Organometallic Insertion Reactions of Diketen; Synthesis of β-Keto-enolates

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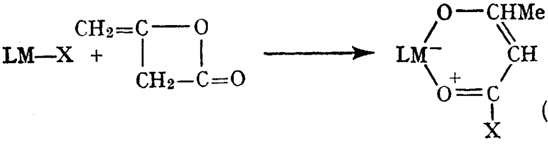
ORGANOMETALLIC insertion reactions have recently attracted much attention.[1] Another active area is that of β-keto-enolates.[2] We now report a general reaction of diketen, which has relevance to both. This is summarised by the following equation (in which L represents the sum of all the ligands other than the univalent atom or group X attached to the metal, metalloid, or non-metal M). It appears at present that, in general, those compounds LM–X which undergo insertion

TABLE

Compound (I)		M.p.
LM	X	
o-$C_6H_4{\cdot}O_2B$	NEt_2	154°
o-$C_6H_4{\cdot}O_2B$	NPr^i_2	222
o-$C_6H_4{\cdot}O_2B$	OEt	108
o-$C_6H_4{\cdot}O_2B$	Cl	98°
Me_3Sn	NMe_2	68–70
$(Et_2O)Cl_2Al$	Cl	—
$(C_5H_5N)Br_2Al$	Br	—

reactions with phenyl isocyanate[1] will also insert diketen.



(I)

The compounds (I) characterised to date are listed in the Table. Evidence for their structures is based on elemental analyses, molecular weights, spectroscopic data (i.r., u.v., n.m.r., and mass spectrometry), and, in some cases, chemical degradation or alternative methods of synthesis. Further illustration is provided by the following example.

Interaction of o-$C_6H_4O_2B{\cdot}NEt_2$ (8·25 g.) and diketen (3·63 g.) in pentane (25 ml.) afforded (I) (LM = o-$C_6H_4O_2B$ and X = NEt_2) (11·66 g., 98%), m.p. 154°, λ_{max} 274 mμ (in CH_2Cl_2) [Found: C, 60·7; H, 6·6; B, 3·8; N, 5·2%; *M* (isopiestic in C_6H_6), 269. $C_{14}H_{18}BNO_4$ requires C, 61·1; H, 6·6; B, 3·9; N, 5·1%; *M*, 275]. The i.r. spectrum showed a strong band at 1620 cm.$^{-1}$, which is within the range normally[2] found for ν(C=O) in β-keto-enolates. The ^1H n.m.r. spectrum showed signals characteristic[2] of exocyclic CH_3 and γ-CH (respectively at τ 2·08 and 5·25) in metal β-keto-enolates. The two ethyl groups of NEt_2 were magnetically inequivalent at 30°, which is consistent[3] with a high barrier to rotation about the amide C–N bond. The ^{11}B n.m.r. spectrum showed absorption at −8·63 p.p.m. with respect to BF_3,OEt_2, as appropriate[4] for a four-co-ordinate boron compound. The mass spectrum showed preferential loss of the β-keto-enolate moiety; thus the ion $[o\text{-}C_6H_4O_2B]^+$, but not $[BOC(CH_3){:}CH{\cdot}C(NEt_2){:}O]^+$, was observed. Refluxing with methanol (the compound, unlike 'normal' alkoxides of boron, did not react in the cold) afforded $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NEt_2$, and this in turn was reconverted into its precursor upon treatment with o-$C_6H_4{\cdot}O_2B{\cdot}Cl$.

It is interesting that diketen behaves quite differently from its monomer [which with LM–X → $LM\text{–}CH_2C({:}O)X$].[1] This may be because of its molecular dissymmetry. By contrast, the symmetrical phenyl isocyanate dimer resembles the monomer in its reaction with $B(NMe_2)_3$ [to give $Me_2N{\cdot}B(NPhCONMe_2)_2$].

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