packed with 100–120 mesh Celite with 10% of Carbowax. The Celite was previously treated with a 5% soda solution in methanol. The analyses were made at 120° with nitrogen as carrier at a flow rate of 12 cc/min. The products were isolated by gas chromatography and characterized by infrared spectrophotometry. The separation was performed with a preparative column 3 m in length and 6 mm in diameter. The infrared analyses were made with a Model 237G Perkin-Elmer apparatus.

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The Transesterification of Acetoacetic Ester Chelates

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Esters of acetoacetic acid are known to undergo facile transesterification without the addition of catalyst.[1-3] It has been suggested[2] that the reaction involves internal acid catalysis by the chelated enolic proton. We have found that metal chelates of acetoacetic esters also undergo uncatalyzed ester interchange. This reaction affords a convenient synthetic route to the higher alcohol derivatives of these metal chelates.

The copper and aluminum chelates of ethyl acetoacetate were converted to the *n*-propyl esters by transesterification with *n*-propyl alcohol. The copper chelate reacted somewhat more slowly than the uncomplexed ester, and the aluminum chelate reacted much more slowly. Neither reacted with isopropyl alcohol under mild conditions. The copper and beryllium chelates of methyl acetoacetate underwent transesterification with 2,2-dimethylpropane-1,3-diol to give polymeric chelates of 2,2-dimethylpropane 1,3-bis(acetoacetate). The products were identified by infrared and ultraviolet spectra (Table I) and by elemental analysis.

Table I

Spectra of Acetoacetic Ester Chelates

		Infrared,[a]	Ultraviolet[b]	
Parent alcohol	Metal	ν_{max}, cm^{-1}	λ_{max}, mμ	$\epsilon_{max} \times 10^{-3}$
CH_3OH	Cu	1600	228	9.8
		1560	262	15.3
		1540		
CH_3OH	Be	1592	260	50.7
		1516		
C_2H_5OH	Cu	1591[c]	229	10.8
		1568[c]	262[d]	15.3
		1516[c]		
C_3H_7OH	Cu	1598	229	13.3
		1531	264	18.0
C_3H_7OH	Al	1605[e]	267	41.0
		1514[e]		
$(CH_3)_2C(CH_2OH)_2$	Cu	1640 (w)		
		1598		
		1520		
$(CH_3)_2C(CH_2OH)_2$	Be	1595	272	34.0[f]
		1510		

[a] Chelate bands in 1500- to 1700-cm^{-1} region, strong except where noted. [b] Copper and aluminum chelates in cyclohexane, beryllium chelates in dichloromethane. Only high-intensity peaks listed. [c] Lit.[12] 1600, 1555, 1538 cm^{-1}; lit.[13] 1591, 1568, and 1516 cm^{-1}. [d] Lit.[12] λ_{max} 254 mμ; (ϵ_{max} 14.0 × 10^3) ($CHCl_3$); lit.[14] λ_{max} 256 and 263 mμ (ϵ_{max} 15.0, 15.1 × 10^3) (cyclohexane). [e] Lit.[13] 1609 and 1528 cm^{-1} (ethyl ester). [f] Based on the repeating unit.

It is somewhat surprising that complexing with metal ions appears to inhibit the transesterification. Metal complexing strongly accelerates the hydrolysis of α-amino esters[4-6] and the transesterification of α-salicylaldimino esters.[7,8] The present reaction may perhaps follow a path analogous to that proposed[4,6] for the amino ester hydrolysis. Alternatively the transesterification may be preceded by the alcoholysis of a metal–oxygen bond. In either case the conjugate carbonyl resonance of the chelate would be lost in the transition state. This could account for the metal ion inhibition, if the assumption is made that enolate resonance is more important in the metal chelates than in the uncomplexed ester.[9]

Experimental Section[10]

Methyl and *n*-propyl alcohols were dried by distillation from the magnesium alkoxides. Benzene and toluene were dried over sodium wire. 2,2-Dimethylpropane-1,3-diol (mp 128–129°) was purified by repeated vacuum sublimation. The transesterifications were carried out in glassware dried at 150°. Bis(ethylacetoacetato)copper(II)[11-14] was recrystallized from benzene, mp 198–200° dec; lit. 193°,[11,12] 195–196°.[13] Tris(ethylacetoacetato)aluminum(III) was purified by distillation, bp 155° (0.7 mm), mp 79–81°; lit.[13] 79–81°. Bis(methylacetoacetato)beryllium(II) was prepared from beryllium chloride, sodium methoxide, and methyl acetoacetate in anhydrous methanol under nitrogen. It melted at 135–136° after repeated vacuum sublimation. Bis(methylacetoacetato)copper(II) was prepared from cupric acetate and methyl acetoacetate in water, and recrystallized from benzene, mp 194–195° dec.

Anal. Calcd for $C_{10}H_{14}CuO_6$: C, 40.88; H, 4.80. Found: C, 40.81; H, 4.80.

Bis(*n*-propylacetoacetato)copper(II).—A solution of 13.0 g (0.0404 mole) of bis(ethylacetoacetato)copper(II) in 35 ml of *n*-propyl alcohol was subjected to slow distillation for 3 hr through a 12-cm column. Propyl alcohol was added continuously to maintain the volume. Fractions of 5 ml each were removed and monitored by vapor phase chromatography (SE 30 on Chromosorb W). Nine fractions were collected containing decreasing amounts of ethanol, and the last fraction was pure *n*-propyl alcohol. The yield of *n*-propyl ester (mp 131.5–132.5°) was 13.2 g (94%) after recrystallization from ether.

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Anal. Calcd for $C_{14}H_{22}CuO_6$: C, 48.06; H, 6.34. Found: C, 47.80; H, 6.27.

Tris(n-propylacetoacetato)aluminum(III).—A solution of 41.4 g (0.1 mole) of tris(ethylacetoacetato)aluminum(III) in 36 g of n-propyl alcohol was subjected to similar transesterification. Nineteen fractions were taken in 16 hr, a trace of ethyl alcohol remaining in the last fraction. The product was purified by distillation through a 64-cm heated column. After a forerun of 12.2 g, bp 152–161° (0.35 mm), the n-propyl ester (21.8 g, 43%) was collected at 161–169° (0.5 mm). It was a colorless, slightly viscous oil of $n^{20}\text{D}$ 1.5030.

Anal. Calcd for $C_{21}H_{35}AlO_9$: C, 55.01; H, 7.26; Al, 5.89. Found: C, 54.57; H, 7.18; Al, 6.04.

Poly[2,2-dimethylpropane-1,3-bis(acetoacetato)]copper(II).—A solution of 28.056 g (0.09551 mole) of bis(methylacetoacetato)-copper(II) and 9.948 g (0.09552 mole) of 2,2-dimethylpropane-1,3-diol in 250 ml of benzene was subjected to very slow distillation at a reflux ratio of 30:1 through a 12-cm column. The volume was maintained by continuously adding benzene. After 4 days the benzene was replaced by toluene and the distillation was continued for 8 days. The product (30.5 g, 91%) was a green powder only slightly soluble in boiling toluene, crystalline by X-ray[15] and decomposing at 228–230°. It had no hydroxyl absorption in the infrared and analyzed satisfactorily for an infinite polymer.

Anal. Calcd for $C_{13}H_{18}CuO_6$: C, 46.77; H, 5.44; Cu, 19.03. Found: C, 46.84; H, 5.45; Cu, 18.84.

Poly[2,2-dimethylpropane-1,3-bis(acetoacetato)]beryllium-(II).—A solution of 2.392 g (0.01 mole) of bis(methylacetoacetato)beryllium(II) and 1.0623 g (0.0102 mole) of 2,2-dimethylpropane-1,3-diol in 15 ml of benzene was subjected to slow distillation for 24 hr, while replacing the solvent which boiled off. The benzene was then replaced by toluene and the distillation was continued for 91 hr. The viscous reaction mixture was freed of solvent by the use of a nitrogen capillary under high vacuum at 110°. After cooling the product was a brittle, colorless glass, amorphous by X-ray,[15] of mol wt 1400 (benzene). No hydroxyl absorption was visible in the infrared spectrum. The product analyzed equally well for an infinite polymer or for a pentamer (mol wt 1428) with one methyl and one diol end group.

Anal. Calcd for $C_{13}H_{18}BeO_6$: C, 55.90; H, 6.50; Be, 3.23. Calcd. for $C_{66}H_{94}Be_5O_{31}$: C, 55.51; H, 6.64; Be, 3.16. Found: C, 55.65; H, 6.60; Be, 3.21.

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[15] We are grateful to Mr. R. Nilberg for the X-ray determinations.

Isomer Distributions in Electrophilic Substitution Reactions of Neopentylbenzene[1]

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In aromatic electrophilic substitution reactions of alkylbenzenes, it has been found that as the bulk of the alkyl substituent is increased the extent of *ortho* substitution is reduced and that of *para* substitution is increased.[2,3] It was therefore somewhat surprising to find that the nitration of neopentylbenzene gave only about 50% of p-nitroneopentylbenzene[4] and that another unidentified isomer was obtained in about equal amount.[5] This result prompted an investigation of the isomer distributions obtained in various electrophilic substitution reactions of neopentylbenzene. It was necessary first to characterize and identify the substitution products of neopentylbenzene, since the only previously identified substitution products were p-nitro-[4a] and p-bromoneopentylbenzene.[4b]

Isomer Distributions.—Analysis of the isomer distributions obtained in the substitution reactions of neopentylbenzene was made by vpc. The areas of the vpc peaks for the various isomers were determined by the triangulation method.[6,7] The results are listed in Table I together with previously reported values for toluene and t-butylbenzene under identical reaction conditions.

TABLE I

ISOMER DISTRIBUTIONS IN SUBSTITUTION REACTIONS OF TOLUENE, t-BUTYLBENZENE, AND NEOPENTYLBENZENE

Reaction	P_f^{Me}		Me	t-Bu	Neop[a]
Nitration, H_2SO_4[b] at 25°	c	o	58.5[d]	15.8[d]	44.9
		m	4.4	11.5	3.2
		p	37.2	72.7	51.8
Cl_2, HOAc at 25°	820[e]	o	59.8[e]	21.5[e]	25.5
		m	0.5	2.3	f
		p	39.7	76.2	74.5
Br_2, 85% HOAc at 25°	2420[e]	o	32.9[e]	1.2[e]	8.5
		m	0.3	1.5	f
		p	67.1	97.3	91.5
CH_3COCl, $AlCl_3$, CS_2 at room temp		o,m	g		5
		p	97.6[g]		95

[a] Average of several values obtained by vpc; maximum deviation in values is ±1.0. [b] Heterogeneous conditions of Brown and Bonner.[3] [c] The value of p_f^{Me} under these conditions is not known. For homogeneous nitration, p_f^{Me} is 48.5 in acetic anhydride at 25°, 58 in 90% acetic acid at 45°, and 45.8 in nitromethane at 25°.[2] [d] Data of Brown and Bonner.[3] For ethylbenzene, the percentages of *ortho, meta,* and *para* are 45.0, 6.5, and 48.5.[2] [e] Data from Tables II and XII of ref 2. [f] No *meta* isomer detected. [g] The *para* yield is reported on p 46 of ref 2; extent of *ortho* and *meta* substitution not reported.

Of much interest is the fact that the degree of *ortho* nitration of neopentylbenzene is considerably greater than that of t-butylbenzene, being comparable to that of ethylbenzene. Brown and Bonner found that the percentage of *ortho* substitution decreases markedly through the series toluene, ethylbenzene, isopropylbenzene, t-butylbenzene, and attributed this to classical steric hindrance to *ortho* substitution.[3] The relatively large *ortho/para* ratio for neopentylbenzene would appear to indicate that there is no great steric hindrance to *ortho* nitration of this hydrocarbon.

In chlorination in acetic acid, the degree of *ortho* substitution of neopentylbenzene is appreciably less than in nitration, becoming comparable to that of t-butylbenzene. Perhaps this could be attributed to greater steric hindrance to *ortho* chlorination as compared to *ortho* nitration of neopentylbenzene. Nowever, note that the *ortho/para* ratio for toluene and t-butylbenzene is comparable in chlorination and nitration. Furthermore, the *ortho/para* ratio in bromination in 85% acetic acid is much greater for neopentylbenzene than for t-butylbenzene. The product ratio is rate controlled and not equilibrium controlled, since o-bromoneopentylbenzene was found to be stable to treatment with excess hydrogen bromide under conditions identical with those used for bromination.

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