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HYDROBORATION OF DIPHENYLKETENE

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Our interest in the hydroboration of cumulated carbon-carbon double bonds[1-3] prompted us to investigate the behaviour of a cumulated system having a hetero atom. Consequently, diphenylketene (I) was synthesized following the recent procedure of Ried and Junker[4], and hydroborated under different conditions. The results of monohydroboration carried out at -5 to 0°, followed by basic hydrogen peroxide oxidation are summarized in TABLE 1.

TABLE 1

Product#		% Yield	
	BH_3-THF	Sia_2BH*	B_2H_6, <u>in situ</u>
Diphenylacetaldehyde (III)	52	74	43
1,1-Diphenylethylene (VIII)	6	1	4
2,2-Diphenylethanol (IX)	5	1	3
Benzophenone (X)	5.5	6.5	5
Diphenylmethane (XI)	1	1	1
1,1,2,2-Tetraphenylethane (XII)	1.5	1	1
Unidentified (XIII)	2	1	1.5
Unidentified (XIV)	1	1	1

* Sia = $(CH_3)_2\ CH\ \overset{|}{C}H\ CH_3$

\# The yields of the products except XII were determined by GLC employing an internal standard. The products were characterized by comparison with authentic samples. Insufficient amounts of XIII and XIV isolated did not allow unambiguous structural assignment.

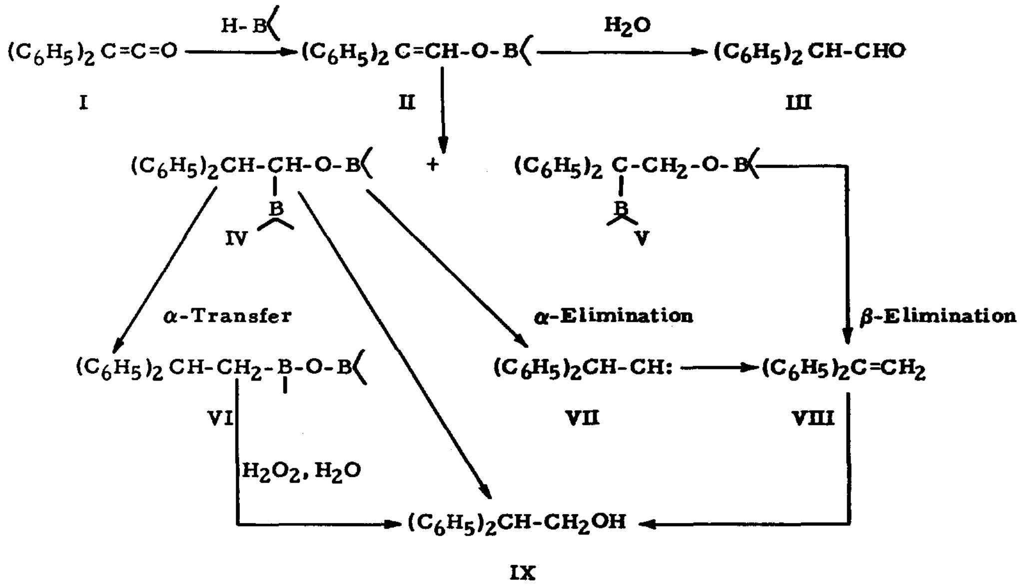
The formation of the various products from monohydroboration-oxidation of I is rationalized in SCHEME 1. The predominant formation of diphenylacetaldehyde (III) suggests that the reaction presumably involves preferential addition of $>$B-H to C = O of I to give mainly the intermediate vinyloxyborane (II). The presence of small amounts of 1, 1-diphenylethylene (VIII) and 2, 2-diphenylethanol (IX) reveals that I is partly undergoing dihydroboration. Further addition of $>$B-H to II can give rise to intermediate organoboranes IV and/or V. However, the amount of formation of V would be expected[5] to be small as the overall electron withdrawing effect of the oxy-boron group would polarize the π-electrons of the alkene bond to aid the preferential formation of IV.[6]

By analogy to the work of Pasto and co-workers[6-8], there are three conceivable pathways for the formation of IX: (1) oxidation-hydrolysis of the new organoboron intermediate (VI), formed by the α-transfer reaction of the intermediate organoborane (IV), (2) a simple hydrolysis of IV, and (3) the base (THF) catalysed β-elimination of V to give VIII, followed by rehydroboration and oxidation. The olefin (VIII) may also arise through the carbene intermediate (VII) produced by the α-elimination of IV. However, this mechanistic pathway <u>via</u> VII is less probable[7]. As expected, dihydroboration of I with BH_3-THF, followed by the usual oxidation work-up afforded 87% of IX and 2% VIII.

Typical radical reactions of III[9] in the presence of hydrogen peroxide suggest that products X, XI and XII may not arise from the initial hydroboration of I. Treatment of III with alkaline hydrogen peroxide gave low yields of these products whilst Fenton's reagent produced mainly X and XII with a low yield of XI. Alternative routes to these products <u>via</u> radical intermediates obtained by fragmentation of C-C from IV or/and V[10], have been ruled out on the basis of the absence of any abnormal oxidation products (X-XII) in the dihydroboration of I. However, X may also arise by the interaction of molecular oxygen with III as observed by Huffman and Elliot[11] <u>via</u> radical intermediates.

SCHEME 1

Possible mechanistic pathways for product formation



$$\text{III} \xrightarrow[\text{NaOH}]{H_2O_2,} \underset{\text{X}}{C_6H_5{-}CO{-}C_6H_5} + \underset{\text{XI}}{(C_6H_5)_2CH_2} + \underset{\text{XII}}{(C_6H_5)_2CH{-}CH(C_6H_5)_2}$$

Further studies are in progress to know the contribution of each mechanistic pathway proposed towards the formation of the individual product and will be described in a subsequent publication in detail.

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