Tetrahedron Letters No.10, pp. 757-760, 1971. Pergamon Press. Printed in Great Britain.

THE BIRCH REDUCTION OF [2.2]PARACYCLOPHANE

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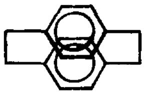
(Received in USA 12 January 1971; received in UK for publication 16 February 1971)

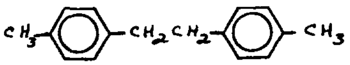
In connection with recent work involving the Birch reduction,[1] we have recently explored the Birch reduction of [2.2]paracyclophane (1). We felt that the reduction of 1 should proceed rather easily, since inherent strain might thereby be removed. We report here our results and compare them with other recent reductions of 1.

When 1 was subjected to the usual Birch conditions[2]--adding sodium to a solution of the substrate in alcohol and liquid ammonia--1 was recovered in 88% yield. The substrate was also recovered unchanged when a cosolvent, tetrahydrofuran,[3] was added to promote the solubility of 1 (72% recovery).

A modified procedure was then attempted that has been successfully used for hydrocarbons;[3] a solution of 1 in tetrahydrofuran was added to a solution of sodium in refluxing ammonia, and then alcohol was added. The result was the cleaved product p,p'-dimethylbibenzyl[4] (2) in 94% yield.



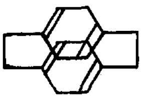
1



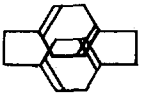
2

A compromise between the reactions used above was sought--it was felt that in the first two reactions the ethanol hindered the reaction, possibly by consuming the sodium before reaction with the substrate could take place; and that in the third reaction the absence of the ethanol led to conditions too drastic. Hence, in a modified procedure, a solution of 1 in tetrahydrofuran and ethanol was added slowly to a solution of sodium and refluxing ammonia.[5] The result was a new product that could be easily sublimed to give a 98% yield, m.p. 120-122°.

The facility of the sublimation led credence to the view that the basic skeleton of a compact molecule was still intact. Dehydrogenation of the product back to 1 proved no cleavage of the basic skeleton had taken place. The mass spectrum exhibited a parent peak at 212, indicating that four hydrogen atoms had been added. The infrared spectrum showed a strong absorption at 794 cm^{-1} (trisubstituted olefin) and the nmr spectrum exhibited two signals (both multiplets) at δ 5.3 and 2.3 in the relative ratio of 1:4. No significant absorption was observed in the ultraviolet spectrum above 260 nm, excluding the possibility of a conjugated chromophore.[6] The only structures consistent with the data were 3a and 3b. At this point it was concluded that either 3a, or 3b, or a mixture thereof was obtained.



3a
"eclipsed"



3b
"staggered"

In structure 3, significant interaction between the π clouds of the upper and lower decks can occur. This interaction is reflected by the unusual ultraviolet spectrum (Figure 1). The absorption of 3 is significantly greater and at longer wavelength than that of norbornadiene, the well-known case of π-interaction of isolated olefins.[7] The ultraviolet spectra of 1 and 2 are also shown,[8] to indicate the change as one goes from a normal system to one involving π-interaction between an upper and a lower ring.

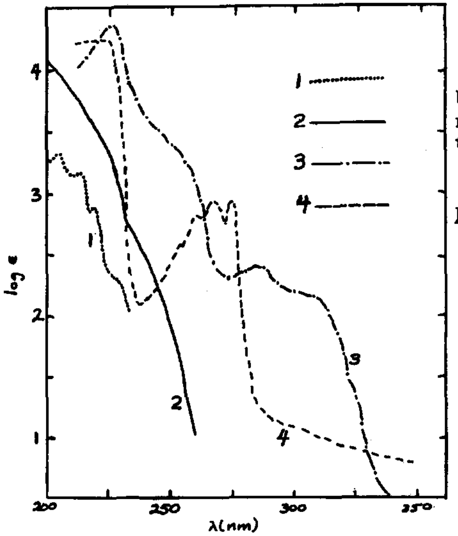
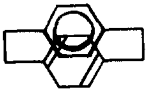


Figure 1. --
Ultraviolet spectrum of:
norbornadiene (line 1);
tetrahydro[2.2]paracyclophane 3 (line 2);
[2.2]paracyclophane 1 (line 3);
p,p'-dimethylbibenzyl 2 (line 4).

Jenny and Reiner have recently reported[9] the Birch reduction of 1. In liquid ammonia at -75°, 3 was obtained (72%) along with a smaller quantity (8%) of the dihydro-product 4, with no appreciable amount of the cleaved dihydro product 2. In view of these differing results, we investigated more closely the reduction of 1 under our conditions. First, we monitored the reduction of 1 using glpc analysis: throughout the reduction, the three components 1, 2, and 3 were seen, and only towards the end of the reduction did a new unknown component (4?) appear, to the extent of 2% (1:2:3=3:8:87). Second, an nmr analysis of the crude reaction product was made. Signals from 1, 2, and 3 were seen in the appropriate ratio of intensities, but no trace of signals existed for 4. Third, authentic samples of 1, 2, and 3 were isolated from the crude reaction product by selective extractions and recrystallizations. Hence, it was concluded that our conditions and those of Jenny and Reiner were sufficiently different to cause entirely different product distributions.



4

Another interesting difference between the two investigations was the melting point behavior. Jenny and Reiner reported a melting point of 3 to be "about 109°", and that after one melting the material now had a new melting point of 160-170° and now contained amounts of 4 and 1. In contrast, our 3 had a sharp melting point of 125-127.5°, and after two or three meltings had no increase in melting point and had no significant change in composition (glpc). Because of the general agreement of nmr, uv and mass spectral data, but because of the sharper and higher melting point of our material, we conclude that the material of Jenny and Reiner is a mixture of 3a and 3b and that our material is predominately one isomer of 3. We can tentatively assign 3a as the correct structure for our isomer of 3, because the ultraviolet spectrum of our material has a significantly greater absorption than that of Jenny and Reiner throughout a greater wavelength range; 3a with its "eclipsed" olefin π-clouds lying together would have greater interaction.

We gratefully acknowledge financial support from the Research Foundation, Frederick G. Cottrell grant, and from the Robert A. Welch Foundation, grant no. B-325.

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