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PHOTOCHEMICAL POLAR ADDITION OF TRIALKYLBORANES

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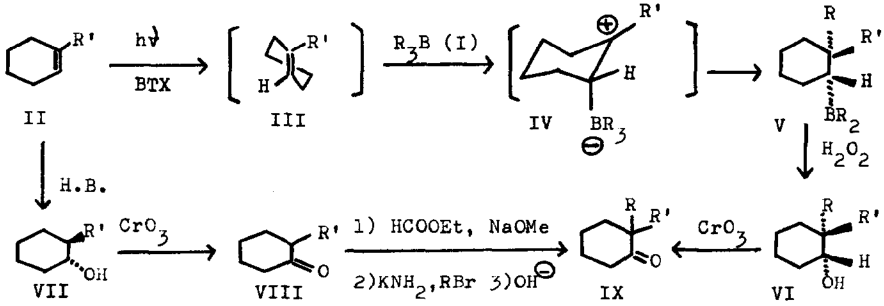
Some instances of photochemical addition are now known to proceed in a polar fashion as exemplified by BTX-sensitized incorporation of protic solvents by cyclohexenes,[1] the polar addition of OH acids to cycloocta-2,7-dienone,[2] and the photoreaction of benzopyridines with carboxylic acids.[3] The present communication deals with a novel photochemical addition of trialkylboranes to such substrates as cyclohexenes, cycloocta-2,7-dienone and acridine, which provides us with a new synthesis of otherwise difficultly accessible compounds.

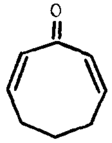
Irradiation [4] (quartz-filtered light, 48 hr) of a mixture of trialkylborane (I, 5 mmol), cyclohexene (II_x, 15 mmol) and p-xylene (5 ml) dissolved in benzene (70 ml) and the successive treatment of the reaction mixture with alkaline H_2O_2 afforded stereoselectively cis-2-alkylcyclohexanol (VI). Triethylborane (I_a) gave the alcohol VI_{ax} in 86% yield (based on 1 mol of the borane) and tri-n-butylborane (I_b) produced VI_{bx} in 80% yield. The structure of alcohols VI_{ax} and VI_{bx} was determined by



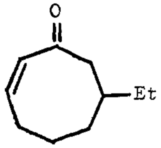
R = (a) Et, (b) n-Bu; R' = (x) H, (y) Et, (z) n-Bu comparison with authentic samples synthesized as follows.[5] Hydroboration [6] of 1-alkylcyclohexenes (II_y, II_z) afforded trans-2-alkylcyclohexanols (VII_y, VII_z), which were oxidized to 2-alkylcyclohexanones ($VIII_y$, $VIII_z$). Hydride-reduction of each ketone gave rise to a cis, trans mixture of 2-alkylcyclohexanols (VI_{ax} or VI_{bx}, VII_y or VII_z), where the isomers were separated on a capillary column (BDS 45 m, 100°) and the cis/trans ratio was 2:3 in both cases. GLC indicated that every photochemically produced alcohol (VI_{ax} or VI_{bx}) was homogeneous and had the cis-configuration. The photoreaction of 1-ethylcyclohexene (II_y) with boranes I_a and I_b under the same condition gave 2,2-dialkylcyclohexanols (VI_{ay}, VI_{by}) in 70% yield in both cases.[7] The alcohols VI [5] were identified by means of spectral data and the following chemical correlation: the alcohols VI were oxidized to ketones IX_{ay} and IX_{by}, which were identical with those independently synthesized from 2-ethylcyclohexanone ($VIII_y$) by the Hauser's method.[8]

Further extention of this reaction was attempted with no success. Tricyclohexyl- and triisopropylborane failed to give the adducts with cyclohexene. Cyclopentene, cyclooctene and cyclododecene (1:1 cis, trans mixture) did not react either with triethyl- or with tri-n-butylborane. This phenomenon is reminiscent of the photochemistry of cycloolefins in protic solvents [1] and points to that the reactive species in the cyclohexene-borane reaction is also very probably trans-cyclohexene (III). The highly strained olefin isomer is much more nucleophilic than ordinary cis-cyclohexene and is prone to be attacked by the strong Lewis acid I to give a zwitterion IV. The least motion migration of alkyl anion occurs from boron to the electron-deficient carbon to result in the observed cis addition. This mechanism is supported by the two facts: the stereoselective cis addition of the boranes and the regiospecific addition to the 1-alkylcyclohexenes. The reaction provides us with a new route to cis-2-alkylcyclohexanols, 2-alkylcyclohexanones and 2,2-dialkylcyclohexanones by means of the appropriate trialkylboranes.

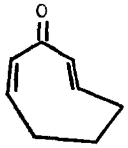
Cycloocta-2,7-dienone [3] was allowed to react with the alkylborane similarly. Irradiation (Pyrex-filtered light, 30 min) [4] of a mixture of the dienone (X, 8.2 mmol) and triethylborane I_a (12.3 mmol) dissolved in ether (20 ml) and the successive treatment with trimethylamine oxide [9, 10] afforded 7-ethylcyclooct-2-enone (XI) in 90% yield. The structure of XI was determined by its spectra.[5] This enone XI was



X



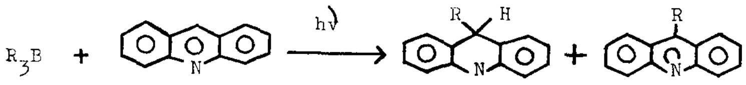
XI



XII

also obtained in the following way. Dienone X was irradiated at -78° for 1 hr in an ethereal solution, the light source was turned off and the borane I_a was added within several minutes. Upon warming up to room temperature and treating the the reaction mixture with trimethylamine oxide the enone XI was obtained in 15% yield, 85% of X being recovered. A mixture of the *cis*,*cis*-dienone X and the borane I_a failed to give the enone XI in the dark after 72 hr and X was totally recovered. Apparently the reactive species is the *cis*,*trans*-dienone XII, which has been shown to be the key intermediate in the protic solvent incorporation by Noyori and Katô.[2] In contrast to the Brønsted acid addition, no ring closure products having the *cis*-bicyclo[3.3.0]octane skeleton were detected in the present reaction.

Finally, the photoreaction with acridine was examined. A mixture of acridine (5 mmol) and the borane I (5 mmol) dissolved in benzene (70 ml) was irradiated[4] with Pyrex-filtered light for 48 hr. The treatment of the reaction mixture with alkaline H_2O_2 afforded 9-alkylacridan and 9-alkylacridine as indicated below the following scheme. Allowing the reaction mixture of acridine and tri-*n*-butylborane to stand for 72 hr at room temperature gave 9-*n*-butylacridan in 10% yield. Thus the addition does proceed thermally but the process is obviously accelerated by irradiation.



I	R	XIII	XIV
	n-Bu	65%	8%
	Cyclohexyl	90%	5%

In sharp contrast to the photochemical reaction of cyclohexene, the thermal reaction of acridine with tricyclohexylborane proceeded much more readily than tri-*n*-butylborane to produce 9-cyclohexylacridan in 90% yield after 72 hr at room temperature. The borane is a good reagent for introducing the α-branched alkyl group at the 9-position of acridine either thermally or photochemically.

REFERENCES AND REMARKS

1) It is commonly accepted that the photoaddition proceeds through protonation of a highly strained species, *trans*-cyclohexene, in the Markovnikov fashion: J. A. Marshall, *Accounts of Chem. Res.*, 2, **33** (1969).

2) Irradiation of the dienone X in acetic acid gives a stereoisomeric mixture of *exo*- and *endo*-2-acetoxy-*cis*-bicyclo[3.3.0]octan-3-one. The reactive species was proven to be the ground-state of *cis,trans*-dienone XII by R. Noyori and M. Katô, *Tetrahedron letters*, 5075 (1968). See also J. K. Crandall and R. P. Haseltine, *J. Amer. Chem. Soc.*, **90**, 6251 (1968).

3) Photoreaction of acridine and carboxylic acids results in decarboxylation and formation of 9-alkylacridans: R. Noyori, M. Katô, M. Kawanisi and H. Nozaki, *Tetrahedron*, **25**, 1125 (1969).

4) Irradiation was effected under N_2 atmosphere externally with a 200 W high press Hg arc at room temperature unless otherwise stated.

5) All isolated products gave correct analyses.

6) G. Zweifel and H. C. Brown, *Organic Reactions*, Vol. 13, John Wiley & Sons, Inc., New York, London, 1963.

7) GLC analyses showed that the photochemically produced alcohol was homogeneous and its positional isomers were absent.

8) S. Boatman, T. M. Harris and C. R. Hauser, *J. Amer. Chem. Soc.*, **87**, 82 (1965).

9) R. Köster and Y. Morita, *Ann. Chem.*, **704**, 70 (1967).

10) Work up of the reaction mixture with alkaline H_2O_2 afforded 2,3-epoxy-7-ethylcyclooctane[5] (85% yield, b.p. 95-97°/0.5 mm, IR (neat) at 1720, 1010 cm^{-1}).