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Bis(acetylacetonato)metal(II)-Catalyzed Addition of Acceptor Molecules to Acetylacetone[1)]

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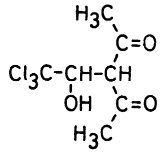
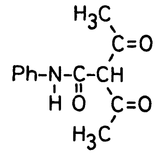
Synopsis. Bis(acetylacetonato)metal(II) (M(acac)$_2$) showed an effective catalytic activity for the addition of various acceptor molecules to acetylacetone to give 3-substituted 2,4-pentanediones.

Collman[2)] found that M(acac)$_n$ undergoes electrophilic substitutions at the 3-position on the chelate ring in a similar manner to that of aromatic compounds and proposed that M(acac)$_n$ has some quasi-aromatic characters. However, the aromaticity of M(acac)$_n$ based on the electrophilic substitution is open to question.[3)] In a previous communication,[4)] we reported that M(acac)$_2$ undergoes an aldol addition of chloral to the 3-position on the chelate ring to give an adduct A and polychloral in the presence and absence of acetylacetone, respectively.

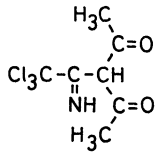
The present paper will show that M(acac)$_2$ undergoes not only the aldol addition but also another electrophilic reaction with a few acceptor molecules such as phenyl isocyanate and trichloroacetonitrile at the 3-position to give adduct B and C in the presence of acetylacetone. It is interesting to note that A can exist only in the keto form and that C is at first isolated as a crystalline keto-form but is easily transformed into an enolic form even in the solid state at room temperature within 24 h.



(A)



(B)

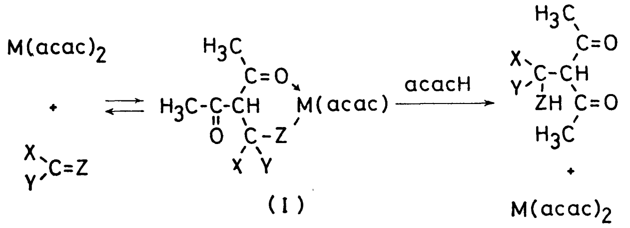


(C)

In the presence of piperidine instead of M(acac)$_2$ as a catalyst, chloral and trichloroacetonitile also reacted with acetylacetone to give the same reaction products (A and C), but not phenyl isocyanate since it reacted with piperidine to form urea. Carbon disulfide did not react with acetylacetone in the presence of M(acac)$_2$, but in the presence of piperidine it reacted to attack the 3-carbon of acetylacetone and the product was isolated as the piperidinium salt of dithiocarboxylic acid.[5)] Acetonitrile was non-reactive to acetylacetone in the presence of either catalyst.

Bloodworth *et al.*[6)] studied systematically the reactions of metal alkoxide with various acceptor molecules such as chloral, phenyl isocyanate, and carbon disulfide. They confirmed that these acceptor molecules were inserted into the oxygen-metal (O–M) bond of metal alkoxide (formation of O-adduct). However, we found that, for the M(acac)$_2$-catalyzed reaction of acetylacetone, the acceptor molecules which are highly polarized or have high polarizability react to attack the 3-position of acetylacetone and form C-adduct. This is not in line with the view that M(acac)$_n$ has the character of metal alcoholate. Hitherto, the initiation mechanisms of the polymerization of chloral and formaldehyde[7)] and of the alternative copolymerization of maleic anhydride with epichlorohydrin[8)] induced by M(acac)$_n$ have been explained in terms of the insertion of these monomers into the O–M bond of M(acac)$_n$ but without definite evidence.

Differing from the electrophilic substitution as reported by Collman,[2)] these acceptors undergo only the electrophilic addition on the 3-carbon of M(acac)$_2$ without subsequent elimination of the proton. The present reaction, therefore, seem to be a novel type of reaction of M(acac)$_n$ as follows:



(I)

Attemps to isolate the adduct I from reaction mixtures were unsuccessful, presumably because the complex is unstable and readily decomposed to the acceptor molecule and M(acac)$_2$. However, there are several spectral evidences to support the existence of I in equilibrium with chloral and M(acac)$_2$. The tetrahydrofuran solutions of Co(acac)$_2$ and Cu(acac)$_2$ rapidly turned from pink to blue and from blue to green, respectively with the addition of chloral. The infrared spectrum (CHCl$_3$) shows the presence of $\nu_{C=O}$ (saturated ketone) at 1700 cm^{-1}, which is not detectable in chloral or M(acac)$_2$ (M=Co, Cu), independently.

Experimental

Materials. Chloral was prepared through the dehydration of commercial chloral hydrate by concentrated sulfuric acid and distilled under nitrogen prior to use. Phenyl isocyanate of G. R. grade was used without further purification. Commercial trichloroacetonitrile and carbon disulfide were distilled before use. Commercial acetylacetone was purified by distillation. M(acac)$_n$ and piperidine of G. R. grade were used without further purification.

Spectral Measurements. The IR spectra were measured with a Model 215 Hitachi grating infrared spectrophotometer. The NMR spectra were taken with a Hitachi Model R-20 spectrometer. Tetramethylsilan was used as an internal standard, and carbon tetrachloride as the solvent. The UV spectra were measured with a Shimadzu UV-200 spectrophotometer. The elemental analyses were carried out with a Yanagimoto Model MT-2 CHN analyzer.

Reaction of Chloral with Acetylacetone. To a mixture of 5.79 g (57.8 mmol) of acetylacetone and 8.48 g (57.5 mmol) of chloral was added 0.339 mmol of $M(acac)_2$(M=Mg(II), Co(II), Ni(II), Zn(II), Cu(II)). An exothermic reaction took place. The solution was cooled to 0 °C until the product was precipitated. The reaction mixture was poured into 20 ml of ligroin to give white crystals of 3-(1-hydroxy-2,2,2-trichloroethyl)-2,4-pentanedione (A). The yield was 91% ($Mg(acac)_2$) to 85% ($Cu(acac)_2$). Mp 83 °C (from benzene–ligroin). Found: C, 34.09; H, 3.62%. Calcd for $C_7H_9O_3Cl_3$: C, 33.97; H, 3.67%. IR spectrum (KBr disk); 3420 (s), 3300 (s), 1690 (vs, C=O), 1410 (m), 1360 (s), 1320 (m), 1275 (m), 1180 (s), 1150 (s), 1090 (s), 940 (m), 830 (w), 805 cm^{-1} (s). UV spectrum ($CHCl_3$); λ_{max} 290 nm, ε_{max} 140. NMR spectrum (CCl_4); 7.67 (6H, s, $COC\underline{H}_3$), 5.35 (3H, m, $O\underline{H}$, $Cl_3CC\underline{H}(OH)$, and $C\underline{H}(COCH_3)_2$). Spectral evidence for the aldol condensate is compatible with the structure A and shows that A exists only in keto form. A is reverted to chloral and acetylacetone in the presence of $M(acac)_2$ and other metal salts. The aldol reaction is also catalyzed by piperidine and gives the same product A in an 85% yield. $Co(acac)_3$ and $Cr(acac)_3$ are ineffective as catalyst.

Reaction of Phenyl Isocyanate with Acetylacetone. Phenyl isocyanate (2.12 ml, 19.5 mmol) was added to a mixture of $M(acac)_2$ (0.194 mmol, M=Mg(II), Co(II)) and acetylacetone (2 ml, 19.5 mmol) in dichloromethane (5 ml). An exothermic reaction took place. Ten ml of ligroin was added to the reaction mixture which was cooled to −78 °C, precipitating 3-phenylcarbamoyl-2,4-pentanedione (B) in a 76% yield (3.24 g). Mp 118—119 °C (lit,[9] 118—119 °C). IR spectrum (KBr disk); 3270 (NH) and 1640 cm^{-1} (C=O). The reaction mixture should not be allowed to stand for a long time in contact with air. In the presence of $M(acac)_2$, B is subject to hydrolysis to give acetic acid and acetoacetanilide as final products. In the presence of piperidine, phenyl isocyanate does not react with acetylacetone because it reacts with piperidine to form urea.

Reaction of Trichloroacetonitrile with Acetylacetone. Trichloroacetonitrile (3.96 g, 27.4 mmol) was added to a mixture of $Co(acac)_2$(0.0705 g, 0.274 mmol) and acetylacetone (2.74 g, 27.4 mmol). An exothermic reaction took place. Ten ml of ligroin was added to the reaction mixture which was cooled in an ice bath, precipitating 3-(1-imino-2,2,2-trichloroethyl)-2,4-pentanedione (C) in an 80% yield (5.37 g). C was precipitated as a keto-form crystal which was purified by the recrystallization from benzene–ligroin. It was easily transformed into the enol form even in the solid state, the color changing from white to pale yellow within 24 h on being left to stand at room temperature; mp of enol-form 58 °C (from benzene–ligroin). Found: C, 34.51; H, 3.07; N, 5.21%. Calcd for $C_7H_8O_2NCl_3$: C, 34.35; H, 3.27; N, 5.73%. IR spectrum of enol-form (KBr disk); 3340 (s, NH), 3080 (m), 1670 (s, C=N), 1595 (s, enol), 1450 (m), 1420 (m), 1360 (s), 1260 (s), 1220 (s), 1100 (m), 1030 (w), 1015 (w), 980 (m), 955 (m), 830 (s), 790 cm^{-1} (s). IR spectrum of keto-form (KBr disk); 3240 (s, NH), 1725 (s, C=O), 1700 (s, C=O), 1645 cm^{-1} (m, C=N). The reaction of trichloroacetonitrile with acetylacetone was also catalyzed by piperidine and gave C in a 1.0% yield.

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