

COMMUNICATIONS TO THE EDITOR

REACTIONS OF METAL CHELATES. II. SYNTHESIS OF THE CHROMIUM(III) CHELATES OF MALONALDEHYDE AND FORMYLACETONE²

Sir:

Previously, we have reported that functional groups substituted on quasiaromatic metal acetylacetonate rings often exhibit abnormal chemical properties which probably manifest the steric crowding at the central carbon of these chelate rings.^{1,3} It seemed desirable to examine the hitherto unknown chromium(III) chelates of malonaldehyde and formylacetone (I and II) in an attempt to differentiate between steric and electronic effects on reactions at the central carbon of such chelate rings. Furthermore, we were interested to discover whether malonaldehyde and formylacetone chelates would undergo electrophilic substitution reactions analogous to the quasi-aromatic acetylacetonate chelates.^{1,3,4}

The malonaldehyde chelate ring can be considered as the parent of all 1,3-dicarbonyl chelate ring systems. Although the ionic sodium salt of malonaldehyde is known,⁵ no authentic metal chelates of this ligand have been reported. We wish to report herein the first known metal chelate of malonaldehyde: tris-(1,3-propanedialono)-chromium(III) (I).

Since attempts to adapt the known methods of preparing chromium(III) acetylacetonate to the synthesis of the malonaldehyde chelate I failed, a new and apparently general method of preparing chromium(III) chelates was developed for the synthesis of I. This method involves generation of a chromium(II)-chromium(III) equilibrium in a donor solvent which contains an ionic salt of the ligand to be chelated. There are many possible variations to this scheme. This method has afforded the chromium(III) chelates of malonaldehyde and formylacetone as well as several other new chromium(III) chelate systems.

An acidic aqueous solution of malonaldehyde (generated from 1,1,3,3-tetraethoxypropane) was treated with triethylamine and the resulting solution then was allowed to come in contact with a suspension of anhydrous chromium(III) chloride and zinc dust in diethyl ether. Workup of the ether layer and recrystallization from 2-propanol-heptane afforded the malonaldehyde chelate I as red-violet needles, m.p. 182–183°, strong infrared maxima at 1600, 1490, 1450, 1370, 1300, and 1134 cm.⁻¹, ultraviolet $\lambda_{\text{max}}^{\text{CHCl}_3}$ 265 and 341 with ϵ of 8,580 and 10,850, 25% yield.

Anal. Calcd. for C₉H₉O₆Cr: C, 40.76; H, 3.42. Found: C, 40.80; H, 3.44.

(1) Previous paper, J. P. Collman, R. A. Moss, H. Maltz and C. C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961).

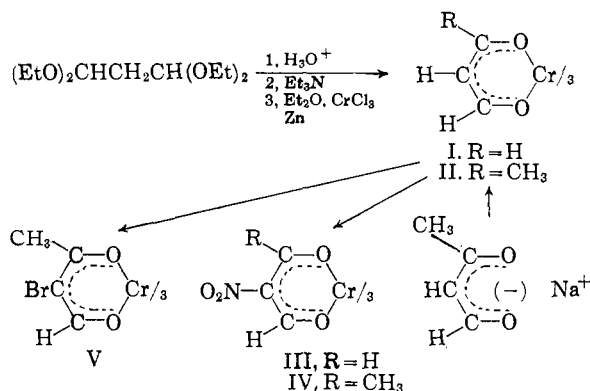
(2) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(3) Abstracts of papers presented at the 139th Meeting of the American Chemical Society in St. Louis, Missouri, March 1961, p. 4M.

(4) J. P. Collman, R. A. Moss, S. D. Goldby and W. S. Trahanovsky, *Chem. and Ind. (London)*, 122 (1959).

(5) R. Hüttel, *Chem. Ber.*, **74**, 1825 (1941).

In a similar manner, treatment of an intimate mixture of a hydrated form⁶ of the sodium salt of malonaldehyde, anhydrous chromium(III) chloride, and zinc dust with dimethylformamide resulted in the formation of I, but in lower yield. This latter procedure also afforded tris-(3-keto-butanalono)-chromium(III) (II) in 41% yield: red-violet crystals, m.p. 168–169°, strong infrared maxima at 1585, 1505, 1420, 1330, and 1230 cm.⁻¹, ultraviolet $\lambda_{\text{max}}^{\text{CHCl}_3}$ 259, 275, 301, 337 m μ with ϵ of 9,950, 9,400, 7,980, and 13,040.



Treatment of I and II with copper(II) nitrate in acetic anhydride afforded the trinitro chelates III and IV. The nitro malonaldehyde chelate III was isolated in 37% yield: red-violet crystals from acetone-heptane, m.p. 294–295°.

Anal. Calcd. for C₉H₆O₁₂N₃Cr: C, 27.01; H, 1.51; N, 10.50. Found: C, 27.67; H, 2.04; N, 10.45.

The nitro formylacetone chelate IV was formed in 26% yield: violet crystals, m.p. 205–207°.

Anal. Calcd. for C₁₂H₁₂O₁₂N₃Cr: C, 32.59; H, 2.74; N, 9.50. Found: C, 32.69; H, 2.90, N, 9.40.

The tribromo formylacetone chelate V was formed in 47% yield by the action of N-bromo-succinimide on II: brown crystals, m.p. 177–178°.

Anal. Calcd. for C₁₂H₁₂O₆Br₃Cr: C, 26.49; H, 2.22. Found: C, 26.73; H, 2.37.

These electrophilic substitution reactions were effected under the same conditions that had been used previously to substitute metal acetylacetonate rings.^{1,3,4} The same infrared patterns that we found to characterize these substitutions in metal acetylacetonates were repeated in the substitution products of I and II.

The ultraviolet spectra of the dialdehyde and formylacetone chelates and their electrophilic substitution products are listed in Table I along with the corresponding acetylacetonates. Examination of these data add credence to our earlier speculation³ that the ultraviolet spectrum of the

(6) T. V. Protopenova and A. P. Skoldinov, *Zhur. Obshchei Khim.*, **28**, 210 (1958).

nitro chromium acetylacetonate is a manifestation of steric inhibition of resonance of the nitro group with the chelate ring. In the case of the nitro chelates III and IV the nitro groups can become coplanar with the chelate ring as is indicated by a bathochromic shift of about 20 m μ ; whereas in the nitro-acetylacetonate the nitro groups probably are forced out of the plane of the chelate ring by the two flanking methyl groups. The bromine atom, being spherical, gives rise to a bathochromic shift in all three cases. The short wave length bands are used in this argument.

TABLE I
ULTRAVIOLET SPECTRA OF METAL CHELATES

R	R'	X	CHCl ₃ , λ_{max}	ϵ
CH ₃	CH ₃	H	335	15,800
CH ₃	CH ₃	Br	358	13,070
CH ₃	H	NO ₂	330	12,260
CH ₃	H	H	259	9,950
			275	9,400
			301	7,980
			337	13,040
CH ₃	H	Br	277	8,710
CH ₃	H	NO ₂	282	27,250
			319	14,650
H	H	H	265	8,580
			341	10,850
H	H	NO ₂	282	31,000
			322	12,500

Work is in progress on further electrophilic substitutions of these new chelate rings, and on the reactions of functional groups substituted on these rings.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, N. C.

JAMES P. COLLMAN
EDMUND T. KITTLEMAN

RECEIVED JULY 17, 1961

THE MECHANISM OF THE REACTION OF GRIGNARD REAGENTS WITH SCHIFF BASES

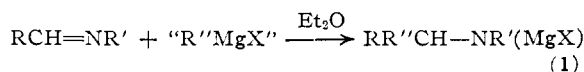
Sir:

Although several kinetic investigations of Grignard reactions have been made¹⁻⁷ none of them has involved systems in which the Grignard reagent added across an unsaturated linkage capable of being substituted at both ends. Data on such a reaction would clearly provide a keener insight into the behavior of organomagnesium compounds.

It is well known that Schiff bases, RCH=NR', react conveniently with "R''MgX" yielding

- (1) D. Ivanoff and J. Abduloff, *Compt. rend.*, **196**, 491 (1933).
- (2) H. Kleinfeller and H. Lohman, *Ber.*, **71**, 2608 (1938).
- (3) C. G. Swain, *J. Am. Chem. Soc.*, **69**, 2307 (1947).
- (4) J. Aston and S. Bernhard, *Nature*, **165**, 485 (1950).
- (5) A. Bruylants, *Bull. Soc. Chim. France*, **1958**, 1291.
- (6) S. J. Storfer and E. J. Becker, personal communication.
- (7) R. E. Dessy, J. H. Wotiz and C. A. Hollingsworth, *J. Am. Chem. Soc.*, **79**, 358 (1957).

halomagnesium salts of amines according to the equation⁸



Using the change in dielectric constant of the reaction mass as function of time as a tool⁹ to follow the rate of reaction of various Schiff bases with ethylmagnesium bromide we have been able to provide such data.

The literature⁸ reports that yields of amines in this reaction are less than 50% when a 1:1 ratio of "RMgX"/Schiff base is employed, although quantitative yields may be obtained when 2/1 ratios are employed.

Employing gas chromatography as an analytical tool we have found that reaction of benzalaniline with ethylmagnesium bromide gives N- α -phenylpropylaniline in 50% yields when a 1/1 ratio of "RMgX"/Schiff base is employed. 100% yields (based on Schiff base) are found at 2/1 ratios.

This suggests that only *one-half* of the available R groups are utilized in the addition of a Grignard reagent across the azomethine link of Schiff bases, and agrees with the work of Becker^{7,10} on the reaction of benzonitrile with Grignard reagents, in which the same phenomenon was noticed. Such a fact is explained easily if one accepts that a Grignard reagent is more accurately portrayed as R₂Mg·MgX₂ than RMgX¹¹.

Addition of one of the R-Mg linkages across the azomethine link leads to a product in which reaction of the second R-Mg linkage is prevented by steric or electronic factors.

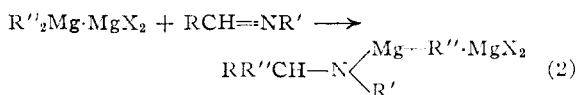


Table I shows the results obtained when various substituents were placed on the rings of benzalaniline.

TABLE I

$$\text{"EtMgBr"} + \text{Z-C}_6\text{H}_4\text{CH=N-C}_6\text{H}_4\text{Z}' \xrightarrow[31.5^\circ]{\text{Et}_2\text{O}}$$

Z	Z'	Schiff base molarity	"EtMgBr" molarity	$k, \text{ l./mole-sec.} \times 10^4$
H	H	0.30	0.15	2.3
H	H	.20	.20	2.7
H	H	.15	.20	2.7
<i>p</i> -CH ₃ O	H	.20	.20	2.8
H	<i>p</i> -CH ₃ O	.20	.20	1.4
H	<i>p</i> -Cl	.20	.20	2.3

* Rate = $k(\text{Et}_2\text{Mg} \cdot \text{MgBr}_2)(\text{Schiff Base})$.

Several kinetic expressions were tested: rate = $k(\text{"EtMgBr"})$, rate = $k(\text{"EtMgBr"})$ (Schiff base), and rate = $k(\text{Et}_2\text{Mg} \cdot \text{MgBr}_2)$ (Schiff base). Only the last of these gave good kinetic plots and consistent k 's, as Table I indicates.

- (8) M. S. Kharasch and O. Reimuth, "Grignard Reactions of Non-Metallic Substances," Prentice Hall, New York, N. Y., 1954.
- (9) R. E. Dessy and R. M. Salinger, *J. Org. Chem.*, in press.
- (10) S. J. Storfer and E. J. Becker, Abstracts, 138th meeting of Am. Chem. Soc., Sept. 11-16, 1960, New York, p. 80-P.
- (11) R. E. Dessy and G. S. Handler, *J. Am. Chem. Soc.*, **80**, 5824 (1958).