SECTION A
Inorganic, Physical, and Theoretical Chemistry

Chloroboration and Allied Reactions of Unsaturated Compounds. Part IX.[1] Organometallic Insertion Reactions of Diketen; Synthesis of β-Keto-enolates

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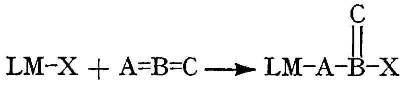
A new general synthesis of β-keto-enolates is described, whereby diketen is caused to react with various organic derivatives of aluminium, boron, and tin. Diketen thus reacts differently from its monomer (which affords *C*-acetyl derivatives). This is attributed to the unsymmetrical structure of the dimer. The symmetrical phenyl isocyanate dimer behaves similarly to its monomer in its reaction with trisdimethylaminoborane. The β-keto-enolates are characterised by elemental analyses, molecular weights, spectroscopic data (i.r., u.v., n.m.r., and mass spectrometry), and, in some cases, by chemical degradation or alternative methods of synthesis.

EARLIER parts of this series have, in the main, been concerned with insertion reactions of organometallic compounds with unsaturated compounds having cumulated double bond systems [see reaction (1),[1] 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].

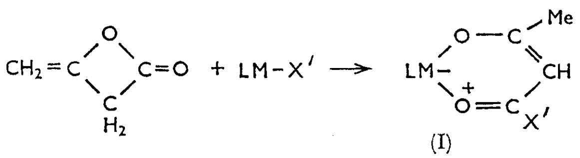


$$LM{-}X + A{=}B{=}C \longrightarrow LM{-}A{-}\overset{\overset{\displaystyle C}{\|}}{B}{-}X \qquad (1)$$

Keten reacts according to this scheme[2] [see reaction (2)]; a new example (LMX = o-$C_6H_4O_2BNEt_2$) is described in the experimental section, and there are indications (i.r.) that $PhBCl_2$ and Ph_2BCl behave similarly.

$$LM{-}X + CH_2{=}C{=}O \longrightarrow LM{-}CH_2COX \qquad (2)$$

Diketen, by contrast, however, reacts according to (3), as we have already briefly described.[3]



(3)

(I)

Thus, addition of diketen to a solution of organometallic reagent LM–X′ gave the β-keto-enolates shown in Table 1.

Insertion reactions with the boron compounds o-$C_6H_4O_2BX'$ proceeded under mild conditions. The order of increasing reactivity of the compounds, qualitatively judged by the ease of reaction and heat liberated, was $X' = Ph, NH_2 \ll OEt < NPr^i_2 < NEt_2 < Cl < Br$. Thus, whereas the chloroborane (X′ = Cl) reacted exothermically and rapidly with diketen, the aminoboranes ($X' = NEt_2$, NPr^i_2) reacted more slowly, and it was necessary to catalyse the reaction of the ethoxyborane (X′ = OEt) with triethylamine. The bromoborane (X′ = Br) reacted exothermically with diketen, giving a product which was not satisfactorily purified. Its ^1H n.m.r. spectrum, however, showed peaks characteristic of the expected ring compound o-$C_6H_4O_2BOC(CH_3)CHCOBr$. No reaction occurred with the compounds $X' = NH_2$ or Ph. The unreactivity of the boron–carbon bond towards diketen was further demonstrated by a failure to obtain insertion products with triethylborane and tri-n-butylborane. The acetylacetonate ($X' = CH_3$) was, therefore, prepared by the more conventional route (4).

TABLE 1

The β-keto-enolates (I)

	LM	X′	M.p.
(Ia)	o-$C_6H_4O_2B$	NEt_2	154°
(Ib)	o-$C_6H_4O_2B$	NPr^i_2	222
(Ic)	o-$C_6H_4O_2B$	OEt	108
(Id)	o-$C_6H_4O_2B$	Cl	98
(Ie)	$Cl_2(Et_2O)Al$	Cl	—
(If)	$Br_2(C_5H_5N)Al$	Br	—
(Ig)	Me_3Sn	NMe_2	68—70

$$o\text{-}C_6H_4O_2BCl + CH_3COCH_2COCH_3 \longrightarrow HCl + o\text{-}C_6H_4O_2BOC(CH_3)CHCOCH_3 \qquad (4)$$

Diketen reacts typically with nucleophilic reagents, and a reaction mechanism involving nucleophilic addition to the carbonyl group has been advanced.[4] As aminoboranes are weak bases, there should be no reaction with diketen if the mechanism depends only on nucleophilic attack by the amino-group. The reaction must be aided by the electrophilic nature of the boron atom, and a concerted mechanism (5) involving both nitrogen and boron is envisaged.

Such a mechanism has been advanced for insertion reactions with phenyl isocyanate. On this basis, the

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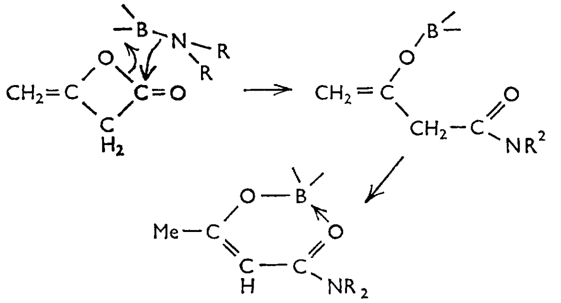
[1] Part VIII, J. R. Horder and M. F. Lappert, *J. Chem. Soc.* (*A*) 1968, 2004.

[2] Cf. M. F. Lappert and B. Prokai, *Adv. Organometallic Chem.*, 1967, **5**, 225.

[3] J. R. Horder and M. F. Lappert, *Chem. Comm.*, 1967, 485.

[4] V. V. Perekalin and T. A. Sokolova, *Uspekhi Khim.*, 1956, **25**, 1351.

high reactivity of the chloroborane ($X' = Cl$) is explained. Although the nucleophilicity of the Cl atom is lower than that of the NEt_2 group, the boron atom is more electrophilic. The interplay of these two factors is apparent, since, whereas the reactivity order of the compounds $X' = NEt_2$, OEt, Ph is appropriate for the nucleophilic character of these groups X′, that of the compounds $X' = Br$, Cl, NEt_2 is appropriate for the electrophilicity of the boron atom. The apparently anomalous failure to obtain insertion with the aminoborane $X' = NH_2$ is presumably due to the oligomeric nature of the compound.[5]



(5)

The products (Ia) and (Ib) were unaffected by boiling water and cold methanol. The resistance to hydrolysis conferred on boron by the β-keto-enolate group[6] and by other chelating groups (*e.g.*, ethanolamine)[7] has been noted previously. Refluxing (Ia) with methanol, however, afforded $CH_3COCH_2CONEt_2$, which was converted into its precursor on treatment with *o*-$C_6H_4O_2BCl$. The chelates could be sublimed under a vacuum, and showed no tendency thermally to decompose to diketen by a reverse of the insertion process. The ethyl acetoacetate (Ic) was slowly hydrolysed, while the chelate (Id) was rapidly hydrolysed, presumably by attack on the acid chloride group of the ring. This compound decomposed at 80°. The free ligand acetoacetyl chloride is not stable at room temperature. It is, therefore, stabilised by co-ordination.

Tris-dimethylaminoborane and tris-t-butylaminoborane reacted rapidly with diketen, forming adducts containing 3 mol. of diketen even when the aminoborane was present in excess. The purity of the products was not satisfactory and their structure is not entirely clear, but their formulation as $B[OC(CH_3)CHCONRR']_3$ seems reasonable because (i) the adduct of $(Bu^tNH)_3B$ gives t-butylacetoacetamide on alcoholysis, and (ii) the C=C and C=O infrared stretching frequencies are at values (broad bands at 1635 and 1620 cm.$^{-1}$) higher than those of the chelated compounds (Ia) to (Id), but lower than those of t-butylacetoacetamide (at 1675 and 1655 cm.$^{-1}$). Ebullioscopic measurements in dichloromethane showed the $(Bu^tNH)_3B$ adduct to be dimeric. There may, therefore, be bridging by some of the t-butylacetoacetamide groups. The adduct of $(Me_2N)_3B$ was monomeric.

Bisdimethylaminophenylborane similarly adds 2 mol. of diketen, to give an ill-defined product ($\nu_{max.}$ 1600 cm.$^{-1}$).

The retention of the donor groups pyridine and diethyl ether in the aluminium halide adducts $Cl_2(Et_2O)AlOC(CH_3)CHCOCl$ (Ie) and $Br_2(C_5H_5N)AlOC(CH_3)CHCOBr$ (If) is peculiar. If these compounds are monomeric, then they are required to be 5-co-ordinate. Such compounds are known, but are rare;[8] 4- or 6-co-ordination should be preferred. The bisacetylacetonate EtOAl $acac_2$ has been shown to be monomeric in benzene,[9] and the aluminium atom has therefore, been postulated to be 5-co-ordinate. The adduct (Ie) was insoluble in benzene, but cryoscopic measurements indicated that it was associated in nitrobenzene (*n* 1·68, 1·45). It appears, therefore, that it is dimeric and the aluminium is 6-co-ordinate. Chlorine-bridging is well known for aluminium compounds, and dimerisation could be explained in this way. A dimeric structure should possess several geometrical isomers, but there is no evidence in the n.m.r. spectrum of any non-equivalence of ether groups, or of any splitting of CH_3 ring resonances, such as observed in the case of unsymmetrical β-keto-enolates.[10]

A patent[11] describes the preparation of trisethylacetonatoaluminium from triethoxyaluminium and diketen. This and other reactions described in the patent are clearly examples of insertion reactions.

$$(EtO)_3Al + C_4H_4O_2 \longrightarrow Al[OC(CH_3)CHCO_2Et]_3$$

It is interesting that diketen behaves quite differently from its monomer, and this may be because of its unsymmetrical structure. By contrast, the symmetrical phenyl isocyanate dimer resembles the monomer in its reaction (6) with trisdimethylaminoborane.

$$B(NMe_2)_3 + (PhNCO)_2 \longrightarrow Me_2N{\cdot}B(NPhCONMe_2)_2 \qquad (6)$$

Spectroscopic Data on β-Keto-enolates.—Some i.r. and n.m.r. data for the boron β-keto-enolates (II) are in Table 2. The ^{11}B n.m.r. shifts are appropriate for 4-co-ordinate boron compounds.[12] The ^1H n.m.r. spectra show signals characteristic of methyl and methine protons of metal acetylacetonates.[13] The spectrum of the chelate $X'' = NEt_2$ shows the two ethyl groups of NEt_2 to be magnetically inequivalent at 30°, which is consistent[14] with a higher barrier to rotation about the amide CN bond. The proton resonances of

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[5] M. F. Lappert, M. K. Majumdar, and B. P. Tilley, *J. Chem. Soc.* (*A*), 1966, 1590.

[6] W. Gerrard, M. F. Lappert, and R. Shafferman, *Chem. and Ind.*, 1958, 722.

[7] Cf. M. F. Lappert, *Chem. Rev.*, 1956, **56**, 959.

[8] E. L. Muetterties and R. A. Schunn, *Quart. Rev.*, 1966, **20**, 245; M. Bonamico, *Chem. Comm.*, 1966, 135.

[9] R. K. Mehrotra and R. C. Mehrotra, *Canad. J. Chem.*, 1961, **39**, 795.

[10] R. C. Fay and T. S. Piper, *J. Amer. Chem. Soc.*, 1963, **85**, 500.

[11] B.P. 789,983 (*Chem. Abs.*, 1958, **52**, 15,566).

[12] Cf. H. Nöth and H. Vahrenkamp, *Chem. Ber.*, 1966, **99**, 1049.

[13] *Cf.* J. P. Fackler, *Progr. Inorg. Chem.*, 1966, **7**, 361.

[14] W. D. Phillips, *J. Chem. Phys.*, 1955, **23**, 1363.

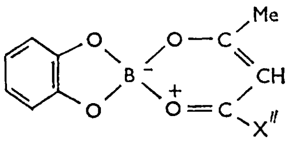
the ethyl groups appear as five lines of relative intensities 1 : 4 : 6 : 4 : 1 (two overlapping quartets due to two non-equivalent $=CH_2$ groups) at τ 6·37, 6·47, 6·59, 6·72, and 6·84, and six lines (two overlapping triplets due to CH_3) at 8·64, 8·72, 8·78, 8·83, 8·89, and 8·95. The spectrum of the chelate X″ = NPr^i_2 shows a broad unresolved band in the region τ 8·0, and two doublets at 8·62, 8·67, 8·73, and 8·77, indicating inequivalence of the isopropyl groups.

TABLE 2

I.r. and n.m.r. data on the β-keto-enolates (II)

X″ in (II)	^{11}B n.m.r.[a] (δ)	^1H n.m.r.[d] τ(CH)	$\tau(CH_3)$	I.r. spectrum $\nu_{C=O}$ and $\nu_{C=C}$
CH_3 ...	−9·4	4·07	7·78	1604w, 1569m, 1554vs
Cl	−8·2	4·48	7·82	1604m, 1548s
OEt	−9·4	4·59	7·86	1598s, 1581m, 1545s
NEt_2 ...	−8·6	4·66	7·86	1606vs
NPr^i_2 ...	−8·6	4·96	7·90	1600vs, 1559m
Br[c]		4·24	7·55	

[a] CH_2Cl_2 solution. [b] $CDCl_3$ solution. Not isolated in a pure state. [d] All signals are singlets.



(II)

Variations in the series are not very large, but the value of the methine proton resonance shows a trend to high field in the order of X″ = CH_3 < Br < Cl < OEt < NEt_2 < NPr^i_2. There is a parallel, but much less significant, trend for the methyl proton resonance. The raising of τ(CH) may be due to a lowering of conjugation within the β-keto-enolate ring caused by conjugation between X″ and the ring. Such exocyclic conjugation is shown to exist by the non-equivalence of the ethyl and isopropyl groups of the chelates X″ = NEt_2 and NPr^i_2. Moreover, the order of groups cited above corresponds to the order with which these groups are expected to conjugate with the ring by a +*M* effect. Dessy, Green, and Toporcer[15] have studied a series of boron β-keto-enolates, and, in agreement with the trend described here, τ(CH) and $\tau(CH_3)$ are at higher field for $Et_2BOC(CH_3)CHCO_2Et$ (at 5·13 and 8·08, respectively) than for $Et_2BOC(CH_3)CHCOCH_3$ (at 4·58 and 8·05).

The infrared spectra show bands characteristic of metal acetylacetonates in the region 1500—1610 cm.$^{-1}$ assigned as C=C and C=O stretching modes.[16] Most of the chelates show only one strong band. The weak band at 1604 cm.$^{-1}$ of the chelate X″ = CH_3 is assigned to the benzodioxo-ring, and this is probably the origin of the medium-intensity band at 1604 cm.$^{-1}$ of the chelate X″ = Cl. No really clear trend is apparent in the variation of these bands, although the π-bonding groups X″ = OEt, NPr^i_2, and NEt_2 have raised $\nu_{C=C}$ relative to the group X″ = CH_3. This increase in frequency could result from an increase in the C–C bond order, indicative of less effective conjugation in the ring.

In a series of unsymmetrical α-substituted copper acetylacetonates,[17] the groups OEt and NEt_2 appear to have opposite effects as they respectively raise and lower $\nu_{C=C}$. The phenyl group, which also exerts a +*M* effect, was previously reported to lower $\nu_{C=C}$,[18] but is now believed to raise $\nu_{C=C}$.[19] It appears that the +*M* groups raise $\nu_{C=C}$.[16]

Ultraviolet spectral data, measured in CH_2Cl_2 solution of 10^{-5}M concentration, are in Table 3. Owing to hydrolysis of the chelates X″ = OEt and Cl in such dilute solutions (10^{-5}M), no results for these are reported.

TABLE 3

U.v. data on some β-keto-enolates (II)

X″ in (II)	CH_3		NEt_2		NPr^i_2	
$\lambda_{max.}$ (mμ) ...	262	213	274	233	276	235
ε	15,800	2080	20,100	4500	21,800	5100

The main band in the u.v. spectra (found at 260—280 mμ) of acetylacetonates has been attributed to a $\pi \longrightarrow \pi^*$ transition of the chelate ring.[13,20] This band shifts to longer wavelength and higher intensity in the order of X″ = CH_3 < NEt_2 < NPr^i_2. Shifts of this kind are normally attributable to an increase in conjugation. In this respect, these measurements appear to contradict the conclusions made on the basis of the n.m.r. and i.r. spectra.

The fragmentation of the chelate X″ = CH_3 in the mass spectrometer followed the scheme shown in Table 4.

The assignment of peaks is supported by the $^{10}B/^{11}B$ isotope pattern (showing the ratio 1 : 4), and the assignment of the transitions by the appearance of metastable peaks.

Fragmentation of the β-keto-enolate ring occurred stepwise, with initial loss of the methyl group as observed with metal acetylacetonates.[21,22] Examination of the spectra of the chelates X″ = NEt_2, NPr^i_2, OEt, shows that fragments of masses 203, 136, and 119 are formed in all cases. These correspond to the species $[o\text{-}C_6H_4O_2BOC(CH_3)CHCO]^+$, $[o\text{-}C_6H_4O_2BOH]^+$, and $[o\text{-}C_6H_4O_2B]^+$). No peaks are found at masses required by the structure $[BOC(CH_3)CHCOX'']^+$, except in the case X″ = CH_3, indicating preferential loss of the β-keto-enolate moiety, rather than loss of the benzodioxo-moiety.

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[15] R. E. Dessy, S. I. E. Green, and L. H. Toporcer, *Inorg. Chem.*, 1965, **4**, 1649.

[16] K. Nakamoto, 'Infrared spectra of Inorganic and Co-ordination Compounds,' Wiley, New York, 1963.

[17] R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nuclear Chem.*, 1956, **2**, 11.

[18] H. F. Holtzclaw and J. P. Collman, *J. Amer. Chem. Soc.*, 1957, **79**, 3318.

[19] K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Phys. Chem.*, 1962, **66**, 346.

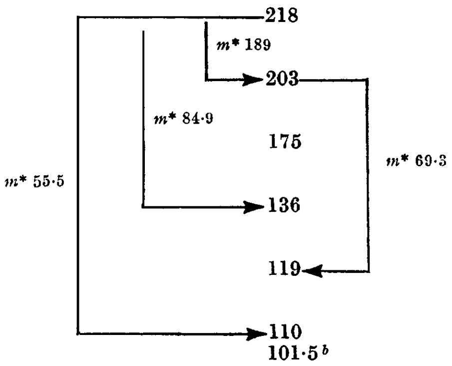
[20] F. A. Cotton and R. H. Holm, *J. Amer. Chem. Soc.*, 1958, **80**, 5658.

[21] J. Macklin and G. Dudek, *Inorg. Nuclear Chem. Letters*, 1966, 403.

[22] C. G. Macdonald and J. S. Shannon, *Austral. J. Chem.*, 1966, **19**, 1545.

TABLE 4

Mass-spectral fragmentation of (II) ($X'' = CH_3$)



m/e	Relative intensity [a]	Assignment
218	100	$C_6H_4O_2BOC(CH_3)CHCOCH_3^+$
203	29	$C_6H_4O_2BOC(CH_3)CHCO^+$
175	7	$C_6H_4O_2BOC(CH_3)CH^+$
136	56	$C_6H_4O_2BOH^+$
119	6	$C_6H_4O_2B^+$
110	17	$BOC(CH_3)CHCOCH_3^+$
101·5 [b]	8	$C_6H_4O_2BOC(CH_3)CHCO^+$

[a] Only those ions containing ^{11}B are considered. [b] This corresponds to a doubly charged ion.

EXPERIMENTAL

General procedures and methods of analysis have been described in earlier Parts. ^1H n.m.r. spectra were measured with a Perkin-Elmer R10 or Varian A60 spectrometer at 60 Mc./sec., with tetramethylsilane as internal standard. ^{11}B n.m.r. spectra were measured with a Perkin-Elmer R10 spectrometer at 19·25 Mc./sec., with $BF_3 \cdot O(C_2H_5)_2$ as external standard. Mass spectra were recorded with an A.E.I. MS 9 spectrometer.

Diketen, obtained as a gift from British Celanese, was distilled under reduced pressure and stored at −15°.

Reactions of Diketen with Various Substrates.—(a) 2-*Diethylamino*-1,3,2-*benzodioxaborole*. Diketen (3·63 g., 1 mol.) was added during 10 min. to a solution of 2-diethylamino-1,3,2-benzodioxaborole (8·25 g., 1 mol.) in n-pentane (15 ml.). The diketen was miscible, and the solution became slightly warm. On standing for 12 hr., yellow, needle-shaped crystals formed. These were removed by filtration (11·66 g., 98%), m.p. 151—154°, washed with n-pentane, and recrystallised from benzene, to give the β-*keto-enolate* (Ia), m.p. 153—154° (Found: C, 60·7; H, 6·65; B, 3·8; N, 5·15%; *M*, 269. $C_{14}H_{18}BNO_4$ requires C, 61·1; H, 6·6; B, 3·95; N, 5·1%; *M*, 275·1).

A sample of (Ia) (3·35 g., 1·00 mol.) was insoluble in cold methanol, but dissolved on heating. Distillation gave methanol and trimethyl borate (0·91 mol., estimated by titration), and a red viscous liquid, b.p. 156·8°/24 mm., identified (i.r. spectrum) as a mixture of catechol and *NN*-diethylacetamide.

(b) 2-*Di-isopropylamino*-1,3,2-*benzodioxaborole*. 2-Di-isopropylamino-1,3,2-benzodioxaborole (5·20 g., 1 mol.) and diketen (2·00 g., 1 mol.) in n-pentane (40 ml.) yielded, after 4 days, the β-*keto-enolate* (Ib) (4·83 g., 67%), m.p. 222° (Found: C, 62·8; H, 7·15; B, 3·5; N, 4·55%; *M*, 303. $C_{16}H_{22}BNO_4$ requires C, 63·3; H, 7·3; B, 3·55; N, 4·6%; *M*, 303·2), as a yellow, crystalline material, which was recrystallised from benzene.

(c) 2-*Ethoxy*-1,3,2-*benzodioxaborole*. A mixture of 2-ethoxy-1,3,2-benzodioxaborole (5·10 g., 1 mol.) and diketen (2·61 g., 1 mol.) in n-pentane (30 ml.) showed no reaction after standing for 12 hr. A drop of triethylamine was added and the mixture was set aside for 6 days. During this time an orange solid (4·93 g.) formed, having i.r. bands at 1760m, 1650m, 1600s, and 1550s. On recrystallising from toluene and then benzene, the β-*keto-enolate* (Ic) (3·02 g., 39%), m.p. 108° (Found: C, 57·9; H, 5·3; B, 4·2%; *M*, 241. $C_{12}H_{13}BO_5$ requires C, 58·1; H, 5·3; B, 4·35%; *M*, 248·0), was obtained. Evaporation of the recrystallising solutions produced a viscous oil.

(d) 2-*Chloro*-1,3,2-*benzodioxaborole*. Slow addition of diketen (4·77 g., 1 mol.) to 2-chloro-1,3,2-benzodioxaborole (8·76 g., 1 mol.) in n-pentane (40 ml.) caused the exothermic formation of a red oil, which solidified after 1 hr. The solid *acetoacetyl chloride adduct* (Id) (13·40 g., 99%), m.p. 98° (Found: C, 51·9; H, 3·5; B, 4·25; Cl, 14·6%; *M*, 202. $C_{10}H_8BClO_4$ requires C, 50·4; H, 3·4; B, 4·55; Cl, 14·85%; *M*, 238·5), was very soluble in dichloromethane, and formed emulsions with toluene and benzene, from which it could not be recrystallised, and so was studied without purification.

(e) *Aluminium chloride–diethyl ether*. Diketen (3·68 g., 1 mol.) was added dropwise with stirring (1 hr.) to aluminium chloride–diethyl ether (10·10 g., 1·1 mol.) in ether (35 ml.). There was an exothermic reaction, and a lower layer of yellow liquid formed. After addition of about half the diketen, the liquid solidified, and further addition of diketen produced more solid. The mixture was filtered. The filtrate contained aluminium chloride–diethyl ether (0·98 g., 0·11 mol.), and the pale yellow residue was the *acetoacetyl chloride adduct* (Ie) (13·02 g., 100%), decomp. <100° (Found: C, 33·6; H, 4·9; Al, 9·15; Cl, 36·0. $C_8H_{14}AlCl_3O_3$ requires C, 33·0; H, 4·85; Al, 9·25; Cl, 36·5%).

Cryoscopic determinations in nitrobenzene gave *M* 491 (*n* 1·68) and *M* 423 (*n* 1·45) for solutions of 0·6 and 2·7 weight %.

(f) *Pyridine–aluminium bromide*. Pyridine–aluminium bromide was obtained as a white solid by condensing pyridine (2·29 g., 1 mol.) on to aluminium bromide (7·74 g., 1 mol.). This was dissolved in dichloromethane (30 ml.), and diketen (2·44 g., 1 mol.) in dichloromethane (10 ml.) added with stirring during 1 hr. There was an exothermic reaction, and a red oil formed. Solvent was decanted, the oil was washed with solvent, and, on pumping, the oil solidified to the *acetoacetyl bromide adduct* (If) (12·18 g., 98%), decomp. <100° (Found: Al, 6·25; Br, 55·0; C_5H_5N, 17·8. $C_9H_9AlBr_3NO_3$ requires Al, 6·3; Br, 55·8; C_5H_5N, 18·3%), as an orange powder.

(g) NN-*Dimethylaminotrimethylstannane*. Diketen (2·28 g., 1 mol.) was added to a solution of dimethylaminotrimethylstannane (5·64 g., 1 mol.) in benzene. Addition of n-pentane precipitated the adduct (Ig) (65·93 g., 75%), m.p. 68—70° (Found: C, 38·1; H, 6·5; N, 5·05. $C_9H_{19}NO_2Sn$ requires C, 37·0; H, 6·5; N, 4·85%).

(h) 2-*Bromo*-1,3,2-*benzodioxaborole*. There was an exothermic reaction producing a brown oil when diketen (2·20 g., 1 mol.) was added to a solution of 2-bromo-1,3,2-benzodioxaborole (5·20 g., 1 mol.) in n-hexane (25 ml.) cooled to 0°. A portion of the product (7·40 g., 100%), obtained by decanting the hexane, was shaken with benzene (50 ml.). The emulsion obtained was added dropwise to vigorously stirred hexane (500 ml.). An orange solid (Found: B, 4·87. $C_{10}H_8BBrO_4$ requires B, 3·78%) was precipitated. The ^1H n.m.r. spectrum showed signals at τ 4·24 and 7·75, assigned to the methine and methyl protons of structure (II), but also signals at 2·74 and 0·90.

(i) 2-*Phenyl*-1,3,2-*benzodioxaborole*. 2-Phenyl-1,3,2-benzodioxaborole was recovered unchanged after refluxing with diketen in ether for 1 day, and then in benzene with a trace of triethylamine for 2 days. When the two reactants were heated together without solvent a black tar was obtained. The phenylborane was sublimed from the tar by heating *in vacuo*.

(j) 2-*Amino*-1,3,2-*benzodioxaborole*. A suspension of 2-amino-1,3,2-benzodioxaborole in benzene and diketen was shaken for 2 days and then filtered off unchanged.

(k) *Trisdimethylaminoborane*. Addition of diketen (5·08 g., 1 mol.) to trisdimethylaminoborane (8·64 g., 1 mol.) in n-pentane (50 ml.) during 2 hr. caused the exothermic formation of a black viscous oil. The pentane solution was siphoned off, and gave, on distillation, pentane and trisdimethylaminoborane (4·67 g., 0·54 mol.), b.p. 63—64°/32 mm., and a residue (0·53 g.). The oil solidified after washing with pentane and pumping for 2 days to a black solid (7·34 g. Required, for addition of 1 mol. of diketen to 0·33 mol. of aminoborane, 7·96 g.).

(l) *Tris-t-butylaminoborane*. Diketen (4·32 g., 3 mol.) was added to tris-t-butylaminoborane (3·88 g., 1 mol.) in benzene (50 ml.). The reaction was less vigorous than with tris(dimethylaminoborane, but the solution turned brown overnight. Removal of benzene *in vacuo* gave an orange solid (8·33 g.), m.p. 76—86° (Found: B, 2·12. $C_{24}H_{22}BN_3O_6$ requires B, 2·25%). The molecular weight, determined ebullioscopically in dichloromethane, was 885 (required for monomer and dimer 479 and 958, respectively).

Methanol (10 ml.) was added to a sample of the adduct (1·5 g.) and the mixture was refluxed for $\frac{1}{2}$ hr. Distillation gave trimethyl borate (Found: 0·00264 mole, estimated by titration. Required: 0·00313 mole) and methanol, and at reduced pressure *N*-t-butylacetoacetamide (0·7 g., 50%), b.p. 95°/2 mm., m.p. 45°. The ^1H n.m.r. of a CCl_4 solution showed singlets at τ 3·17br (NH), 6·84 (CH_2), 7·85 (CH_3), and 8·74 (Bu^t).

(m) *Bisdimethylaminophenylborane*. Addition of diketen (2·55 g., 1 mol.) to a solution of bisdimethylaminophenylborane (5·33 g., 1 mol.) gave a brown oil (5·52 g., corresponding approximately to addition of 2 moles of diketen) and a solution which, on removal of solvent, contained unreacted bisdimethylaminophenylborane (2·01 g., 0·38 mol.). The oil ($\nu_{max.}$ 1600 cm.$^{-1}$) did not solidify on pumping.

Preparation of 2-*Acetoacetonato*-1,3,2-*benzodioxaborole*.—Addition of freshly distilled acetylacetone (6·15 g., 1 mol.) to 2-chloro-1,3,2-benzodioxaborole (9·50 g., 1 mol.) in n-pentane (25 ml.) produced gaseous hydrogen chloride and yellow solid (13·35 g., 100%). This crystallised from benzene as the pale yellow, air-stable 2-*acetoacetonato*-1,3,2-*benzodioxaborole* (II; $X'' = CH_3$), m.p. 193° (Found: C, 60·7; H, 5·05; B, 4·9. $C_{11}H_{11}BO_4$ requires C, 60·6; H, 5·1; B, 4·95%).

Alternative synthesis of (Ia).—On adding *NN*-diethylacetoacetamide (4·95 g., 1 mol.) to 2-chloro-1,3,2-benzodioxaborole (5·93 g., 1 mol.) in dichloromethane (30 ml.), hydrogen chloride was evolved. Compound (Ia) (8·73 g., 92%), m.p. 153—154°, was obtained after removal of dichloromethane and recrystallisation from benzene.

Reaction of Trisdimethylaminoborane with Phenyl Isocyanate Dimer.—A mixture of trisdimethylaminoborane (5·45 g., 1 mol.) and phenyl isocyanate dimer (9·08 g., 1 mol.) in benzene (30 ml.) was refluxed for 1 hr. On cooling, white crystals of the *substituted amidoborane* $Me_2N{\cdot}B(NPhCONMe_2)_2$ (10·90 g., 75%), m.p. 199—200° (Found: C, 63·0; H, 7·25; B, 2·8; N, 18·1. $C_{20}H_{28}BN_5O_2$ requires C, 63·0; H, 7·4; B, 2·85; N, 18·35%), were obtained, and collected by filtration. Benzene was removed from the filtrate, to produce more crystalline material (2·72 g.) which was washed with hexane and identified (i.r. spectrum) as the amidoborane and unreacted phenyl isocyanate dimer. The infrared spectrum of a nujol mull showed bands at : 1670sh, 1655vs, 1610m, (1595m—s), 1585vw, 1545w, 1530m, 1505s, (1470s), 1450w, 1420m, 1395s, 1350w, 1335w, 1310w, 1285s, 1265s, 1215w, 1195w, 1175m, 1165w, 1150w, 1090w, 1075m, 1025w, 1010w, 985w, 935w, 805w, 785s, 715s, and 670m.

A weighed sample of this amidoborane (approx. 0·6 g.) was refluxed with methanol and dilute acid (40 ml. of 0·1M-solution) for 5 min. The amount of amine released [Found: easily hydrolysable N, 3·15. $Me_2N{\cdot}B(NPhCONMe_2)_2$ requires easily hydrolysable N, 3·7%] was determined by titration with alkali.

The amidoborane (3·70 g., 1·00 mol.) was dissolved in boiling methanol. Liquid was distilled, giving methanol and trimethyl borate (0·98 mol., estimated by titration) until ~10 ml. remained. On cooling, white crystals (2·67 g., 84 %), identified as *NN*-dimethyl-N′-phenylurea, m.p. 135°, were obtained.

Interaction of Keten and Various Boranes.—Keten was passed (experiment of Dr. B. P. Tilley) through 2-diethylamino-1,3,2-benzodioxaborole (2·45 g.) in light petroleum (20 ml.). The mixture was set aside for 24 hr. at 20°, and, after filtration, afforded the *C-borylamide* *o*-$C_6H_4O_2BCH_2C(O)NEt_2$ (2·64 g., 88·3%), m.p. 139° (Found: C, 61·2; H, 7·1; N, 5·8. $C_{12}H_{16}BNO_3$ requires C, 61·9; H, 6·9; N, 6·0%).

In a similar way (experiments of Dr. B. Prokai), keten was passed severally through dichlorophenylborane and chlorodiphenylborane. The products were only characterised by their i.r. spectra [both had $\nu_{max.}$ 1786 cm.$^{-1}$ (CO) and ~1350 cm.$^{-1}$].

[8/555 *Received, April* 16*th*, 1968]