Analytical Method.—The product from each cleavage reaction was carefully rectified to remove the lower boiling alcohol. The end-run fractions were analyzed quantitatively by their infrared spectra by a slight modification of the technique described previously.[1] In the case of a mixture of 3-ethoxy-1,1,1-trifluoro-2-butanol (VII) and 3-ethoxy-4,4,4-trifluoro-2-butanol (IX), a base line was drawn across absorption minima characteristic of both spectra at 6.05 and 13.35 μ. A calibration curve was established on the basis of the ratio of the distance measured from the base line to the absorption minimum at 10.3 μ and to the curve at 11.5 μ. The latter point is an absorption minimum for VII and an absorption maximum for IX. The calibration data are summarized in Table II.

Quantitative estimation of mixtures of 3-ethoxy-2-methyl-1,1,1-trifluoro-2-propanol (VIII) and 2-ethoxy-2-methyl-3,3,3-trifluoro-1-propanol (X) was accomplished on the basis of a shift in the location of a peak at 13.15 μ in VIII and 13.35 μ in the latter. The general shape of the spectra was also used since no technique analogous to the above was applicable.

TABLE II

INFRARED DATA FOR MIXTURES OF 3-ETHOXY-1,1,1-TRIFLUORO-2-BUTANOL (VII) AND 3-ETHOXY-4,4,4-TRIFLUORO-2-BUTANOL (IX)

Composition, %		Distance to base line[a]		
VII	IX	B (10.3 μ)	A (11.5 μ)	A/B
100.0	0.0	17.1	7.0	0.41
94.0	6.0	17.0	15.2	0.90
88.4	11.6	16.5	19.3	1.17
0.0	100.0	15.3	67.0	4.28

[a] Base line between absorption minima at 6.05 and 13.35 μ.

WEST LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

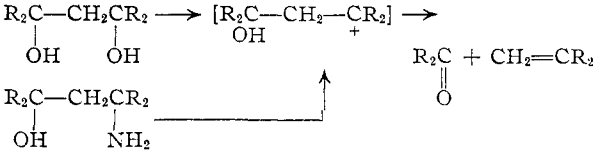
The Preparation and Deamination of Some 1,3-Amino Alcohols

BY JAMES ENGLISH, JR., AND ARTHUR D. BLISS[1]

RECEIVED JANUARY 17, 1956

Some 1,3-amino alcohols have been synthesized and their deamination with nitrous acid studied. Evidence is presented for the cleavage of some of these substances into carbonyl compounds and olefins, analogous to the reaction observed in the dehydration of 1,3-diols.[2]

The mechanism recently proposed[2] for the acid-catalyzed cleavage of 1,3-diols leads to the prediction that other compounds capable of producing carbonium ions of analogous structure to those derived from 1,3-diols should also exhibit cleavage of carbon-to-carbon bonds. One such example would be 1,3-amino alcohols, which with nitrous acid should behave as



We have undertaken, therefore, the study of the synthesis and nitrous acid deamination of some substituted 1,3-amino alcohols. It was predicted from the diol work[2] that substitution, especially by aromatic groups, would be favorable to the cleavage reaction and several synthetic approaches capable of leading to the desired types were investigated. The compounds synthesized are shown in Table I.

The reaction of β-amino ketones with Grignard reagents[3] and also their reduction[4] has been reported to give poor yields of amino alcohols due to loss of ammonia. Our experience has confirmed this in the reaction of diacetoneamine with methylmagnesium iodide, which gave only 2% of crude amine, and its reduction to 2-methyl-2-amino-4-pentanol (I) in 14% yield. The reduction of cyano-ketones leads in general to 1,3-amino alcohols, and this method was applied to the preparation of 1-phenyl-3-amino-1-propanol (IV). In view of the failure of these amino alcohols having the amino group on primary carbon atoms (IV and V) to undergo cleavage, this method was not further pursued. Attempts were made to react nitroethane and 2-nitropropane with ethylene oxide and with styrene oxide in basic media. This would lead to 1,3-nitro alcohols, presumably reducible to amino alcohols; in all cases, however, the nitro paraffins were recovered unchanged, accompanied by some polymerized epoxide.

A promising and apparently general method for the preparation of 1,3-amino alcohols in which R_3 and R_4 are the same (VII and VIII) was found in the reaction of Grignard reagents with acetylated β-aminoesters. Adamson[5] and McKenzie[6] report relatively poor yields in this type of reaction with free amino esters where the amino group is primary, although the secondary and tertiary analogs seem satisfactory. Protection of the amino group by acetylation apparently decreases the amount of elimination of ammonia (or amide), and we obtained the N-acetylated amino alcohols in 40–60% yield; hydrolysis to the free bases occurred smoothly and almost quantitatively.

Stühmer and Frey[7] have reported the preparation of both diastereomers of 1,3-diphenyl-1-amino-3-propanol (VI) by reduction of 3,5-diphenylisoxazoline derived from benzal-acetophenone. An analogous reduction of 3,5-diphenylisoxazole (prepared from dibenzoylmethane) gave satisfac-

---

[1] Taken from the dissertation submitted by Arthur D. Bliss to the Graduate School of Yale University in partial fulfillment of the requirements for the Ph.D. degree (1955).

[2] H. E. Zimmerman and J. English, THIS JOURNAL, **76**, 2285, 2291, 2294 (1954).

[3] A. W. Ruddy and J. S. Buckley, Jr., *ibid.*, **72**, 718 (1950).

[4] M. Kohn, *Monatsh.*, **25**, 141 (1904); C. E. Rehberg and H. R. Henze, *ibid.*, **63**, 2785 (1941).

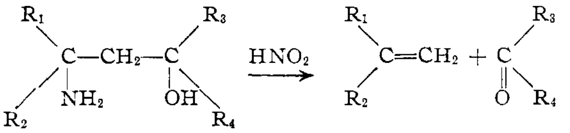
[5] D. W. Adamson, *J. Chem. Soc.*, S 144 (1949).

[6] A. McKenzie and A. C. Richardson, *ibid.*, **79** (1923).

[7] W. Stühmer and H. H. Frey, *Arch. Pharm.*, **286** [58], 8 (1953).

TABLE I

1,3-AMINO ALCOHOL REACTIONS WITH NITROUS ACID

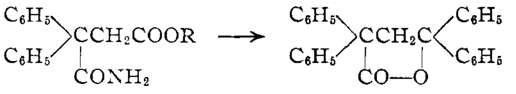


	R_1	R_2	R_3	R_4	Reagent[a]	Cleavage product isolated	Yield of cleavage product, %
I	CH_3	CH_4	H	CH_3	HOAc	....	-0-
II	CH_3	H	CH_3	CH_3	HOAc	....	-0-
III	C_6H_5	H	H	H	HOAc	CH_2O[b]	5.2
IV	H	H	H	C_6H_5	H_2SO_4	....	-0-
V	H	H	C_6H_5	C_6H_5	HOAc	....	-0-
VI	C_6H_5	H	H	C_6H_5	H_2SO_4	....	16.0–18.9
					HOAc	α-C_6H_5CHO[c]	17.6
					H_2SO_4	β-C_6H_5CHO[c]	12.3
					HOAc		11.8
VII	C_6H_5	H	C_6H_5	C_6H_5	HOAc	$(C_6H_5)_2CO$[c]	18.5
VIII	$p(OCH_3)C_6H_4$	H	C_6H_5	C_6H_5	HOAc	$(C_6H_5)_2CO$[c]	22.0

[a] HOAc refers to 50% acetic acid plus 3 equivalents of $NaNO_2$; H_2SO_4 refers to 0.3 N H_2SO_4 plus 3 equivalents of $NaNO_2$. Dimedone derivative. [c] 2,4-Dinitrophenylhydrazone.

tory yields in our hands, and the separation of the diastereomers was carried out according to Stühmer and Frey. It was observed that the hydrolysis in 2 N acid of the Schiff base of "α"-1,3-diphenyl-1-amino-3-propanol was accompanied by equilibration to a mixture of the two forms (85% "β"); the use of 0.5 N hydrochloric acid and rapid removal of the benzaldehyde produced led to the isolation of the pure "α"-form. The free amino alcohols were found to be unchanged by treatment with 2 N hydrochloric acid.

A number of possible schemes were examined for the synthesis of a di-tertiary 1,3-amino alcohol ($R_1R_2R_4R_5$ = aryl) which on deamination was expected to undergo cleavage as the main reaction.[2] For one reason or another, all of these have failed so far and the scarcity of literature on tertiary carbinamines leads us to believe that this type of 1,3-amino alcohol is unavailable at present. Only unchanged starting material could be obtained from attempted Ritter[8] reactions with β,β-diphenylacrylic ester. Attempts to convert the α,α-diphenylsuccinic acid derivatives of Salmon-Legagneur[9] to suitable β,β-diphenyl-β-amino acid intermediates, for instance the rearrangement of α,α-diphenylsuccinamic acid, were unsuccessful; the tendency to form stable cyclic compounds is very marked in this series. α,α-Diphenylsuccinimide is formed very readily from the corresponding succinamic acid. Reaction of the ester amide IX with Grignard reagents even at −10° gave a very stable lactone X rather than the hoped-for amide alcohol.



IX X

Only two previous reports could be found of the deamination of 1,3-amino alcohols. McKenzie and Richardson[6] deaminated 1,1,3-triphenyl-3-amino-1-propanol and reported only the isolation of the corresponding diol in 30% yield. Stühmer and Frey[7] deaminated two of the diastereomeric 1,3-diphenyl-3-amino-1-propanols in optically active form and report the isolation in each case of only one, optically active, diol in about 40% yield. Repetition of their experiments with the two *dl*-1,3-diphenyl-1-amino-3-propanols showed the presence of both *dl* (40%) and *meso* (10–20%) diols in the mixture. The latter diol, which is more soluble and crystallizes only slowly from solution, was apparently overlooked by the previous workers and, as expected, the nitrous acid reaction in this case is accompanied by considerable racemization.

Neither of these reports contain any evidence of the occurrence of the cleavage reaction. Table I indicates the degree of cleavage observed in the present work.

The deaminations were carried out at room temperature for 6 hr. with either 0.3 N sulfuric acid or 50% acetic acid and 3 equivalents of sodium nitrite. Control experiments with a typical diol, 1,3-diphenyl-1,3-propanediol (VI), showed that negligible cleavage of diols occurred under these conditions, and hence the products obtained were formed directly from the amino alcohols rather than by way of the diols. Also, in the case of unsymmetrical amino alcohols VII and VIII, it is to be noted that different cleavage products (benzophenone) are produced than from the acid-catalyzed reaction of the corresponding diols (benzaldehyde and anisaldehyde). Measurement of N_2 evolved indicated substantially complete reaction (97%) after 6 hr. Except in the case of 1,3-diphenyl-3-amino-1-propanol, only the carbonyl components of the cleavage reactions were isolated; the yields in Table I represent isolated pure carbonyl derivatives and were found reproducible.

Control experiments with benzaldehyde and with benzophenone showed that the reproducible yields of dinitrophenylhydrazones were 87 and 94%, re-

---

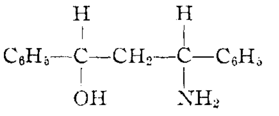
[8] C. J. Ritter, *et al.*, THIS JOURNAL, **73**, 1044, 2804 (1951).

[9] F. Salmon-Legagneur, *Compt. rend.*, **208**, 1507 (1939); **218**, 681 (1944).

spectively. The yields of cleavage products listed in Table I, therefore, are minimum values, since no correction has been made for these losses.

The difference in cleavage yields between the two diastereomers VI we believe to be significant. Until the configurations of the two forms are placed on a sounder basis, it is difficult to interpret these results. Stühmer and Frey have assigned the "β"-form the *threo* configuration on the basis of the ease of migration of acyl groups from oxygen to nitrogen by analogy with 1,2-amino alcohols. Wendler[10] has questioned this on the ground that the transition state in the case of 1,3-migration is six-membered and not planar.

The (+)-"β"- and (−)-"α"- 1,3-diphenyl-3-amino-1-propanols have been shown[7] to have the same configuration about C_3, and this configuration is that of (−)-β-amino-β-phenylpropionic acid (XI). The (+)-1,3-diphenyl-1,3-diol obtained from the (+)-"β"-amino alcohol was found[7] to have the configuration (on both carbons) of D-(+)-β-hydroxy-β-phenylpropionic acid (XII). Therefore, unless racemization occurred at the hydroxy center during the deamination,[11] (+)-"β"-1,3-diphenyl-3-amino-1-propanol has the configuration of (−)-XI and (+)-XII on the amino and hydroxyl centers, respectively. Fischer, Scheibler and Groh[12] have reported the deamination of (+)-XI and of its ester to yield a partly racemized (−)-XII. If we assume, as has been shown by numerous workers,[13] that deaminations of this sort, except in the case of free α-amino acids, proceed by inversion and extensive racemization, the configuration of (+)-XI and (+)-XII are the same and hence the configuration of (+)-"β"-VI must be *erythro*-XIII.



$$C_6H_5-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-CH_2-\overset{\displaystyle H}{\underset{\displaystyle NH_2}{C}}-C_6H_5$$

XIII

This is in agreement with Wendler's[10] postulation and contrary to that of Stühmer and Frey.[7] It is worthy of note that the corresponding diol isomer, *erythro-(meso)*-1,3-diphenyl-1,3-propanediol, like XIII is also cleaved to a lesser extent than the *threo* isomer.[2]

The extent of the cleavage reactions in this series of compounds appears to be controlled by the nature of the substituents on the carbon atom which bears the amino group, an aryl group at this point being necessary. Di-aryl substitution on the carbon bearing the hydroxyl group alone is not sufficient to promote cleavage and, indeed, appears to have little effect on the extent of cleavage of those compounds which do undergo the reaction. The *p*-anisyl group, as opposed to phenyl, has only a slight effect in promoting cleavage (VII, VIII).

Experimental[14]

Diacetonealkamine (I) was prepared in 14% yield by the method of Kohn,[15] b.p. 81–83° at 24 mm., $n^{26}D$ 1.4321.

2 Methyl-4-amino-2-pentanol (II) was obtained in 12% yield by reduction of diacetone alcohol oxime according to Kohn and Lindauer,[16] b.p. 120° at 23 mm., sinters 29–30°, melts 35–36°.

3-Phenyl-3-amino-1-propanol (III).—To a solution of 7.0 g. (0.18 mole) of lithium aluminum hydride in 140 ml. of dry ether was added, dropwise with stirring, 11.2 g. (0.06 mole) of ethyl β-aminohydrocinnamate[17] in 105 ml. of anhydrous ether. When the addition was complete, the mixture was stirred at room temperature for 15 minutes, cooled, decomposed with a slight excess of water, the ether decanted and the gummy residue extracted twice with 100-ml. portions of hot benzene. After removing the solvent from the combined ether and benzene extracts, there was obtained an oil, b.p. 117–118° at 0.5 mm., which crystallized. Recrystallization from benzene–petroleum ether gave 7.2 g. (80% yield) of white needles, m.p. 74.5–75°.

Anal. Calcd. for $C_9H_{13}ON$: C, 71.49; H, 8.66; N, 9.27. Found: C, 71.84; H, 8.55; N, 9.65.

1-Phenyl-3-amino-1-propanol (IV).—This substance was prepared by lithium aluminum hydride reduction of benzoylacetonitrile, 14.5 g. (0.1 mole), in ether–benzene solution and the product worked up as above III. 1-Phenyl-3-amino-1-propanol, b.p. 107–110° at 0.5 mm., m.p. 63–64°,[18] was obtained in about 40% yield. The infrared spectrum showed no carbonyl bonds and was consistent with the proposed structure.

1,1-Diphenyl-3-amino-1-propanol (V) was prepared in 30% yield by the method of Adamson,[19] m.p. 143–144.5°.

1,3-Diphenyl-3-amino-1-propanol isomers (VI).—A glazed crock of about 10-l. capacity was equipped with two stirrers (stainless steel, 2 inch, four-bladed paddles) reaching into a shallow dish imbedded in plaster of paris in the bottom (to contain the amalgam). A third (Hershberg) stirrer was arranged to stir the liquid higher up in the crock. There was added 81 g. (0.37) mole of 3,5-diphenylisoxazole[20] and 3.5 liters of methanol. Over a period of 6 hr. there was added in small portions and with very vigorous stirring 7 kg. of powdered 3% sodium amalgam. After 30 minutes and again after 2 hr., 100 ml. of water was added. The temperature remained at 30–35° during this process; the mixture was then stirred overnight at room temperature, decanted, filtered and acidified. About 2 l. of methanol was removed *in vacuo* and the residue diluted with water and extracted with ether. The aqueous layer was then made basic to precipitate the mixture of 1,3-diphenyl-3-amino-1-propanols which, after one crystallization from ethanol, weighed 66.6 g. (80.6%), m.p. 101–105°. Without vigorous stirring of the amalgam, yields are much lower.

The separation of diastereomers was carried as described by Stühmer and Frey[7]; the "α"-isomer was isolated as the Schiff base, m.p. 124–125°, and the "β"-isomer as the tartrate.

Hydrolysis of the pure "α"-Schiff base by boiling 2 *N* hydrochloric acid (5-fold excess) gave a mixture of amino alcohols. This mixture, m.p. 108–110°, was re-converted to the Schiff bases and fractionally crystallized from ethanol. From 19.2 g. there was obtained 4.0 g. of pure "α"-Schiff base, m.p. 124–125°, and 14.8 g. of a Schiff base, m.p. 82–83°, identical with that prepared from the pure "β"-amino alcohol, m.p. 82–83°. This equilibration is not observed with the free amino alcohols under these conditions and could be avoided by use of 0.5 *N* hydrochloric acid (2-fold excess) and immediate removal of benzaldehyde by steam distillation.

Methyl β-Acetamidohydrocinnamate.—To 23.8 g. (0.13 mole) of methyl β-aminohydrocinnamate was added 8.1 g. (0.13 mole) of glacial acetic acid and 27.2 g. (0.27 mole) of freshly distilled acetic anhydride. The solution was warmed on a water-bath at a temperature of 50° for 1 hr. The

---

[10] N. L. Wendler, *Experientia*, **9**, 416 (1953).

[11] Model experiments have indicated that this occurs to a negligible extent.

[12] E. Fischer, A. Scheibler and R. Groh, *Ber.*, **43**, 2020 (1910).

[13] P. Brewster, F. Hiron, E. Hughes, C. Ingold and P. Rao, *Nature*, **66**, 178 (1950).

[14] All boiling points and melting points are corrected.

[15] M. Kohn, *Monatsh.*, **25**, 135 (1904).

[16] M. Kohn and G. Lindauer, *ibid.*, **23**, 74 (1902).

[17] C. S. Marvel and W. A. Noyes, THIS JOURNAL, **42**, 2265 (1920).

[18] R. E. Davies and G. Powell, *ibid.*, **67**, 1466 (1945).

[19] D. W. Adamson, *J. Chem. Soc.*, S 144 (1949).

[20] T. Posner, *Ber.*, **34**, 3985 (1901).

acetic acid and excess anhydride were removed by distillation at reduced pressure, leaving a slightly greenish, viscous oil, which crystallized after standing overnight in the refrigerator. Two recrystallizations from benzene–petroleum ether (60–90°) gave white plates melting at 90–91°, yield 26.4 g. (92%).

Anal. Calcd. for $C_{12}H_{15}O_3N$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.07; H, 6.63; N, 6.36.

1,1,3-Triphenyl-3-acetamido-1-propanol.—A solution of phenylmagnesium bromide was prepared from 7.8 g. (0.3 atom) of magnesium turnings and 51.8 g. (0.33 mole) of bromobenzene in 300 ml. of anhydrous ether. To this was added, dropwise with stirring, a solution of 10.0 g. (0.045 mole) of methyl β-acetaminohydrocinnamate in 60 ml. of dry benzene. About 5 minutes after completion of the addition, a white solid began to appear. The mixture was refluxed for 2 hr., then cooled in ice and hydrolyzed with excess ice-cold aqueous ammonium chloride solution. A substantial amount of white solid was filtered off. The organic layer of the filtrate was separated, washed with water and dried over sodium sulfate. Removal of the ether gave a small amount of slightly yellow solid, which was combined with the solid material previously isolated and recrystallized from acetone. There was obtained 8.2 g. (53% yield) of white needles melting at 198–199°. Three recrystallizations from ethanol raised the melting point to 205–205.4°. The infrared spectrum showed both hydroxyl and amide absorptions.

Anal. Calcd. for $C_{23}H_{23}O_2N$: C, 79.97; H, 6.71; N, 4.06. Found: C, 79.90; H, 6.54; N, 3.96.

1,1,3-Triphenyl-3-amino-1-propanol (VII) was prepared by hydrolysis of 8.2 g. (0.024 mole) of the acetyl derivative in 60 ml. of boiling 10% potassium hydroxide for 24 hr. A part of the product, 5.7 g., crystallized on cooling and the remainder was recovered by pouring into water and recrystallization from methanol. The total yield was 6.0 g. (83%) of pure VIII, m.p. 154–155°. A mixed melting point with material prepared by the method of McKenzie and Richardson,[21] m.p. 154–155°, showed no depression.

Methyl β-(*p*-Anisyl)-β-acetamidopropionate.—To 31.4 g. (0.15 mole) of methyl β-(*p*-anisyl)-β-aminopropionate was added a mixture of 9.0 g. (0.15 mole) of acetic acid and 30.6 g. (0.3 mole) of acetic anhydride. The solution was maintained at 50° for 2 hr. Acetic acid and the excess anhydride were removed at reduced pressure, leaving a viscous, yellow oil, which soon crystallized. Recrystallization from benzene–petroleum ether (60–90°) gave white plates melting at 95.5–96°. The infrared spectrum confirmed the presence of both ester and amide groups. The yield was 35.7 g. (95%).

Anal. Calcd. for $C_{13}H_{17}O_4N$: C, 62.13; H, 6.82; N, 5.58. Found: C, 62.37; H, 6.65; N, 5.42.

1,1-Diphenyl-3-(*p*-anisyl)-3-acetamido-1-propanol was prepared in the same manner as described above for the phenyl analog, m.p. 227–227.5°. The yield was 40% of theoretical.

Anal. Calcd. for $C_{24}H_{25}O_3N$: C, 76.77; H, 6.71; N, 3.73. Found: C, 76.96; H, 6.64; N, 3.54.

1,1-Diphenyl-3-(*p*-anisyl)-3-amino-1-propanol (VIII) was prepared in the same manner described for VII above. The yield of pure product, m.p. 167–168°, was nearly quantitative.

Anal. Calcd. for $C_{22}H_{23}O_2N$: C, 79.25; H, 6.95; N, 4.20. Found: C, 79.41; H, 6.80; N, 4.10.

Nitrous Acid Deaminations, General Procedure.—Compounds VI, VII and VIII were treated as follows. About 1 g. of amino alcohol was dissolved in 30 ml. of 50% acetic acid and the solution treated with 0.7 g. (3-fold excess) of sodium nitrite in 5 ml. of water. The mixture was allowed to stand at least 6 hr. at room temperature before neutralization and extraction with ether. Evaporation of the ether, solution of the residue in ethanol and addition of saturated alcoholic solution of 2,4-dinitrophenylhydrazine containing 1% of concentrated hydrochloric acid yielded crystalline derivatives of benzaldehyde (from VI) or benzophenone (from VII and VIII). In all cases mixed melting points with authentic samples showed no depression.

In the case of III, the deamination was carried out below 5° for 4 hr. and the formaldehyde isolated by distillation of the neutralized mixture into a cold solution of dimedon in water. After some time a small precipitate of formaldehyde-dimedon derivative (0.102 g.) separated, m.p. 185–186°; no depression was observed on mixed melting point with an authentic sample.

Nitrous Acid Deaminations, Modified Procedures.—The 1,3-diphenyl-3-amino-1-propanol isomers were also separately deaminated exactly as described by Stühmer and Frey. There was obtained on recrystallization of the product from 0.5 g. of "α"-amino alcohol, 0.1 g. of pure racemic 1,3-diphenyl-1,3-propanediol, m.p. 130–131°, and 0.05 g. of the *meso* isomer, m.p. 98–99°. These showed no depression of melting point on mixing with authentic samples.[2] The remainder of the material was an intractable gum showing evidence of unsaturation which was not further investigated. The "β"-isomer gave slightly more racemic diol (0.12 g.) and less of the *meso* form (0.01 g.) under the same conditions.

The deamination of both "α"- and "β"-1,3-diphenyl-3-amino-1-propanol was also carried out with 1.9-g. samples in 15 ml. of 1 *N* sulfuric acid. To this was added 1.2 g. of sodium nitrite in 7 ml. of water and the mixture was steam distilled and benzaldehyde isolated from the steam distillate as the 2,4-dinitrophenylhydrazone. The yields are given in Table I.

A deamination was carried out on a large scale with 11.2 g. of the more available "β"-1,3-diphenyl-3-aminol-1-propanol in 150 ml. of 50% acetic acid. The mixture was worked up as above by ether extraction and a careful fractional distillation carried out. Most of the styrene apparently had polymerized or did so during the distillation as only 0.2 g. of pure styrene, b.p. 83–84° at 40 mm., $n^{25}\text{D}$ 1.5441, was obtained. The identity of this fraction was established by comparison of its infrared spectrum with that of pure styrene. Benzaldehyde was isolated by steam distillation of the residue after removal of the styrene fraction, yield 12%.

In order to convert any 1,3-diphenyl-3-propene-1-ol that might have been formed to 1,3-diphenyl-1-propanone[22] the residue from steam distillation of benzaldehyde was boiled with 20% alcoholic potassium hydroxide for 5 hr. On cooling, pouring into water and extracting with ether, there was obtained from the ether extract an oil which crystallized and on recrystallization from benzene–petroleum ether yielded 9.2 g. of a mixture of the diastereomeric 1,3-diphenyl-1,3-propane diols, m.p. 115–118°, showing the infrared absorption pattern and solubilities expected of these compounds; no carbonyl absorption bands appeared. An attempt was made to isolate any carbonyl compounds from the mother liquors of this recrystallization, but only a small amount (0.06 g.) of a semicarbazine, m.p. 141–143°, could be isolated. The melting point of 1,3-diphenyl-1-propanone semicarbazone is reported[23] as 144°.

α,α,γ,γ-Tetraphenylbutyrolactone (X).—α,α-Diphenyl succinamic acid methyl ester was prepared from 7.0 g. of the acid by action of diazomethane in dry ether. To the ether solution was added a solution of phenylmagnesium bromide prepared from 17.3 g. of bromobenzene in 100 ml. of dry ether. After standing 1 hr. at room temperature, the mixture was decomposed with cold ammonium chloride solution and worked up in the usual way by ether extraction. There was obtained, after three recrystallizations from ethanol, 7.1 g. (72%) of a crystalline product, m.p. 197–198°. The analysis and infrared absorption at 5.65 μ leads to the assignment of the α,α,γ,γ-tetraphenylbutyrolactone structure to this substance.

Anal. Calcd. for $C_{28}H_{22}O_2$: C, 86.12; H, 5.88. Found: C, 86.19; H, 5.73.

NEW HAVEN, CONN.

---

[21] A. McKenzie and A. C. Richardson, *ibid.*, 79 (1923).

[22] H. Burton and C. K. Ingold, *ibid.*, 907 (1928).

[23] C. W. Shoppee, *ibid.*, 2571 (1928).