Olefins from Metal Xanthates

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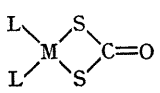
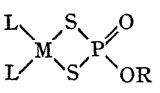
Summary Olefin formation is shown to occur when nickel(II) xanthates are thermally decomposed.

WHILE several studies of decomposition reactions of metal *OO*-dialkyldithiophosphates, have been reported to produce olefins,[1] olefinic decomposition products from metal xanthates, or metal dithiocarbamates, have not been identified.

We have observed[2] that R–O cleavage of palladium(II) and platinum(II) xanthates and dithiophosphates occurs when these species react with certain arylphosphines. The resultant inorganic products are (I) and (II), where L is the phosphine. The organic species, when R is a primary alkyl group, are *S*-alkylated xanthates and dithiophosphates.

(I) 

 (II)

The thermal decomposition of certain metal xanthates

produces olefinic products. Dickert and Rowe[1a] concluded that olefin formation in the decomposition of the dithiophosphates probably involves a two-step process in which isomerization precedes an intramolecular (*cis*) elimination.[3] Our data for the decomposition of the nickel(II) xanthates as well as the nickel(II) dithiophosphates (see Table) are not sufficiently sensitive on this point, since olefin isomerizations are promoted by transition metals.[4] However, nickel(II) and other metal ions promote xanthate decomposition, and high olefin yields may be obtained. The sensitivity of the xanthate to the metal ion is seen from the fact that even aqueous solutions of potassium t-butylxanthate produce 10—15% yields of isobutene when various metal halides are added. While a mesomeric charge shift toward the metal is more pronounced in the dithiocarbamates than in the xanthates,[5] olefin formation on decomposition is not as pronounced.

Pyrolysis of metal xanthate and dithiophosphate derivatives of butanols[a]

Compound	Reaction[b]	Olefin yield
$KS_2CO{\cdot}CH_2{\cdot}CHMe_2$	A	No olefin identified
$KS_2CO{\cdot}CMe_3$	Aqueous Sn^{IV}, Ni^{II} or Cr^{III} at ambient temperature	10—15% Isobutene
$KS_2CO{\cdot}CH(Me)Et$	B	15% (1 : 3 : 3)[c]
$Ni[S_2CO{\cdot}CHMeEt]_2$	B	20% (*ca.* 1 : 1 : 1)[c]
	C	50% (2 : 3 : 3)[c]
$Ni[S_2P(OCMe_3)_2]_2$	A	30% Isobutene
	C	60% Isobutene
$Ni(S_2CNHCH_2{\cdot}CHMe_2)_2$	A	No olefin identified
$Ni(S_2CNHCMe_3)_2$	B	Small yield isobutene
$Ni[S_2CO{\cdot}CH(Me)Et]_2$	175° dry	20—30% Butenes
$Ni\{S_2P[OCH(Me)Et]_2\}_2$	160° in butanol	>50% (1 : 5 : 5)[b]

[a] Metal xanthates were prepared and analysed. Thermal decomposition was conducted in such a way that the olefins produced could be trapped at −70° in anhydrous ether containing a pent-1-ene standard. G.l.c. on Chromosorb-P (9 ft. column) and 30% Dowtherm on firebrick (10 ft. column) was used to separate and identify the products.
[b] Pyrolysis at 160° in; A, dry; B, Nujol; C, diglyme.
[c] Ratio of but-1-ene to *trans*- and to *cis*-but-2-ene.

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