1:1:1; $C_6H_6:N(C_2H_5)_3$, 2:1. Found: C, 75.77; H, 9.68; Al, 8.98; N, 5.67; active H, 0.33; mol. wt., 370; Al:N:active H, 1:0.83:0.92; $C_6H_6:N(C_2H_5)_3$, 2:0.95.

Preparation of $C_6H_5AlH_2\cdot N(CH_3)_3$ (III).—The preparation of I was repeated with $ClAlH_2\cdot N(CH_3)_3$ to produce 15.9 g. of yellow, viscous liquid (96.4% of theory) which decomposed slowly at room temperature and rapidly above 50°.

Anal. Calcd. for $C_9H_{16}AlN$: Al, 16.33; N, 8.48; active H, 1.22; Al:N:active H, 1:1:2. Found: Al, 15.47; N, 8.08; active H, 1.21; Al:N:active H, 1:1:2.1.

Acknowledgment.—We wish to acknowledge the assistance of Raymond N. Storey in the determination and interpretation of the infrared spectra.

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CONTRIBUTION FROM THE U. S. ARMY NATICK
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The Synthesis of a New Series of Zinc Compounds

BY GÜNTER RUDOLPH[1] AND MALCOLM C. HENRY

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In a recent communication[2] we reported the existence of a compound $Zn_2(CH_3CO_2)(C_5H_7O_2)_3$ formed either by (a) the thermal decomposition of bis(acetylacetonato)-zinc(II) hydrate or (b) heating zinc acetate with acetylacetone. We have now found a superior synthetic route and have applied it to the preparation of a homologous series of compounds having the generalized formula $Zn_2(RCO_2)(C_5H_7O_2)_3$ where R = CH_3, C_2H_5, $C(CH_3){=}CH_2$, C_6H_5, *m*-$CH_3C_6H_4$, *p*-$CH_3C_6H_4$, *p*-ClC_6H_4, and *p*-BrC_6H_4 (Table I).

The general route to these compounds is *via* the reaction of anhydrous bis(acetylacetonato)zinc(II) with the calculated amount of an organic acid according to the equation

$$2Zn(C_5H_7O_2)_2 + RCOOH \longrightarrow Zn_2(RCO_2)(C_5H_7O_2)_3 + C_5H_8O_2$$

These white crystalline compounds are only slightly soluble in organic solvents at ambient temperatures. They are, however, soluble in chloroform. The acetate and methacrylate derivatives are sufficiently soluble in benzene to conduct molecular weight measurements. Polar solvents generally decompose these new compounds.

It is interesting to note that the molecular weights obtained in chloroform are not in agreement with the calculated formula weight. The two derivatives sufficiently soluble in benzene, however, gave molecular weights in agreement with theoretical. The acetate derivative described earlier[2] has been determined at varying concentrations in chloroform. The experimentally found molecular weight does not vary with concentration (7.17 g./l., mol. wt. found 346; 4.51 g./l., mol. wt. found 348; 19.66 g./l., mol. wt. found 386; 6.45 g./l., mol. wt. found 319).

Attempts to prepare similar compounds with other fatty acids higher than propionic acid were unsuccessful.

We assume that the three acetylacetonate groups of these compounds are attached to one zinc atom, leading to a structure with hexacoordinated zinc such as $Zn(RCO_2)[Zn(C_5H_7O_2)_3]$. This salt-like structure could account for the poor solubility in organic solvents and the anomalous molecular weights obtained in chloroform. The existence of the $[Zn(C_5H_7O_2)_3]^-$ anion, and its low stability in ionizing solvents, has been noted previously.[3]

In this connection sodium tris(acetylacetonato)-zincate(II) was prepared by combining methanol

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[2] G. Rudolph and M. C. Henry, *Inorg. Chem.*, **3**, 1317 (1964).

[3] F. P. Dwyer and A. M. Sargeson, *J. Proc. Roy. Soc. N.S. Wales*, **90**, 29, 141 (1956).

TABLE I

$Zn_2(RCO_2)$-$(C_5H_7O_2)_3$, R =	Yield, %	M.p., °C.	Mol. wt.			% C		% H	
			Calcd.	Found[a] in C_6H_6	Found[a] in $CHCl_3$	Calcd.	Found	Calcd.	Found
CH_3	78	198–200	487.14	*b*	319	41.92	42.31	4.97	5.06
CH_3CH_2	67	159–160	501.17	528	328	43.14	43.95	5.23	5.23
$CH_2{=}C(CH_3)$	55	193–194	513.18	498	446	44.47	44.03	5.11	4.99
C_6H_5	88	243–245 dec.	549.21	*b*	340	48.11	49.12	4.77	4.79
m-$CH_3C_6H_4$	72	219–220	563.24	*b*	422	49.05	50.94	5.01	4.95
p-$CH_3C_6H_4$	83	244 dec.	563.24	*b*	397	49.05	50.78	5.01	4.87
p-ClC_6H_4	80	257 dec.	583.66	*b*	*b*	45.27	45.35	4.32	4.12
p-BrC_6H_4	91	251 dec.	628.12	*b*	*b*	42.07	41.74	4.01	3.93

[a] Mechrolab vapor pressure osmometer. [b] Insoluble.

solutions of sodium acetylacetonate and zinc acetate according to the procedure given by Dwyer and Sargeson.[3] The desired compound was obtained in poor yield; the major product was a compound of the empirical formula $Zn(C_5H_7O_2)_2 \cdot NaC_2H_3O_2 \cdot CH_3OH$ and unknown structure.

It was not possible to carry out any further reactions with the sodium tris(acetylacetonato)zincate(II) thus prepared, due to its low solubility in alcohol and instability in the presence of water.

Experimental

Anhydrous Bis(acetylacetonato)zinc(II).—Reports about this product in the literature are rather inconsistent.[2,4] We prepared it in large runs *via* the unstable methanol adduct of bis(acetylacetonato)zinc(II).

Bis(acetylacetonato)zinc(II) hydrate (100 g.) was dissolved in 600 ml. of methanol. The flask containing the solution was packed in Dry Ice and stored with occasional shaking, until the temperature dropped to −50°. The crystals formed were filtered rapidly through a precooled Büchner funnel and transferred to a round-bottom flask; extended contact with moist air was avoided. After 24 hr. drying under high vacuum 80 g. of anhydrous bis(acetylacetonate)zinc(II), m.p. 127°, was obtained. Unlike the monohydrate, this product dissolved readily in common organic solvents.

Preparation of Compounds $Zn_2(RCO_2)(C_5H_7O_2)_3$. General Procedure.—Anhydrous bis(acetylacetonato)zinc(II) (10.5 g., 40 mmoles) was dissolved in benzene. A solution of 20 mmoles of the acid in benzene was added and the mixture allowed to stand overnight. The resulting crystals were filtered, washed with benzene and petroleum ether, and dried. Recrystallization did not significantly improve the elemental analyses.

When the acid is not sufficiently soluble in benzene, as in the case of *p*-chloro- and *p*-bromobenzoic acids, the components could be dissolved in hot xylene before being poured together.

Preparation of $NaZn(C_5H_7O_2)_3$ and $Zn(C_5H_7O_2)_2 \cdot NaC_2H_3O_2 \cdot CH_3OH$.—Methanol solutions of sodium acetylacetonate (0.32 mmole) and zinc acetate (0.16 mmole) were combined. Sodium acetylacetonatozincate(II) (11.5 g., 0.03 mmole) precipitated immediately and was filtered and dried. The mother liquor, set aside in a freezer overnight, precipitated a crystalline colorless compound (decomposes above 225°); the yield was 31.1 g. or 0.082 mole. The formula $Zn(C_5H_7O_2)_2 \cdot NaC_2H_3O_2 \cdot CH_3OH$ was established by elemental analysis, by potentiometric titration of acetylacetone and acetic acid after aqueous phosphoric acid decomposition and steam distillation, and by v.p.c. detection of methanol in the decomposed aqueous solution.

Anal. Calcd. for $ZnNaC_{13}H_{20}O_7$: C, 41.34; H, 5.60; Zn, 17.31; Na, 6.09. Found: C, 41.05; H, 5.30; Zn, 17.17; Na, 5.69.

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The Synthesis and Resolution of *cis*-Difluorobis(ethylenediamine)chromium(III) Iodide

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In 1960 Fehrmann and Garner[2] reported the first successful synthesis of *cis*-difluorobis(ethylenediamine)-chromium(III) iodide. The assignment of the *cis* arrangement of the fluoro ligands was on the basis of the color of the complex, its visible absorption spectrum, and the behavior of the complex on ion-exchange columns. Absolute proof of the *cis* structure was not presented by these authors and, in addition, the synthesis, while ultimately yielding a pure product, was tedious and gave the desired compound in a low yield.

During the course of stereochemical studies in this laboratory, it was necessary to prepare *cis*-difluorobis(ethylenediamine)chromium(III) iodide in quantity and to establish unequivocally the *cis* configuration of the complex.

Experimental

Preparation and Source of Starting Materials.—Aqueous (95%) ethylenediamine, 1,2-propanediamine, and 1,3-propanediamine were dried according to the method of Putnam and Kobe.[3] Anhydrous chromium(III) fluoride was used as received.[4]

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[1] Taken in part from a thesis submitted by B. J. K. to the Graduate School of Northern Illinois University in partial fulfillment of the requirements for the degree of Master of Science.

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