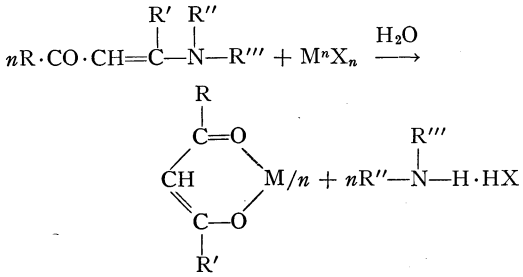
Convenient synthesis of metal chelates[1]

V. W. GASH

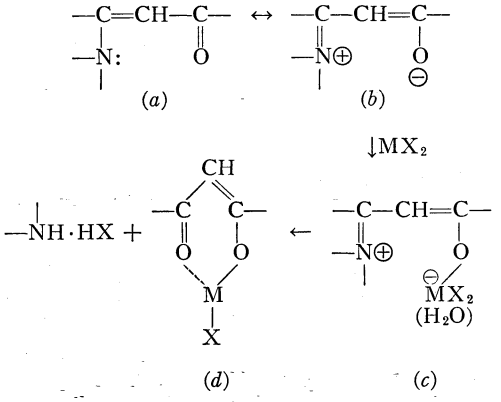
During an investigation into the chemistry of β-tertiary aminoketones, it was found that these compounds provide a convenient route to the metal chelates of the parent diketones. The general utility of this reaction (illustrated for a divalent cation) and its simplicity warrant its use whenever difficulty is encountered in the usual techniques.



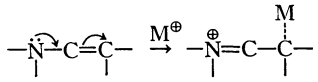
A comparison with known syntheses of metal chelates (1, 2) shows several advantages for this technique characterized by homogeneous systems (the tertiary aminoketones are generally soluble in both polar and nonpolar solvents), intrinsic pH control, very fast reactions at ordinary temperatures, convenience of operation, and high yields. Table I describes yields and properties of several metal chelates made by this procedure. A polymeric iron chelate made from the bis-aminoketone (XIV) was completely intractable and is not included in the table.

It is difficult to explain this reaction in terms of a simple hydrolysis of the aminoketone. Relevant evidence includes the fact that the secondary aminoketone (XIII) (Table II) reacted sluggishly with Cu(II) and not at all with Mg(II). Calvin (3) has also shown that a β-tertiary aminocrotonic ester is stable in aqueous solution precluding a simple hydrolysis. Finally, it was found that the anion (X) in the metal salt (M^nX_n) had no apparent effect on the reaction.

The reaction rate suggests an *ionic* reaction and the following reaction scheme involving the attack of a metal cation on the ionic resonance form (*b*) is proposed.



Subsequent reaction of the immonium salt (*c*) with a water molecule (possibly from the hydrated metal ion) would yield the chelate (*d*). Evidence (4) exists for the ionic resonance form (*b*), and the known (5) double bond shift (with protonic acids) of α,β-unsaturated amines to yield immonium salts suggests a similar type of reaction with a metal cation (acting as a Lewis acid).



The infrared spectra of the metal chelates exhibited two bands in the 1 500 – 1 600 cm^{-1} region for the acetylacetonates and three bands for the unsymmetrical diketones similar to the behavior (3, 6) of acetoacetic ester chelates.

[1]Presented in part at the 138th Meeting of the American Chemical Society, New York, New York, September 1960.

TABLE I

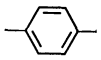
Chelation reactants and products

	Reactants		Product	Yield (%)	Color	Analysis (%)	
	Aminoketone	Metal salt				Calcd.	Found
I	4-Diethylamino-3-pentene-2-one	$NiCl_2 \cdot 6H_2O$	Bis(2,4-pentanediono)-nickel(II)	87	Blue-green	C, 43.69 H, 5.87	C, 44.09 H, 6.24
II	1-(2-Thienyl)-3-*N*-morpholino-2-butene-1-one	$CaCl_2$	Bis[1-(2-thienyl)-1,3-butanediono]calcium*	81	Gold	—	—†
III	1-(2-Thienyl)-3-*N*-morpholino-2-butene-1-one	$Al(NO_3)_3 \cdot 9H_2O$	Tris[1-(2-thienyl)-1,3-butanediono]aluminium	89	Yellow	C, 54.53 H, 4.05	C, 54.75 H, 4.53
IV	1-(2-Thienyl)-3-*N*-morpholino-2-butene-1-one	$CuCl_2 \cdot 2H_2O$	Bis[1-(2-thienyl)-1,3-butanediono]copper(II)	96	Green	C, 48.29 H, 3.55	C, 48.38 H, 4.10
V	1-(2-Thienyl)-3-*N*-morpholino-2-butene-1-one	$MgSO_4 \cdot 7H_2O$	Bis[1-(2-thienyl)-1,3-butanediono]magnesium	95	Cream	C, 53.57 H, 3.93	C, 53.35 H, 4.54
VI	1-(2-Thienyl)-3-*N*-morpholino-2-butene-1-one	$Ni(OAc)_2$‡	Bis[1-(2-thienyl)-1,3-butanediono]nickel(II)§	73	Green	C, 48.90 H, 3.59	C, 48.57 H, 4.01
VII	1-(2-Thienyl)-3-*N*-morpholino-2-butene-1-one	$CoCl_2 \cdot 6H_2O$	Bis[1-(2-thienyl)-1,3-butanediono]cobalt(II)§	—	Yellow-orange (with $2H_2O$)	C, 44.76 H, 4.23	C, 45.07 H, 4.58
VIII	3-*N*-Piperidino-3-(2-furyl)-1-phenyl-2-propen-1-one	$ZnCl_2$	Bis[1-phenyl-3-(2-furyl)-1,3-propanediono]zinc(II)	78	Lemon (with 1.5 H_2O)	C, 60.19 H, 4.08	C, 60.28 H, 4.08

*This calcium chelate had the unique property of gelling many solvents, e.g. a 1% solution in benzene gave an immobile gel.
†All carbon analyses obtained on this calcium chelate were extremely erratic. A correct sulfur analysis was possible: for S, calcd. 17.12; found 17.00.
‡Nickel chloride gave the same chelate, indicating unimportance of the anion.
§Both the solid nickel(II) and cobalt(II) chelates changed color and physical appearance upon drying. The anhydrous cobalt(II) chelate was a greyish tan, somewhat unstable material that was soluble in a variety of solvents to yield different colored solutions.

TABLE II

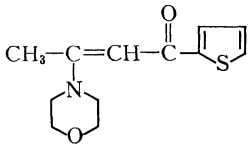
β-Amino-α,β-unsaturated ketones $R \cdot CO \cdot CH{=}C(R')\text{—}N(R'')\text{—}R'''$

	R	R′	R″	R‴	Yield (%)	Boiling point (°C)	Melting point (°C)	Infrared bands in double bond region (cm^{-1})*	Nitrogen analysis (%) Calcd.	Nitrogen analysis (%) Found
IX	CH_3	CH_3	—$CH_2CH_2CH_2CH_2CH_2$—		57 (7)	90–91 at 0.2 mm	51–54	1625, *1540*	8.38	8.46
X	CH_3	CH_3	C_2H_5	C_2H_5	59 (8)	75–80 at 0.3 mm	—	1640, *1565*	9.02	9.13
XI	CH_3	CH_3	—$(CH_2)_2$—O—$(CH_2)_2$—		82	110 at 0.3 mm	46–48	—	8.34	8.16
XII		CH_3	—$(CH_2)_2$—O—$(CH_2)_2$—		90	—	95–98.5	1615, *1550*	5.90	5.70
XIII	CH_3	CH_3	H		95	90–94 at 0.04 mm	—	1630, 1590 (equal intensity)	7.72	7.64
XIV†		CH_3	—$CH_2CH_2CH_2CH_2CH_2$—		49	—	203–205	1625, *1540*	7.37	7.08
XV			—$CH_2CH_2CH_2CH_2CH_2$—		59	—	90–106‡	—	—	—

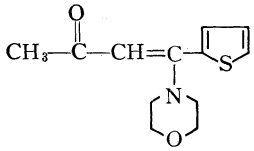
ADDITIONAL CONSTANTS: IX, λ_{max}(alc) 314 mμ; X, n_D^{26} 1.5385; XII, λ_{max}(alc) 258 mμ, 355 mμ; XIII, λ_{max}(alc) 316 mμ, n_D^{25} 1.5315.
*The frequency in italics is the one with the higher intensity in the double bond region.
†This is a bis-enamine from *p*-bis[3-oxo-butyryl]benzene.
‡Possibly a mixture of *cis–trans* isomers (10) or position isomers XV* and XV† (see text).

The aminoketones (IX–XV) described in Table II were obtained by condensation of the amine with the appropriate diketone.

Structural assignments for the β-aminoketones derived from the unsymmetrical diketones were made by analogy to the work of Beyer and Claisen (9). Thus compound XII is assigned as XII*a* rather than

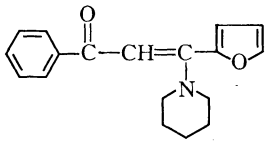


XII*a*

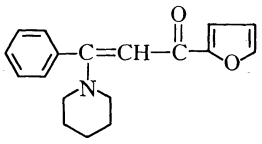


XII*b*

XII*b*. An additional β-amino-α,β-unsaturated ketone (XV*a*, XV*b*) was prepared from reaction of piperidine with benzoyl-2-furoyl methane. Although structure XV*a* is favored, definite proof of the direction of preferred enolization of this type diketone is not available.



XV*a*



XV*b*

1. L. E. Marchi. Inorg. Syn. **2**, 10 (1946).
2. W. E. Fernelius and B. E. Bryant. Inorg. Syn. **5**, 105 (1957).
3. R. L. Belford, A. E. Martell, and M. Calvin. J. Inorg. Nucl. Chem. **2**, 11 (1956).
4. N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank, and D. J. Wallace. J. Am. Chem. Soc. **71**, 3337 (1949).
5. N. J. Leonard and V. W. Gash. J. Am. Chem. Soc. **76**, 2781 (1954).
6. R. P. Dryden and A. Winston. J. Phys. Chem. **62**, 636 (1958).
7. B. Ohta and H. Kawasaki. J. Pharm. Soc. Japan, **71**, 1309 (1951).
8. A. Combes and C. Combes. Bull. Soc. Chim. France, Ser. 3, **7**, 782 (1892).
9. C. Beyer and L. Claisen. Ber. **20**, 2180 (1887).
10. J. Weinstein and G. Wyman. J. Org. Chem. **23**, 1618 (1958).

Received August 3, 1966.
Central Research Department,
Monsanto Company,
St. Louis, Missouri.

Effect of ion association upon the electron spin resonance spectrum of durosemiquinone in 1,2-dimethoxyethane

P. S. Gill and T. E. Gough

Many of the results and interpretations contained in a recent paper (1) concerning the effect of ion association upon the electron spin resonance spectra of semiquinone anions are in conflict with similar studies in progress in our laboratories. The present communication is confined to the systems sodium–duroquinone and potassium–duroquinone, both dissolved in 1,2-dimethoxyethane. Reduction of duroquinone by sodium or potassium was performed by standard methods (2) and electron spin resonance spectra were recorded with a J.E.O.L. 3BX spectrometer.

The electron spin resonance spectra of the present systems are temperature and concentration dependent. All such spectra are readily interpreted in terms of two kinds of radicals in equilibrium with one another. However, since the spectra of both radicals contained narrow lines ($\Delta H_{\text{m.s.}} = 0.04$ G) (where m.s. represents maximum slope), the interconversion of these radicals must take place at rates slow in comparison with electron spin resonance correlation times.

One of the radicals with 12 equivalent protons exhibited a hyperfine interaction