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## Addition Reactions of Conjugated Double Bonds. Part II.<sup>1</sup> The Occurrence of 1,4- or 1,2-Addition in the Reduction of Some Aryl $\alpha\beta$ -Unsaturated Ketones with Metal Hydrides

By K. Iqbal and W. R. Jackson, Department of Chemistry, Queen's University, Belfast

Some substituted *trans*-chalcones, crotonophenone, benzylideneacetone, and 3-phenylcyclohex-2-enone have been reduced with sodium borohydride in three solvents. In diglyme and propan-2-ol the proportion of attack at the  $\beta$ -carbon atom (1,4-addition) is less in the last two compounds than in the others. Reduction of the chalcones or crotonophenone in pyridine led to almost exclusive double-bond saturation. The related allylic alcohols are also reduced under these conditions. The ease of borohydride reduction of allylic alcohols appears to be connected with the ease of the base-catalysed allylic alcohol-saturated ketone rearrangements, though the allylic alcohols are stable to rearrangement in pyridine solution. An explanation is suggested.

In a previous paper <sup>1</sup> the reduction of  $\alpha\beta$ -unsaturated ketones with sodium borohydride was examined and the ratio of 1,4- to 1,2-addition was shown to be sensitive to the size of the reducing species and to the relative steric hindrance to nucleophilic attack at the the two possible sites. We have now investigated the



influence of electronic effects on the amounts of doublebond saturation in the borohydride reduction of  $\alpha\beta$ -unsaturated ketones. *trans*-Chalcone, *trans*-4-methoxychalcone (4-MeO·C<sub>6</sub>H<sub>4</sub>·CH·COPh), and *trans*-4'- methoxychalcone (PhCH:CH·CO·C<sub>6</sub>H<sub>4</sub>·OMe-4') were reduced with sodium borohydride in propan-2-ol, diglyme, and pyridine. The resulting mixtures of saturated and allylic alcohols could not be conveniently analysed, and were oxidised to mixtures of dihydrochalcones and chalcones, which were separated both by chromatography on alumina and by gas-liquid chromatography. The products of 1,4-addition from these and all other compounds studied were always saturated alcohols; in no case was the presence of saturated ketone detected. This indicates that a proton source, probably traces of moisture, was available in the aprotic solvents, diglyme and pyridine, to convert the metal hydride salt of the enolate into the enol, which could then be reduced, probably through the keto-form (see Scheme). The results (Table 1) showed that a methoxy-group in the 4-position of either of the benzene rings in chalcone had little influence on the position of hydride attack. A

<sup>1</sup> W. R. Jackson and A. Zurquiyah, J. Chem. Soc., 1965, 5280 is to be considered as Part I.

similar study on the influence of the nitro-group was attempted but neither the mixtures of nitro-alcohols nor the nitro-ketones could be analysed satisfactorily.

The results for chalcone reductions showed two surprising solvent effects. Reduction in methanol gave almost exclusive 1,2-addition in agreement with previous work,<sup>2</sup> whereas reduction in propan-2-ol gave large amounts of 1,4-addition. Sodium borohydride reacts slowly with methanol<sup>3</sup> and reduction by the product, sodium trimethoxyborohydride, may therefore be responsible for this preponderance of 1,2-addition. However, reduction of chalcone with a solution of sodium trimethoxyborohydride gave after oxidation a 75:25 mixture of dihydrochalcone and chalcone. This ratio is very similar to that obtained for reduction of chalcone with sodium borohydride in either diglyme or tetrahydrofuran. The usual sequence for increasing doublebond saturation was methanol < propan-2-ol < diglyme  $\approx$  tetrahydrofuran. Chalcone reduction was the only exception to this sequence, in that its reduction in propan-2-ol gave more saturated products than its reduction in the ether solvents. The proportion of carbonyl attack appears to increase with increasing solvent polarity. This trend is compatible with a greater reduction by the more polar solvents in the energy of the transition state leading to 1,2-addition than of that leading to 1,4-addition. The former transition state could be expected to have a more localised charge than the latter and thus to be more effectively solvated by polar solvents.

The extensive double-bond saturation obtained when pyridine was used as solvent or when pyridine was added in small amounts to reduction mixtures in diglyme was surprising in view of the previously proposed reasons for exclusive 1,4-addition of borohydride in pyridine to some cyclic ketones.<sup>1</sup> The previous work indicated that in a series of alkyl substituted cyclohexenones there was an inherent tendency for the borohydride ions to add in a conjugate manner. However, the presence of bulky β-alkyl substituents caused adverse steric interactions in the transition stages leading to 1,4-additions, and only when reduction was limited to the small borohydride nucleophile, BH<sub>4</sub><sup>-</sup>, was exclusive 1,4-addition obtained. The presence of pyridine and other Lewis bases limits reduction to the following step: 4

$$R_2CO + Na^+BH_4^- + C_5H_5N - C_5H_5N \rightarrow BH_3 + R_2CHO^-Na^+$$

Under these conditions the more bulky alkoxyborohydride species, e.g., R<sub>2</sub>CHO·BH<sub>3</sub><sup>-</sup>, is not formed and does not participate in the reduction.

In *trans*-chalcone the  $\beta$ - and carbonyl carbon atoms have very similar steric environments and it was not anticipated that the effective size of the nucleophile would significantly influence the site of nucleophilic

attack. The previously mentioned reduction of chalcone with sodium trimethoxyborohydride in diglyme substantiated this suggestion. The extensive doublebond saturation with pyridine as solvent was more clearly understood when it was shown that the allylic

TABLE 1

alcohol from chalcone, chalcol, was reduced under the

reaction conditions. The allylic alcohol was also re-

duced when set aside for 3 days with sodium boro-

Reductio	ons with	sodium	borohydride *	in (A	A) propan-	-2-ol,
(B)	diglyme,	(C) te	etrahydrofuran,	(D)	pyridine,	and
$(\mathbf{F})$	methano					

Ketone	Temp.	Solvent	Ratio of 1,4- to 1,2-addition products †	Recovery $\binom{0}{0}$ †
Chalcone	20°	$\mathbf{A}$	82:18	83
	20	В	71:31	86.5
	<b>70</b>	в	100:0	88
	<b>20</b>	в‡	100:0	80
	<b>20</b>	В§	100:0	69
	<b>20</b>	C	75:25	80
	<b>70</b>	С	90:10	98
	<b>20</b>	D	98:2	82
	<b>65</b>	E	13:87	87
4-Methoxychalcone	<b>20</b>	А	63:37	87
-	<b>20</b>	в	73:27	81
	<b>20</b>	D	98:2	<b>78</b>
4'-Methoxychalcone	<b>20</b>	Α	68:32	80
-	<b>20</b>	в	69:31	93.5
	<b>20</b>	$\mathbf{D}$	98:2	80

\* Molar ratio of sodium borohydride to ketone, 4:1.  $\dagger$  Average of at least two values; the ratio was independent of % recovery ( $\pm 3\%$ ).  $\ddagger$  Pyridine (4 mol.) added. § Triphenylphosphine (4 mol.) added.

hydride (4 mol.) in diglyme in the presence of pyridine or triphenylphosphine (4 mol.). The alcohol was not reduced in diglyme under these conditions when a Lewis base was absent. The allylic alcohol was, however, reduced by sodium borohydride in diglyme in 3 days at 70°.

Recent work<sup>2</sup> describes the apparent 1,4-addition of sodium borohydride to some 4-benzylpyrrolidine-2,3-di-The authors showed that this apparent 1,4-addiones. tion was in fact a 1,2-addition to carbonyl followed by rapid isomerisation of the product to an enol and subsequent reduction of the enol. It was thought that our results might be explained in a similar manner, especially as chalcol rearranges in aqueous alcoholic alkali to dihydrochalcone.<sup>5,6</sup> However, though the rearrange-

ment proceeded readily when chalcol was briefly heated in aqueous alkali, no rearrangement had occurred in pyridine after 3 days at 20°. This result was to be expected; since previous workers reported that chalcol was stable when refluxed in triethylamine, a stronger

- 4 W. M. Jones and H. E. Wise, J. Amer. Chem. Soc., 1962, 84, 997.

  - <sup>5</sup> H. Nomura, Bull. Soc. chim. France, 1925, 37, 1245.
     <sup>6</sup> W. Davey and J. A. Hearne, J. Chem. Soc., 1964, 4978.

<sup>&</sup>lt;sup>2</sup> P. L. Southwick, N. Latif, B. M. Fitzgerald, and N. M.

Zaczek, J. Org. Chem., 1966, **31**, 1. <sup>3</sup> H. C. Brown, E. J. Mead, and B. C. Subba Rao, J. Amer. Chem. Soc., 1955, **77**, 6209.

base than pyridine.<sup>6</sup> Also a small amount of triphenylphosphine, a strong Lewis but a weak Brønsted base, caused reduction of the allylic alcohol.<sup>1</sup> This latter result also lessened the possibility that the reduction in pyridine may occur by way of a hydride transfe from dihydropyridine-borine. Similarly, addition of pyridine-borine to a mixture of the allylic alcohol and sodium borohydride in diglyme was much less effective than addition of pyridine in promoting the reduction of the allylic alcohol.

In an attempt to test the generality of the results for chalcone, reductions of trans-crotonophenone, transbenzylideneacetone, and 3-phenylcyclohex-2-enone, were studied under similar conditions (Table 2). The experi-

## TABLE 2

## Reductions with sodium borohydride in (A) propan-2-ol, (B) diglyme, and (D) pyridine \*

Ketone	Solvent	Ratio of 1,4- to 1,2-addition products	Recovery (%)
Crotonophenone	А	58:42	87
1	$\mathbf{B}$	75:25	91
	D	95:5	78
Benzylideneacetone	Α	23:77	93
\$	$\mathbf{B}$	42:58	92
	$\mathbf{D}$	28:72	76
3-Phenylcyclohexenone	Α	35:65	94
5-5	в	67:33	80
	D	30:70	76

\* Sodium borohydride and ketone were in molar ratio 4 : 1. All reactions were at 20°. Each value represents the average of at least two reactions. The ratios were independent of yield  $(\pm 3\%).$ 

mental procedure was similar to that for chalcone reductions. Care was taken to ensure that the isolation procedure did not involve an acidification step, as the allylic alcohols from these compounds are acid labile. The products from benzylideneacetone and phenylcyclohexenone were usually analysed as alcohols and those from crotonophenone as ketones. The allylic alcohols from all three compounds were stable when treated with sodium borohydride in propan-2-ol or diglyme under the standard conditions. The allylic alcohols from benzylideneacetone and phenylcyclohexenone were also stable towards sodium borohydride in pyridine solution but 1-phenylbut-2-en-1-ol, the allylic alcohol from crotonophenone, was reduced under the standard conditions in pyridine. This last allylic alcohol also rearranged smoothly to the corresponding saturated ketone when heated with aqueous alcoholic alkali, whereas the other two were recovered unchanged.

Thus allylic alcohols of general structure RCH:CH·CH(OH)Ph can apparently be reduced by sodium borohydride in non-polar solvents in the presence of small amounts of strong Lewis bases. Such alcohols all rearrange under basic conditions to give ketones.<sup>5,7,8</sup> The mechanism proposed for this rearrangement involves formation of the alkoxide of the allylic alcohol, a 1,2-hydride transfer, and reprotonation at the carbon atom  $\beta$  to the ketone.<sup>9</sup>

$$Ph CHOH \cdot CH: CHR + OR^{-} \longrightarrow Ph C - CH = CHR$$

$$Ph CO \cdot CH_{2} \cdot CH_{2}R + OR^{-}$$

When ketones are reduced in non-polar solvents by sodium borohydride the final product is usually the corresponding alkoxyborate,  $4R_2CO + Na^+BH_4^- \rightarrow$  $Na^+B(O\cdot CHR_2)_4^-$ , and free alkoxide ions are not present in solution. When a strong Lewis base is present, the boron is removed as a borine, e.g., pyridine-borine, and the free alkoxide is present in solution (see above). Similarly the reduction of allylic alcohols can be visualised as an initial attack of borohydride on the acidic hydrogen of an allylic alcohol. Sodium borohydride has been

$$\begin{array}{c} \mathsf{RCH:CH:CH(OH)Ph} + \mathsf{BH}_{4}^{-} \longrightarrow \mathsf{RCH:CH:CHPh} + \mathsf{H}_{2} \\ \downarrow \\ \mathsf{OBH}_{3} \end{array}$$

shown to react rapidly with methanol and more slowly with ethanol. The allylic alcohols from chalcone and crotonophenone are both allylic and benzylic and could thus be expected to be as strongly acidic as methanol.<sup>10</sup> In the presence of a strong Lewis base the rapid formation of a borine and the alkoxide ion could be anticipated. As in our previous work, the protons necessary to complete the reaction sequence are probably available from small amounts of impurity in the pyridine.

The values in Table 2 show that reductions of benzylideneacetone and phenylcyclohexenone give less double-bond saturation than those of the chalcones or crotonophenone. The transition state for 1,4-addition to the system PhCH:CH-COR, present in both benzylideneacetone and in phenylcyclohexenone, must involve loss of the phenyl-double bond conjugation energy. This energy is retained in the transition state leading to 1,2-addition.

Finally, it is of interest to compare the ratios of 1,4to 1,2-addition for phenylcyclohexenone reduction with those for carvenone reduction (39:61 in propan-2-ol, 64:36 in diglyme). The effective size of a phenyl group is usually considered to be slightly less than that of an isopropyl group [conformational energies ca. 2.6 kcal. mol.<sup>-1</sup> for phenyl<sup>11</sup> and 3.3 kcal. mol.<sup>-1</sup> (average value) for isoporpyl<sup>12,13</sup>]. The similar results for the two compounds are then consistent with compensation for the gain in 1,4-addition from the less adverse steric interactions in phenylcyclohexenone by the increase in transition state energy due to loss of conjugation. The importance both of steric effects and of the desire to

- 82, 1367.
  <sup>12</sup> W. G. Dauben and K. S. Pitzer in 'Steric Effects in Organic
  <sup>13</sup> W. G. Dauben and K. S. Pitzer in 'Steric Effects in Organic
  <sup>14</sup> W. G. Dauben and K. S. Pitzer in 'Steric Effects in Organic
- <sup>13</sup> R. D. Stolow, J. Amer. Chem. Soc., 1964, 86, 2170.

 <sup>&</sup>lt;sup>7</sup> E. Tiffeneau, Bull. Soc. chim. France, 1907, 1, 1209.
 <sup>8</sup> H. Burton and C. K. Ingold, J. Chem. Soc., 1928, 904.
 <sup>9</sup> C. K. Ingold and C. W. Shoppee, J. Chem. Soc., 1928, 365.

<sup>&</sup>lt;sup>10</sup> J. Hine and M. Hine, J. Amer. Chem. Soc., 1952, 74, 5266.

<sup>&</sup>lt;sup>11</sup> E. L. Eliel and M. N. Renick, J. Amer. Chem. Soc., 1960,

preserve the most conjugated system in the transition state has been previously noted in additions of Grignard reagents to  $\alpha\beta$ -unsaturated ketones.<sup>14</sup>

## EXPERIMENTAL

Materials .--- Sodium borohydride and solvents were as described previously.<sup>1</sup> The chalcones and related dihydrochalcones had the properties listed in Table 3. 3-Phenylcyclohex-2-enone, m. p. 64° was prepared by the method of

Table	3
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	М. р.	Lit. m. p.
Chalcone	$56^{\circ}$	55—57° a
Dihydrochalcone	72 - 73	72—73 <sup>b</sup>
4-Methoxychalcone	<b>74</b> ·5	74·3—74·6 °
4-Methoxydihydrochalcone	64	66 <sup>d</sup>
4'-Methoxychalcone	106	105—106 °
4'-Methoxydihydrochalcone	95	95 d
4-Nitrochalcone	163	164 /
4-Nitrodihydrochalcone	98	99.5-100.5

<sup>a</sup> E. P. Kohler and H. M. Chadwell, Org. Synth., 1941, Coll. Vol. I, 79. <sup>b</sup> R. Adams, J. W. Kern, and R. L. Shriner, Org. Synth., 1941, Coll. Vol. I, 101. <sup>c</sup> D. S. Noyce and W. A. Pryor, J. Amer. Chem. Soc., 1959, **81**, 618. <sup>d</sup> D. Bar and E. Debruyne, Ann. pharm. franç., 1958, **16**, 235. <sup>e</sup> H. Staudinger and N. Kom, Annalen, 1911, **384**, 38. <sup>f</sup> W. Davey and J. R Cwilt L. Chem. Soc. 1957, 1008. <sup>g</sup> P. 6f. 6 Gwilt, J. Chem. Soc., 1957, 1008. 9 Ref. 6.

Novello, Christy, and Sprague,<sup>15</sup> who quote m. p. 63-8-64.6°. 3-Phenylcyclohexanone, prepared by hydrogenation of the unsaturated ketone over palladium-charcoal, had b. p. 169-169.5°/18 mm.; [2,4-dinitrophenylhydrazone, m. p. 183-185° (lit.,<sup>16</sup> 183-186°)]. 3-Phenylcyclohex-2-enol, prepared by lithium aluminium hydride reuction of the unsaturated ketone, had m. p. 59-60° (lit.,<sup>17</sup> 60-61). A mixture of cis- and trans-3-phenylcyclohexanols, m. p. 77-78° (lit.,<sup>17</sup> 78-80°), probably mainly the cis-isomer, was obtained by hydrogenation of the unsaturated alcohol over palladium-charcoal.

Benzylideneacetone (Lights) had m. p. 42° (from light petroleum). 4-Phenylbutan-2-one, prepared by hydrogenation of the above ketone, had b. p.  $115^{\circ}/13$  mm.,  $n_{\rm p}^{21}$ 1.5104 (lit.,<sup>18</sup> b. p. 115°/13 mm.,  $n_{\rm p}^{22}$  1.511). Reduction of the saturated ketone with lithium aluminium hydride gave 4-phenylbutan-2-ol, [phenylurethane: m. p. 112-113° (lit.,<sup>18</sup> 113°)]. 4-Phenylbut-3-en-2-ol, prepared as by Klages,<sup>18</sup> had b. p.  $85^{\circ}/0.25$  mm.,  $n_{\rm p}^{19}$  1.5719 (lit.,<sup>18</sup> b. p. 1178) 117°/4 mm.,  $n_{\rm p}^{31}$  1.5530) [phenylurethane: m. p. 90–91° (lit.,<sup>19</sup> 92–93°)]. Crotonophenone, b. p. 90–95°/3.0 mm.,  $n_{\rm D}^{24}$  1.5572 (lit.,<sup>20</sup> b. p. 114°/11.5 mm.,  $n_{\rm D}^{25}$  1.5582), butyrophenone, b. p. 115—123°/18 mm.,  $n_{\rm D}^{18}$  1.5251 (lit.,<sup>21</sup> b. p. 125—130°/21 mm.,  $n_{\rm D}^{20}$  1.524), 1-phenylbut-2-en-1-ol, b. p. 113—114°/7.5 mm. (lit.,<sup>22</sup> 121—123°/14 mm.), and 1-phenylbutan-1-ol, b. p. 90—93°/3·5 mm.,  $n_{\rm D}^{18}$  1·5139, (lit.,<sup>12</sup> b. p. 110°/15 mm.) were prepared by similar methods.

Reduction of Chalcones.-Solutions of sodium borohydride in diglyme (diethyleneglycol dimethyl ether), propan-2-ol, and pyridine were made up as before.<sup>1</sup> Solutions of sodium borohydride in methanol (0.73 g., 20 mmoles/100 ml.) and in tetrahydrofuran (0.1 g., 2.8 mmoles/100 ml.) were

<sup>14</sup> J. Klein, Tetrahedron, 1964, 20, 465.
 <sup>15</sup> F. C. Novello, M. E. Christy, and J. M. Sprague, J. Amer. Chem. Soc., 1953, 75, 1330.
 <sup>16</sup> G. F. Woods and I. W. Tucker, J. Amer. Chem. Soc., 1948,

**70**, 2174.

<sup>17</sup> G. F. Woods, N. C. Bolgiano, and D. E. Duggan, J. Amer. Chem. Soc., 1955, 77, 1800.

made up in dry solvents and used immediately. Reductions were carried out by adding a solution of the chalcone (ca. 1.5 g.) in diglyme (15 ml.), pyridine (15 ml.), propan-2-ol (50 ml.), or methanol (25 ml.) to sodium borohydride (4 mol.) dissolved in the appropriate solvent. Reductions in tetrahydrofuran were on a smaller scale: chalcone (0.25 g.) in tetrahydrofuran (25 ml.). The solutions were stirred at 20 or 70° under nitrogen. The reduction mixture in methanol was refluxed for 5 hr. The products were isolated in ether as previously described for carvenone.<sup>1</sup> The complete absence of chalcones in the products was checked by infrared analysis. The products were then dissolved in ether and oxidised with a solution of chromic acid in sulphuric acid. Small portions of the products, chalcones and dihydrochalcones, were separated with a Pye Argon Chromatograph [column (4 ft) of 6% Apiezon condensate on 100-120 mesh Celite at 225°]. The detector was calibrated with authentic mixtures. The main bulk of the product was chromatographed on Spence grade H alumina deactivated with dilute acetic acid (10%); 5% w/w of alumina). Elution with benzene-light petroleum (1:9 for dihydrochalcone; 3:7 for methoxydihydrochalcones) gave saturated ketones. Elution with benzene gave the unsaturated ketones. The results by this method agreed  $(\pm 3\%)$  with those from gas chromatography. The ketones were obtained in combined yield 78-98% (one exception), each experiment was repeated at least twice, and the ratio of saturated to unsaturated ketones was independent of vield (+3%). A mixture of dihydrochalcols and chalcols of known composition was subjected to the procedures for oxidation and analysis. The determined ratio of dihydrochalcones to chalcones was unchanged  $(\pm 3\%)$ . In some reductions in pyridine it was necessary to chromatograph the reduction product prior to oxidation, in order to remove pyridine-borine. The product from the reduction in diglyme to which triphenylphosphine had been added was isolated as described previously.<sup>1</sup> The yields and product ratios for these reactions are summarised in Table 1.

Chalcone (0.5 g.) was refluxed with a solution of sodium trimethoxyborohydride in tetrahydrofuran (60 ml.) for 2 days under nitrogen. The solution of sodium trimethoxyborohydride was prepared from the same quantities and by the same procedure as described previously.<sup>1</sup> The excess of reagent was decomposed with dilute sulphuric acid and the product isolated in ether. Oxidation gave a mixture of ketones (0.465 g., 93%) which was chromatographed on alumina (90 g.). Dihydrochalcone (0.36 g., 71%), m. p. 72°, and chalcone (0.096 g., 22%), m. p. 55°, were obtained.

Attempted Rearrangements and Reductions of 1,3-Diphenylprop-2-en-1-ol (Chalcol).--(a) Rearrangements. (i) Chalcol (1.0 g) was refluxed with a solution of potassium hydroxide (5 g.) in ethanol-water (3:2; 25 ml.) for 3 hr. Acidification with dilute hydrochloric acid and ether extraction gave dihydrochalcone (0.95 g., 95%).

(ii) A solution of chalcol (1.0 g.) in pyridine (25 ml.) was stirred under nitrogen for 3 days at 20°. Isolation and oxidation gave chalcone (0.98 g., 98%).

(b) Reduction. (i) A solution of chalcol (0.5 g., 2.4

<sup>18</sup> A. Klages, Ber., 1904, 2301.

<sup>19</sup> E. A. Bruade, E. R. H. Jones, and E. S. Stern, J. Chem. Soc., 1946, 396.

<sup>20</sup> T. M. Patrick, J. Org. Chem., 1952, 1269.

<sup>21</sup> R. L. Shriner and T. A. Turner, J. Amer. Chem. Soc., 1930, **52**, 1267.

<sup>22</sup> H. Burton, J. Chem. Soc., 1929, 455.

mmoles) in diglyme (10 ml.) was added to a solution of sodium borohydride (0.36 g., 9.4 mmoles) in diglyme (15 ml.) and the mixture was kept at 20° for 3 days. Isolation followed by oxidation gave chalcone (0.43 g., 86%).

(ii) A similar mixture was kept at  $70^{\circ}$  for 3 days. Isolation and oxidation gave dihydrochalcone (0.49 g., 98%).

(iii) Pyridine (0.85 g., 9.4 mmoles) was added to a mixture of chalcol (0.5 g., 2.4 mmoles) and sodium borohydride (0.36 g., 9.4 mmoles) in diglyme (25 ml.). The resulting solution was kept at 20° for 3 days. The usual orange colour associated with reductions in pyridine quickly developed. Isolation of the alcohols and oxidation gave dihydrochalcone (0.43 g., 86%).

(iv) A similar reaction to (iii) but to which pyridineborine (1 g., 9.4 mmoles) was added in place of pyridine gave a gummy mixture (0.48 g., 96%) of chalcone and dihydrochalcone (76: 24) (g.l.c.).

Reduction of 3-Phenvlcvclohex-2-enone.—The ketone (0.5 g.) was reduced by the general method prevously used for carvenone,<sup>1</sup> though in this case a much better separation of alcohols was achieved and the oxidation to ketones was only used to confirm that both analytical procedures gave similar results. Both alcohols and ketones were separated with a Griffin and George Gas Density Balance Chromatograph [column (4 ft.) of 6% Apiezon condensate on 100-120 mesh Celite at 175°]. Calibration of the detector with authentic samples showed a relative peak area response of unity for either the two alcohols or the two ketones. This instrument was also used to analyse the alcohols obtained by reduction of benzylideneacetone and crotonophenone (see below). In both cases authentic mixtures of saturated and unsaturated alcohols showed equal peak area response. The products from a larger scale reduction (2 g. of ketone) were separated on a column (10 ft.) of silicone oil (30%)w/w) on acid-washed 45–60 mesh Chromosorb W at  $200^{\circ}$ helium flow rate 200 ml./min. Three poorly resolved peaks were obtained. Material from the first, very broad peak was collected as a gum. It showed no hydroxylic absorption in the i.r. and its n.m.r. spectrum was that expected for an impure sample of 3-phenylcyclohexa-1,3-diene [ $\tau$  2·7 (5H, m), 3·5-4·3 (2H, m), and 7·0-8·9 (5H, m)]. Two alcohol-containing fractions were obtained ( $v_{max}$ , 3600 cm.<sup>-1</sup>) but pure samples could not be isolated.

Attempted Reduction of 3-Phenylcyclohex-2-enol.—A solution of the allylic alcohol (62.5 mg., 0.36 mmole) in diglyme (5 ml.) was added to a solution of sodium borohydride (55 mg., 1.44 mmole) in diglyme (10 ml.) and the mixture was set aside under the usual conditions. Isolation in ether gave starting material (50 mg., 80%).

Reduction of Benzylideneactone.—The ketone (0.5 g.) was reduced as described above and the alcohols were separated on a column (4 ft.) of Apiezon condensate (6% w/w) on 100—120 mesh Celite at 125°. The products from a larger scale reduction (5 g.) were separated on a column (20 ft.) of poly(diethanolamine succinate) (30% w/w) at 160°. 4-Phenylbut-3-en-2-ol, m. p. and mixed m. p. 31—33° [phenylurethane: m. p. 89—91°, mixed m. p. 90—91° (lit.,<sup>13</sup> 92—93°)], waseluted first and followed by the saturated alcohol [phenylurethane: m. p. 107—108°, mixed m. p. 109—111<sup>1</sup> (lit.,<sup>12</sup> 113°)].

Attempted Rearrangement and Reduction of 4-Phenylbut-3-en-2-ol.—(a) The alcohol (1.0 g.) was refluxed with potassium hydroxide (5 g.) in 40% aqueous ethanol (25 ml.) for 3 hr., Acidification with dilute hydrochloric acid and ether extraction gave starting material (0.92 g., 92%).

(b) A solution of the alcohol (1.0 g., 6.7 mmoles) in propan-2-ol (60 ml.) was added to a stirred solution of sodium borohydride (1.02 g., 26.8 mmoles) in propan-2-ol (400 ml.) and stirring was continued for 3 days at 20° under nitrogen. Isolation by the usual procedure gave a clear liquid (0.82 g.) which gave a single peak (starting material) on gas chromatography.

(c) A reaction with similar quantities of alcohol and sodium borohydride but with pyridine (50 ml.) as solvent also gave starting material (0.92 g., 92%).

Reduction of Crotonophenone.—The ketone (0.5 g.) was reduced as described above and the alcohols were separated on a column (4 ft.) of silicone oil condensate (10% w/w) on 100-120 mesh Celite at 90%.

Rearrangement and Reduction of 1-Phenylbut-2-en-1-ol.— (a) Rearrangement of the allylic alcohol (1.0 g.) under the previously described conditions gave butyrophenone (0.94g., 94%) [semicarbazone; m. p.  $184-185^{\circ}$  (lit.,<sup>21</sup>  $184^{\circ}$ )].

(b) A solution of the allylic alcohol (0.5 g., 3.38 mmoles) in pyridine (10 ml.) was added to a solution of sodium borohydride (0.514 g., 13.3 mmoles) in pyridine (40 ml.); the reaction was performed under the usual conditions at 20°. The product (0.46 g., 92%) was 1-phenylbutan-1-ol (gas chromatography).

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