We have found that this can indeed be a good synthetic approach and report here on its application, with "quantitative" conversion to the desired products, to the acid chlorides acetyl chloride, propionyl chloride, and benzoyl chloride and to the ketones acetophenone, propiophenone, and isobutyrophenone. The results are summarized in Table I. In all cases the ketone was shown to be inert to triphenyltin hydride and to the acid chloride under the reaction conditions.

Acknowledgment. We are grateful to Farbwerke Hoechst AG. and M & T Chemicals for gifts of chemicals.

Leonard Kaplan
Department of Chemistry, University of Chicago
Chicago, Illinois 60637
Received February 10, 1966

Reactions of Organoboron Compounds with Phenyl(bromodichloromethyl)mercury. The Conversion of C_n-Terminal Olefins to C_{2n+1}-Internal Olefins

Sir:

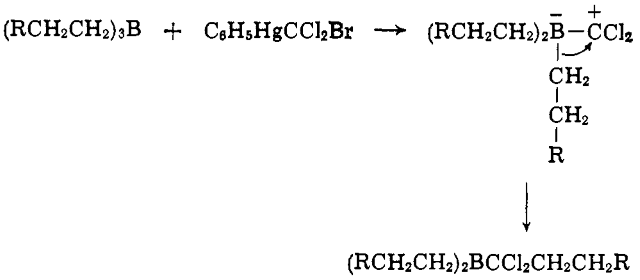
The known chemistry of dichlorocarbene has provided many examples of its action as an electrophilic reagent, leading to its description in terms of a singlet state ($sp^2 + p$) configuration.[1] If, however, dichlorocarbene could be generated in the absence of nucleophilic reagents and in the presence of strong electrophilic substrates, one might expect to see nucleophilic reactions of dichlorocarbene, *i.e.*, reagent interaction with the lone pair sp^2 orbital rather than with the vacant p orbital. We have shown that at 80° in benzene solution phenyl(bromodichloromethyl)mercury inserts CCl_2 into the O–H bond of carboxylic acids and into HCl.[2] It was suggested tentatively that this was the first example of a reaction in which CCl_2 acts as a nucleophile. Whether or not this postulate was correct, it suggested to us that the reactions of phenyl(bromodichloromethyl)mercury with electrophilic reagents other than protonic acids might provide a fruitful area of investigation. This is the case, and we report here concerning novel and potentially useful reactions of organoboranes with $C_6H_5HgCCl_2Br$.

When a benzene solution (under argon) containing 25.6 mmoles each of phenyl(bromodichloromethyl)mercury[3] and tri-*n*-butylborane[4] was heated slowly to 60–70°, phenylmercuric bromide precipitated. After 40 min, thin layer chromatography[3] showed that the starting mercurial had been consumed. The mixture was hydrolyzed and the organic layer analyzed by gas–liquid partition chromatography (silver nitrate column). The presence of one major product, as well as of several minor products, was indicated. The major product, obtained in 68% yield based on the mercurial, was identified as 4-nonene (58% *cis*, 42% *trans*) by analysis and infrared, nmr, and mass spectra, and ultimately by comparison with an authentic mixture of *cis*- and *trans*-4-nonene prepared by reaction of triphenylphosphine-*n*-butylidene with *n*-valeraldehyde. A similar reaction of $C_6H_5HgCCl_2Br$ with tri-*n*-propylborane[4] gave 3-heptene (66% *cis*, 34% *trans*) in 68% yield. In principle, we should now be able to convert any C_n-terminal olefin to the C_{2n+1}-internal olefin by a sequence of hydroboration and reaction of the triorganoborane produced with phenyl(bromodichloromethyl)mercury.

$$RCH{=}CH_2 \xrightarrow{B_2H_6} (RCH_2CH_2)_3B \xrightarrow{C_6H_5HgCCl_2Br} RCH_2CH_2CH{=}CHCH_2R$$

This was shown to be the case with 1-hexene, which was converted to tri-*n*-hexylborane by reaction with diborane in THF.[5] Subsequent reaction of tri-*n*-hexylborane (obtained in 86% yield) with $C_6H_5HgCCl_2Br$ gave 6-tridecene (52% *cis*, 48% *trans*) in 58% yield.

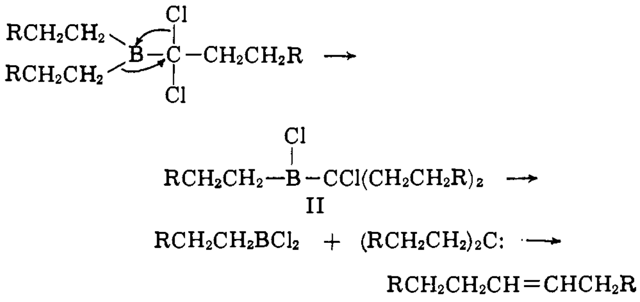
A possible mechanism for these conversions involves nucleophilic attack by CCl_2 (or a CCl_2–C_6H_5HgBr complex) at boron, followed by alkyl group migration from boron to carbon.[6]



$$(RCH_2CH_2)_3B + C_6H_5HgCCl_2Br \longrightarrow (RCH_2CH_2)_2\overset{-}{B}{-}\overset{+}{C}Cl_2(CH_2CH_2R) \longrightarrow (RCH_2CH_2)_2BCCl_2CH_2CH_2R$$

I

The α,α-dichloroalkylborane then undergoes further intramolecular rearrangement to give II, which gives a dialkylcarbene by α-elimination; the latter undergoes subsequent rearrangement[1] to olefin.



$$(RCH_2CH_2)_2B{-}CCl_2{-}CH_2CH_2R \longrightarrow \underset{\text{II}}{RCH_2CH_2{-}BCl{-}CCl(CH_2CH_2R)_2} \longrightarrow RCH_2CH_2BCl_2 + (RCH_2CH_2)_2C{:} \longrightarrow RCH_2CH_2CH{=}CHCH_2R$$

The rearrangement of I to II finds analogy in organosilicon chemistry ($Me_3SiCH_2Cl \xrightarrow{AlCl_3} Me_2EtSiCl$).[10] A mechanism in which I eliminates a *free* alkylchlorocarbene, $RCH_2CH_2\ddot{C}Cl$, which then "inserts" into a boron–carbon bond appears to be eliminated by the fact that only 3-heptene and 4-nonene (but *not* 3- or 4-

---

(1) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

(2) D. Seyferth, J. Y.-P. Mui, and L. J. Todd, *J. Am. Chem. Soc.*, **86**, 2961 (1964).

(3) D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, **4**, 127 (1965).

(4) Prepared by the Grignard procedure.

(5) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

(6) Migration of an organic group from a quaternary boron atom to an attached, electron-deficient carbon atom is well established, occurring in the reactions of triorganoboranes with carbon monoxide,[7] isonitriles,[8] and diazomethane.[9]

(7) M. E. D. Hillman, *J. Am. Chem. Soc.*, **84**, 4715 (1962); **85**, 982, 1626 (1963).

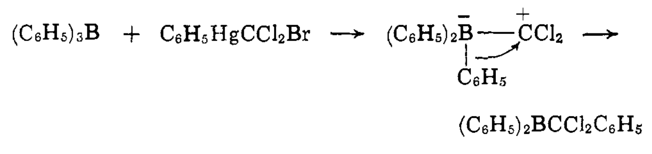
(8) (a) G. Hesse and H. Witte, *Angew. Chem.*, **75**, 791 (1963); *Ann.*, **687**, 1 (1965); (b) J. Casanova, Jr., and R. E. Schuster, *Tetrahedron Letters*, 405 (1964); (c) J. Casanova, Jr., H. R. Kiefer, D. Kuwada, and A. H. Boulton, *ibid.*, 703 (1965).

(9) C. E. H. Bawn and A. Ledwith, *Progr. Boron Chem.*, **1**, 345 (1964).

(10) F. C. Whitmore, L. H. Sommer, and J. R. Gould, *J. Am. Chem. Soc.*, **69**, 1976 (1947).

octene) were obtained when $C_6H_5HgCCl_2Br$ (30.9 mmoles) was allowed to react with a mixture of 15.4 mmoles each of tri-*n*-propyl- and tri-*n*-butylborane. It may be noted that decarboxylation of sodium trichloroacetate in the presence of tri-*n*-propylborane also gave 3-heptene (*cis*/*trans* = 1.56), but the yield was only 15%.

The initially formed $RCCl_2B<$ products appeared to be more stable in the case of arylboranes. With triphenylborane a dark reaction mixture was formed when it was heated at *ca.* 60° in benzene for 1 hr with an equimolar quantity of $C_6H_5HgCCl_2Br$. Addition of an excess of cyclohexene and further heating at reflux for 16 hr followed. The major volatile products were 7-chloro-7-phenylnorcarane (21.4% yield, a mixture of the *exo* and *endo* isomers) and trichlorostyrene (C_6H_5-$CCl{=}CCl_2$; 35% yield). The products obtained can be rationalized in terms of initial CCl_2 transfer to boron followed by B to C phenyl migration.

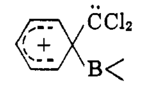


$$(C_6H_5)_3B + C_6H_5HgCCl_2Br \longrightarrow (C_6H_5)_2\overset{-}{\underset{\substack{|\\ C_6H_5}}{B}}-\overset{+}{C}Cl_2 \longrightarrow (C_6H_5)_2BCCl_2C_6H_5$$

Reaction of the α,α-dichlorobenzylboron intermediate with cyclohexene, either in a bimolecular process or *via* α elimination to give phenylchlorocarbene, would produce 7-chloro-7-phenylnorcarane. The formation of trichlorostyrene is best explained by further CCl_2 "insertion" into the $C_6H_5CCl_2$–B linkage to give the $>BCCl_2CCl_2C_6H_5$ system, which in analogy to the known chemistry of (β-chloroalkyl)boron compounds[11,12] should undergo facile β elimination ($\rightarrow >B{-}Cl + Cl_2C{=}CClC_6H_5$). Formation of trichlorostyrene must have been complete by the time the $C_6H_5HgCCl_2Br$ was consumed and prior to the addition of cyclohexene, since 7,7-dichloronorcarane was not among the reaction products. Attempts to isolate an intermediate α,α-dichlorobenzylborane were not successful. However, it was found that tris(α,α-dichlorobenzyl)borane (prepared *in situ* by reaction of boron trifluoride etherate and α,α-dichlorobenzyllithium[13]) reacted with 3 molar equiv of phenyl(bromodichloromethyl)mercury in benzene at reflux to give trichlorostyrene in fair yield.

An experiment in which phenyldimethoxyborane and $C_6H_5HgCCl_2Br$ were allowed to react in benzene at 60–70° and the resulting reaction mixture then was heated with cyclohexene at reflux for 20 hr produced 7-chloro-7-phenylnorcarane (27.3%), trichlorostyrene (22.4%), and 1,2-dichloro-1-methoxy-2-phenylethylene (C_6H_5-$CCl{=}CClOCH_3$; 34.7%). The formation of the latter implies that after CCl_2 attack at boron both phenyl and methoxy groups migrate from boron to carbon, giving $C_6H_5CCl_2B<$ and $CH_3OCCl_2B<$ intermediates. The absence of 7-chloro-7-methoxynorcarane among the products suggests that the methoxydichloromethylborane intermediate is less stable than the α,α-dichlorobenzylboron species to the extent that, once formed, it decomposes immediately to give $CH_3O\ddot{C}Cl$ which then could "insert" into a $C_6H_5CCl_2$–B linkage. β elimination would then give the observed olefin.

The reactions occurring between $C_6H_5HgCCl_2Br$ and phenylboranes also could be rationalized in terms of electrophilic attack of CCl_2 at carbon to give III,



III

subsequent rearrangement of which could lead to the α,α-dichlorobenzylboron species. However, the fact that such reactions occur very readily with trialkylboranes, which are much less susceptible to electrophilic attack,[14] would tend to speak against this view.

Syntheses of novel olefins based on reactions of phenyl(trihalomethyl)mercurials with organoboranes are being investigated. We also find that use of an excess of $C_6H_5HgCCl_2Br$ in reactions with trialkylboranes allows direct synthesis of *gem*-dichlorocyclopropanes derived from the internal olefins produced. Details of this and related work will be reported at a later date.

Acknowledgment. The authors are grateful to the U. S. Army Research Office (Durham) for generous support of this work.

---

(11) M. F. Hawthorne and J. A. Dupont, *J. Am. Chem. Soc.*, **80**, 5830 (1958).

(12) P. Binger and R. Köster, *Tetrahedron Letters*, 156 (1961).

(13) D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *J. Am. Chem. Soc.*, **87**, 4147 (1965).

(14) L. H. Toporcer, R. E. Dessy, and S. I. E. Green, *ibid.*, **87**, 1236 (1965).

(15) Alfred P. Sloan Foundation Fellow, 1962–1966.

(16) Postdoctoral Research Associate, 1964–1966.

Dietmar Seyferth,[15] Bela Prokai[16]
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received February 5, 1966

Novel Photocyclization of a Highly Phenylated β,γ-Unsaturated Ketone to a Cyclopropyl Ketone, Involving Benzoyl Group Migration

Sir:

The photolytic rearrangement of bis-(2,3,5,5-tetraphenyl-2-dihydrofuranyl)-1,2-hydrazine to 1,3,4,4-tetraphenyl-3-buten-1-one (III, 60%)[1] and its 1,2,4,4 isomer (I, 25%)[2] invited investigation of β,γ-unsaturated ketones themselves, and we report herewith the preliminary results and their significance relative to current photochemical literature.[3]

Among the products of irradiation[4] of the 1,2,4,4-tetraphenyl β,γ-unsaturated ketone I, we have isolated the cyclopropyl ketone II[5] consistently in *ca.* 7% yields.[5b]

---

(1) (a) R. E. Lutz, J. I. Dale, and D. W. Boykin, Jr., *J. Am. Chem. Soc.*, **85**, 2340 (1963); (b) R. E. Lutz and C. L. Dickerson, *J. Org. Chem.*, **27**, 2041 (1962).

(2) (a) D. W. Boykin, Jr., and R. E. Lutz, *J. Am. Chem. Soc.*, **86**, 5046 (1964), ref 2a; (b) R. E. Lutz, R. G. Bass, and D. W. Boykin, Jr., *J. Org. Chem.*, **29**, 3660 (1964), ref 8; (c) D. W. Boykin, Jr., Ph.D. Dissertation, University of Virginia, 1965.

(3) (a) Photointerconversion of phenylated propenes and cyclopropanes: G. W. Griffin, *et al.*, *J. Am. Chem. Soc.*, 87, 1410 (1965), ref 17; (b) *Tetrahedron Letters*, **34**, 2951 (1965); (c) photocyclization of desyl compounds: J. C. Sheehan and R. M. Wilson, *J. Am. Chem. Soc.*, **86**, 5277 (1964); (d) irradiation of 4-hexen-2-one with *trans–cis* inversion: H. Morrison, *Tetrahedron Letters*, **48**, 3653 (1964); (e) photocyclization of a γ,δ-unsaturated ketone: R. Srinivasan, *J. Am. Chem. Soc.*, **82**, 775 (1960); (f) N. C. Yang, M. Nussim, and D. R. Coulson, *Tetrahedron Letters*, **20**, 1525 (1965); (g) photocyclization of a β,γ-epoxyketone: A. Padwa, *J. Am. Chem. Soc.*, **87**, 4205 (1965).

(4) Hanovia high-pressure Hg arc lamp, Type L, 450 w, Pyrex filter; I in benzene (1.3 m*M*), under N_2, 1.5 hr.

(5) (a) II had been identified before we learned of Griffin's work,[3a] but at that time it had been erroneously assumed to stem from phenyl rather than benzoyl group migration. (b) The major products were noncrystalline. Compounds arising evidently from radical fragmentation (*cf.* VII) include biphenyl and dimeric hydrocarbons $C_{42}H_{34}$ (*ca.* 15%).