approaching the tertiary hydrogen atoms of this hydrocarbon. Taft has shown that these hydrogen atoms should be more hindered than the tertiary hydrogens of 2,3-dimethylpentane.[9] The high experimental value for *p*-xylene may be a result of the small steric hindrance in *p*-xylene combined with the resonance stabilization of the *p*-xylyl radical.

Acknowledgment.—The authors wish to thank Mr. John G. Ehlers and Mr. Frank P. Hochgesang of these Laboratories for the infrared analyses. Thanks are also due to Dr. Charles C. Price of the University of Pennsylvania for his helpful advice.

PAULSBORO, NEW JERSEY

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[9] Robert W. Taft, Jr. (Pennsylvania State University); presented at a seminar, University of Pennsylvania, February, 1955.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Mechanism of Halide Reductions with Lithium Aluminum Hydride. III. Reduction of α-Chloro Acids and Esters[1,2]

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RECEIVED JUNE 24, 1955

A series of chloroacids, RR'CClCOOH (where R and/or R' = hydrogen, alkyl or phenyl) and their esters were reduced with lithium aluminum hydride in excess. The products were chlorohydrins, $RR'CClCH_2OH$, alcohols, $RR'CHCH_2OH$, aldehydes, RR'CHCHO and glycols, $RR'COHCH_2OH$ with the glycols being formed in substantial amounts only if at least one of the R-groups is phenyl. Preliminary evidence was obtained that the chlorohydrins are intermediate in the reduction of chloroacids to alcohols. The ease of reduction of the chlorine (as measured by the ratio: yield of alcohol/yield of chlorohydrin) is greater in either primary or tertiary chloroacids than in secondary, suggesting that two different mechanisms account for the removal of the halogen. Aldehydes are formed when R is phenyl and R' is phenyl or methyl; their origin was traced to the primary formation of an enolate salt. Chlorohydrins can be obtained from a number of chloroesters RR'CClCOOR" in good yield by the inverse addition of one-half mole of lithium aluminum hydride to one mole of ester.

The reduction of simple primary alkyl chlorides with lithium aluminum hydride in ether solution is usually ineffective, although the reduction can be performed quite readily in boiling tetrahydrofuran.[4] Thus *n*-butyl chloride is reported[5] not to be reduced in ether solution at 25° and in the present work it was found that the phenyl- and phenoxy-substituted halides shown in Table I were reduced only to the extent of 17% or less.

TABLE I

REDUCTION OF ALKYL CHLORIDES WITH LITHIUM ALUMINUM HYDRIDE IN BOILING ETHER[6]

Chloride	Reduction, %	Recovery, %
$PhCH_2CH_2Cl$	4	79
$PhCH_2CH_2CH_2Cl$	8	75
$PhOCH_2CH_2Cl$	2	89
$PhOCH_2CH_2CH_2Cl$	17	77
n-C_4H_9Cl	No redn. at 25°[5]	

Secondary and tertiary halides are reduced even more sluggishly,[4,7,8] as would be expected in view of the fact that the lithium aluminum hydride reduction of alkyl halides is a bimolecular nucleophilic displacement reaction.[7,9] In contrast, we have observed[1] that the tertiary chloride 2-phenyl-2-chloropropionic acid, $CH_3CCl(Ph)COOH$ (I) is reduced readily, the principal reduction product of I or its methyl ester being the chlorine-free alcohol 2-phenylpropanol, $CH_3CH(Ph)CH_2OH$. Fragmentary results of other investigators suggest that reduction of chlorine in reactions where chloroalcohols are the expected products is fairly general. Thus poor yields were reported in the reduction of chloroacetic acid and its ethyl ester to ethylene chlorohydrin (13 and 37%, respectively)[10] and of chloroacetone[11a] and bromoacetone[11b] to the corresponding 1-halo-2-propanols (44 and 48%, respectively). Low boiling fractions (probably having the chloride function reduced) were reported in the reduction of 4-chloro-2-butanone[12] and of ethyl (1-hydroxy-2-methyl)-cyclohexylchloroacetate.[13] Moreover, the reduction of epichlorohydrin gives the chlorine-free product propanol-2 in 88% yield.[7] In all these instances the "direct addition" technique was employed, yet chloroacid chlorides can be reduced to chlorohydrins in good yields even by the ordinary technique of adding the halide to a slight excess of ethereal lithium aluminum hydride. Thus chloroacetyl chloride is reduced to ethylene chlorohydrin in 62% yield[10] and the corresponding reduction of 2-chloropropionyl chloride gives the chloro-

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[1] Previous paper in this series: E. L. Eliel and J. P. Freeman, THIS JOURNAL, **74**, 923 (1952).

[2] Presented in part before the Organic Division of the American Chemical Society at Atlantic City, N. J., on September 17, 1952.

[3] This paper is taken in part from the Ph.D. dissertation of Sr. M. Carolyn, R.S.M.

[4] J. E. Johnson, R. H. Blizzard and H. W. Carhart, THIS JOURNAL, **70**, 3664 (1948).

[5] R. F. Nystrom and W. G. Brown, *ibid.*, **70**, 3738 (1948).

[6] The chlorides in this table as well as ethylene chlorohydrin are of about the same reactivity as *n*-butyl chloride in typical S_N2 reactions, such as the reaction with iodide ion in acetone: J. B. Conant and W. R. Kirner, *ibid.*, **46**, 232 (1924); W. R. Kirner, *ibid.*, **48**, 2745 (1926).

[7] L. W. Trevoy and W. G. Brown, *ibid.*, **71**, 1675 (1949).

[8] See also W. G. Brown in R. Adams, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. VI, p. 469 (1951).

[9] Exceptions are some highly fluorinated and phenylated halides: J. C. Tatlow and R. E. Worthington, *J. Chem. Soc.*, 1251 (1952); J. Roylance, J. C. Tatlow and R. E. Worthington, *ibid.*, 4426 (1954), and ref. 8, p. 481.

[10] C. E. Sroog, C. M. Chih, F. A. Short and H. M. Woodburn, THIS JOURNAL, **71**, 1710 (1949).

[11] (a) C. A. Stewart and C. A. VanderWerf, *ibid.*, **76**, 1259 (1954); (b) K. Kakemi, F. Kusuda and R. Morii, *J. Pharm. Soc. Japan*, **75**, 110 (1955).

[12] F. Sondheimer and R. B. Woodward, THIS JOURNAL, **75**, 5438 (1953).

[13] J. D. Billimoria, *J. Chem. Soc.*, 2626 (1953).

TABLE II

PRODUCTS OF THE REDUCTION OF CHLORO-ACIDS RR'CClCOOH AND THEIR ESTERS WITH LITHIUM ALUMINUM HYDRIDE

R	R'	Compound reduced	Method	Mole[e] ratio	Decomp.	Products, %			
						RR'CH-CH$_2$OH	RR'CCl-CH$_2$OH	RR'COH-CH$_2$OH	RR'-CHCHO
H	H	Chloroacetic acid	Direct	1.25s	Acid	16–38	<5	....	......
CH$_3$	H	α-Chloropropionic acid	Direct	1.45s	Acid	44	46	....	......
		Methyl α-chloropropionate	Inverse	0.52	Acid	Trace?	78	....	......
C$_2$H$_5$	H	α-Chloro-*n*-butyric acid	Direct	1.5s	Acid	52	38	....	......
		Methyl α-chloro-*n*-butyrate	Inverse	0.55	Acid	?	89	....	......
CH$_3$	CH$_3$	α-Chloroisobutyric acid	Direct	1.5(s)	Acid	70	?	Trace?	......
		Ethyl α-chloroisobutyrate	Inverse	0.52	Acid	?	74	....	[a]
		Methyl α-chloroisobutyrate	Inverse	1.1	Acid	82	Present	....	......
C$_6$H$_5$	H	Phenylchloroacetic acid	Direct	1.5s	Acid	83	..	Trace[b]	......
		Ethyl phenylchloroacetate	Inverse	0.5	Tartrate[c]	..	*ca.* 68	....	......
		Ethyl phenylchloroacetate	Inverse	0.5	Base[d]	...	..	....	......
		Ethyl phenylchloroacetate	Inverse or direct	1.1	Base	70–82	?	....	......
C$_6$H$_5$	CH$_3$	2-Chloro-2-phenylpropionic acid	Direct	2.1s	Base	50–60	..	<10	10–20
C$_6$H$_5$	C$_6$H$_5$	Diphenylchloroacetic acid	Direct	1.5(s)	Acid or base	*ca.* 55(?)	..	20	*ca.* 25(?)
		Ethyl diphenylchloroacetate	Direct	0.85 or 1.2	Acid	*ca.* 45	..	....	*ca.* 55

[a] Isobutyraldehyde was isolated when alkali carbonate was not added during the distillation of the chlorohydrin. [b] 8% in THF. [c] Also gave 6% of what seemed to be styrene oxide. [d] Product was styrene oxide (80%). [e] Moles LiAlH$_4$/mole halide. s means that the hydride was employed as a slurry; where no notation appears, a clear standardized solution of the hydride was used. (s) indicates that both procedures were studied with essentially identical results.

hydrin in 72–82% yield.[11,14] The same is not necessarily true of bromoacid chlorides: β-bromopropionyl chloride is reduced to the corresponding bromohydrin in a yield of only 46%.[15] In this reduction, a large excess of lithium aluminum hydride was employed, however. Even so, the bromohydrin can be obtained in 77% yield, provided aluminum chloride is added to the lithium aluminum hydride solution prior to reduction.[15]

In order to gain a better understanding of these reactions, we undertook a systematic study of the reduction of a number of α-chloroacids of the general formula RR'CClCOOH and their esters, using all possible combinations with R and/or R' being hydrogen, alkyl (methyl in all cases but one) and phenyl. The results are summarized in Table II. Both "direct reductions" (by addition of the halogen compound to an excess of ethereal lithium aluminum hydride) and "inverse reductions" (by addition of a limited amount, or, in a few instances, an excess of ethereal lithium aluminum hydride to the compound) are included in the table, and the method of decomposition of the lithium aluminum complexes is also indicated. (In some instances, several decomposition methods—with acid, with base and with tartrate—were studied so as to minimize the possibility that the products isolated resulted from secondary transformations during the decomposition of the complexes). The products of reduction of the acids RR'CClCOOH or their esters are listed under four headings: alcohols, RR'CHCH$_2$OH, chlorohydrins, RR'CClCH$_2$OH, glycols, RR'COHCH$_2$OH and aldehydes RR'CHCHO, since our previous investigation[1] had indicated that all these could be formed in major amounts.

Several facts are apparent from Table II. First of all, the halogen in a variety of α-chloroacids unlike that in simple alkyl chlorides (Table I) is substantially, if not completely, removed by an excess of lithium aluminum hydride. Where chlorohydrins are the desired products, reduction of esters of chloroacids with the theoretical amount of lithium aluminum hydride (standardized solution) by the "inverse addition" technique is to be recommended.[16]

Secondly, it appears that the ease of reduction of primary, secondary and tertiary chloroacids is in the order primary > secondary < tertiary. This suggests strongly that reduction of the halogen in the primary and tertiary chloroacids proceeds by a different mechanism.[17] A mechanism for the reduction of tertiary chloroacids already has been proposed.[1] The present work lends support to the earlier hypothesis[1] that chlorohydrins are intermediate in the reduction of chloroacids or chloroesters to halogen-free alcohols. Thus the reduction of methyl α-chloroisobutyrate by the (inverse) addition of one-half mole of lithium aluminum hydride gave 2-chloro-2-methylpropanol in good yield, while the addition of an excess of lithium aluminum hydride to the same chloroester gave largely isobutyl alcohol. Similar results were obtained in the case of ethyl phenylchloroacetate, a benzylic halide. Further discussion of the mechanism of alcohol formation from primary and secondary as well as tertiary chloroacids will be deferred until experiments presently under way on the reduction of halohydrins with lithium aluminum hydride and deuteride and on the reduction of β-, γ-, δ- and ε-chloroacids are completed.

The appearance of glycols among the reduction products of chloroacids (but not esters) containing

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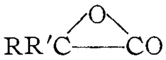
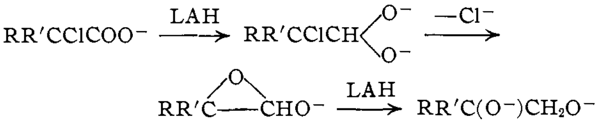
(14) W. Fickett, H. K. Garner and H. J. Lucas, THIS JOURNAL, **73**, 5063 (1951).

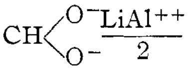
(15) R. F. Nystrom, *ibid.*, **77**, 2544 (1955).

(16) The addition of aluminum chloride[15] also seems to be beneficial in increasing the yield of chlorohydrin but was not tried out in this work.

(17) *Cf.* C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 316.

α-phenyl groups extends our earlier observation with 2-chloro-2-phenylpropionic acid.[1] The proportion of glycol obtained from RR'CClCOOH increases in the series R = R' = Me < R = Ph, R' = H < R = Ph, R' = Me < R = R' = Ph. A decision whether this is due to a steric effect or to an electrical factor in the phenyl group must await study of more highly branched tertiary alkyl chloroacids. As to the mechanism of glycol formation, previously it had been assumed to proceed through the α-lactone .[1] An alternative path involving an α-epoxyalcoholate (as shown in the formulations) cannot, however, be excluded on the basis of evidence presently available. This problem is under further study.



It had been observed[1] previously that in the reduction of 2-chloro-2-phenylpropionic acid with excess lithium aluminum hydride, 2-phenylpropionaldehyde is one of the products. This observation has now been confirmed and extended to the reduction of diphenylchloroacetic acid and its ethyl ester. In fact, in the reduction of ethyl diphenylchloroacetate with excess hydride, diphenylacetaldehyde is the major product. The aldehyde cannot have been present in the reaction mixture as such, since it was shown in a separate experiment to be reduced to 2,2-diphenylethanol in nearly quantitative yield. Three alternatives are suggested regarding the origin of these aldehydes: They might be present in the reaction mixture as enolates $RR'C{=}CHO^{-}\frac{LiAl^{+}}{4}$, as aldehydrol salts RR'CH-  $CH(O^{-})_2\frac{LiAl^{++}}{2}$ or as chlorohydrin salts, $RR'CClCH_2O^{-}\frac{LiAl^{+}}{4}$ Two items of experimental evidence suggest that the first alternative (enolate intermediate) is the correct one. Thus when the crude reaction mixture was treated with acetic anhydride instead of being hydrolyzed, diphenylacetaldehyde enol acetate could be isolated from the product mixture. The analytical yield of the enol acetate (established by conversion to diphenylacetaldehyde dinitrophenylhydrazone and weighing of the hydrazone) was about equal to the analytical yield of free diphenylacetaldehyde (similarly established) in reactions where the hydride mixture was decomposed with water.

Even more significant is the fact that in the formation of the enolate one molar equivalent of hydrogen should be formed also, according to the stoichiometry

$$RR'CClCOOEt + {}^{1}/_{2}LiAlH_4 \longrightarrow \left[RR'CClCH_2O^{-}\frac{LiAl^{+}}{4}\right] + EtO^{-}\frac{LiAl^{+}}{4}$$

$$\left[RR'CClCH_2O^{-}\frac{LiAl^{+}}{4}\right] + {}^{1}/_{4}LiAlH_4 \longrightarrow RR'C{=}CHO^{-}\frac{LiAl^{+}}{4} + \frac{LiAl^{+}}{4}Cl^{-} + H_2$$

In fact, it was observed that the reaction of one mole of ethyl diphenylchloroacetate with excess hydride gave 0.58 mole of a combustible gas, presumably hydrogen This amount is in good agreement with the *ca.* 55% yield of aldehyde obtained in this reduction.

When this work was initiated, lithium aluminum hydride slurries were employed in all reductions save those where a measured amount of the hydride had to be added to the compound to be reduced ("inverse reduction"). In the later phases of the work, however, clear standardized hydride solutions were used in *all* reductions. This ensures an accurate knowledge of the amount of hydride employed as well as the substantial absence of impurities in the slurry. In view of uncertainty[4,15,18] as to the exact stoichiometry of the reduction of halides with lithium aluminum hydrides, in those reductions where the hydride was used in excess, a rather *large* excess was usually employed.

Experimental[19]

Reduction of Chloroacetic Acid.—Using 28.3 g. (0.3 mole) of chloroacetic acid and 14.2 g. (0.375 mole) of lithium aluminum hydride in ether solution (990 ml.) in the usual procedure,[8] boiling for one hour, decomposing the reaction mixture with sulfuric acid and continuously extracting with ether for two days, there was obtained, on fractional distillation, 2.15 g. (16%) of ethanol, b.p. 75-77°, n^{25}D 1.3619, 3,5-dinitrobenzoate m.p. 98–99°, undepressed by admixture of an authentic sample (lit. b.p. 78°, n^{25}D 1.3610, 3,5-dinitrobenzoate m.p. 97°). A fraction boiling between 77 and 126° was also collected and had n^{25}D 1.4304. Ethylene chlorohydrin boils at 128° and has n^{25}D 1.4401. If all of this fraction were the chlorohydrin, the yield would be 5%. Other investigators[10] have reported a 13% yield of ethylene chlorohydrin in this reduction.

In a repeat run, as much as 38% of ethanol was recovered. The actual yield of ethanol is believed to be higher, since much is undoubtedly lost during the extraction and fractionation procedure.

Reduction of α-Chloropropionic Acid.—The acid (32.6 g., 0.3 mole) was reduced in the usual way by an ethereal slurry of 17.1 g. (0.45 mole) of lithium aluminum hydride (total ether volume 1150 ml., reflux time two hours) and the products isolated as described for chloroacetic acid. There was obtained 4.1 g. of propanol-1, b.p. 94–100°, n^{25}D 1.3829–1.3850, 3,5-dinitrobenzoate m.p. 72–73°, undepressed by admixture of an authentic sample (lit. b.p. 97°, n^{25}D 1.3834, 3,5-dinitrobenzoate m.p. 74°). There were also isolated 6.61 g. of a fraction boiling from 100–130°, n^{25}D 1.4052, and 10.20 g., boiling at 130–131°, n^{25}D 1.4358; the higher-boiling fraction giving a 3,5-dinitrobenzoate melting at 74–75°. Literature values for 2-chloro-1-propanol are[14,20]: b.p. 121–124° (613 mm.), n^{25}D 1.4368, m.p. of 3,5-dinitrobenzoate 78.0–78.3°. If the fraction boiling from 100 to 130° is assumed to be a mixture of propanol-1 and 2-chloro-1-propanol, its composition can be calculated from the refractive index (assuming linear dependence on composition) to be 3.9 g. of alcohol and 2.7 g. of chlorohydrin. Thus the total yield of alcohol is 8.0 g. (44%) and that of the chlorohydrin 12.9 g. (46%).

Reduction of α-Chloro-*n*-butyric Acid.—The acid (51 g., 0.415 mole, supplied by Sapon Laboratories) was reduced in the usual way by means of 23.7 g. (0.6 mole) of lithium

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[18] See also E. Wiberg and A. Jahn, *Z. Naturforsch.*, **7b**, 580 (1952).

[19] All melting and boiling points are uncorrected. Microanalyses by Micro-Tech Laboratories, Skokie, Ill. Many of the infrared analyses in this work were recorded by Dr. Barbara K. Campbell to whom we are indebted for her help in this matter. Other spectra were recorded by Mr. Anthony Verbiscar, Mr. Rolland Ro and E. L. E. on a Baird double-beam instrument. All fractional distillations were carried out by means of a helix-packed column, 20 cm. in length. Ether was fractionated from reaction mixtures containing low-boiling materials through a 97-cm. helix-packed column.

[20] S. J. Cristol and K. R. Eilar, THIS JOURNAL, **72**, 4353 (1950).

aluminum hydride (ether volume 1250 ml., two-hours reflux). Fractional distillation gave 13.3 g. of butanol-1, b.p. 95–133°, n^{25}D 1.3970–1.3985, 3,5-dinitrobenzoate m.p. 62–63° (lit. b.p. 118°, n^{25}D 1.3974, 3,5-dinitrobenzoate m.p. 64°). There were also obtained fractions boiling at 133–143°, n^{25}D 1.4141 (2.52 g.); 143–148°, n^{25}D 1.4311 (4.56 g.); and 66–72° (21–23 mm.), n^{25}D 1.4429–1.4462 (12.66 g.). The last fraction gave a 3,5-dinitrobenzoate melting at 75.5–76.5°. Literature values[21,22] for 2-chloro-1-butanol are b.p. 52–53° (19 mm.) or 74–76° (25 mm.), n^{25}D 1.4410, 3,5-dinitrobenzoate m.p. 76.2–77.0°. Assuming the last fraction to be essentially pure 2-chloro-1-butanol (n^{25}D 1.4462) and apportioning the intermediate fractions according to refractive index, one calculates the yield of butanol-1 to be 15.4 g. (52%) and that of 2-chloro-1-butanol as 16.7 g. (38%).

Reduction of α-Chloroisobutyric Acid.—This acid (28 g., 0.23 mole, supplied by Sapon Laboratories) was reduced by means of 13.3 g. (0.35 mole) of lithium aluminum hydride (ether volume 900 ml., two-hours reflux). The only product of this reduction identified with certainty was isobutyl alcohol (12.0 g., 70%), b.p. 106–109°, n^{25}D 1.3965, 3,5-dinitrobenzoate m.p. 87–88°, not depressed by admixture of an authentic specimen. Literature data for isobutyl alcohol are b.p. 108°, n^{25}D 1.3939, 3,5-dinitrobenzoate m.p. 87°. On one occasion 1 g. of a high-boiling fraction (b.p. 82° (26 mm.), n^{25}D 1.4272) was obtained, and since this fraction gave a positive periodate test,[23] it was believed to be isobutylene glycol, reported[24] to have b.p. 178°, n^{25}D 1.4358, phenylurethan m.p. 140.5°. The phenylurethan of the above material melted at 140–143°, but was obtained in too small quantity for positive identification.

Attempts to increase the proportion of the supposed glycol by carrying out the reduction in tetrahydrofuran[1] were unsuccessful.

Reduction of Phenylchloroacetic Acid.—The acid[25] (27 g., 0.16 mole) was reduced by means of 9 g. (0.24 mole) of lithium aluminum hydride (ether volume 700 ml., reflux time two hours). There was obtained 16.0 g. (83%) of 2-phenylethanol, b.p. 100–110° (10–13 mm.), n^{25}D 1.5310–1.5315, 3,5-dinitrobenzoate m.p. 104–105° not depressed by admixture of an authentic specimen. Literature values are b.p. 104° (14 mm.), n^{20}D 1.5240, 3,5-dinitrobenzoate m.p. 108°. The high refractive index of the 2-phenylethanol obtained here and the fact that it gave a positive Beilstein test for halogen suggest a slight contamination, possibly with a chlorohydrin; but the infrared spectrum of the sample was identical with that of an authentic specimen.

From the distillation residue, a small amount of styrene glycol, m.p. 66–67° (lit. 67–68°) undepressed by admixture of an authentic sample, was isolated. In a run carried out in tetrahydrofuran as a solvent, the crude glycol, b.p. 143–145° (3 mm.), m.p. 54–56°, was obtained in 8% yield (1.87 g.) along with 15.9 g. (83%) of 2-phenylethanol.

Reduction of 2-Chloro-2-phenylpropionic Acid.—This reduction was carried out on a 0.12-mole scale as described previously,[1] except that the reaction mixture was decomposed with 10% sodium hydroxide. It gave 3.21 g. of material boiling at 82–105° (8 mm.), n^{25}D 1.5261–1.5280, semicarbazone m.p. 152–154° (lit. for 2-phenylpropanal, b.p. 84–86° (10 mm.), n^{18}D 1.5176, semicarbazone m.p. 153°) and 8.86 g. of material boiling at 106–116° (8 mm.), n^{25}D 1.5257–1.5271, 3-nitrophthalate m.p. 138–139° (lit. for 2-phenyl-1-propanol, b.p. 113–114° (14 mm.), n^{25}D 1.5245, 3-nitrophthalate m.p. 147°). The distillation residue was combined with material obtained from the aqueous residue of the hydride reduction by continuous extraction with ether and yielded 2.15 g. of material boiling at 101–143° (17 mm.) from which 2-phenyl-1,2-propanediol, m.p. 44–45° undepressed by admixture of an authentic specimen, was obtained by crystallization (literature values for the glycol are b.p. 158–160° (25 mm.), m.p. 44.5°). Although no analytical data were obtained for the various fractions, one can estimate the yield of the alcohol as about 50–60% (previously reported[1] 69.5%), that of the aldehyde about 10–20% and that of the glycol under 10%.

Reduction of Diphenylchloroacetic Acid.—The acid, m.p. 106–118°, was obtained in 72% yield by treatment of benzylic acid with acetyl chloride.[26] Recrystallization from ether–hexane gave material melting at 115–121° (lit.[26] 117–118° dec.) in 55% over-all yield; neut. equiv.: calcd.[27] 123.3; found 124.7, 124.7.

Reduction of 37 g. (0.15 mole) of the acid was effected by means of 8.7 g. (0.23 mole) of lithium aluminum hydride in the usual way (ether volume 750 ml., reflux time two hours). The reaction mixture was decomposed with either 10% sulfuric acid or 10% sodium hydroxide, the type of decomposition having little effect on the nature of the product. Distillation of the product gave 11.2 g. of material boiling at 150–168° (3 mm.), n^{25}D 1.5922. The infrared spectrum of the distillate suggested the presence of 2,2-diphenylethanol and diphenylacetaldehyde.[28] The presence of the alcohol was confirmed by the preparation of a phenylurethan,[28] m.p. 135–137° undepressed by admixture of an authentic specimen prepared from alcohol obtained by the reduction of diphenylacetic acid with lithium aluminum hydride.[29] The presence of aldehyde was proved by the preparation of a semicarbazone,[30] m.p. 161–163° undepressed by admixture of an authentic sample prepared from aldehyde obtained by the treatment of 1,1-diphenylethylene glycol with 20% sulfuric acid.

A residue amounting to 15.5 g. was obtained in the above distillation. Treatment of this with hot ethanol gave three crops of crystals totalling 4.8 g. (15%) of 1,1-diphenylethylene glycol melting in the 108–113° range. Recrystallization from ethanol raised the melting point to 120–121.5° (lit.[29] 121°), undepressed by admixture of an authentic specimen prepared by the reduction of benzilic acid with lithium aluminum hydride.[29]

In an attempt to obtain better data on the composition of the product of this reduction, the reaction was repeated and the crude product subjected to analysis. Analysis by means of periodic acid[31] indicated the product to contain about 20% of 1,1-diphenylethylene glycol. Unfortunately the glycol interfered in the gravimetric analysis of the aldehyde as dinitrophenylhydrazone, as well as in the gravimetric analysis of the alcohol as phenylurethan, and even after the bulk (70%) of the glycol was removed by crystallization, satisfactory analytical data could not be obtained. Attempts to analyze the mixture by comparing its infrared spectrum in a solution of standard concentration (300 mg. per ml. of chloroform) with infrared spectra of synthetic mixtures also were not entirely satisfactory. On the basis of such analyses, it was estimated that the mixture might contain about 25% of diphenylacetaldehyde and 55% of 2,2-diphenylethanol. However, spectra of synthetic mixtures of that composition, while having about the correct *relative* intensity of the characteristic bands, had a higher over-all absolute intensity of all bands than the product mixture. From this and from the fact that less than 50% of the crude reaction mixture could be distilled, it would appear that some other, non-volatile component might be present in the mixture, but if so it was not identified.

Reduction of Methyl α-Chloropropionate.[32]—To 49 g. (0.40 mole) of the ester in 100 ml. of sodium-dried ether, was added 210 ml. (0.21 mole) of a 1.0 *M* solution of lithium aluminum hydride in ether[33] at such a rate as to produce

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[21] B. I. Halperin, H. B. Donahoe, J. Kleinberg and C. A. VanderWerf, *J. Org. Chem.*, **17**, 623 (1952).

[22] H. M. Waddle and H. Adkins, This Journal, **61**, 3361 (1939).

[23] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," third edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 115.

[24] K. A. Krasuskii and M. Movsum-Zade, *J. Gen. Chem.* (*U.S.S.R.*), **6**, 1203 (1936); *C. A.*, **31**, 1377 (1937).

[25] E. L. Eliel, M. Fisk and Th. Prosser, *Org. Syntheses*, in press.

[26] F. E. King and D. Holmes, *J. Chem. Soc.*, 164 (1947).

[27] Assuming complete hydrolysis of the chlorine.

[28] The literature reports the following physical constants: For 2,2-diphenylethanol, b.p. 190–195° (20 mm.), m.p. 62°, phenylurethan m.p. 138–139°: P. Ramart and P. Amagat, *Ann. chim.*, [10] **8**, 290 (1927). For diphenylacetaldehyde, b.p. 166° (9 mm.), n^{21}D 1.5920, semicarbazone m.p. 160–161°: A. Klages and J. Kessler, *Ber.*, **39**, 1755 (1906).

[29] M. Protiva, *Chem. Listy*, **45**, 20 (1951); *C. A.*, **45**, 8997 (1951).

[30] R. Stoermer, *Ber.*, **39**, 2293 (1906).

[31] S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1954, p. 16.

[32] This experiment was performed by Mr. Thomas Prosser.

[33] Lithium aluminum hydride solutions were standardized early in the work by the gasometric procedure of J. A. Krynitsky, J. E. Johnson and H. W. Carhart, *Anal. Chem.*, **20**, 311 (1948), and later by the more convenient iodimetric procedure of H. Felkin, *Bull. soc. chim. France*, 347 (1951).

gentle reflux. After the addition was complete, the mixture was stirred for 30 minutes and then decomposed with water and 10% sulfuric acid. The ether layer was separated and the aqueous layer extracted continuously with ether for 24 hours. The combined ether layers were concentrated through a Vigreux column and the residue fractionated. After a small forerun (0.77 g.) there was collected 29.4 g. (78%) of 2-chloro-1-propanol, b.p. 59–62° (51–53 mm.), $n^{20}\mathrm{D}$ 1.4370–1.4382, 3,5-dinitrobenzoate m.p. 77–78°. The literature[11] reports b.p. 53.0–53.6° (29 mm.), $n^{30}\mathrm{D}$ 1.4356, 3,5-dinitrobenzoate m.p. 77.0–77.9°.

Reduction of Methyl α-Chloro-*n*-butyrate.—This ester[34] (30 g., 0.22 mole) was dissolved in 500 ml. of dry ether and reduced by the addition of 113 ml. of 0.98 *M* ethereal lithium aluminum hydride (0.11 mole), reflux time one hour. The product was continuously extracted for 48 hours with ether after decomposition of the reaction mixture with acid. Distillation yielded 21.3 g. (89%) of 2-chloro-1-butanol, b.p. 67–70° (26 mm.), $n^{25}\mathrm{D}$ 1.4430, 3,5-dinitrobenzoate m.p. 75.5–76.5°, in good agreement with the literature values (see above).

Methyl α-Chloroisobutyrate.—Nitrogen gas was passed for six hours through a mixture of 500 g. (3.8 moles) of ethyl α-hydroxyisobutyrate[35] and 491 g. (4.16 moles) of thionyl chloride contained in a flask equipped with a reflux condenser, so as to entrain the hydrogen chloride and sulfur dioxide evolved. Pyridine (1 ml.) was then added and the mixture was heated on the steam-bath for four hours and then poured onto ice. The product was extracted with two 250-ml. portions of ether which, in turn, were washed successively with 250-ml. portions of water, 10% hydrochloric acid, water, saturated sodium bicarbonate solution, and water. The ether solution was then dried over sodium sulfate, concentrated and fractionated through a 20-cm. helix-packed column. After a fraction of methyl methacrylate weighing 203 g. (51%), the desired ethyl α-chloroisobutyrate was collected at 68–79° (56–57 mm.) (mostly 68–74°), $n^{20}\mathrm{D}$ 1.4150–1.4159, yield 155 g. (36%). The infrared spectrum showed this material to be free of impurities containing hydroxyl groups (starting material) or double bonds (methacrylate).

The methyl ester could be similarly prepared from methyl α-hydroxyisobutyrate. It was also prepared from α-chloroisobutyric acid and methanol in the presence of sulfuric acid[36] (77% yield, b.p. 62° (58 mm.), $n^{25}\mathrm{D}$ 1.4164; lit.[36] b.p. 64–65° (55 mm.), $n^{25}\mathrm{D}$ 1.4122) or from α-chloroisobutyric acid and diazomethane. Samples prepared by the three routes had identical infrared spectra, ruling out the possibility that the route from the α-hydroxyester led to the β-chloroester.[37]

Reduction of α-Chloroisobutyrates. (a) With a Limited Amount of Hydride.—To 60 g. (0.4 mole) of ethyl α-chloroisobutyrate in 200 ml. of ether was added 210 ml. (0.21 mole) of ethereal lithium aluminum hydride. The mixture was worked up in the usual way (without continuous extraction, which did not improve the yield). Concentration of the ether layer and subsequent distillation were performed in the presence of small amounts of solid anhydrous potassium carbonate, since 2-chloro-2-methylpropanol tends to decompose in the presence of traces of acid. After a forerun weighing 4.88 g. consisting largely of ethanol there was collected 31.9 g. (74%) of 2-chloro-2-methyl-1-propanol, b.p. 60–62.5° (53–54 mm.), $n^{20}\mathrm{D}$ 1.4367–1.4385. The material was collected in several fractions which had similar infrared spectra but differed somewhat in freezing point, the highest point observed being 28–32°. The material appears to have a high cryoscopic constant. The literature[38] reports a boiling point of 132–133°, but in our hands the material tended to decompose on atmospheric distillation. Even distillation at reduced pressure in a few instances produced an extensive forerun of isobutyraldehyde.

The phenylurethan of 2-chloro-2-methyl-1-propanol melted at 92.5–94°.

Anal. Calcd. for $C_{11}H_{14}ClNO_2$: C, 57.99; H, 6.19; Cl, 15.60; N, 6.15. Found: C, 58.01; H, 6.21; Cl, 15.70; N, 6.68.

(b) **Reduction with Excess Hydride.**—The hydride solution (198 ml., 1.095 *M*, 0.216 mole) was added to methyl α-chloroisobutyrate (26.3 g., 0.193 mole) in 300 ml. of ether. The reflux time was two hours after completion of the addition. The reaction mixture was decomposed with dilute acid and extracted continuously for 22 hours. The product was collected in three fractions: 2.41 g., b.p. 87–105°, $n^{25}\mathrm{D}$ 1.3941; 4.76 g., b.p. 105–114°, $n^{25}\mathrm{D}$ 1.4009; 4.56 g., b.p. 114–120°, $n^{25}\mathrm{D}$ 1.4112. Infrared spectra and the preparation of 3,5-dinitrobenzoates indicated all three fractions to be principally isobutyl alcohol (b.p. 108°, $n^{25}\mathrm{D}$ 1.3939) with a considerable amount of impurity, probably the chlorohydrin, in the third fraction (all fractions gave precipitates with alcoholic silver nitrate). The yield, calculated as isobutyl alcohol, was 11.7 g. (82%), the actual yield being, of course, somewhat lower because of the presence of impurities.

Reduction of Ethyl Phenylchloroacetate. (a) With a Limited Amount of Hydride.—Ethereal lithium aluminum hydride (69.3 ml., 1.08 *M*, 0.075 mole) was added to a solution of 29.8 g. (0.15 mole) of ethyl phenylchloroacetate in 250 ml. of ether. After completion of the addition, the solution was stirred for one hour and then decomposed by the addition of 20% sodium potassium tartrate solution. Distillation of the product gave a forerun, b.p. 58–63°, $n^{25}\mathrm{D}$ 1.5312, weighing 1.1 g. (probably styrene oxide, see below), and a main fraction, b.p. 106–120° (5–6 mm.), $n^{25}\mathrm{D}$ 1.5481–1.5501, weighing 15.9 g. A high boiling fraction, b.p. 164–174° (4 mm.), $n^{25}\mathrm{D}$ 1.5669 (1.2 g.) also resulted. 2-Chloro-2-phenylethanol (68% yield, if pure) was identified in the main fraction by the preparation of a 3,5-dinitrobenzoate, m.p. 121–123°.

Anal. Calcd. for $C_{15}H_{11}ClN_2O_6$: C, 51.35; H, 3.16; Cl, 10.09. Found: C, 51.37; H, 3.22; Cl, 9.78.

In one instance where the reaction mixture was decomposed by 10% aqueous sodium hydroxide with vigorous stirring, the only product of the reaction was styrene oxide, b.p. 62–66° (5 mm.), $n^{25}\mathrm{D}$ 1.5301 (lit.[39] b.p. 84–85° (15 mm.), $n^{25}\mathrm{D}$ 1.5329) isolated in 80% yield (14.4 g.), identified by its infrared spectrum which was identical with that of an authentic specimen. Ring closure of the chlorohydrin had apparently taken place during the isolation process. On another occasion where basic decomposition was employed (with less vigorous stirring), extensive ring closure did not occur.

(b) With Excess Lithium Aluminum Hydride.—Addition of 140 ml. of 1.095 *M* (0.153 mole) of ethereal lithium aluminum hydride to 27 g. (0.136 mole) of the chloroester in 200 ml. of ether, with two hours of reflux followed by basic decomposition gave 12.1 g. (73%) of slightly impure 2-phenylethanol, b.p. 110–115° (19 mm.), $n^{25}\mathrm{D}$ 1.5308. The 3,5-dinitrobenzoate melted at 103° (lit. 108°) after one recrystallization and was undepressed by admixture of an authentic sample. Essentially the same result (82% yield of 2-phenylethanol) was obtained when the ethyl phenylchloroacetate was added to a hydride slurry.

Reduction of Ethyl α-Chlorodiphenylacetate.—A solution of 27.4 g. (0.10 mole) of ethyl α-chlorodiphenylacetate[40] in 100 ml. of ether was added to 85 ml. (0.085 mole) of 1.0 *M* ethereal lithium aluminum hydride. After a 1.5-hour reflux, the mixture was decomposed by means of 10% sulfuric acid. The crude product weighed 19.75 g.

Fourteen grams of the product was subjected to distillation which yielded 8.9 g. of distillate, b.p. 110–117° (0.25 mm.), $n^{20}\mathrm{D}$ 1.5914–1.5980. A black distillation residue (4.9 g.) also resulted. The infrared spectrum of the distillate indicated it to be a mixture of diphenylacetaldehyde and 2,2-diphenylethanol. Presence of the alcohol was proved by formation of the phenylurethan, m.p. 133–134°, not depressed by admixture of an authentic sample.[29]

In order to obtain a more accurate idea as to the composition of the crude product, a dinitrophenylhydrazone was prepared quantitatively from the undistilled material. There was obtained 63% of diphenylacetaldehyde 2,4-dinitrophenylhydrazone melting at 125–138°. (The pure derivative, obtained after several recrystallizations, melted at 150–151°.)

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(34) E. Fischer and A. Speier, *Ber.*, **28**, 3252 (1895).

(35) Kindly supplied by Rohm & Haas Co.

(36) Y. S. Zal'kind and I. F. Markov, *J. Appl. Chem.* (*U.S.S.R.*), **10**, 1042 (1937); *C. A.*, **32**, 1652 (1938).

(37) Acetone cyanohydrin with phosphorus pentachloride yields β-chloroisobutyronitrile: C. L. Stevens, THIS JOURNAL, **70**, 165 (1948).

(38) L. Henry, *Compt. rend.*, **142**, 495 (1906).

(39) M. Tiffeneau and M. Fourneau, *ibid.*, **146**, 697 (1908).

(40) Prepared in similar fashion as ethyl phenylchloroacetate.[22]

Anal. Calcd. for $C_{20}H_{16}N_4O_4$: C, 63.81; H, 4.28. Found: C, 63.58; H, 4.17.

In some cases, benzophenone dinitrophenylhydrazone, identified by mixed melting point determination was also isolated.[41] Comparison of the infrared spectrum of the crude reaction product with that of synthetic mixtures of diphenylacetaldehyde and 2,2-diphenylethanol suggested a composition of 55% aldehyde and 45% alcohol. A synthetic mixture of that composition had a spectrum very similar to that of the reaction product.

According to the mechanism presented in the Discussion, hydrogen gas should be evolved in the formation of diphenylacetaldehyde from ethyl diphenylchloroacetate. The combustible gas evolved from a reduction involving 21.93 g. (0.08 mole) of the ester was found to occupy 1190 cc. at 25° and 750 mm. over water, which amounts to 0.047 mole, the expected amount, assuming a 55% yield of aldehyde, being 0.044 mole.

Isolation of Diphenylacetaldehyde Enol Acetate.—The reduction of 44.6 g. (0.16 mole) of ethyl diphenylchloroacetate was effected by means of 0.16 mole of ethereal lithium aluminum hydride. After completion of the addition the reaction mixture was boiled and stirred for one hour, then 20 ml. of ethyl acetate was added to remove excess lithium aluminum hydride and boiling and stirring was continued for 15 minutes. Acetic anhydride (128 ml., 138.7 g., 1.36 moles) was then added dropwise and stirring under reflux continued for another half hour. The reaction mixture was then treated with water and sodium potassium tartrate solution, allowed to settle and filtered, the precipitated salt being washed once with water and twice with 100-ml. portions of ether. The combined water layers were extracted three times with 100-ml. portions of ether and the combined ether fractions were dried over sodium sulfate and concentrated. The residue weighed 32.6 g. (85%, assuming it to be a mixture of diphenylacetaldehyde enol acetate and 2,2-diphenylethanol acetate—see below) and on distillation yielded 28.1 g. (86% recovery) of distillate boiling at 121–125° (0.07–0.09 mm.), $n^{20}D$ 1.5817–1.5820. No acetic acid was found in the cold traps.[42] On standing, the fraction deposited crystalline material. Half the fraction was dissolved in ethanol and chilled; in this way a total of 2.27 g. of crystalline material was recovered which, after two further crystallizations from ethanol, melted at 57–59°. The melting point was not depressed by admixture of an authentic sample[43] of diphenylacetaldehyde enol acetate, m.p. 60–61° (lit.[43] 59°).

From the mother liquor of the crystallization of the above enol acetate there was isolated another 0.52 g. of material which after four recrystallizations from ethanol melted at 53–57°, depressed by admixture of diphenylacetaldehyde enol acetate but not depressed by admixture of an authentic sample of 2,2-diphenylethyl acetate, m.p. 56–57°, prepared from 2,2-diphenylethanol, acetic anhydride and pyridine.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.95; H, 6.71. Found: C, 80.03; H, 6.76.

The presence of diphenylacetaldehyde enol acetate was further confirmed by basic hydrolysis of the above crude distillate to a compound which had the infrared bands of diphenylacetaldehyde and by preparation of diphenylacetaldehyde semicarbazone, m.p. 164–165°, undepressed by admixture of an authentic sample and diphenylacetaldehyde 2,4-dinitrophenylhydrazone. The latter derivative was prepared quantitatively and suggested that the crude distillate contained about 70% of the enol acetate. The enol acetate evidently was cleaved in the acidic media employed in the preparation of the aldehyde derivatives.

Reduction of Diphenylacetaldehyde.—The aldehyde (19.6 g., 0.1 mole, in 150 ml. of ether) was added to 0.06 mole of ethereal lithium aluminum hydride over a period of 1.5 hours and the solution boiled for another 1.5 hour. The amount of gas (hydrogen?) evolved from the reaction mixture during this time was less than 0.01 mole, indicating little, if any, reaction of the hydride with the acidic (enolic) hydrogen of the aldehyde. The product of the reaction, isolated in the usual way, solidified to a crystalline solid melting at 45–54°, weighing 18.7 g. (94.5%). The infrared spectrum of the crude solid suggested that it was essentially pure 2,2-diphenylethanol with no recovered diphenylacetaldehyde. Attempts to prepare a dinitrophenylhydrazone from the crude material failed. Three recrystallizations of the crude material raised the melting point to 60–62°, undepressed by admixture of an authentic sample (lit.[28] 62°).

Reduction of γ-Phenoxypropyl Chloride.—The chloride was prepared[44] from phenol and 1-chloro-3-bromopropane in 67% yield, m.p. 12–13° (lit.[45] 11.8–12°).

Reduction of 42.6 g. (0.25 mole) of the chloride by means of 16 g. (0.42 mole) of lithium aluminum hydride (total ether volume 500 ml., four-hours reflux) gave 3.9 g. of material boiling at 101–107° (45 mm.), $n^{24}D$ 1.5004 (lit. $n^{20}D$ 1.5011 for phenyl propyl ether) whose infrared spectrum was identical with that of authentic phenyl propyl ether, 2.8 g. boiling at 107–151° (45 mm.), $n^{24}D$ 1.5085, and 31.7 g. boiling at 151–154° (45 mm.), $n^{24}D$ 1.5240, m.p. 10.5–12°, undepressed by admixture with starting material. If the intermediate fraction is apportioned according to refractive index, the yield of phenyl propyl ether is 5.8 g. (17%) and the recovery of starting chloride is 32.6 g. (77%).

Reduction of β-Phenoxyethyl Chloride.—This chloride was prepared[46] similarly to the higher homolog, but the yield of product melting at 25–25.5° (lit. 25°) was only 23%. A substantial amount of 1,2-diphenoxyethane, m.p. 97.5–99° (lit. 98°), also was isolated.

Reduction of 31.3 g. (0.2 mole) of the chloride with 8 g. (0.21 mole) of lithium aluminum hydride (ether volume 450 ml., 4 hours reflux) gave only 0.55 g. (2%) of material boiling at 89–110° (45 mm.), $n^{23.5}D$ 1.5082 (lit. $n^{21}D$ 1.5076 for phenetole) whose infrared spectrum was identical with that of phenetole and 27.7 g. (89% recovery) of starting material, b.p. 133–134° (45 mm.), $n^{23.5}D$ 1.5325, m.p. 23.5–25°, undepressed by admixture of the starting chloride.

Reduction of γ-Phenylpropyl Chloride.—The reduction of 7.8 g. (0.05 mole) of the chloride in 50 ml. of ether was effected by means of 0.06 mole of ethereal lithium aluminum hydride solution, reflux time 2.25 hours. The product was collected in two fractions: 0.50 g. (8%) of *n*-propylbenzene, b.p. 54–80° (20–22 mm.), $n^{20}D$ 1.4930 (lit. b.p. 67–68° (15 mm.), $n^{20}D$ 1.4920), and 5.87 g. (75% recovery) of γ-phenylpropyl chloride, b.p. 100–105° (20–22 mm.), $n^{20}D$ 1.5219 (lit. b.p. 106–106.5° (22 mm.), $n^{25}D$ 1.5203). The infrared spectrum of the first fraction was identical with that of *n*-propylbenzene and that of the second fraction with the spectrum of the starting material.

Reduction of β-Phenylethyl Chloride.—The chloride (28.2 g., 0.20 mole) was reduced by means of 8.5 g. (0.22 mole) of lithium aluminum hydride in ethereal slurry, total ether volume 400 ml., reflux time 3 hours. Distillation yielded 0.71 g., b.p. 70–72° (100 mm.), $n^{20}D$ 1.4960 (lit. b.p. 79° (121 mm.), $n^{20}D$ 1.4959 for ethylbenzene), and 22.40 g. (79% recovery) of β-phenylethyl chloride, b.p. 86–90° (20 mm.), $n^{20}D$ 1.5281 (lit. b.p. 91–92° (20 mm.), $n^{20}D$ 1.5294). The infrared spectrum of the second fraction was identical with that of the starting material. That of the first fraction suggested that the fraction contained ethylbenzene, but was not pure ethylbenzene. The yield of this hydrocarbon is therefore under 4%.

Acknowledgment.—This work was supported by Frederic Gardner Cottrell Grants of Research Corporation over a period of several years. We are deeply grateful for this support.

NOTRE DAME, INDIANA

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[41] Occasionally, the presence of benzophenone was also evident through its characteristic infrared bands. Because of the erratic appearance of benzophenone, it is believed to be due to a process of oxidative degradation of primary reaction products. Acetophenone had similarly been found in the reduction of 2-chloro-2-phenylpropionic acid[1] and probably results from oxidation of the primary product 2-phenylpropionaldehyde. In fact it is known that 2-phenylpropionaldehyde is converted to acetophenone by oxidation with gaseous oxygen: L. A. Wetzel, C. H. McKeever and C. L. Levesque, THIS JOURNAL, **72**, 4939 (1950). Samples of diphenylacetaldehyde aged in our laboratories were found to show the characteristic bands of benzophenone in the infrared.

[42] Looked for because the primary product might have been aldehyde diacetate yielding the enol acetate and acetic acid on distillation.

[43] M. Tiffeneau, *Compt. rend.*, **150**, 1181 (1910).

[44] S. Gabriel, *Ber.*, **25**, 415 (1892).

[45] L. Henry, *Bull. soc. chim. France*, [3] **15**, 1224 (1896).

[46] L. Henry, *Bull. soc. chim., France*, [2] **40**, 323 (1883).