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Synthesis and Reactions of Chromium(III) Chelates of β-Amino-α,β-unsaturated Ketones[1,2]

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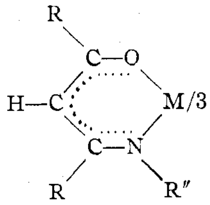
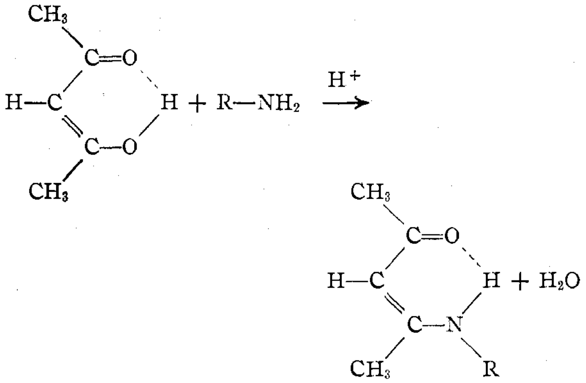
A series of chromium(III) chelates of β-amino-α,β-unsaturated ketones has been prepared by a new non-aqueous chelation reaction. Several of these chelates have been brominated in the manner of a quasi-aromatic system.

Recent reports from these and other laboratories have described the electrophilic substitution of chromium(III), cobalt(III), and rhodium(III) acetylacetonates[4–10] and of the chromium(III) chelates of malonaldehyde[11] and formylacetone.[11] Halogenation,[5,9] thiocyanogenation,[7,9,10] nitration,[4,6] dimethylaminomethylation,[10] chloromethylation,[10] acylation,[4,6,10] and formylation[6,10] reactions have been carried out on these reactive quasi-aromatic substrates. An investigation of the chemistry of the inert metal chelates of β-amino-α,β-unsaturated ketones (I), the mononitrogen analogs of acetylacetonates, seemed a logical sequel to these earlier studies.[12]



I

A large number of imine derivatives of acetylacetone are known. These substances are easily formed by treatment of acetylacetone with a primary amine. Acid catalysis and azeotropic removal of the water formed in the condensation make this a general procedure. The principal interest in these Schiff bases has been due to their application in the synthesis of heterocyclic compounds. Cromwell included this class of compounds in a review of amino ketones.[13] The tautomerization of these compounds has recently been studied by n.m.r. spectroscopy.[14]



In spite of the large number of well characterized Schiff bases[15,16] of acetylacetone, the

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[2] The authors gratefully acknowledge financial support from the Petroleum Research Fund, administered by the American Chemical Society.

[3] Hampden Sydney College, Hampden Sydney, Virginia; Petroleum Research Fund Fellow, 1960–1961.

[4] J. P. Collman, R. A. Moss, S. D. Goldby, and W. S. Trahanovsky, *Chem. Ind.* (London), 1213 (1960).

[5] J. P. Collman, R. A. Moss, H. Maltz, and C. C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961).

[6] J. P. Collman, R. A. Moss, S. D. Goldby, R. L. Marshall, and W. L. Young, III, Abstracts of the 139th National Meeting of the American Chemical Society, St. Louis, Mo., March, 1961.

[7] J. P. Collman and R. P. Blair, Abstracts of the 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961, p. 4-N.

[8] R. W. Kluiber, *J. Am. Chem. Soc.*, **82**, 4839 (1960).

[9] R. W. Kluiber, *ibid.*, **83**, 3030 (1961).

[10] J. P. Collman, unpublished results.

[11] J. P. Collman and E. T. Kittleman, *J. Am. Chem. Soc.*, **83**, 3529 (1961).

[12] As a matter of convenience these ligands will be referred to as β-ketoimines.

[13] N. H. Cromwell, *Chem. Rev.*, **38**, 83 (1946).

[14] G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 3914 (1961).

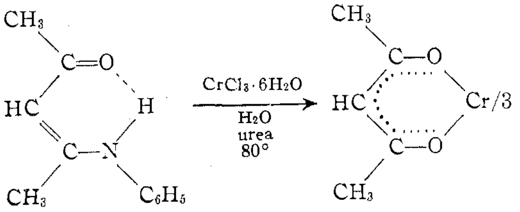
[15] R. F. C. Brown, V. M. Clark, I. O. Sutherland, and A. R. Todd, *J. Chem. Soc.*, 2116 (1959).

[16] (a) A. Combes and C. Combes, *Compt. rend.*, **106**, 142 (1888); (b) A. Combes, and C. Combes, *Bull. soc. chim. France*, [3] **7**, 781 (1892); (c) C. Burlow and G. Issler, *Ber.*, **36**, 4015 (1903); (d) W. Koenigs and A. Mengel, *ibid.*, **37**, 1333 (1904); (e) L. Rugheimer and G. Ritter, *ibid.*, **45**, 1332 (1912); (f) E. E. Turner, *J. Chem. Soc.*, 1 (1917); (g) J. Braun, W. Gmelin, and A. Petzold, *Ber.*, **57**, 382 (1924); (h) G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 610 (1925); (i) E. Roberts and E. E. Turner, *ibid.*, 1832 (1927); (j) H. Lempert and R. Robinson, *ibid.*, 1419 (1934); (k) W. S. Johnson and F. J. Mathews, *J. Am. Chem. Soc.*, **66**, 210 (1944); (l) C. R. Hauser and M. J. Weiss, *J. Org. Chem.*, **14**, 453 (1949); (m) R. Adams and J. Campbell, *J. Am. Chem. Soc.*, **72**, 1021 (1950); (n) W. Suida, *J. prakt. Chem.*, [2] **83**, 241 (1911); (o) E. Knoevenagel and W. Rushhaup, *Ber.*, **31**, 1030 (1898); (p) L. Knorr and K Rossler, *ibid.*, **36**, 1278 (1903); (q) F. Lions, W. H. Perkin, and R. Robinson, *J. Chem. Soc.*, 1162 (1925).

metal chelates of these β-amino-α,β-unsaturated ketones have been relatively neglected. Combes[16d] reported the copper(II) salt of 4-amino-3-penten-2-one. Kishita[17] measured the magnetic susceptibility of the copper(II) chelate of 4-*o*-hydroxyanilino-3-penten-2-one. The synthesis and infrared spectra of several copper(II) chelates of such β-ketoimines were studied by Holtzclaw.[18] Martin[19] recently has determined the dissociation constants of several copper(II) chelates of β-ketoimines, but the complexes were not isolated and characterized. A considerable amount of work has appeared on the chelates of bisacetylacetoneëthylenediimine.[20]

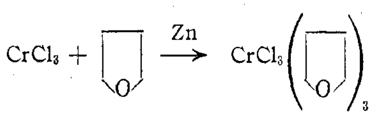
It is significant that the preceding studies have described only the β-ketoimine chelates of divalent metals. Such chelates of trivalent metals have not been reported. From the aspect of treating metal chelate rings as reactive metal heterocycles this lack of synthetic background is unfortunate since such chemical studies are best carried out with the inert molecular chelates of chromium(III), cobalt(III), and rhodium(III).

The first attempts to prepare chromium(III) and cobalt(III) chelates of β-ketoimines by modification of known aqueous chelation methods failed. For example, when a mixture of 4-anilino-3-penten-2-one (II) was treated with a hot aqueous solution of chromium(III) chloride and urea, only chromium(III) acetylacetonate was isolated. It soon became apparent that non-aqueous chelation procedures were more promising.



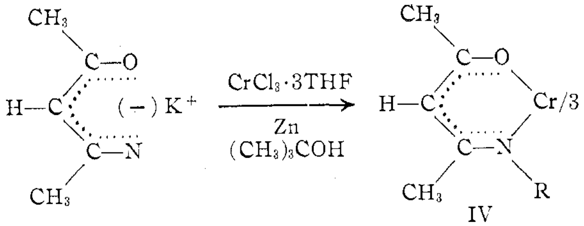
II

Anhydrous chromium(III) chloride reacts with Lewis donor solvents such as ethers, alcohols and amides to form a series of solvates which are soluble in many polar organic solvents.[21] These solvation reactions proceed only when a small amount of zinc is in contact with the chromium(III). Although a number of these materials have been characterized, many more remain to be investigated. The solvate III proved useful in preparing the desired chelates



III

The chelation reaction was successful when potassium *t*-butoxide in *t*-butyl alcohol was used as the base—provided the correct order of addition was used. An equimolar mixture of potassium *t*-butoxide and the β-ketoimine in *t*-butyl alcohol immediately became a solid mass—probably the potassium salt of the β-ketoimine. The solid chromium solvate III (mixed with a small amount of zinc dust) was added to this slurry and the mixture was heated. Work-up of this crude mixture afforded a modest yield of the β-ketoimine chromium(III) chelate (IV). All other modes of addition failed to give tractable products. Subsequent experiments showed that zinc dust is not necessary for the reaction, but the yields are higher when zinc dust is present.



IV

This reaction scheme proved to be a generally useful process for the preparation of β-ketoimine chelates of chromium(III). Table I summarizes the complexes that have been synthesized by this method. In most cases the β-ketoimines were derivatives of aromatic amines (IV, R = aryl), but aliphatic amines also can be used—for example, benzylamine (IV, R = $C_6H_5CH_2$). In another instance the imine of a β-ketoaldehyde was converted into a chromium(III) chelate.

Several β-ketoimines failed to form chromium(III) chelates under these conditions. For example, 4-*p*-carbethoxyanilino-3-penten-2-one (V, R = *p*-$(C_2H_5O_2C)C_6H_4$); 4-*m*-nitroanilino-3-penten-2-one (V, R = *m*-$NO_2C_6H_4$); and 4-ethanolamino-3-penten-2-one (V, R = $HOCH_2CH_2$) gave intractable products. Each of these ligands contains an additional group that would be expected to react with the strong base.

The initial attempts to use other bases and the solvate III to form chromium(III) chelates of

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(17) M. Kishita, Y. Muto, and M. Kubo, *Naturwissenschaften*, **44**, 372 (1957).

(18) H. F. Holtzclaw, Jr., J. P. Collman, and R. M. Alire, *J. Am. Chem. Soc.*, **80**, 1100 (1958).

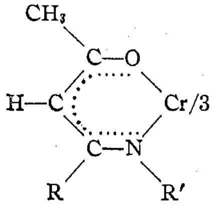
(19) D. F. Martin, G. A. Janusonis, and B. B. Martin, *ibid.*, **83**, 73 (1961).

(20) R. J. Hovey, J. J. O'Connell, and A. E. Martell, *ibid.*, **81**, 3189 (1959).

(21) W. Herwig and H. H. Zeiss, *J. Org. Chem.*, **23**, 1404 (1958).

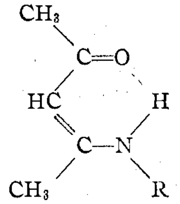
TABLE I

CHROMIUM(III) CHELATES FROM SCHIFF BASE LIGANDS



		Calcd.			Found			%	
R	R′	C	H	N	C	H	N	yield[a]	M.p., °C.
CH_3	C_6H_5	68.96	6.32	7.32	69.06	6.29	7.15	23	187–188
CH_3	p-$CH_3C_6H_4$	70.11	6.87	6.81	70.18	6.68	6.90	38	179–181
CH_3	o-$CH_3C_6H_4$	70.11	6.87	6.81	70.28	6.78	6.87	48	197–199
CH_3	o-ClC_6H_4	58.46	4.91	6.20	58.38	4.83	6.17	25	241–244
CH_3	m-ClC_6H_4	58.46	4.91	6.20	58.10	4.85	6.28	50	168–170
CH_3	p-ClC_6H_4	58.46	4.91	6.20	57.48	4.92	6.03	20[a]	219–221
CH_3	p-$CH_3OC_6H_4$	65.04	6.37	6.32	65.14	6.34	6.56	39	185–187
CH_3	$C_6H_5CH_2$	70.11	6.87	6.82	69.62	6.80	6.89	54	137–139
CH_3	p-C_6H_5–C_6H_4	76.29	6.03	5.23	76.91	6.01	5.10	30	261–263
CH_3	β-naphthyl	74.56	5.84	5.80	73.16	5.79	5.74	27[b]	225–228[b]
H	p-$CH_3C_6H_4$	68.97	6.32	7.31	68.83	6.27	7.48	14	170–171

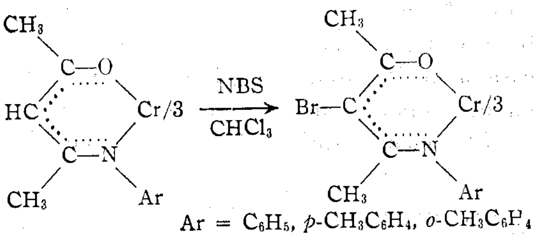
[a] % yield is based on chromium solvate II. [b] Analyses indicate that this compound may not have been obtained in a pure form. We occasionally have experienced great difficulty in obtaining accurate carbon analyses on metal chelates. Many of these compounds explode upon ignition.



V

β-ketoimines failed. Each base was chosen to function as a proton abstractor with a minimum tendency to attack the metal as a ligand. Sodium acetate in tetrahydrofuran, potassium carbonate in ethanol, magnesium oxide in t-butyl alcohol, collidine in isopropyl alcohol, sodium ethoxide in ethanol, and sodium isopropoxide all failed.

The β-ketoimine chromium(III) chelates were found to undergo facile bromination with N-bromosuccinimide (NBS) in the same manner as the quasi-aromatic metal acetylacetonates.[5] It is interesting to note that the benzene ring was not substituted under these conditions, even though this ring should be activated by the nitrogen atom.



Ar = C_6H_5, p-$CH_3C_6H_4$, o-$CH_3C_6H_4$

Preliminary attempts to carry out nitration and formylation of this new chelate system failed. Under the same conditions that previously had effected nitration and formylation of chromium(III) acetylacetonate, the β-ketoimine chelates were destroyed. The latter showed much less stability under acidic conditions. It is probable, however, that suitable conditions can be found to carry out other electrophilic substitutions on these β-ketoimine chelates.

The infrared spectrum of a typical β-ketoimine exhibits strong, characteristic peaks at 1570, 1540, and 1490 cm.$^{-1}$, whereas the corresponding chromium chelate shows major bands at 1565, 1490, and 1450 cm.$^{-1}$. The 1490-cm.$^{-1}$ band in the chelate spectra is the strongest peak. This characteristic pattern of infrared maxima is shown by all of the β-ketoimine chelates examined. The substitution of hydrogen by bromine at the central carbon atom resulted in the disappearance of the bands at 1565 and 1490 and their replacement by a strong peak at 1545 cm.$^{-1}$. This behavior is analogous to the spectra of the metal acetylacetonates. Dryden[22] observed that replacement of the hydrogen by other groups at the central carbon of metal acetylacetonate rings caused the infrared doublet in the 1500–1600-cm.$^{-1}$ region to become a singlet at about

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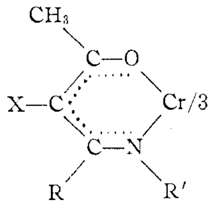
(22) R. P. Dryden and A. Winston, *J. Phys. Chem.*, **62**, 635 (1958)

1550 cm.$^{-1}$. Many examples of this empirical rule have been observed in this Laboratory.

The ultraviolet spectra of the chromium(III) chelates of β-ketoimines are summarized in Table II, whereas the spectra of a few representative examples of the Schiff base ligands are listed in Table III. Inspection of these data reveals a significant change in ultraviolet spectra in going from ligand to chelate, but the spectra of the individual chelates are very similar. Introduction of bromine into the chelate rings gives rise to a bathochromic shift in each of the ultraviolet maxima suggesting an increased conjugated system. The data in Table II also indicate that the aryl groups on the nitrogen are not coplanar with the chelate ring except in the case of the chelate derived from a β-ketoaldimine. In each case the β-ketoimine chelates exhibit maxima near 270 and 363 mμ. Substration of naphthyl, biphenyl, phenyl, or even benzyl at the ring nitrogen has little effect on these maxima. *o*- and *p*-substituted aryl groups give rise to the same spectra but models show that there is little possibility of coplanarity with the chelate ring in the case of *o*-substituted aryl groups on the chelate ring nitrogen. The adjacent methyl group on the chelate ring provides steric interaction which prevents coplanarity of the aryl and chelate rings. Replacement of this methyl group by hydrogen (the β-ketoaldimine chelate) gives rise to a bathochromic shift of the lower ultraviolet maximum from 263 to 280 mμ. It would seem that the upper maximum is not sensitive to conjugation with groups on nitrogen. The molecular extinction coefficient of the lower maximum is sensitive to extended conjugation.

TABLE II

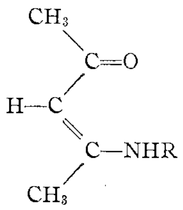
ULTRAVIOLET SPECTRA OF CHROMIUM(III) CHELATES OF β-KETOIMINES



X	R	R′	CHCl$_3$ $\lambda_{\max}$	ϵ
H	CH$_3$	C$_6$H$_5$	266	19,900
			362	12,500
Br	CH$_3$	C$_6$H$_5$	274	15,600
			377	10,400
H	CH$_3$	2-CH$_3$C$_6$H$_4$	269	21,500
			362	13,200
Br	CH$_3$	2-CH$_3$C$_6$H$_4$	275	16,600
			377	11,700
H	CH$_3$	4-CH$_3$C$_6$H$_4$	268	22,500
			362	12,500
Br	CH$_3$	4-CH$_3$C$_6$H$_4$	272	18,200
			377	10,900
H	CH$_3$	2-ClC$_6$H$_4$	270	21,000
			363	13,400
H	CH$_3$	3-ClC$_6$H$_4$	271	20,000
			363	12,700
H	CH$_3$	4-ClC$_6$H$_4$	272	22,000
			362	12,500
H	CH$_3$	4-CH$_3$OC$_6$H$_4$	270	26,400
			363	12,400
H	CH$_3$	C$_6$H$_5$CH$_2$	268	17,500
			361	12,300
H	CH$_3$	β-naphthyl	270	49,000
			366	14,500
H	CH$_3$	4-C$_6$H$_5$C$_6$H$_4$	272	67,500
			363	15,900
H	H	4-CH$_3$C$_6$H$_4$	280	21,300
			373	14,900

TABLE III

ULTRAVIOLET SPECTRA OF β-KETOIMINES



R	CHCl$_3$ $\lambda_{\max}$	ϵ
C$_6$H$_5$	323	17,000
4-CH$_3$C$_6$H$_4$	323	18,500
4-ClC$_6$H$_4$	327	20,000
4-BrC$_6$H$_4$	328	20,000
β-naphthyl	334	20,600
	290	14,100
	280	11,600
4-C$_6$H$_5$C$_6$H$_4$	336	24,400
	255	11,000

Our preliminary attempts to detect the two diastereoisomeric racemates which should be possible in this system have not been successful. We have separated such *cis* and *trans* forms in unsymmetrical trisacetylacetonates and in the chromium(III) chelate of formylacetone.[10] Piper recently has separated and assigned structures to *cis* and *trans* isomers of rhodium(III) and cobalt(III) chelates of unsymmetrical β-diketones by an elegant use of n.m.r. spectra.[23] In the case of the β-ketoimine chelates the bulky groups on the donor atoms should greatly increase the relative energy difference between the *cis* and

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(23) R. C. Fay and T. S. Piper, Abstracts of the 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

trans forms. This is beautifully illustrated by molecular models. For this reason the less stable *cis* form may not be present in significant amounts. However, some of our crude, but analytically pure, reaction products exhibited wide melting ranges suggestive of such diastereoisomers.

Experimental[24]

Synthesis of β-Ketoimines. General Procedure.—A mixture of 0.1 mole of 2,4-pentanedione, 0.1 mole of primary amine, 2 drops of concentrated HCl, and 150 ml. of benzene was placed in a flask equipped with a Dean-Stark trap and reflux condenser fitted with a calcium chloride drying tube. Overnight heating at reflux resulted in azeotropic removal of water. The reaction mixture was cooled to room temperature, filtered, and concentrated to an oil or a solid on a rotating evaporator. Crystallization of these oils was effected by solution in ether and chilling to −10°. The solid residues were recrystallized from ether and/or heptane. Liquid products were purified by vacuum distillation. New β-ketoimines are described below.

4-*p*-Phenylanilino-3-penten-2-one.—Yield 30%; white crystals, m.p. 89–90°; infrared ($CHCl_3$): 1595, 1565, 1550, 1475, and 1270 cm.$^{-1}$; ultraviolet ($CHCl_3$): λ_{max} 336 (ϵ 11,000).

Anal. Calcd. for $C_{17}H_{17}NO$: N, 5.57. Found: N, 5.58.

4-(2-Carbethoxyethylamino)-3-penten-2-one (Sodium Salt).—Yield 75%; white needles from isopropyl alcohol–water, m.p. 191–193°.

Anal. Calcd. for $C_7H_{10}NNa$: N, 7.82. Found: N, 7.63.

4-*p*-Bromoanilino-3-penten-2-one.—Yield 35%; white crystals, m.p. 56–57°; infrared ($CHCl_3$): 1600, 1550, 1475, 1430, 1350, and 1270 cm.$^{-1}$; ultraviolet ($CHCl_3$): λ_{max} 328 (ϵ 20,000).

Anal. Calcd. for $C_{11}H_{12}ONBr$: N, 5.51. Found: N, 5.45.

4-*p*-Carbethoxyanilino-3-penten-2-one.—Yield 60%; yellow crystals; m.p. 83–84°; infrared ($CHCl_3$): 1770, 1605, 1565, and 1275 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{17}NO_3$: N, 5.66. Found: N, 5.62.

4-*m*-Nitroanilino-3-penten-2-one.—Yield 69%; yellow crystals; m.p. 78–80°; infrared ($CHCl_3$): 1615, 1565, 1530, 1350, and 1275 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{12}N_2O_3$: N, 12.72. Found: N, 1275.

Tristetrahydrofuranotrichlorochromium(III).—A mixture of 1 g. of zinc dust and 20 g. (0.127 mole) of anhydrous chromium(III) chloride was placed in the thimble of a Soxhlet extraction apparatus. Approximately 218 ml. of tetrahydrofuran (freshly distilled from calcium hydride) was placed in a 300-ml. flask which was attached to the Soxhlet apparatus. A calcium chloride drying tube was fitted on the reflux condenser. The tetrahydrofuran was heated at reflux for 4 hr., after which the heating was interrupted and an additional gram of zinc was added to the thimble. The heating at reflux then was maintained for 8 hr. (or until the recycling liquid was colorless). The tetrahydrofuran solution was cooled and allowed to stand for 12 hr. The purple powder was filtered and washed repeatedly with dry heptane. The powder was dried under vacuum for 24 hr.; yield 28.6 g. (60%).

General Procedure for Preparing Chromium(III) Chelates. Tris-(4-*p*-toluidine-3-penten-2-one)-chromium (III).—To 50 ml. of dry *t*-butyl alcohol in a 100-ml. flask fitted with a reflux condenser and a calcium chloride drying tube was added 0.85 g. (0.0217 mole) of potassium metal. After 10 hr. the metal had completely dissolved. While this solution was stirred with a magnetic bar, a mixture of 3.97 g. (0.021 mole) of 4-*p*-toluidine-3-penten-2-one, 1.37 g. (0.021 mole) of zinc dust, and 2.62 g. (0.007 mole) of tristetrahydrofuranotrichlorochromium(III) was added in one portion. The mixture was boiled under reflux for 2 hr. (continuous stirring). The mixture was cooled to room temperature, poured into 400 ml. of ether, and left in a deep freeze (−15°) overnight. The cold ether solution was filtered and then concentrated to a volume of 45 ml. on a rotating evaporator.

The resulting solution was diluted with 45 ml. of ethanol and then concentrated to 45 ml. This was repeated two times, and the material then was concentrated to a sticky red solid in order to remove the last amounts of *t*-butyl alcohol. The red solid was dissolved in benzene and put on a 10-in. chromatography column of activated alumina. Elution with 80/20 benzene–heptane afforded a red solution. This solution was concentrated to a red grease which crystallized in hot ethanol. Recrystallization from ethanol afforded 1.8 g. (41%) of red crystals, m.p. 179–181°.

Tris-(3-bromo-4-anilino-3-pentene-2-ono)-chromium-(III).—A solution of 0.574 g. (0.001 mole) of tris-(4-anilino-3-pentene-2-ono)-chromium(III) and 0.53 g. (0.003 mole) of N-bromosuccinimide in 25 ml. of chloroform was boiled 5 min. and then evaporated to dryness. The crude chelate was separated from succinimide by carbon tetrachloride extraction. Removal of the carbon tetrachloride afforded a benzene-soluble residue which was chromatographed on alumina. The benzene eluate was concentrated to a red oil. Crystallization was effected by dissolving the oil in ether–isopropyl alcohol and allowing this solution to stand for 12 hr. The dark green crystals were dried *in vacuo* at 80°; 60% yield (0.5 g.); m.p. 159–162° dec.; infrared (KBr pellet) 1545, 1440, and 1375 cm.$^{-1}$.

Anal. Calcd. for $C_{33}H_{33}O_3Br_3N_3Cr$: C, 48.85; H, 4.10; Br, 29.55; N, 5.18. Found: C, 49.03; H, 4.05; Br, 29.59; N, 5.19.

Tris-(3-bromo-4-*o*-toluidino-3-pentene-2-ono)-chromium(III).—This bromo chelate was prepared by the above procedure. The pure green crystals, m.p. 183–186° dec., were isolated in 14% yield.

Anal. Calcd. for $C_{36}H_{39}Br_3O_3N_3Cr$: C, 50.66; H, 4.61; Br, 28.09; N, 4.92. Found: C, 51.15; H, 4.82; Br, 27.52; N, 4.86.

Tris-(3-bromo-4-*p*-toluidino-3-pentene-2-ono)-chromium(III).—This bromo chelate was prepared by the above procedure. The dark crystals, m.p. 170° dec., were isolated in 23% yield.

Anal. Calcd. for $C_{36}H_{39}Br_3N_3O_3Cr$: C, 50.66; H, 4.61; Br, 28.09; N, 4.92. Found: C, 50.25; H, 4.63; Br, 29.19; N, 5.14.

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(24) All melting points are uncorrected.