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PHOTOCHEMICAL REACTION OF TRIALKYLBORANES AND ß-DICARBONYL COMPOUNDS

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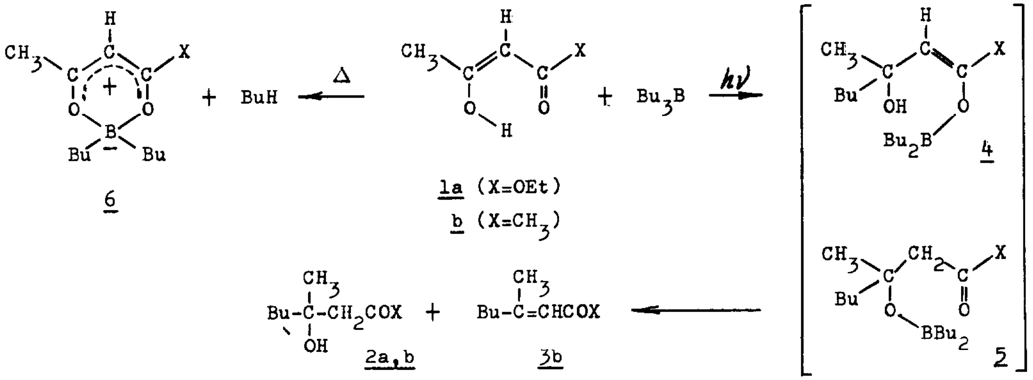
The discovery of now well-known reaction[1] of trialkylboranes and carbon monoxide motivated an extensive investigation on the synthetic applications of the boranes.[2] In continuation of the interest of photochemical reaction with cyclohexene,[3] research has been made on the reaction with photoexcited state of the enolic ß-dicarbonyl compounds[4] in expectation of possible conjugate addition to form 4. This communication reports that the expected reaction occurs to provide us with a novel method for the preparation of ß-alkylated ß-hydroxycarbonyl compounds 2.

Irradiation[5] of a benzene (25 ml) solution of ethyl acetoacetate (1a, 650 mg, 5 mmol) and tributylborane (910 mg, 5 mmol), followed by work-up,[6] gave ethyl 3-hydroxy-3-methylheptanoate[7] (2a, bp 74°/ 4 mm) in 37% yield.[8] Gas chromatogram of the crude product indicated that this was the only product isolable from the higher boiling fraction. Duplicated reaction with three times quantity of ethyl acetoacetate gave the hydroxyester 2a in 60% yield. Equimolar reaction of tricyclohexylborane and ethyl acetoacetate gave ethyl 3-cyclohexyl-3-hydroxybutyrate in 33% yield.



Irradiation of benzene (25 ml) solution of acetylacetone (1b, 500 mg, 5 mmol) and tributylborane (910 mg, 5 mmol) and the following work-up[6] gave (Z)- and (E)-4-methyl-3-octen-2-one (3b, 35%) and 4-methyloctan-4-ol-2-one (2b, 15%). When three times quantity of acetylacetone was used, the yield was increased to 45% each.[9] As the olefinic ketones 3b could be detected by glc of the reaction mixture before work-up, at least a part of 3b was formed during irradiation.[10] Possible route to the observed products is speculated as shown in equation: conjugate addition of trialkylborane to the enol to give 4, intramolecular alcoholysis[11] to 5, and the elimination of dibutylboronic acid to give 3b. The thermal reaction of acetylacetone and tributylborane was reported[12] to give an acetylacetonate complex 6 and butane, both of which could not be detected from the photochemical reaction mixture.

The reaction with non-enolizable keto ester was also attempted. Irradiation of a benzene solution of ethyl 2,2-dimethylacetoacetate (2.47 g, 15.6 mmol) and tributylborane (950 mg, 5.2 mmol) and the succesive work-up gave ethyl 2,2,3,3-tetramethylsuccinate (55% yield) as the only isolable product. Formation of this diester would be explained as the coupling reaction of the α-fission fragment of the keto ester.[13] This result also suggested that the reaction of tributylborane and enolizable ß-dicarbonyl compounds could be explained to proceed via photoexcited state of the enol.

The attempted reaction of tributylborane with both ethyl acetoacetate and acetylacetone under oxygen-catalyzed thermal conditions[14] failed to afford any addition products in sharp contrast with those toward α,ß-unsaturated carbonyl compounds.[14] Treatment of the reaction mixture with alkaline hydrogen peroxide gave only 1-butanol.

References and Remarks

1) H. C. Brown and M. W. Rathke, J. Am. Chem. Soc., 89, 2737 (1967).
2) H. C. Brown, Accts. Chem. Res., 2, 65 (1969); Chem. Britain, 7, 458 (1971).
3) N. Miyamoto, S. Isiyama, K. Utimoto and H. Nozaki, Tetrahedron Letters, 4597 (1971).
4) For photochemical behaviour of enolizable ß-diketones, especially reaction with olefins, see P. de Mayo, Accts. Chem. Res., 4, 41 (1971).
5) Irradiation was effected under nitrogen atmosphere externally with Pyrex-filtered 200 w high pressure mercury lamp at room temperature for 5 days.
6) The mixture was simply hydrolyzed with water or alternatively, hydrolysis and oxidation were carried out with alkaline hydrogen peroxide. The yields given refer to those obtained in the latter process, which is more convenient for isolation of products, i.e., the reaction mixture was treated with 10 ml of 6N sodium hydroxide and 10 ml of 30% hydrogen peroxide under stirring for 2 hr at 40°.
7) Determined by spectral and elemental analyses: ir (liquid film) 3480, 1710 cm^{-1}, nmr and ms also supported the structure.
8) Yields were calculated based on trialkylborane.
9) In this case acetophenone was detected from the reaction mixture. This origin is being investigated.
10) Reaction of 3b and tributylborane under the same reaction conditions did not give addition product and 3b was recovered.
11) Conversion of enol borinate to corresponding carbonyl compounds by the material containing protolytic hydrogen, see H. C. Brown, M. M. Rogić, M. W. Rathke and G. W. Kabalka, J. Am. Chem. Soc., 89, 5709 (1967).
12) M. F. Hawthorne and M. Raintjes, J. Org. Chem., 30, 3851 (1965).
13) For photochemical reaction of non-enolizable β-diketones, in which the coupling products of this sort are recorded, see H. Nozaki, Z. Yamaguti, T. Okada, R. Noyori and M. Kawanisi, Tetrahedron, 23, 3993 (1967).
14) H. C. Brown and G. W. Kabalka, J. Am. Chem. Soc., 92, 714 (1970).