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THE REACTION OF DIPHENYLCYCLOPROPENONE WITH DIBORANE

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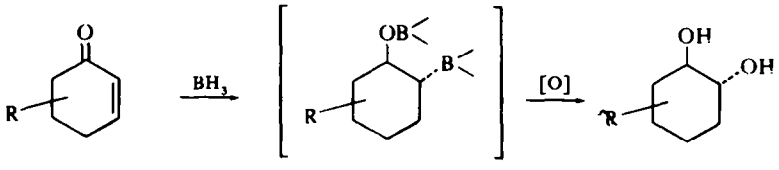
Abstract—The reaction of diphenylcyclopropenone (**1**) with excess of diborane has been shown to proceed by a stepwise mechanism. The formation of a cyclopropenyl cation intermediate **8** is postulated. Reduction of **8** with B_2H_6 generates 1,2-diphenyl-1-cyclopropene (**9**) which is the key intermediate in the hydroboration of **1**. Deuteroborane has been used to support the proposed mechanism. Both oxidation and protonolysis of the hydroboration and deuteroboration products have been performed.

WE WERE interested in the behaviour of diphenylcyclopropenone (**1**) towards diborane and derivatives as these reagents can react with both the carbonyl group and the double bond.[1] Diphenylcyclopropenone (**1**) is an α,β-unsaturated ketone of unique structure. The proximity of the CO group to both ends of the double bond makes the system different from normal α,β-unsaturated ketones.[2] Previous studies[3,4] on the hydroboration of conjugated cyclic ketones, in particular cyclohex-2-enones showed that *trans*-1,2-borane-borates are the main products and these can be oxidized to *trans*-1,2-cyclohexandiols. We anticipated different results in the hydroboration of **1** due to its unique structure.



Hydroboration of **1** with excess diborane in THF and oxidation with H_2O_2/OH^- gave as the main product benzylacetophenone (**2**) in 55–65% yield (Scheme 1). The unexpected product was identified through its spectroscopic properties* and by comparison with an authentic sample prepared from benzylacetophenone.[6]

The cleavage of the cyclopropane ring of **1** to yield **2** can be explained by two paths:

(A) Opening of the ring by diborane.

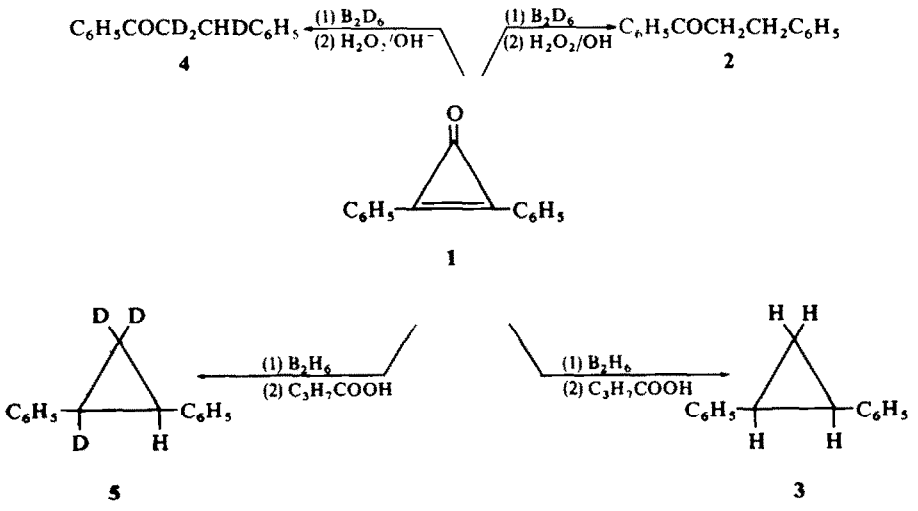
(B) Cleavage of an intermediate during or after oxidation.

To answer this question the hydroboration product of **1** was submitted to protonolysis.[1] Excess of diborane was destroyed with methanol and all volatile materials were removed; the residue was heated with diglyme and butyric acid at 150° (butyric

* The $-CH_2CH_2\overset{\overset{O}{\|}}{C}-$ part of the NMR spectrum of **2** is a good example of an A_2B_2 spin system with all 14 lines clearly separated.[5]

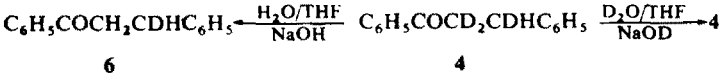
acid gave higher yields than the frequently used acetic acid). Purification by GLC gave 1,2-*cis*-diphenylcyclopropane (**3**), m.p. 34–35°,* in 45–50% yield. The structure of **3** was deduced from its NMR spectrum† (CCl_4): δ – 6·90/m (10H) aromatic, 2·39/d × d; J_1 = 8·5, J_2 = 6·5 Hz, (2H) benzylic 1·55–1.20/m; 10 lines; (2H) homobenzylic; mass spectrum and microanalysis.

The isolation of **3** from the hydroboration of **1** proves that diborane does not cleave the cyclopropane ring. It has been shown recently that cyclopropanes are cleaved by diborane only under drastic conditions.[8]



SCHEME 1

To obtain more information on the reaction deuterodiborane was used. Deuteroberation of **1** and subsequent oxidation (Scheme 1) gave trideuterobenzylacetophenone (**4**) which has only one nonaromatic proton. The position of this proton was found from exchange reactions. When **4** was stirred in H_2O/THF with NaOH at 40°—two deuterons could be exchanged to yield monodeuterobenzylacetophenone **6**. The same treatment in D_2O/THF with NaOD caused no change in **4**.



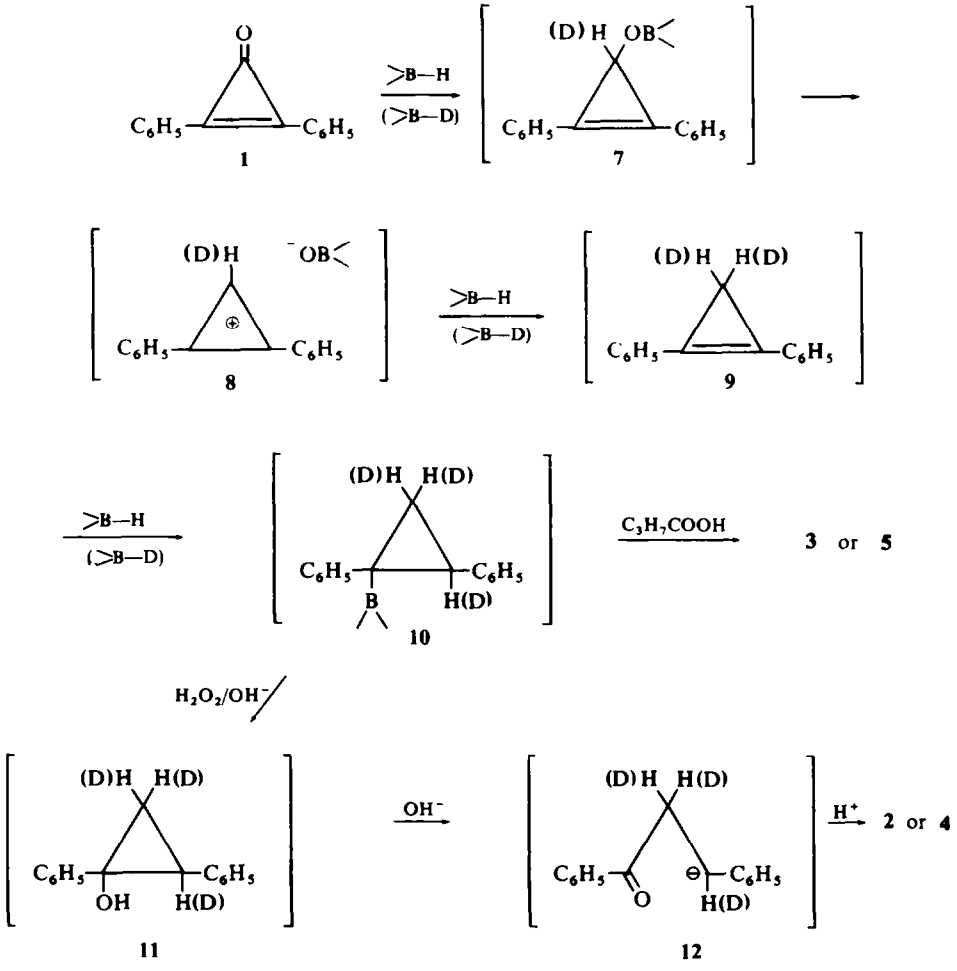
These two reactions prove that two of the three deuterons in **4** are α to the carbonyl group and that the proton which is introduced into **4** during workup after the deuteroboration is β to the ketone function. Further confirmation for the position of this proton was acquired from the mass spectrum of both **4** and **6**. In addition to M^+ 213 *m/e* for **4** and M^+ 211 *m/e* for **6** both spectra have several major peaks, one of them being 92 *m/e* which corresponds to $C_6H_5CHD^+$. Deuteroboration of **1**

* Both *cis*- and *trans*-1,2-diphenylcyclopropanes are known compounds,[7] the *cis*-isomer has a reported m.p. of 38–39° whereas the *trans*-isomer is a liquid.

† Partial NMR data, of *cis*- and *trans*-1,2-diphenylcyclopropanes has been reported, namely the chemical shifts of the aromatic and benzylic protons: *cis*, δ 6·96 (aromatic), 2·45 (benzylic); *trans*, 7·13 and 2·13 respectively.[7] The chemical shifts we obtained for **3** are in good agreement with those published for the *cis*-isomer.

and subsequent protonolysis (Scheme 1) gave *cis*-1,2-diphenyl-1,3,3-trideuterocyclopropane (**5**) in 50% yield. The position of the proton introduced from the buturic acid is clearly evident from the NMR spectrum of **5**. There is one benzylic proton at δ 2·39 and no homobenzylic protons.

A possible mechanism, which correlates all the data obtained, for the reaction of **1** with diborane is presented in Scheme 2. The first step of the reaction sequence is the reduction of the carbonyl function to yield **7**. This is in accord with previous work[3] and is even more plausible in the case of **1** because of its highly polarized CO group.[2]



SCHEME 2

Loss of an $^{-}OB<$ group generates the stabilized diphenylcyclopropenyl cation **8** which is subsequently reduced to 1,2-diphenyl-1-cyclopropene (**9**). A similar reaction, namely reduction of diphenylcyclopropenyl fluoroborate with $NaBH_4$ to yield **9** was reported recently.[9] 1,2-Diphenyl-1-cyclopropene (**9**) is the key intermediate in the reaction of **1** with diborane. Hydroboration of **9** yields, as expected,

10.* Protonolysis of **10** yields **3** or **5** without affecting the cyclopropane ring, whereas basic oxidation gives, as primary product, *cis*-1,2-diphenyl-1-cyclopropanol **11** which under these conditions ring opens[11] and yields **2** or **4**. The proposed mechanism is strongly supported by the following facts: (A) formation of **3** without the isomeric *trans*-1,2-diphenylcyclopropane, in accord with the *cis*-sterochemistry of the hydroboration reaction[1], (B) introduction of one proton in **5** only in a benzylic position, (C) introduction of one proton in **4** β to the carbonyl group[11] which confirms the sequence **11** → **12** → **2** or the analogous trideutero sequence leading to **4**.

Further work on the reaction of **1** with boranes and possible trapping or isolating of intermediates as **8** and **9** is in progress.

EXPERIMENTAL

B.ps and m.ps are uncorrected. NMR spectra of compounds **2**,**3** and **6** were measured on a Varian HA-100 spectrometer; the spectra of **4** and **5** were measured on a Varian T-60 spectrometer with TMS as internal standard. They are recorded in δ units, ppm/multiplicity† (number of hydrogens). Mass spectra were recorded on an Atlas, Mat CH4 spectrometer. GLC was performed on an Aerograph A-700 apparatus; the column used was SE 30 20% on Chromosorb W, 2 m long. All hydroboration reactions were carried out under nitrogen. Deuteroborane was prepared from LiD, 99% D (Fluka) and BF_3OEt_2. Diphenylcyclopropenone (**1**) was synthetized from dibenzylketone according to Breslow's procedure.[12] Authentic benzylacetophenone **2** was prepared by catalytic hydrogenation of benzalacetophenone[6]), m.p. 70–71° (EtOH).

Hydroboration-oxidation of diphenylcyclopropenone (**1**). B_2H_6 (5 ml, 1M) was added dropwise to **1** (1·03 g, 5 mmol) in 5 ml THF cooled in an ice bath with magnetic stirring; the mixture was stirred for 1 hr at 0° and, then 1 hr at room temp. Excess B_2H_6 was decomposed carefully with ice and the mixture was oxidized with 5 ml 10% NaOH and 5 ml 30% H_2O_2 for 1 hr at room temp. K_2CO_3 was added to saturation and the layers separated; the aqueous layer was extracted several times with CH_2Cl_2 and the combined extracts were dried over $MgSO_4$ and concentrated to dryness *in vacuo*. Crystallization from EtOH gave (in two crops) 0·470 g (46%) of **2** m.p. 69–70° (lit.[6] m.p. 72–73°); IR (CCl_4): 1700 cm^{-1} (>C = O); NMR (CCl_4): 8·10–7·20/m (10H), 3·37–2·96/m (4H). (Found: C, 85·3; H, 6·5. Calc. for $C_{15}H_{14}O$: C, 85·7; H, 6·7). The mother liquors from the above crystallization contained 0·140 g of **2** as found by GLC, at 220° He 100 ml/min, using a weighed amount of dibenzylketone as internal standard. The total yield of **2** was 60%.‡

Hydroboration–protonolysis of **1**. (2·06 g, 10 mmol) in 5 ml THF was treated with B_2H_6 (20 ml, 0·5 M) as described above. Excess B_2H_6 was decomposed with dry MeOH, diglyme (15 ml) was added and the mixture was concentrated to a small volume *in vacuo*. Butyric acid (20 ml) was added dropwise and the mixture was kept at 150° for 16 hr under N_2. The acid was neutralized with 10% NaOH and the product was extracted several times with hexane, dried over $MgSO_4$ and distilled to yield 1·05g of crude **3** b.p. 90–100°/0·3, (ball-oven). Purification by GLC§ at 170° He 100 ml/min gave pure **3** m.p. 34–35° in 45% yield as calculated using a weight amount of 1,3-diphenylpropyne as internal standard. NMR (CCl_4) 6·90/m (10H), 2·38/d × d; $J = 8·5$, $J_2 = 6·5$ Hz; (2H), 1·55–1·20/m (2H); MS, *m/e* 194M^+. (Found: C, 93·0; H, 7·3. Calc. for $C_{15}H_{14}$: C, 92·8; H, 7·2).

Deuteroboration–oxidation of **1**. (1·03 g, 10 mmol) in 5 ml THF with B_2D_6 (15 ml, 0·35M) gave (in two crops from EtOH) 0·450 g (44%) of **4** m.p. 68–69°. (Total yield of **4** was 58%; GLC with dibenzyl ketone as internal standard). NMR (CCl_4) 8·10–7·20/m (10H), 3·15/bs (1H); MS, *m/e* 213(M^+, 36%), 105($C_6H_5CO^+$, 100%), 92($C_6H_5CHD^+$, 9%) and 77($C_6H_5^+$, 29%).

* Hydroboration of 1-methylcyclopropene gives tris (*trans*-2-methylcyclopropyl) borane.[10]

† s = singlet, d = doublet, m = multiplet, b = broad.

‡ A number of small peaks present were not analyzed.

§ An unidentified compound (12% of the volatile fraction) which did not contain phenyl groups was also isolated.

Exchange experiments

(A) *Reaction of* **4** *with* H_2O/OH^-. Trideuterobenzylacetophenone **4** (73 mg) in 2 ml THF and 10% NaOH (4 ml) was stirred at 40° for 16 hr. The mixture was saturated with anhyd K_2CO_3 and extracted several times with CH_2Cl_2, dried and concentrated to dryness to yield 60 mg of **6**. NMR (CCl_4): 8·10–7·20/m (10H), 3·29–2·90/m (3H); MS, *m/e* 211 (M^+, 34%), 105($C_6H_5CO^+$, 100%), 92($C_6H_5CHD^+$, 10%) and 77($C_6H_5^+$, 40%).

(B) *Reaction of* **4** *with* D_2O/OD. Treatment of **4** (50 mg) in 1 ml THF with a sol of D_2O (2 ml) and Na (200 mg) as described above caused no change in **4** (checked by NMR).

Deuteroboration–protonolysis of **1**. (1·53 g, 7·5 mmol) was treated with B_2D_6 (30 ml, 0·25M) and heated with butyric acid (30 ml) as described for the hydroboration–protonlysis of **1**. The yield of **5** m.p. 30–31°, was 50% (GLC with 1,3-diphenylpropyne as internal standard). NMR (CCl_4): 6·95/m (10H), 2·39/bs (1H); MS, *m/e* 197M^+.

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REFERENCES

[1] H. C. Brown, *Hydroboration*. Benjamin (1962)
[2] G. L. Closs, *Advances in Alicyclic Chemistry* **1**, 114 (1966)
[3] J. Klein and E. Dunkelblum, *Tetrahedron* **24**, 5701 (1968); E. Dunkelblum, R. Levene and J. Klein, *Ibid* **28**, 1009 (1972)
[4] H. C. Brown and R. U. Gullivan Jr., *J. Am. Chem. Soc.* **90**, 2906 (1968)
[5] J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution NMR Spectroscopy* **1**, 347 (1965)
[6] R. Adams, J. W. Kern and R. L. Shriner, *O. S. Coll.* **1**, 101 (1941)
[7] D. Y. Curtin, H. Gruen, Y. G. Hendrickson and H. E. Knipmeyer, *J. Am. Chem. Soc.* **83**, 4838 (1961)
[8] B. Rickborn and S. E. Wood, *Ibid.* **93**, 3940 (1971)
[9] D. T. Longone and D. M. Stehouwer, *Tetrahedron Letters* 1017 (1970)
[10] R. Koster, S. Arora and P. Binger, *Angew. Chem.* **81**, 185 (1969)
[11] C. H. DePuy, F. W. Breitbeil and K. R. De Bruin, *J. Am. Chem. Soc.* **88**, 3397 (1967); C. H. DePuy, *Acc. Chem. Research* **1**, 33 (1968)
[12] R. Breslow, T. Eicher, A. Krebs, R. A. Peterson and J. Possner, *J. Am. Chem. Soc.* **87**, 1320 (1965)