

## Hydrogenolyses with Chloroaluminum Hydrides. I. Diphenylallyl Alcohols

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Received June 7, 1963

The hydrogenolysis of *cis*- and *trans*-2,3-diphenyl-2-propen-1-ol and also of 1,2-diphenyl-2-propen-1-ol with mixtures of aluminum chloride and lithium aluminum hydride gives in each case, *cis*- and *trans*- $\alpha$ -methylstilbene and  $\alpha$ -benzylstyrene. The relative amounts of the three olefins vary with the structure of the starting alcohol in a way that indicates that previous assignments of configurations to the olefins are correct. The results indicate that there is an appreciable, but not insurmountable, barrier to geometric interconversion of allylic carbonium ions in this system.

Mixtures of lithium aluminum hydride and aluminum chloride in ether show promise as selective reducing agents,<sup>2</sup> being less active than lithium aluminum hydride toward nitro groups,<sup>3,4</sup> simple halides,<sup>2,3</sup> and tosylates,<sup>2</sup> but more active in the hydrogenolysis<sup>5</sup> of acetals, ketals,<sup>2,15,16</sup> allylic and benzylic alcohols,<sup>6-13</sup> and ethers.<sup>14</sup> In addition, these reagents show interesting attributes in the epimerization of alcohols<sup>2</sup> and the reduction of epoxides.<sup>2</sup> It seems probable that the hydrogenolysis reactions involve the formation and reduction of carbonium ions,<sup>2</sup> the effective reagents being chloroaluminum hydrides<sup>17</sup>; the latter substances would be expected to behave both as Lewis acids and as hydride donors.

The possibility that the hydrogenolysis reactions involve the generation of carbonium ions<sup>2</sup> in the presence

of hydride donors suggested that results of synthetic, theoretical, and stereochemical interest might be obtained from a broad study of them. Taken as a whole, the data presented in this series and in the earlier papers<sup>2-16</sup> would seem to leave little room for doubt that the formation of a carbonium ion is required if any significant reaction is to occur. Thus, aliphatic alcohols react only under the most vigorous conditions, and even then *n*-hexyl alcohol can be recovered unchanged<sup>18</sup>; with secondary and tertiary saturated alcohols the formation of olefins and rearranged products is prominent.<sup>18</sup> *p*-Methoxy groups produce a strong acceleration in reductions of benzyl alcohols.<sup>19</sup> The reduction of allylic alcohols gives mixtures of products which may be relatively rich in thermodynamically less stable isomers (following); such mixtures may be of synthetic interest as potential sources of olefins otherwise difficult of access. The reduction of allylic alcohols can occur with some inversion of geometric configuration at the original double bond, but there appears to be enough of a barrier to such interconversion<sup>20</sup> to permit the use of this reaction in the correlation of geometric configurations (following).

Our first studies in this field were aimed at confirming the configurations of the  $\alpha$ -methylstilbenes<sup>21</sup> (*trans*, I; *cis*, II),<sup>22</sup> upon which rest the configurations assigned to the alcohols,<sup>21</sup> halides,<sup>23</sup> epoxides,<sup>24</sup> and diols<sup>24</sup> of the 1,2-diphenylpropane series. The configurations of the 2,3-diphenylacrylic acids (*trans*, IV; *cis*, V)<sup>22</sup> have been determined by chemical methods<sup>25</sup>; reduction of the two acids with lithium aluminum hydride gave *trans*

(1) The authors gratefully acknowledge the financial support of this research by the National Science Foundation (NSF-G 10051).

(2) For a review, see E. L. Eliel, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **22**, 129 (1961).

(3) R. F. Nystrom, *J. Am. Chem. Soc.*, **77**, 2544 (1955).

(4) See P. Newman, P. Rutkin, and K. Mislow, *ibid.*, **80**, 465 (1958), for an application of this reagent in reduction of a nitro acid.

(5) Certain aromatic carbinols undergo slow hydrogenolysis with excess lithium aluminum hydride alone at high temperatures. L. H. Conover and D. S. Tarbell, *ibid.*, **72**, 3586 (1950).

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(7) J. Broome and B. R. Brown, *Chem. Ind.* (London), 1307 (1956).

(8) A. J. Birch and M. Slaytor, *ibid.*, 1524 (1956).

(9) O. H. Wheeler and J. L. Mateos, *ibid.*, 395 (1957).

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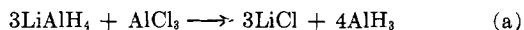
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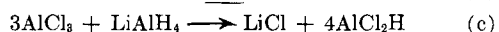
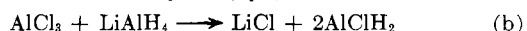
(15) H. M. Doukas and T. D. Fontaine, *J. Am. Chem. Soc.*, **75**, 5355 (1953).

(16) E. L. Eliel and M. Rerick, *J. Org. Chem.*, **23**, 1088 (1958); E. L. Eliel, V. G. Badding, and M. N. Rerick, *J. Am. Chem. Soc.*, **84**, 2371 (1962); M. N. Rerick and E. L. Eliel, *ibid.*, **84**, 2356 (1962).

(17) Lithium aluminum hydride reacts with aluminum chloride in ether to form aluminum hydride [A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *ibid.*, **69**, 1199 (1947)], presumably by way of intermediate chlorohydrides.



The latter have been formed by reaction of aluminum chloride with aluminum hydride [E. Wiberg, *Angew. Chem.*, **65**, 16 (1953); E. Wiberg, K. Mödritzer, and R. U. Lacal, *Rev. acad. cienc. exact. fis.-quim. nat. Zaragoza*, [1] **9**, 91 (1954); *Chem. Abstr.*, **52**, 3584a (1958)] and have been isolated as etherates. On this basis, the commonly used 1:1 (ratio of aluminum chloride to lithium aluminum hydride) reagent conveniently may be considered to consist essentially of monochloroaluminum hydride (eq. b), while the 3:1 reagent which we have used extensively may be considered to consist essentially of dichloroaluminum hydride (eq. c).



It is to be recognized that these are convenient oversimplifications since some mixtures are more strongly conducting than these equations would suggest they should be [G. G. Evans, J. K. Kennedy, Jr., and F. P. Del Greco, *J. Inorg. Nucl. Chem.*, **4**, 40 (1957)].

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(19) J. H. Brewster, H. O. Bayer, and S. F. Osman, *ibid.*, **29**, 110 (1964).

(20) See W. G. Young, S. H. Sharman, and S. Winstein, *J. Am. Chem. Soc.*, **82**, 1376 (1960).

(21) The higher melting isomer has been assigned the *trans*<sup>22</sup> configuration I on the ground that it is the more stable of the two [E. Ellingboe and R. C. Fuson, *ibid.*, **55**, 2964 (1933); D. J. Cram, F. D. Greene, and C. H. Depuy, *ibid.*, **78**, 790 (1956)]. The ultraviolet spectra of the two isomers are consistent with this assignment [D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5828 (1952)], since they show differences similar to those observed with *cis*- and *trans*-stilbene [G. N. Lewis, T. T. Magel, and D. Lipkin, *ibid.*, **62**, 2973 (1940)].

(22) We are concerned in this paper with geometrical configurations about stilbenoid double bonds and use the terms *cis* and *trans* throughout to indicate the geometrical relationships of phenyl groups to one another about such bonds. The nomenclature of acids IV and V is thoroughly confused in the earlier literature, the more readily available and higher melting isomer V being called " $\alpha$ -phenyl-*trans*-cinnamic acid" in some sources (*e.g.*, Beilstein, "Handbuch der Organischen Chemie," IX, p. 691) and "*cis*- $\alpha$ -phenylcinnamic acid" in others [*e.g.*, L. F. Fieser, *J. Chem. Educ.*, **31**, 291 (1954)]. We, therefore, adopt the approach of *Chemical Abstracts* and term acid V, "*cis*-2,3-diphenylacrylic acid" and the alcohol VII, "*cis*-2,3-diphenylallyl alcohol" (*Chemical Abstracts* name, *cis*-2,3-diphenyl-2-propen-1-ol).

(23) D. J. Cram and F. A. Abd Elhafez, *J. Am. Chem. Soc.*, **74**, 5851 (1952).

(24) J. H. Brewster, *ibid.*, **78**, 4061 (1956).

(25) R. Stoermer, *Ann.*, **409**, 13 (1915).

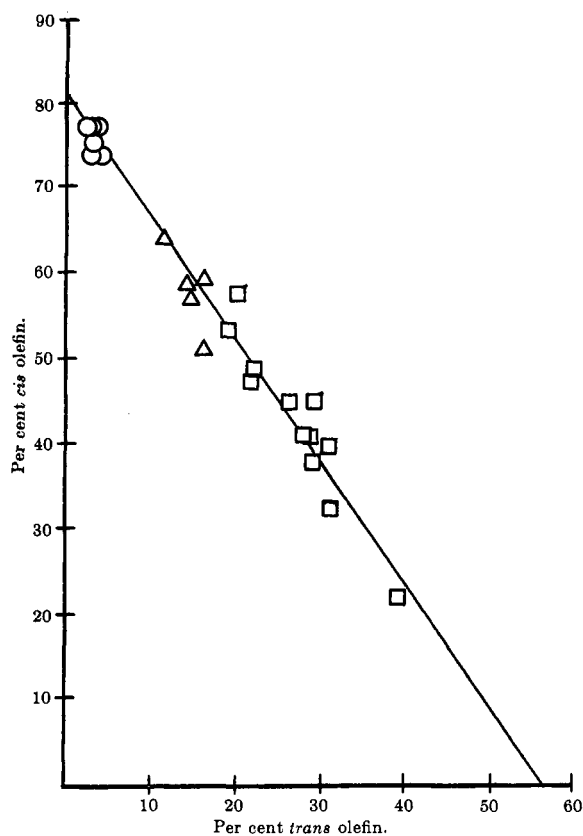
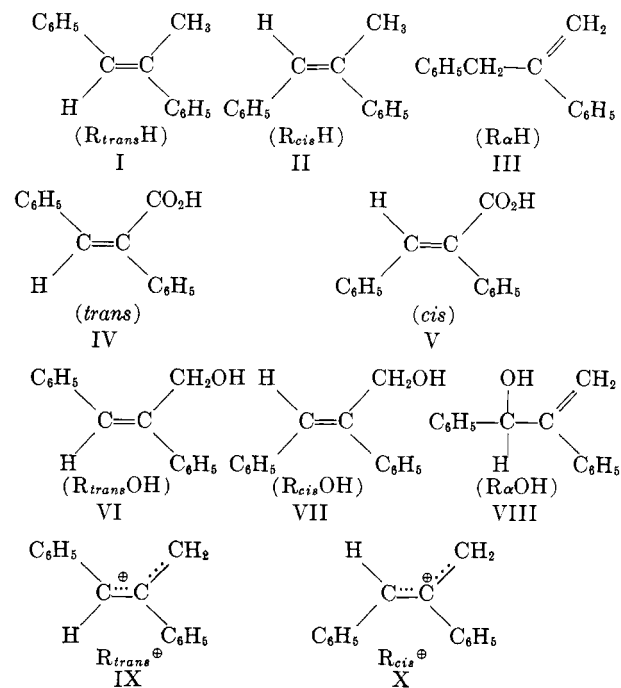


Fig. 1.—Composition of hydrocarbon mixtures from hydrogenolyses of diphenylallyl alcohols with "mixed hydride" reagents in ether. The per cent of *cis*- and *trans*- $\alpha$ -methylstilbenes in the hydrocarbon products is shown; the per cent of  $\alpha$ -benzylstyrene in each case is that required to total 100%: O, products from *cis*-2,3-diphenylallyl alcohol; □, products from *trans*-2,3-diphenylallyl alcohol;  $\Delta$ , products from  $\alpha$ -styrylphenylcarbinol.

alcohol<sup>26</sup> VI ( $\lambda_{\max}^{\text{EtOH}}$  273  $m\mu$ ,  $\epsilon$  19,800) and *cis* alcohol<sup>26</sup> VII ( $\lambda_{\max}^{\text{EtOH}}$  222  $m\mu$ ,  $\epsilon$  15,900; 257  $m\mu$ ,  $\epsilon$  12,500), the ultraviolet spectra of which are very similar to those of, respectively, the more stable and the less stable of the  $\alpha$ -methylstilbenes.<sup>21,26</sup> Although this seemed a satisfactory confirmation of the earlier assignments of configuration, we then attempted to buttress this argument by reduction of the alcohols with aluminum chloride-lithium aluminum hydride mixtures. Surprisingly, the less stable of the  $\alpha$ -methylstilbenes was the predominant product in the reduction of *both* alcohols at or near room

(26) The above-mentioned confusion in nomenclature<sup>22</sup> enters into the literature dealing with these alcohols. R. E. Lutz and E. H. Rinker, Jr., *J. Am. Chem. Soc.*, **77**, 366 (1955), reduced "*cis*- $\alpha$ -phenylcinnamic acid" (no melting point or literature cited, but indicated as having the *trans* configuration IV) to "*cis*- $\alpha$ -phenylcinnamyl alcohol," m.p. 73–74° (formula VI given) which is described as having the ultraviolet spectrum to be expected of an  $\alpha$ -substituted *cis*-stilbene ( $\lambda_{\max}$  222, 258  $m\mu$ ,  $\epsilon$  14,500). Our *cis* alcohol (VII), prepared from the more readily available *cis* acid (V, m.p. 172–173°) has properties agreeing closely with those reported for this substance (m.p. 72–73°), and there seems little reason to doubt that these alcohols are the same and that the formulas in the text of the paper of Lutz and Rinker are in error. H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *ibid.*, **81**, 108 (1959), have prepared this same alcohol from the corresponding aldehyde, the latter having been oxidized to the *cis* acid (V, m.p. 174–175°), but give m.p. 68–69° for the alcohol and regard it as different from that of Lutz and Rinker, apparently on the basis of the formulas and nomenclature of the latter workers. Zimmerman, Singer, and Thyagarajan also have prepared the *trans* alcohol (VI) from the *trans* acid (IV, m.p. 137°) and, on the basis of melting point (73–74°), conclude it is the same as the product of Lutz and Rinker. Our values for the melting point (77–78°) and the absorption spectrum (text) indicate that it is different from the product of Lutz and Rinker.

temperature. A third olefin, identified as  $\alpha$ -benzylstyrene (III) by way of an independent synthesis, was always formed in amounts ranging from 20–40% of the hydrocarbon product. As seen from the data in Fig. 1, however, the less stable  $\alpha$ -methylstilbene was formed in largest amounts (ca. 75% of the hydrocarbon product) from the *cis* alcohol (VII) while the more stable was formed in largest amounts (20–32% of the hydrocarbon product) from the *trans* alcohol (VI). Reduction in ether at 80° (sealed tube) gave a more decisive result since the *trans* alcohol (VI) gave 39% of the more stable and 22% of the less stable olefin, while the *cis*



alcohol (VII) gave 2.4 and 69%, respectively. No simple pathway for specific inversion of geometric configuration being apparent, it must be concluded that the last-mentioned reductions occur with predominating retention of geometric configuration and that the more stable  $\alpha$ -methylstilbene has, indeed, the *trans* configuration (I). It also must be concluded, however, from the results of reduction at room temperature, that a pathway for interconversion of geometrical isomers is available. This pathway cannot involve equilibration of the olefins since it favors formation of the less stable  $\alpha$ -methylstilbene and allows formation of quite large amounts of  $\alpha$ -benzylstyrene (III), which should be the least stable of the three products. A control experiment showed that the olefins were not isomerized at all under the reaction conditions. It seems most likely that this interconversion involves the formation of some derivative of  $\alpha$ -styrylphenylcarbinol (VIII). In this regard it is of interest to note that VIII is reduced more rapidly than the other two alcohols (Table I) and gives a distribution of olefins intermediate between those from VI and VII.

The olefin distribution in the product from the *trans* alcohol (VI) was found to be sensitive to the ratio of hydride to alcohol (Table II) and to the concentration of initial reactants (Table III); that from the *cis* alcohol (VII) was almost invariant. The rate of reduction increased markedly as the initial ratio of aluminum chloride to lithium aluminum hydride was increased

TABLE I  
RELATIVE REACTIVITY<sup>a</sup> OF DIPHENYLALLYL ALCOHOLS

Alcohol <sup>a</sup>	Conversion, <sup>b</sup> %	Product composition <sup>b</sup>		
		R <sub>cis</sub> H (II)	R <sub>trans</sub> H (I)	R <sub>α</sub> H (III)
R <sub>trans</sub> OH (VI)	15	40	29	31
R <sub>cis</sub> OH (VII)	27	74	4	22
R <sub>α</sub> OH (VIII)	72	51	16	33

<sup>a</sup> In diethyl ether, 4 hr. at 20°; 3:1 reagent; 0.5 mmole "AlCl<sub>3</sub>H"/ml.; 0.05 mmole ROH/ml. <sup>b</sup> Determined by v.p.c. at 220° on polyadipate with naphthalene internal standard.

TABLE II  
INFLUENCE OF REACTANT RATIO ON PRODUCT COMPOSITION  
(*trans* ALCOHOL VI)

Initial concentrations, <sup>a</sup> mmoles/ml.		Conversion, <sup>b</sup> %	Product composition <sup>b</sup>		
"AlCl <sub>3</sub> H" <sup>c</sup>	R <sub>trans</sub> OH		R <sub>cis</sub> H (II)	R <sub>trans</sub> H (I)	R <sub>α</sub> H (II)
0.4	0.2	62	71	15	14
.4	.133	85	48	22	30
.4	.10	82	45	29	26
.4	.089	75	41	29	30

<sup>a</sup> In diethyl ether; 16 hr. at 34°. <sup>b</sup> Determined by v.p.c. at 220° on polyadipate with naphthalene internal standard. <sup>c</sup> 3:1 reagent.

TABLE III  
INFLUENCE OF CONCENTRATION ON CONVERSION AND PRODUCT COMPOSITION (*trans* ALCOHOL VI)

Initial concentrations <sup>a</sup> mmole/ml.		Conversion, <sup>b</sup> %	Product composition <sup>b</sup>		
"AlCl <sub>3</sub> H" <sup>c</sup>	R <sub>trans</sub> OH		R <sub>cis</sub> H (II)	R <sub>trans</sub> H (I)	R <sub>α</sub> H (III)
0.55	0.11	24.0	32.5	31.0	36.5
.30	.06	15.3	41.0	28.0	31.0
.20	.04	11.3	44.7	25.9	29.4
.15	.03	8.9	49.0	22.4	28.7
.10	.02	8.8	53.4	19.3	27.3

<sup>a</sup> In diethyl ether; 8 hr. at 20°. <sup>b</sup> Determined by v.p.c. at 220° on polyadipate with naphthalene internal standard. <sup>c</sup> Prepared from stock solutions of 3:1 reagent, assayed by hydrogen evolution as being 0.55 *N* and 0.069 *N* in hydride.

TABLE IV  
EFFECT OF REAGENT COMPOSITION ON CONVERSION  
(*cis* ALCOHOL V)

Reagent <sup>a</sup> AlCl <sub>3</sub> -LiAlH <sub>4</sub> (molar ratio)	Concentrations, mmole/ml.		Conversion, <sup>b</sup> %
	"H"	ROH	
1:1	0.30	0.060	0.6
2:1	.24	.048	15
3:1	.20	.040	34
4:1	.17	.034	48

<sup>a</sup> In diethyl ether; 16 hr. at 20°. <sup>b</sup> Determined by v.p.c. at 220° on polyadipate with naphthalene internal standard. Product composition: 75.5 ± 1.5% R<sub>cis</sub>H; 3.0 ± 0.3% R<sub>trans</sub>H; 22 ± 1% R<sub>α</sub>H.

(Table IV). These facts are consistent with a carbonium ion mechanism (see Discussion of Results) as is the result of a control experiment indicating that, although neither the alcohol nor the olefin react appreciably with naphthalene (the analytical internal standard), there is apparently a small amount of a nondiscriminating reaction between the alcohol (or some substance derived from it) and preformed olefin to give high molecular weight products. The extent of this side reaction appears to be so small that it can be ignored in drawing qualitative conclusions from our results.

## Experimental<sup>27</sup>

*cis*- and *trans*-2,3-Diphenylacrylic Acids.—*cis*-2,3-Diphenylacrylic acid (V), m.p. 172–173°, was prepared in 51% yield by the method of Buckles, Bellis, and Coder.<sup>28</sup> The *trans* isomer (IV), m.p. 136.5–137.5°, was isolated in 1.3% yield from the crude reaction product by the procedure of Stoermer and Voht.<sup>29</sup>

*cis*-2,3-Diphenylallyl alcohol (VII) was prepared by reduction of the *cis* acid (m.p. 172–173°) with lithium aluminum hydride in ether. The product was first crystallized from methanol and water and then from petroleum ether (b.p. 60–70°) to give a 75% yield of crude product, m.p. 70–71°. The analytical sample had m.p. 72–73°, λ<sub>max</sub><sup>OH</sup> 257 (ε 12,500) and 222 mμ (15,900). This product is, thus, the same as that of Lutz and Rinker.<sup>26</sup>

Anal. Calcd. for C<sub>15</sub>H<sub>14</sub>O: C, 85.68; H, 6.71. Found: C, 86.01; H, 7.00.

*trans*-2,3-Diphenylallyl alcohol (VI) was prepared in low yield from the corresponding acid (m.p. 136.5–137.5°) by the previous method. Better yields were obtained by use of a mixture rich in aluminum hydride. Aluminum chloride (0.60 g., 4.5 mmoles) was dissolved with cooling in 40 ml. of anhydrous ether and 9.4 ml. of ether containing 9 mmoles of lithium aluminum hydride was added. Immediately a solution of 1.0 g. (4.5 mmoles) of *trans*-2,3-diphenylacrylic acid in 10 ml. of ether was added. The mixture was heated at reflux for 1 hr. (magnetic stirring) and hydrolyzed at ice temperature by dropwise addition of 20 ml. of 20% aqueous sodium potassium tartrate. The ether layer was washed with dilute base and concentrated to give a solid which was recrystallized from petroleum ether (b.p. 60–70°) to give 0.67 g. (72%) of almost pure *trans* alcohol, m.p. 76.5–77.5°. A second recrystallization gave 0.57 g., m.p. 77–78°, λ<sub>max</sub><sup>OH</sup> 273 mμ (ε 19,800).

Anal. Calcd. for C<sub>15</sub>H<sub>14</sub>O: C, 85.68; H, 6.71. Found: C, 85.75; H, 6.96.

α-Bromostyrene was prepared from styrene dibromide,<sup>30</sup> m.p. 71–73° (lit.<sup>31</sup> m.p. 72–73°), by a method essentially that of Ashworth and Burkhardt,<sup>32</sup> except that equimolar amounts of dibromide and potassium hydroxide were used. The product was obtained in 71% yield in several fractions, b.p. 76–78° (10 mm.), n<sub>D</sub><sup>20</sup> 1.5895–1.5920; lit.<sup>33</sup> b.p. 71° (7–8 mm.), n<sub>D</sub><sup>19.5</sup> 1.5881.

α-Styrylphenylcarbinol (VIII).—Lithium wire (0.50 g., 0.072 g.-atom) was cut into very small pieces and placed into 50 ml. of anhydrous ether. The mixture was cooled to –45° and maintained there during the dropwise addition of 5.0 g. (0.028 mole) of α-bromostyrene (about 1 hr.), 1 drop of methyl iodide having been added just prior to the bromide. The mixture was stirred magnetically at –45° for 2.5 hr., and then 2.9 g. (0.028 mole) of benzaldehyde was added dropwise (0.5 hr.). After an additional half hour at –45°, the mixture was allowed to warm to room temperature and was then filtered. The ether solution was extracted with water, aqueous sodium bisulfite, sodium hydroxide, and finally saturated sodium chloride, dried over sodium sulfate, and concentrated under vacuum to give 4 g. of viscous orange-yellow oil. Molecular distillation of 3.0 g. of this crude product gave 1.5 g. of viscous colorless oil in several fractions. The main fraction (1.2 g.) gave a solid, m.p. 44–49°, on seeding. α-Styrylphenylcarbinol (0.45 g.) was obtained in the form of white needles, m.p. 53–54°, after four recrystallizations from petroleum ether (b.p. 60–70°).

Anal. Calcd. for C<sub>16</sub>H<sub>14</sub>O: C, 85.68; H, 6.71. Found: C, 85.53; H, 6.75.

*cis*- and *trans*-α-Methylstilbenes.—Samples of *cis*-α-methylstilbene (m.p. 43–47°, lit.<sup>21</sup> m.p. 48°) and *trans*-α-methylstilbene (m.p. 79–81°, lit.<sup>21</sup> m.p. 81–82°), prepared earlier by Rudesill,<sup>34</sup> had deteriorated slightly on standing but could be purified by gas chromatography; after such purification their melting points agreed with those in the literature. Additional amounts were accumulated by isolation from gas chromatographic analyses.

(27) All melting points are uncorrected. Microanalyses were by Dr. C. S. Yeh, Mrs. I. Groten, and Mrs. V. Kebly; infrared spectra by Mrs. M. Dilling and author H. O. B.

(28) R. E. Buckles, M. P. Bellis, and W. D. Coder, *J. Am. Chem. Soc.*, **73**, 4972 (1951).

(29) R. Stoermer and G. Voht, *Ann.*, **409**, 36 (1915). Our attention has since been called to the improved method by Fieser.<sup>27</sup>

(30) C. Glaser, *ibid.*, **154**, 154 (1870).

(31) R. Fittig and E. Erdmann, *ibid.*, **216**, 194 (1882).

(32) F. Ashworth and G. N. Burkhardt, *J. Chem. Soc.*, 1801 (1928).

(33) C. Dufraisse, *Ann. chim. (Paris)*, [9] **17**, 171 (1922).

(34) J. T. Rudesill, Ph.D. thesis, Purdue University, 1957.

**$\alpha$ -Benzylstyrene. 2,3-Diphenylpropanoic Acid.**—A solution of 22.4 g. (0.10 mole) of *cis*-2,3-diphenylacrylic acid in 150 ml. of ethanol was hydrogenated in a Paar apparatus over 2.5 g. of palladium on charcoal. The catalyst was removed by filtration, the filtrate was concentrated on a steam bath, and water was added. The precipitate was thrice recrystallized from petroleum ether (b.p. 60–70°) to give 15.6 g. (70%) of 2,3-diphenylpropanoic acid, m.p. 87–89° (crystal modifications with m.p. 82°, 88–89°, and 95–96° are reported<sup>35</sup>).

**2,3-Diphenylpropyl Acetate.**—A solution of aluminum hydride was prepared by adding 3.8 g. (0.10 mole) of lithium aluminum hydride to a solution of 4.4 g. (0.033 mole) of aluminum chloride in 50 ml. of anhydrous ether, using magnetic stirring. Immediately thereafter a solution of 15.6 g. of 2,3-diphenylpropanoic acid in 60 ml. of anhydrous ether was added slowly, the mixture being stirred and maintained at reflux by gentle heating. After 1.5 hr. at reflux the solution was cooled with ice. Excess hydride was destroyed by dropwise addition of 5 ml. of ethyl acetate. Hydrolysis was completed by addition of 100 ml. of a 20% solution of sodium potassium tartrate. The layers were separated, and the aqueous layer was extracted with ether. The ether extract was extracted with base, dried over sodium sulfate, and concentrated under reduced pressure. The crude alcohol was heated to reflux directly with 25 ml. of acetic anhydride. After 12 hr. of reflux, acetic acid and anhydride were removed by distillation, and the residue was distilled through a short Vigreux column to give 15.3 g. (87%) of 2,3-diphenylpropyl acetate, b.p. 123–125° (1 mm.), m.p. 46.2–47.8°,  $n_D^{20}$  1.5478.

*Anal.* Calcd. for  $C_{17}H_{18}O_2$ : C, 80.28; H, 7.13. Found: C, 80.41; H, 7.19.

**$\alpha$ -Benzylstyrene.**—The ester was pyrolyzed by a method similar to that of Bailey and King,<sup>36</sup> 4.7 g. being passed dropwise through a column packed with glass beads which was maintained at 480–485°. There was obtained, after vacuum distillation of the effluent, 2.1 g. of olefin, collected in several fractions,  $n_D^{20}$  1.5887–1.5940. Analysis by v.p.c. indicated the presence of small amounts of *cis*- and *trans*- $\alpha$ -methylstilbenes. A small sample, purified by v.p.c. fractionation, had  $n_D^{20}$  1.5917 (lit.<sup>37</sup>  $n_D^{20}$  1.5903). The infrared spectrum showed no significant bands in the regions 3200–3500 (hydroxy), 1700–1800, 1200–1300 (acetate), 1300–1400  $cm^{-1}$  (methyl). A strong band at 896  $cm^{-1}$ , with a weak band at 1790  $cm^{-1}$  (possible overtone) indicates the presence of a disubstituted vinyl group ( $R_2C=CH_2$ ). Other bands at 695, 725, 781, 1560, 1590, 1615, 2850, and 3000  $cm^{-1}$  are consistent with the assigned structure.

**Reagent solutions** were prepared by dissolving powdered lithium aluminum hydride (Metal Hydrides) in anhydrous ether (Mallinckrodt, dried over sodium hydride) and decanting the solution through glass wool into a previously cooled (0°) solution of granular aluminum chloride (Baker) in anhydrous diethyl ether. The mixture was allowed to stand at 0° for 4 hr., at which time the formation of sediment appeared to be complete, and carefully decanted through a small amount of glass wool into a flask for storage. The solution was assayed for hydride by measurement of the hydrogen evolved when methanol was added to an aliquot. Reagent solutions prepared in liter amounts in this way (usually ca. 1 M in hydride) were clear and could be stored at –4° for several months without forming further sediment or changing in hydride content. If, however, the solutions were left in contact with the sediment (which possesses some hydride activity), they decomposed slowly with the evolution of hydrogen.

**Reductions** were carried out in screw-cap vials held in a constant temperature bath for a specified amount of time. In the reactions reported here 10–200-mg. samples of the alcohols were placed in the vials with 3–30-mg. amounts of naphthalene as internal standard (all weighed out on an analytical balance). The required ether solutions of stock reagent (and in some cases, of aluminum chloride) were introduced by means of a calibrated syringe. A little hydrogen was evolved rapidly, from reaction of the alcohol with the reagent, but this reaction was usually complete by the time the screw cap had been tightened. After the desired reaction time a little water was added to decompose unchanged hydride, and the ether solutions were dried over Drierite and analyzed by gas chromatography (following). The

reaction conditions used in particular studies are indicated in the footnotes in the tables of results presented in the text.

**Analysis by Vapor Phase Chromatography.**—All analyses were carried out with an Aerograph Model A-90-C equipped with a manual preheater control. Sharp symmetrical peaks were obtained with a 5-ft. Craig polyadipate column and flow rates of 20–40 ml. of helium per minute. A typical analysis at oven temperature of 220–240° and preheater temperature of 220° required about 15 min. The *cis*- and *trans*-2,3-diphenylallyl alcohols could not be separated under these conditions but gave a single peak. Naphthalene was used as an internal standard and, prior to each sequence of analyses, a determination of the area to weight ratios of the internal standard and each of the olefins was made using standard mixtures, areas being computed by the triangle method (height  $\times$  base width/2). Thus, in a typical analysis, it was first determined that, for *cis*- $\alpha$ -methylstilbene, the area to weight ratio was

$$R = \frac{\text{area (olefin)}}{\text{g. (olefin)}} \times \frac{\text{g. (standard)}}{\text{area (standard)}} = 0.855$$

In a particular reduction, using 182.6 mg. of the *trans* alcohol and 31.4 mg. of naphthalene, analysis of the product gave areas of 6.72  $cm^2$  for naphthalene and 1.1  $cm^2$  for *cis*- $\alpha$ -methylstilbene. The product thus contained

$$\frac{1.10 \text{ cm.}^2}{6.72 \text{ cm.}^2} \times \frac{31.4 \text{ mg.}}{0.855} = 6.03 \text{ mg. } \textit{cis } \alpha\text{-methylstilbene}$$

**Control Experiments. Stability of Internal Standard.**—Equal amounts (31.2 mg., 0.15 mmole) of  $\alpha$ -styrylphenylcarbinol were placed in two screw-cap vials. In the first was placed 2.0 mg. (0.0156 mmole) of naphthalene, while in the second was placed 19.3 mg. (0.15 mmole). Then 1.5 ml. (0.75 mmole) of standard ethereal dichloroaluminum hydride solution (3:1 reagent) was added with a syringe. The vials were closed and held at 20° for 2 hr. and then worked up and analyzed in the usual way. In the first run the analysis indicated the formation of 66% of the theoretical amount of olefin: 14% I, 57% II, and 29% III; in the second run, the analysis indicated the formation of 70% of the theoretical amount of olefin: 14% I, 58% II, 28% III. We assume that any reaction of olefin or alcohol with naphthalene would occur on a mole-for-mole basis (*e.g.*, alkylation); if so, such reaction would not affect the analysis in the second run, but as little as 1% of such reaction in the first run would consume 10% of the standard and give an apparent yield of 77%. The reproducibility of yield and composition, thus, indicate that the internal standard does not interfere appreciably with the reaction.

**Stability of Olefins.**—A synthetic mixture containing 39.6 mg. (0.204 mmole, 51.3%) of *trans*- $\alpha$ -methylstilbene, 19.0 mg. (0.098 mmole, 24.6%) of *cis*- $\alpha$ -methylstilbene, and 18.6 mg. (0.096 mmole, 24.1%) of  $\alpha$ -benzylstyrene was dissolved in 4 ml. of 0.4 N ethereal dichloroaluminum hydride together with 11.2 mg. (0.0875 mmole) of naphthalene. The solution was kept at 34° for 16 hr. and then worked up and analyzed in the usual way; this analysis showed the recovered olefin mixture to contain 51.3% of *trans*- $\alpha$ -methylstilbene, 24.4% of *cis*- $\alpha$ -methylstilbene, and 24.2% of  $\alpha$ -benzylstyrene. The recovery of olefin was 100.5%, this meaning simply that there was virtually no change in relative amounts of olefin and naphthalene. Since the solution originally contained a total of 0.396 mmole of olefin and 0.0875 mmole of naphthalene any mole-for-mole reaction of olefin with naphthalene would raise the apparent recovery above 100%. The value obtained corresponds to no more than 1.3% of such reaction. The olefins are not isomerized under these conditions.

**Reaction of Olefin Precursors with Olefins.**—A solution of 52.5 mg. (0.25 mmole) of *trans*-2,3-diphenylallyl alcohol and 11.1 mg. (0.087 mmole) of naphthalene in 10 ml. of an ether solution of 3:1 reagent containing 1.24 mmoles of active hydride was kept at 20° for 24 hr. and then worked up and analyzed as before. The analysis indicated formation of 0.0608 mmole of *cis*- $\alpha$ -methylstilbene, 0.0268 mmole of *trans*- $\alpha$ -methylstilbene, and 0.0318 mmole of  $\alpha$ -benzylstyrene (0.1194 mmole of olefin in all, or 47.8%). An otherwise identical solution, containing in addition 0.0572 mmole of *cis*- $\alpha$ -methylstilbene, 0.1405 mmole of *trans*- $\alpha$ -methylstilbene, and 0.0603 mmole of  $\alpha$ -benzylstyrene (0.2580 mmole in all) was simultaneously subjected to the same conditions. Analysis of the product from the second reaction showed the presence of 0.108 mmole of *cis*- $\alpha$ -methylstilbene, 0.152 mmole of *trans*- $\alpha$ -methylstilbene, and 0.0845 mmole of

(35) W. v. Miller and G. Rohde, *Ber.*, **25**, 2017 (1892).

(36) W. J. Bailey and C. King, *J. Am. Chem. Soc.*, **77**, 75 (1955).

(37) J. v. Braun, J. Seemann, and A. Schultheiss, *Ber.*, **55**, 3814 (1922).

$\alpha$ -benzylstyrene (0.3445 mmole in all). The amount of mixed olefin obtained in the second run was thus, 0.033 mmole less than that expected from the results of the first run and the amount of preformed olefin used. We assume that this loss arises from diversion of 0.0165 mmole of preformed olefin (6.4%) and 0.0165 mmole (13.8%) of alcohol into a 1:1 reaction of carbonium ion with olefin, and that this reaction is not discriminating among olefins or possible carbonium ions. On this basis the amount of each olefin to be expected in the second run becomes 0.1059 mmole of *cis*- $\alpha$ -methylstilbene, 0.1547 mmole of *trans*- $\alpha$ -methylstilbene, and 0.0838 mmole of  $\alpha$ -benzylstyrene. These values are within 2% of those observed. These results indicate that a side reaction of this nature will occur in all reactions, being presumably most important when about 50% conversion of alcohol to olefin has occurred. Since this side reaction appears not to be discriminating, it should have little effect on ratios of olefins obtained.

**Hydrogenolyses at 80°.**—*trans*-2,3-Diphenylallyl alcohol (VI) (0.017 g., 0.080 mmole) and 2 mg. of naphthalene were placed in a 10-mm. i.d. glass tube which was then cooled in a Dry Ice-acetone bath. While a slow stream of dry nitrogen was passed into the tube, 1 ml. of 3:1 reagent (0.4 mmole/ml. in hydride) was added. The tube was quickly sealed and placed in an oil bath set at 80°. The solution turned cloudy and then a clear second liquid layer separated. After a reaction time of 0.5 hr., the tube was cooled and opened. The solution was hydrolyzed and analyzed in the usual way by v.p.c. The hydrocarbon fraction (*ca.* 100% conversion) consisted of 22% *cis*- $\alpha$ -methylstilbene, 39% *trans*- $\alpha$ -methylstilbene, and 39%  $\alpha$ -benzylstyrene. In a parallel experiment the *cis* alcohol gave *ca.* 93% of olefin containing 69% *cis*- $\alpha$ -methylstilbene, 2.4% *trans*- $\alpha$ -methylstilbene, and 29%  $\alpha$ -benzylstyrene.

### Discussion of Results

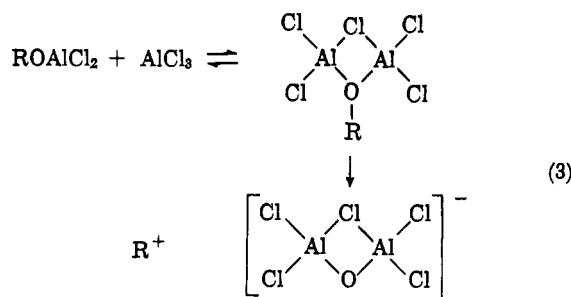
The reaction of an alcohol with an aluminum chloride-lithium aluminum hydride mixture occurs in several distinct steps, the first of which is very rapid, giving one mole of hydrogen per mole of alcohol in a few minutes, presumably according to eq. 1 (following).



An aldehyde or ketone also would react rapidly with one mole of a chloroaluminum hydride to give the same alkoxy compound, without releasing hydrogen (eq. 2).

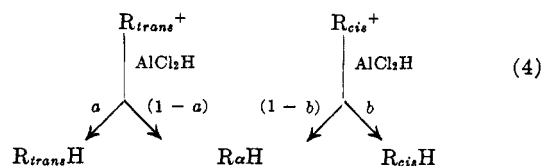


Provided that these steps are much faster than the following ones, the hydrogenolysis reactions of alcohols and of carbonyl compounds should be indistinguishable as to rate and product<sup>38</sup>; it is our experience that this is the case. The rate of conversion to hydrocarbons decreases with dilution (Table III) indicating that the slow step in hydrogenolysis is not simple ionization of the chloroaluminum alkoxide but involves additional chloroaluminum hydride. The relative reactivity of variously substituted benzylic alcohols<sup>6-13</sup> (see also part II<sup>19</sup>) and of saturated alcohols (part IV<sup>18</sup>), together with the distribution of products observed in the present work, suggest strongly that the slow step involves the formation of a carbonium ion. Accordingly, we suggest that ionization is preceded by coordination of the oxygen atom with a second molecule of Lewis acid, for example, as in eq. 3.<sup>39</sup> On this basis, the Lewis acidity of the initial reagent (considered either in terms of the amount of aluminum chloride present as such in a re-



distribution equilibrium or in terms of the Lewis acidity of the individual chloroaluminum hydrides) would be of great importance, as, in fact, it seems to be (Table IV). These results are reminiscent of those of Conover and Tarbell<sup>5</sup> who found that in hydrogenolyses with lithium aluminum hydride alone an excess of the hydride accelerated the reaction.

The distribution of olefins in the products of reduction of the three diphenylallyl alcohols near room temperature falls into a pattern (Fig. 1) which is that to be expected from reactions leading to varying amounts of the two allylic carbonium ions ( $\text{R}_{\text{trans}}^+$ , IX;  $\text{R}_{\text{cis}}^+$ , X) each of which is reduced in characteristic proportions to two olefins. (See eq. 4 following).



In such a case the amounts of *cis* ( $\text{R}_{\text{cis}}\text{H}$ , II) and *trans* ( $\text{R}_{\text{trans}}\text{H}$ , I) olefin will be related to the total amount of olefin formed (RH) as follows. (See eq. 5 and 6).

$$\text{R}_{\text{cis}}\text{H}/b + \text{R}_{\text{trans}}\text{H}/a = \text{RH} \quad (5)$$

whence

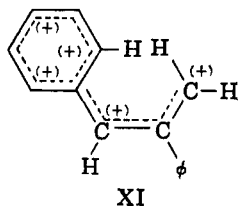
$$a(\text{R}_{\text{cis}}\text{H}/\text{RH}) + b(\text{R}_{\text{trans}}\text{H}/\text{RH}) = ab \quad (6)$$

From the data used in preparing Fig. 1, we obtain the values  $a = 0.55$  and  $b = 0.82$ , indicating that, while the *trans* carbonium ion is reduced almost statistically at either end, the *cis* carbonium ion is reduced chiefly to *cis*- $\alpha$ -methylstilbene. The data of Tables I-III indicate that the *trans* carbonium ion (IX) has a strong tendency to isomerize to the *cis* (X); this might most simply occur by reversal of the ionization shown in eq. 3 to form the  $\alpha$ -styrylphenylcarbanyl derivative. Any such process, it would appear, is interrupted by reductive attack of a hydride donor before equilibration can occur. It is expected from this analysis that an increase in the concentration of hydride donor (*at this stage of the reaction*) would produce a decrease in the fraction of *cis* olefin (II) in the product of reduction of the *trans* alcohol (VI). This is observed (Tables II and III).

These conclusions indicate that there is an appreciable, but not unsurmountable, barrier to interconversion of geometrically isomeric allylic carbonium ions. It would appear that *in the present system* the *cis* carbonium ion (X) is the more stable and retains its geometric configuration to the extent of about 90%. The *trans* carbonium ion (IX) is less stable, perhaps because of coulombic repulsions or perhaps because of steric hindrance to coplanarity (XI), and so, depending on the

(38) Certain results of Nystrom and Berger<sup>12</sup> which seem to be inconsistent with this conclusion are considered in the following paper.<sup>19</sup>

(39) The structures shown for the complex and the anion are speculative, of course, but are in reasonable analogy to the bridged structures possessed by many aluminum compounds. Analogous structures with hydrogen in place of chlorine can be imagined for cases where the reagent is richer in hydride.



rate at which it is consumed by reduction, is converted in part to the *cis* ion (40–70% conversion in reductions at room temperature). We may, in general, then, ex-

pect that one geometrical isomer of an allylic alcohol will be reduced with a high degree of retention of geometric configuration, but that the other isomer will give sizeable amounts of the same products, the nature of these products being determined, first, by the relative stability of the two allylic carbonium ions (*not* to stability of the olefins) and, second, by the extent to which reduction occurs at either end of the allylic systems. The use of this reaction in the assignment of configuration is, thus, not without hazard, and some care should be exercised in its use for this purpose.

## Hydrogenolyses with Chloroaluminum Hydrides. II. Benzylic Alcohols

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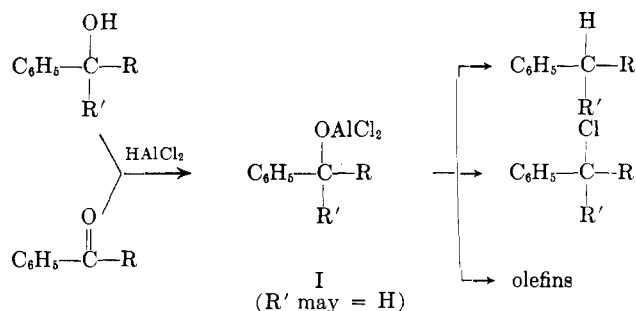
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*Received June 7, 1963*

Benzylic alcohols are reduced to hydrocarbons by mixtures of aluminum chloride and lithium aluminum hydride. The ease of reduction is sensitive to the structure of the alcohol and the Lewis acidity of the reagent, the influence of these factors suggesting that the slow step involves formation of a benzylic carbonium ion. Chlorides, which may be formed in a side reaction, appear to be reduced more slowly than alcohols by "dichloroaluminum hydride." Olefins are prominent by-products in the reduction of tertiary benzylic alcohols; in at least one case the elimination reaction follows the Hofmann rule.

Since allylic alcohols undergo hydrogenolysis with mixtures of aluminum chloride and lithium aluminum hydride,<sup>2</sup> it seemed likely that benzylic alcohols would also undergo this reaction. Hydrogenolysis of activated aromatic carbinols has been observed to occur with excess lithium aluminum hydride alone at temperatures of 60–90°.<sup>3</sup> Reductions in which such hydrogenolysis might reasonably be considered to be the final step have been reported to occur when aromatic acids, aldehydes, and ketones are treated with "mixed hydride" reagents.<sup>4,5</sup> The latter papers, however, give the impression that carbinols are not always intermediates and may well be reduced less easily than carbonyl compounds. Thus Nystrom and Berger<sup>5</sup> report that methylphenylcarbinol is not reduced when treated with a large amount of a reagent that reduces acetophenone to ethylbenzene; they also report that benzyl alcohol is not reduced although triphenylcarbinol and benzhydrol are reduced with ease. Brown and White<sup>4</sup> suggest that reduction to the carbinol stage may be a deleterious side reaction leading to the formation of chlorides and olefins. We have, therefore, investigated this matter in more detail and have found that benzylic alcohols in general can be reduced by "mixed hydrides" (Table I). This indicates that the alcohols or, more probably, alkoxyaluminum compounds derived from them (as I) are at least sufficient as intermediates in the reduction of the more highly oxidized compounds. In several cases it was observed that alcohols and ketones are essentially equivalent as starting materials in preparative applications of this reaction.

In accord with an earlier report<sup>5</sup>, we found that benzyl alcohol was not detectably reduced by 3:1 reagent<sup>6</sup>



after three days in refluxing diethyl ether; it was reduced (in part) to toluene at 70–80°. Under these conditions a higher-boiling product, apparently identical with that formed on benzylation of toluene, also was obtained. In contrast, *p*-methoxybenzyl alcohol was cleanly reduced to *p*-methoxytoluene in half an hour at room temperature, confirming the strong activating effect of methoxy groups observed by Conover and Tarbell<sup>3</sup> and by Brown and White.<sup>4</sup> Methylphenylcarbinol also was more easily reduced than benzyl alcohol. With excess 3:1 reagent the alcohol was almost completely consumed in two hours at room temperature, but virtually no reduction occurred when the ratio of chloride to hydride was low (Table II). We have calculated the chloride-to-hydride ratios obtaining in the reaction mixtures used by Nystrom and Berger<sup>5</sup>, assuming rapid formation of I, and find (Table III) that their experimental results are consistent with ours. When the chloride-to-hydride ratio was higher than 2, acetophenone was reduced to ethylbenzene; when it was lower, the ketone was reduced only to the alcohol in the short reaction time allowed. Their failure to obtain hydrogenolysis with the alcohol is now seen to have resulted from the use of *too much* of their 1:1

(1) The authors gratefully acknowledge the financial support of this research by the National Science Foundation (Grant NSF-G 10051).

(2) J. H. Brewster and H. O. Bayer, *J. Org. Chem.*, **29**, 116 (1964). References to earlier examples of this reaction are cited in this paper.

(3) L. H. Conover and D. S. Tarbell, *J. Am. Chem. Soc.*, **72**, 3586 (1950).

(4) B. R. Brown and A. M. S. White, *J. Chem. Soc.*, 3755 (1957).

(5) R. F. Nystrom and C. R. A. Berger, *J. Am. Chem. Soc.*, **80**, 2896 (1958).

(6) This is the molar ratio of aluminum chloride to lithium aluminum hydride used in preparing stock solutions<sup>2</sup> of "mixed hydride" reagents. The 3:1 reagent has the composition of  $\text{AlCl}_2\text{H}$  and also will be referred to as "dichloroaluminum hydride." In most of this work we have used amounts of this reagent corresponding to 4 moles of this species per mole of alcohol.