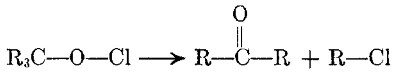
Stereochemistry of the Decomposition of 1,1-Dimethyl-2-phenylpropyl Hypochlorite[1]

Donald B. Denney and William F. Beach

Received June 18, 1958

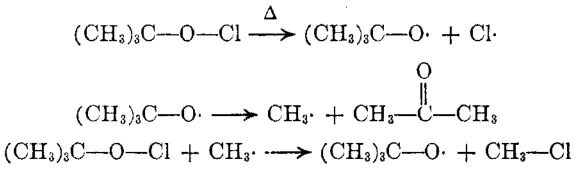
The decomposition of tertiary alkyl hypochlorites proceeds in the following manner:



$$R_3C—O—Cl \longrightarrow R—\overset{\displaystyle O}{\overset{\|}{C}}—R + R—Cl$$

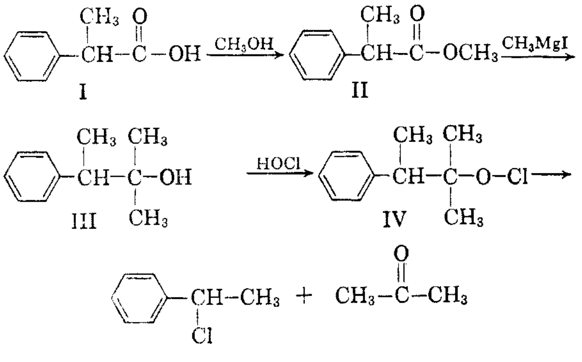
The reaction has considerable synthetic value as has been pointed out by Cairns and Englund.[2]

The gas phase decomposition of *t*-butyl hypochlorite has been studied by Yoffe[3], and he has suggested the following mechanism:



$$(CH_3)_3C—O—Cl \xrightarrow{\Delta} (CH_3)_3C—O\cdot + Cl\cdot$$
$$(CH_3)_3C—O\cdot \longrightarrow CH_3\cdot + CH_3—\overset{\displaystyle O}{\overset{\|}{C}}—CH_3$$
$$(CH_3)_3C—O—Cl + CH_3\cdot \longrightarrow (CH_3)_3C—O\cdot + CH_3—Cl$$

It seemed possible that some of the alkyl halide might be formed by an intramolecular process similar to that found for the decomposition of some peroxides.[4] In order to investigate this point, it was decided to study the sterochemistry of the decomposition. An intramolecular decomposition would lead to optically active halide of retained configuration. The reaction sequence started with (−)-hydratropic acid (I), which was converted to (−)-methyl hydratropate (II). II was allowed to react with methylmagnesium iodide to afford the alcohol, III. A solution of III in carbon tetrachloride was allowed to react with hypochlorous acid to effect the conversion to the hypochlorite IV. Distillation of the carbon tetrachloride solution of IV afforded α-phenethyl chloride (V) and acetone, the expected products of the decomposition of IV.



The hydratropic acid used in this series had 47% of the possible optical activity. The α-phenethyl chloride isolated had 1.1% of the activity which could have been obtained by a stereospecific series of reactions. Although there may have been small amounts of racemization in the formation of II and III, the majority most probably occurred during the decomposition of III. Yoffe's mechanism predicts racemization during this reaction and these results support his mechanism.

The α-phenethyl chloride isolated from this reaction series had an observed rotation of + 0.69°. The alcohol, III, used in preparing the α-phenethyl chloride had an observed rotation of + 8.62°; all of the other compounds were levorotatory. If the rotation of the chloride is due to contamination by III, it must comprise 8% of the sample. A careful inspection of the infrared spectrum of the α-phenethyl chloride showed it to be identical to that of a known sample and it indicated that there was no III present.

It can be shown by a suitable combination of stereochemical data available in the literature[5] that (−)-hydratropic acid has the same absolute configuration as (+)-α-phenethyl chloride. This correlation shows that the small amount of optically active halide present is of the same configuration as the starting acid. This small amount of retention of configuration may have arisen by an intramolecular decomposition or by combination of an unracemized α-phenethyl radical and a chlorine atom in a solvent cage. It is clear though that the most favorable reaction path is not stereospecific and is best represented by Yoffee's mechanism.

EXPERIMENTAL

(−)-*Methyl hydratropate* (II). A solution of 47.0 g. (0.313 mole) of (−)-hydratropic acid, $[\alpha]^{21}_{D}$ −37.8° (lit.[6] $[\alpha]^{20}_{D}$ −81.10), in 190 ml. of methanol and 4 ml. of concentrated sulfuric acid was refluxed for 4 hr. Methanol, 145 ml., was removed by distillation and the residue was poured into 200 ml. of water. The ester was taken up in ether. The ether was extracted with a solution of potassium carbonate and then dried over anhydrous sodium sulfate. Distillation afforded 46.6 g. (87%) of (−)-methyl hydratropate, b.p. 71–75° (4.5 mm.), n^{25}_{D} 1.5012 (lit.[7] n^{18}_{D} 1.5008), α^{21}_{D} −44.5° (1 = 1 dm.).

Preparation of (+)-*1, 1-dimethyl-2-phenylpropan-1-ol* (III). To a solution of methylmagnesium iodide in ether prepared from 154 g. (1.085 mole) of methyl iodide and 26.4 g. (1.085 mole) of magnesium was added 44.5 g. (0.271 mole) of II in 100 ml. of dry ether. After the addition was completed, the reaction mixture was allowed to reflux for 2 hr. with stirring. The reaction mixture was treated with an aqueous ammonium chloride solution and then dried over

---

(1) Taken from a dissertation submitted by William F. Beach in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry, Rutgers, The State University.

(2) T. L. Cairns and B. E. Englund, *J. Org. Chem.*, **21**, 140 (1956).

(3) A. D. Yoffe, *Chem. & Ind.* (*London*), 963 (1954).

(4) C. Walling, *Free Radicals in Solution*, John Wiley and Sons, New York, N. Y., 1957, p. 501–503.

(5) W. Klyne, *Progress in Stereochemistry*, Butterworths Scientific Publications, London, 1954, p. 187.

(6) H. S. Raper, *J. Chem. Soc.*, 2557 (1923).

(7) A. Campbell and J. Kenyon, *J. Chem. Soc.*, 436 (1947).

sodium sulfate. Distillation afforded 44.7 g. (88%) of (+)-1, 1-dimethyl-2-phenylpropan-1-ol, b.p. 78–84° (5 mm.) n_D^{23} 1.5147 (lit.[7] n_D^{22} 1.5162), α_D^{23} +8.62° (1 = 1 dm.).

Preparation and decomposition of 1,1-dimethyl-2-phenylpropyl hypochlorite. A solution of 10.0 g. (0.0606 mole) of III in 50 ml. of carbon tetrachloride was stirred with 1200 ml. of 0.3 *M* hypochlorous acid solution[8] for 3 hr. at 0°. The yellowish-green carbon tetrachloride solution was separated, washed with water, and dried over calcium chloride. The carbon tetrachloride was removed under reduced pressure. The infrared spectrum of the carbon tetrachloride solution indicated the presence of a carbonyl compound, presumably acetone. The residue was distilled to yield 4.5 g. of material, b.p. 73–78° (11 mm.), n_D^{23} 1.5248, α_D^{26} +0.69° (1 = 1 dm.) (lit.[9] α_D^{25} 126°). The infrared spectrum of this material was identical to that of a known sample of α-phenethyl chloride.

SCHOOL OF CHEMISTRY
RUTGERS, THE STATE UNIVERSITY
NEW BRUNSWICK, N. J.

---

[8] R. Fort and L. Denivelle, *Bull. soc. chim. France*, **21**, 1104 (1954).

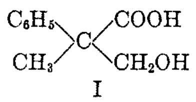
[9] R. L. Burwell, Jr., A. D. Shields, and H. Hart, *J. Am. Chem. Soc.*, **76**, 908 (1954).

A Convenient Synthesis of α-Methyltropic Acid

ALBERTO VECCHI AND GAETANO MELONE

Received June 24, 1958

A synthesis of α-methyltropic acid (I) has been recently reported by Zaugg and DeNet.[1]

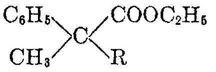


I

However, according to these authors, when α-phenylpropionic acid was treated with formaldehyde under the conditions of the Ivanov reaction, α-methyltropic acid was obtained in only trace amounts. Dimethyldiphenylsuccinic anhydride was the main end product, although yields were generally poor.

An attempted synthesis by the action of nitrous acid on ethyl β-amino-α-methyl-α-phenylpropionate[2] failed to give the expected compound, since rearrangement occurred with formation of α-benzyllactic acid.[3]

We have now ascertained that α-methyltropic acid may be prepared in reasonable yield through a way already described by Fusco and Testa for α-ethyltropic acid.[4] The starting compound was diethyl phenylmethylmalonate[5] (II), which was partially hydrolyzed to the monoester (III) in an alcohol solution of potassium hydroxide at room temperature. The monoester was then converted into the ester-chloride (IV) by reaction with thionyl chloride. Reduction of the acyl chloride with sodium borohydride gave the alcohol-ester (V), which was finally hydrolyzed to the free acid.



II. R = $COOC_2H_5$
III. R = COOH
IV. R = COCl
V. R = CH_2OH

The over-all yields ranged between 26 and 28%, based on the starting diethyl phenylmethylmalonate.

EXPERIMENTAL

Monoethyl phenylmethylmalonate (III). To a solution of 37.8 g. of potassium hydroxide in 250 ml. of water and 700 ml. of ethyl alcohol, 117.6 g. of diethyl phenylmethylmalonate was added quickly with stirring and the mixture was allowed to stand for about 100 hr. at room temperature. After this time hydrochloric acid was added to *p*H about 7.0, the ethyl alcohol was distilled off under reduced pressure, and the residue was diluted with an equal volume of water. After extraction with ethyl ether of some unreacted diethyl ester, the water layer was made acidic to *p*H 3–3.5 with hydrochloric acid. The separated oil was extracted with ethyl ether and the solvent removed *in vacuo;* the residue was sufficiently pure for the following step.

α-Phenyl-α-carbethoxypropionyl chloride (IV). The above crude ester (81 g.) was mixed cautiously with 81 ml. of thionyl chloride and refluxed for 2 hr. The excess thionyl chloride was then removed under reduced pressure. Distillation of the residue yielded 57.5 g. (66% based on the crude monoester) of IV, b.p. 135–136° (5 mm.).

Ethyl α-phenyl-α-hydroxymethylpropionate (V). To a well stirred suspension of 13.4 g. of sodium borohydride in 135 ml. of anhydrous dioxane a solution of 57.5 g. of IV in 250 ml. of anhydrous dioxane was added slowly in about 1 hr. Then the mixture was refluxed for 2.5 hr. on an oil bath. After cooling the mixture was cautiously poured into 500 ml. of ice water, taking care that the temperature did not exceed 25°. Hydrochloric acid was added to *p*H about 4, then the mixture was extracted with four 200-ml. portions of ethyl ether. The combined ether extracts were washed to neutral reaction and the solvent was removed *in vacuo*. The residue was distilled in a Claisen flask collecting at 130–132° (2 mm.); clear colorless oil. Yield 36 g. (72%).

α-Methyltropic acid (I). The above ester V (36 g.) was hydrolyzed by refluxing it for 5 hr. under rapid stirring with 720 ml. of 10% aqueous sodium hydroxide. After cooling the mixture was extracted with ethyl ether, the aqueous layer was made acidic to Congo red with hydrochloric acid, and the separated oil was extracted with ethyl ether. The solvent was removed *in vacuo* and the oily residue dissolved in equal volume of anhydrous benzene. The benzene solution was poured with stirring and cooling into 5 volumes of petroleum ether. An oil precipitated which crystallized after prolonged stirring and cooling. The white crystals were collected, washed with petroleum ether, and dried *in vacuo*. Yield 21.5 g. (70%); m.p. 86–87°.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.28; H, 6.80.

Acidimetric assay: 99%. The infrared spectrum was entirely consistent with the formula. After a further crystal-

---

[1] H. E. Zaugg and R. W. DeNet, *J. Org. Chem.*, **23**, 498 (1958).

[2] R. Foster and H. R. Ing., *J. Chem. Soc.*, 938 (1956).

[3] R. Foster and H. R. Ing., *J. Chem. Soc.*, 925 (1957).

[4] R. Fusco and E. Testa, *"Il Farmaco" Sci.*, **12**, 3 (1957).

[5] W. Wislicenus and K. Goldstein, *Ber.*, **28**, 815(1895).