

scribed flow method¹ and low conversion to products.

Alkylborane Systems.—The four isomeric trimethylamine-butylboranes were examined in their reaction with I. The iso- and *n*-butyl systems were too slow to measure at 29.6° and rate data obtained at 49.8 and 40.1° were employed to estimate their rates³ at 29.6° (see Table I). In all of these systems, with the single exception of *t*-butyl, the over-all rate expression was composed of first- and second-order kinetic terms. The *t*-butyl system gave only first-order kinetics at 29.6°. This is not surprising in view of the fact that the reaction site is analogous to that present in the neopentyl carbon system which does not enter into bimolecular nucleophilic displacement reactions.

The *sec*-butyl system presents the highest bimolecular reactivity in the butyl series. This probably reflects a large internal steric compression in a system which is not seriously encumbered toward bimolecular attack by a nucleophile. As in the case of triethylamine-borane,⁴ the *sec*-butyl system was labeled at boron with deuterium⁵ and the resulting substrate was examined kinetically. As previous work would suggest,⁶ the second-order kinetic term remained unchanged while the first-order term gave rise to a k_H/k_D of 1.29. These data further support the idea that the first-order term represents a dissociative process and that the second-order term represents an S_N2 process. Further work is in progress which will deal with possible β-deuterium isotope effects.

Arylborane Systems.—The reactions of phenyl, *p*-tolyl, *p*-bromophenyl, *p*-anisyl, *o*-tolyl, and mesityl (trimethylamine)boranes with I were studied at 30°. As seen in Table I, the mesityl and *p*-anisyl systems produced rate expressions which contained a predominant second-order term and a small first-order term. The other compounds studied in this series most probably have smaller first-order terms in their rate expressions which lie within the region of experimental error. The effect of *para* substituents upon the rates of the second-order reactions was surprisingly small and suggests transition states of low polarity. The most striking result pertained to the effect of *o*-methyl substituents upon rate. Thus, the *o*-tolyl and mesityl systems were approximately 4.2 and 47 times, respectively, as reactive as the phenyl system. Such substituent effects on bimolecular displacement reactions have been noted before⁷ in similar benzyl systems and ascribed to the operation of London dispersion forces. The observation of first-order terms in the rate expressions of the *p*-anisyl and mesityl systems might be attributed to enhanced electronic stabilization of the borane intermediate and to steric acceleration of dissociation, respectively.

Further work is in progress and will be reported at a later date.

(3) Approximate activation parameters for these two systems are: *n*-butyl, first-order term, $\Delta H^*_1 = 30$ kcal./mole, $\Delta S^*_1 = 38$ e.u.; second-order term, $\Delta H^*_2 = 22$ kcal./mole, $\Delta S^*_2 = 0$ e.u.; isobutyl, first-order term, $H_1 = 32$ kcal./mole, $\Delta S^*_1 = 18$ e.u., second-order term, $\Delta H^*_2 = 26$ kcal./mole, $\Delta S^*_2 = 2$ e.u.

(4) M. F. Hawthorne and W. L. Budde, *J. Am. Chem. Soc.*, **86**, 5337 (1964).

(5) The deuterium compound was prepared by lithium aluminum deuteride reduction of the corresponding boroxine. See ref. 1.

(6) See A. Streitwieser, Jr., Supplement, "Solvolytic Displacement Reactions," McGraw-Hill Book Company, Inc., New York, N. Y., 1962, for collected examples.

(7) J. F. Bunnett and J. D. Reinheimer, *J. Am. Chem. Soc.*, **84**, 3284 (1962).

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(8) Alfred P. Sloan Research Fellow.

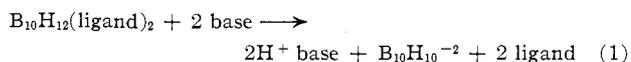
DEPARTMENT OF CHEMISTRY M. FREDERICK HAWTHORNE⁸
THE UNIVERSITY OF CALIFORNIA WILLIAM L. BUDDE
RIVERSIDE, CALIFORNIA DONALD WALMSLEY

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A Mechanism Study of B₁₀H₁₀⁻² Formation

Sir:

The preferred synthetic route to B₁₀H₁₀⁻² involves the reaction of B₁₀H₁₂(ligand)₂ compounds with bases such as triethylamine,¹ triphenylphosphorane,² and



ammonia.³ Yields of B₁₀H₁₀⁻² as high as 90% may be obtained on a large preparative scale accompanied by variable amounts of displacement products, B₁₀H₁₂(base)₂, and less well-defined materials.

We have initiated a kinetic study aimed at elucidating the mechanism of B₁₀H₁₀⁻² formation. Previous deuterium tracer work⁴ indicated the course of the over-all geometrical change which accompanies the reaction.

A reliable and very sensitive spectrophotometric method was devised⁵ for the determination of B₁₀H₁₀⁻². With this method, and where necessary by the use of initial reaction rates, it was possible to study the kinetics of B₁₀H₁₀⁻² formation essentially uncomplicated by competitive reactions.

The reaction of B₁₀H₁₂(NEt₃)₂ (I) with triethylamine (II) was examined in acetonitrile solution at 100°. This system employed an amine base identical with the attached ligand. Thus, with reference to eq. 1, the amine concentration remained constant throughout each kinetic run. Reactions were followed to at least 80% completion. The observed kinetics were first order in I and zero order in II over a wide range of initial concentration ratios and with a first-order rate constant of 5.4×10^{-5} sec.⁻¹. These results indicated that the external base molecule was not incorporated in the rate-determining transition state.

The reaction of B₁₀H₁₂(SMcE₂)₂ (III) with II was examined at 20.0° in toluene solution. A preparative-scale experiment carried out under these conditions for 4.5 days with 0.02 *M* III and 0.15 *M* II produced 70% B₁₀H₁₀⁻², 15% I, and 15% unidentified oil. In another series of experiments, the infinite time yields of B₁₀H₁₀⁻² were determined under kinetic conditions with 0.01 *M* III and varied initial concentrations of II. Maximum yields (80%) of B₁₀H₁₀⁻² were obtained at 0.05 *M*, or higher, initial [II]. Below 0.05 *M*

(1) A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.*, **81**, 5519 (1959).

(2) Unpublished results.

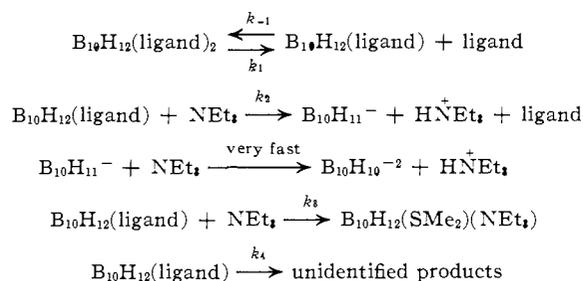
(3) E. L. Muettterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).

(4) J. A. Dupont, M. F. Hawthorne, A. R. Pitochelli, and R. Ettinger, *J. Am. Chem. Soc.*, **84**, 1037 (1962).

(5) This method makes use of the quantitative formation of a red azo coupling product (ϵ 19,400, λ_{max} 520 m μ) which is formed from a large excess of phenyldiazonium ion and B₁₀H₁₀⁻² in acetonitrile acidified with trifluoroacetic acid. The nature of this coupling product is presented elsewhere: M. F. Hawthorne and F. P. Olsen, *J. Am. Chem. Soc.*, **86**, 4219 (1964).

initial [II], yields decreased with decreasing initial [II] to a value of 50% at 0.01 M II.

The initial-rate method was employed and reactions were followed to approximately 5% completion. A series of rate determinations carried out at constant II concentration and varying III concentrations proved this reaction to be first order in III. A plot of pseudo-first-order rate constant *vs.* initial II concentration indicated that the reaction became essentially zero order in II at high II concentrations. The addition of dimethyl sulfide (IV) depressed the reaction rate at all concentrations of II and III. Three series of kinetic runs were carried out at different [IV], in which [II] was varied within each series and [III] was held constant. Plots of $[III]/(d[B_{10}H_{10}^{-2}]/dt)$ *vs.* $[II]^{-1}$ for each [IV] were linear and gave a common intercept of 2.1×10^{-4} sec. at $[II]^{-1} = 0$. The slopes (*z*) of each of these plots were plotted *vs.* [IV] present in each series of rate runs and a straight line described by the equation, $z = 3.45 \times 10^4 [Me_2S] + 140$ sec. mole l.⁻¹ was obtained. The intercept of the latter line was identical with the slope obtained in the first series of plots with no added IV. This intercept requires the operation of a process (*k*₄) which removes the B₁₀H₁₂(ligand) intermediate from the system without producing B₁₀H₁₀⁻² or regenerating III. The results obtained with I and III are consistent with the following rationale⁶ in which the *k*₁ process



may become rate determining at high II concentrations.

It seems probable that the *k*₂ process involves proton abstraction by II with or without the concerted ejection of the second ligand molecule.

The proposed B₁₀H₁₂(ligand) intermediate formally resembles B₁₀H₁₃⁻. That the B₁₀H₁₂(SM_e)₂ (V) reported by Knoth and Muettterties⁷ is not the intermediate involved in B₁₀H₁₀⁻² formation was shown by the fact that authentic V formed B₁₀H₁₀⁻² more than 10³ times slower than III under the same conditions. As suggested by Lipscomb,⁸ two reasonable structures exist for B₁₀H₁₃⁻ and two tautomeric B₁₀H₁₂(ligand) structures may well exist. The formation of B₁₀H₁₀⁻² from V may involve the slow conversion of V to the reactive isomer. Conversely, the *k*₄ process may involve the moderately rapid conversion of the reactive intermediate to V.

Further work is in progress and will be reported at a later date.

(6) Where L = ligand and $d[B_{10}H_{12}L]/dt = 0$, $d[B_{10}H_{10}^{-2}]/dt = k_1 [B_{10}H_{12}L] \{ k_2 [Et_3N] / ((k_2 + k_3) [Et_3N] + k_{-1}[L] + k_4) \}$ or $[B_{10}H_{12}L] / (d[B_{10}H_{10}^{-2}]/dt) = (1/[Et_3N]) \{ (k_{-1}[L] + k_4)/k_1k_2 + (k_2 + k_3)/k_1k_2 \}$. In the first series of plots, the slopes = $(k_{-1}[L] + k_4)/k_1k_2$ sec. mole l.⁻¹, and the intercepts = $(k_2 + k_3)/k_1k_2$ sec. In the second plot, the slope = k_{-1}/k_1k_2 sec., and the intercept = k_4/k_1k_2 sec. mole l.⁻¹. Elimination of the *k*₁*k*₂ term gives $(k_2 + k_3)/k_{-1} = 0.44 \pm 0.02$ and (rate of *k*₄ process)/(rate of *k*₋₁ process) = $k_4/(k_{-1}[L]) = 2.5 \pm 0.5 \times 10^{-4}/[L]$.

(7) W. H. Knoth and E. L. Muettterties, *J. Inorg. Nucl. Chem.*, **20**, 66 (1961).

(8) W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 117 (1959).

(9) Alfred P. Sloan Research Fellow.

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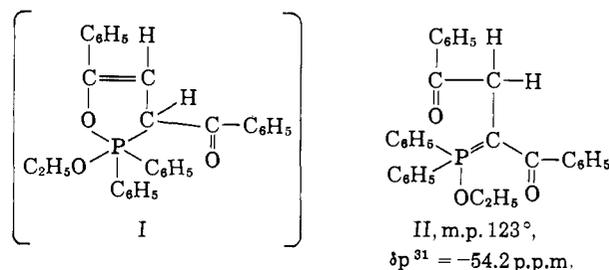
DEPARTMENT OF CHEMISTRY M. FREDERICK HAWTHORNE⁹
THE UNIVERSITY OF CALIFORNIA RICHARD L. PILLING
RIVERSIDE, CALIFORNIA RUSSELL N. GRIMES

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A Crystalline Alkoxydiarylalkylidenephosphorane from the Reaction of Ethyl Diphenylphosphinite with an α - β -Unsaturated Ketone¹

Sir:

Harvey and Jensen² ascribed the *cyclic dialkoxydiarylalkylphosphorane* structure³ I to the adduct, "m.p. 116–118°," which is formed from ethyl diphenylphosphinite and *trans*-dibenzoyl ethylene in an ether solution.⁴ We should like to report that this substance is actually the *alkoxydiarylalkylidenephosphorane*³ II, a moderately stable phosphinitemethylene.



Equimolar amounts of ethyl diphenylphosphinite⁵ and *trans*-dibenzoyl ethylene were allowed to react at 20° in anhydrous 1,2-dimethoxyethane (*ca.* 1.6 M). The infrared spectrum of the resulting clear, red solution after 3 hr. showed that the reaction was nearly complete. The 1:1 adduct crystallized and was filtered after 2 days; yield, 42%; m.p. 118–120° (crude). Recrystallization from benzene–hexane gave II, m.p. 122–123°. Spectral characteristics are: infrared bands, (CH₂Cl₂, μ): 5.97 (strong C=O) and 6.65 (broad and strong "enolate" C=O⁶); $\delta_{P^{31}} = -54.2$ p.p.m.⁷ (CH₂Cl₂); H¹ n.m.r. (CDCl₃; p.p.m. in the τ -scale): multiplet at 2.65 (aromatic), 2H¹

(1) This investigation was supported by the National Science Foundation (G 1509) and by Public Health Service Research Grant No. CA-04769-05 from the National Cancer Institute.

(2) R. G. Harvey and E. V. Jensen, *Tetrahedron Letters*, **No. 26**, 1801 (1963).

(3) Structure I: 2-ethoxy-2,2-diphenyl-3-benzoyl-5-phenyl- Δ^4 -oxaphospholene; structure II: ethoxydiphenyl-(benzoyl-, phenacyl-) methylenephosphorane.

(4) For other reactions of α - β -unsaturated carbonyl compounds with trivalent phosphorus compounds: (a) V. A. Kukhtin and K. M. Orekhova, *J. Gen. Chem. USSR*, **30**, 1539 (1960); (b) G. Kamai and A. V. Kukhtin, *ibid.*, **31**, 1621 (1961), and earlier papers; (c) V. A. Ginsburg and A. Ya. Yakubovich, *J. Gen. Chem. USSR*, **30**, 3944 (1960); (d) E. R. DeSombre, R. G. Harvey, and E. V. Jensen, Abstracts, Division of Organic Chemistry, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan., 1964, p. 21C.

(5) R. Rabinowitz and J. Pellon, *J. Org. Chem.*, **26**, 4624 (1961).

(6) Triphenylbenzoylmethylenephosphorane [F. Ramirez and S. Der-showitz, *J. Org. Chem.*, **22**, 41 (1957)] has an "enolate" carbonyl at 6.63 μ . The P³¹ n.m.r. shift (*vs.* 85% H₃PO₄) is -16.7 p.p.m. (CHCl₃). Its hydrochloride has -20.7 p.p.m. (CHCl₃). A. J. Speziale and K. W. Ratts [*J. Am. Chem. Soc.*, **85**, 2790 (1963)], however, reported -21.6 p.p.m. for the former *ylid*, and -16.9 p.p.m. for the latter *hydrochloride* (both in CHCl₃).

(7) All P³¹ n.m.r. spectra were determined at 40.5 Mc./sec. and are expressed in p.p.m. *vs.* 85% H₃PO₄.