

Spanish origin and a 3-year-old sample of Mexican origin showed only the presence of **1** by thin layer chromatography.

The *trans*- $\Delta^6$ -tetrahydrocannabinol (**2**),  $[\alpha]^{27D} -260^\circ$  (*c* 0.700, absolute EtOH),  $\lambda_{\max}^{\text{EtOH}}$  283 ( $\epsilon$  1390), 276 ( $\epsilon$  1330), and 209  $m\mu$  ( $\epsilon$  41000) (*Anal.* Calcd for  $C_{21}H_{30}O_2$ : C, 80.21; H, 9.62. Found: C, 79.9; H, 9.8), had the same optical rotation as a tetrahydrocannabinol Adams, *et al.*,<sup>3</sup> obtained from the treatment of cannabidiol with *p*-toluenesulfonic acid in refluxing benzene. Treatment of cannabidiol with *p*-toluenesulfonic acid under the conditions described by Adams yielded a product identical in all respects (infrared, ultraviolet, nmr, and optical rotation) with the natural product **2**. This material was also identical in all respects except optical rotation with the totally synthetic *dl-trans*- $\Delta^6$ -tetrahydrocannabinol prepared by Taylor, *et al.*<sup>6</sup> Adams<sup>3</sup> assigned a  $\Delta^6$  position for the double bond in **2**, but did not make any stereochemical assignments at C-3 and C-4.

The stereochemistry at C-3 and C-4 in **1** and **2** was shown to be identical. Hydrogenation of **2** in the presence of a platinum catalyst yielded a colorless resin,  $[\alpha]^{27D} -109^\circ$  (*c* 0.502, absolute EtOH), which had an infrared spectrum that was identical with the infrared spectrum of the colorless resin,  $[\alpha]^{27D} -108^\circ$  (*c* 0.507, absolute EtOH) (*Anal.* Calcd for  $C_{21}H_{32}O_2$ : C, 79.68; H, 10.19. Found: C, 79.5; H, 10.5), obtained by the catalytic hydrogenation of **1**. This result established that **1** and **2** had the same stereochemistry at C-3 and C-4, but different positions of the double bond. Treatment of **1** with a catalytic amount of *p*-toluenesulfonic acid in toluene for 10 hr at 100° resulted in over 90% conversion to **2**. This also indicated that **1** and **2** differed only in the position of the alicyclic double bond.

(6) E. C. Taylor, K. Lenard, and Y. Shvo, *J. Am. Chem. Soc.*, **88**, 367 (1966).

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## Reductive Acylation of Ketones<sup>1</sup>

Sir:

We wish to report some one-step transformations of the type



brought about in high yield under neutral, mild, and convenient conditions.

Although ketone-to-ester conversions involving reduction of the ketone followed by acid- or base-catalyzed esterification in a separate step have been extensively investigated, very few reports have appeared in the literature describing the occurrence of such conversions under free-radical conditions.<sup>2</sup> In all of these cases,

(1) This work was supported by American Cancer Society Institutional Grant 41-F.

(2) Rust, Seubold, and Vaughan<sup>3</sup> treated benzaldehyde with *t*-butyl peroxide for 30 hr at 130° and obtained 35% conversion to *sym*-diphenylethylene glycol dibenzoate; Beckwith and Evans<sup>4</sup> carried out

Table I. Summary of Results

Reactants (mmole)	Reaction conditions <sup>a</sup>	Product <sup>b</sup>
In 0.148 g of $C_6H_6$ $CH_3COCl$ (0.396) $C_6H_5COCH_3$ (0.410) $(C_6H_5)_3SnH$ (0.528) <sup>d</sup>	0.5 hr	$OCOCH_3$   $C_6H_5CHCH_3$
In 0.187 g of $C_6H_6$ $CH_3CH_2COCl$ (0.492) $C_6H_5COCH_3$ (0.491) $(C_6H_5)_3SnH$ (0.500)	2 hr	$OCOCH_2CH_3$   $C_6H_5CHCH_3$
In 0.153 g of $C_6H_6$ $CH_3COCl$ (0.436) $C_6H_5COCH_2CH_3$ (0.432) $(C_6H_5)_3SnH$ (0.703) <sup>d</sup>	15 hr	$OCOCH_3$   $C_6H_5CHCH_2CH_3$
In 0.230 g of $C_6H_6$ $CH_3COCl$ (0.654) <sup>c,d</sup> $C_6H_5COCH(CH_3)_2$ (0.445) $(C_6H_5)_3SnH$ (0.657)	40 hr	$OCOCH_3$   $C_6H_5CHCH(CH_3)_2$
In 0.196 g of $C_6H_6$ $C_6H_5COCl$ (0.619) <sup>c</sup> $C_6H_5COCH_3$ (0.383) $(C_6H_5)_3SnH$ (0.625)	0.5 hr <sup>a</sup> 122°	$OCOC_6H_5$   $C_6H_5CHCH_3$

<sup>a</sup> It was not determined whether a shorter reaction time would be adequate. <sup>b</sup> In all cases the ketone was quantitatively converted to the single product indicated, as judged by nmr spectroscopy and gas chromatographic analysis. <sup>c</sup> Use of equimolar amounts of reagents resulted in only 70% conversion. <sup>d</sup> It was not determined whether this large an excess was necessary for "quantitative" conversion. <sup>e</sup> Ambient temperature unless indicated otherwise.

however, per cent conversions to the desired product were not high and the  $R''CO-$  group was, by the nature of the reaction, derived from the starting carbonyl compound.

In order to determine the feasibility of a free-radical approach to effecting this conversion, it was desired to have the acyl radical which was to be added to the ketone generated in a clean reaction (no other radicals formed) at a reasonably low temperature. The method of generation used, which appears to meet these criteria, is the reaction of an organic halide with an organotin hydride, conditions which are known to bring about reduction of the halide, presumably by a free-radical mechanism.<sup>8</sup>

It was thought that the following reactions would occur.<sup>9</sup>



the same reaction for 72 hr at 132° and obtained 31% conversion. Huang and Lee<sup>5</sup> treated *o*-tolualdehyde with *t*-butyl peroxide for 32 hr at 125° and obtained 5% conversion to  $\alpha,\alpha'$ -di( $\alpha$ -methylbenzoyloxy)-2,2'-dimethylbibenzyl. Urry, Trecker, and Hartzler<sup>6</sup> treated 2-phenyl-1,2-dimethylbutanal with *t*-butyl peroxide for 20 hr at 140° and obtained 38% conversion to  $\alpha,\alpha,\beta$ -trimethyl- $\beta$ -phenethyl  $\beta'$ -phenyl, $\alpha',\beta'$ -dimethylbutyrate. Kupchik and Kiesel<sup>7</sup> treated benzoyl chloride with triphenyltin hydride and obtained 87% conversion to benzyl benzoate; they also treated *p*-methylbenzoyl chloride similarly and obtained 79% conversion to *p*-tolyl *p*-toluate.

(3) F. F. Rust, F. H. Seubold, and W. R. Vaughan, *J. Am. Chem. Soc.*, **70**, 3258 (1948).

(4) A. L. J. Beckwith and G. W. Evans, *J. Chem. Soc.*, 130 (1962).

(5) R. L. Huang and H. H. Lee, *ibid.*, 2500 (1964).

(6) W. H. Urry, D. J. Trecker, and H. D. Hartzler, *J. Org. Chem.*, **29**, 1663 (1964).

(7) E. J. Kupchik and R. J. Kiesel, *ibid.*, **29**, 3690 (1964).

(8) D. H. Lorenz, P. Shapiro, A. Stern, and E. I. Becker, *ibid.*, **28**, 2332 (1963); E. P. Kupchik and R. J. Kiesel, *ibid.*, **29**, 764, 3690 (1964); L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964).

(9) Although the reactions in Table I appear to be most easily visualizable in these terms, no evidence in favor of this scheme can be offered in addition to that already given.

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.

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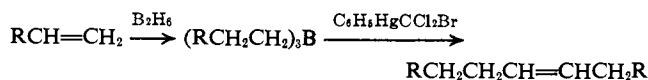
### Reactions of Organoboron Compounds with Phenyl(bromodichloromethyl)mercury. The Conversion of $C_n$ -Terminal Olefins to $C_{2n+1}$ -Internal Olefins

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.<sup>1</sup> 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.<sup>2</sup> 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  $C_6H_5HgCCl_2Br$ .

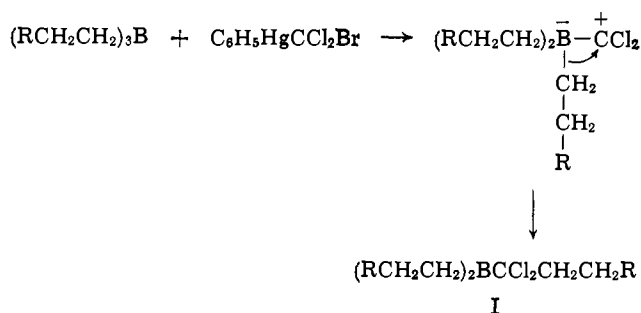
When a benzene solution (under argon) containing 25.6 mmoles each of phenyl(bromodichloromethyl)mercury<sup>3</sup> and tri-*n*-butylborane<sup>4</sup> was heated slowly to 60–70°, phenylmercuric bromide precipitated. After 40 min, thin layer chromatography<sup>5</sup> showed that the starting mercurial 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 triphenyl-

phosphine-*n*-butylidene with *n*-valeraldehyde. A similar reaction of  $C_6H_5HgCCl_2Br$  with tri-*n*-propylborane<sup>4</sup> 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.

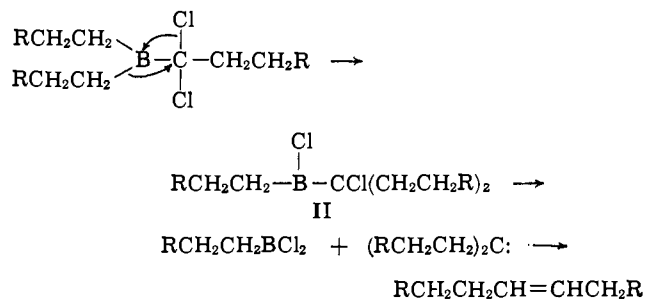


This was shown to be the case with 1-hexene, which was converted to tri-*n*-hexylborane by reaction with diborane in THF.<sup>5</sup> Subsequent reaction of tri-*n*-hexylborane (obtained in 86% yield) with  $C_6H_5HgCCl_2Br$  gave 6-tridecene (52% *cis*, 48% *trans*) in 58% yield.

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.<sup>6</sup>



The  $\alpha,\alpha$ -dichloroalkylborane then undergoes further intramolecular rearrangement to give II, which gives a dialkylcarbene by  $\alpha$ -elimination; the latter undergoes subsequent rearrangement<sup>1</sup> to olefin.



The rearrangement of I to II finds analogy in organosilicon chemistry ( $Me_3SiCH_2Cl \xrightarrow{AlCl_3} Me_3EtSiCl$ ).<sup>10</sup> A mechanism in which I eliminates a *free* alkylchlorocarbene,  $RCH_2CH_2\overset{-}{C}Cl$ , 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-

(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,<sup>7</sup> isonitriles,<sup>8</sup> and diazomethane.<sup>9</sup>

(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).

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(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.