of these, the corresponding 4-(*p*-diethylaminobenzylamino)-quinolines were obtained by hydrogenation of the azomethine double bond.

Three new azomethines of quinoline-4-aldehyde are also described; it was found that they resist acid hydrolysis.

A series of reactions is given for the preparation of 4-amino-7-methylquinoline from 7-methylquinoline.

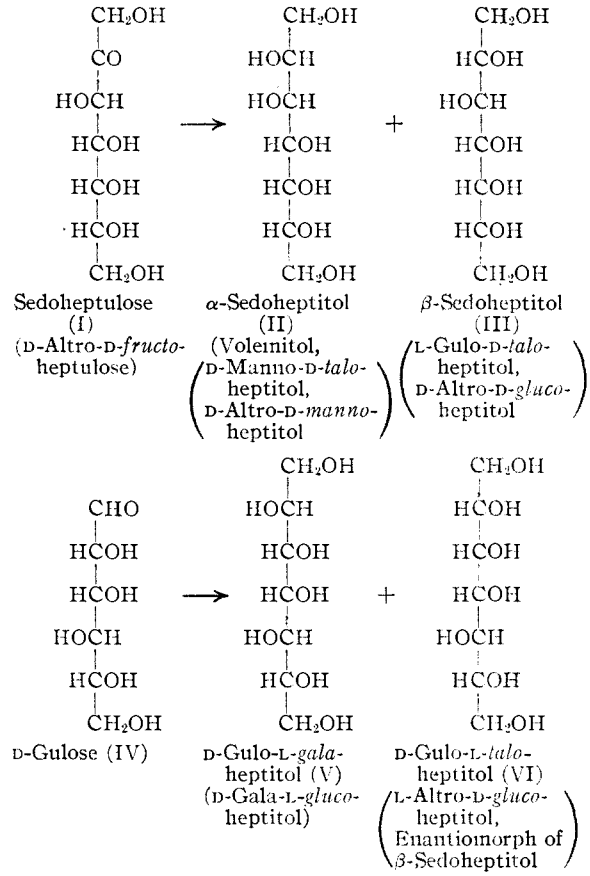
PITTSBURGH 13, PA. RECEIVED SEPTEMBER 7, 1946

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

L-Gulo-D-*talo*-heptitol (β-Sedoheptitol) and its Enantiomorph

BY ALICE T. MERRILL, W. T. HASKINS, RAYMOND M. HANN AND C. S. HUDSON

LaForge and Hudson[1] showed that the reduction of sedoheptulose, the seven-carbon ketose that occurs in the free state in *Sedum spectabile* Bor. and many related plants,[2] yields two heptitols which they named α- and β-sedoheptitol. It was found later[3] that α-sedoheptitol is identical with volemitol, a heptitol which occurs in the mushroom *Lactarius volemus* Fr. and in several species of *Primula*,[4] but the configuration of this heptitol remained unknown until Ettel[5] proved that volemitol (*syn.*, α-sedoheptitol) is D-manno-D-*talo*-heptitol (II). It then became evident that if the configuration of β-sedoheptitol could be determined, the configuration of sedoheptulose would become established. LaForge and Hudson[1] had reported that β-sedoheptitol melts at 127–128° and shows no rotation in water or in borax solution; these data did not correspond with the properties of any known heptitol, a fact which led LaForge[6] to synthesize the two D-guloheptitols from D-gulose (IV) through the epimeric D-guloheptoses. One D-guloheptitol proved to be identical with D-gala-L-*gluco*-heptitol and was therefore D-gulo-L-*gala*-heptitol (V); accordingly the other D-guloheptitol could be assigned the epimeric configuration that is represented by the name D-gulo-L-*talo*-heptitol (VI). LaForge reported that D-gulo-L-*talo*-heptitol melted at 128–129° and that it showed no rotation in borax solution, even though the configuration, which is unsymmetrical, represents a substance that should possess some rotatory power; its rotation seemed to be so small that it remained undetected. When Ettel proved that volemitol and α-sedoheptitol are D-manno-D-*talo*-heptitol it became evident to him from configuration II that β-sedoheptitol could not be LaForge's D-gulo-L-*talo*-heptitol (VI) but might be the enantiomorph, namely, L-gulo-D-*talo*-heptitol (III). The melting



points of these possible enantiomorphs were alike and if one of them fortuitously exhibited no detected rotation the other would also show no rotation under like conditions of observation. Ettel therefore concluded from LaForge's data that β-sedoheptitol is L-gulo-D-*talo*-heptitol and therefore that sedoheptulose has the configuration I. Conclusive and independent evidence that the ketose possesses this configuration was obtained subsequently by Richtmyer, Hann and Hudson[7] through the oxidative degradation of sedoheptulose to D-altronic acid, which was identified by its characteristic crystalline calcium salt. The work that is reported in the present article was undertaken for the purpose of deciding whether

(1) LaForge and Hudson, *J. Biol. Chem.*, **30**, 61 (1917).

(2) References concerning its wide occurrence in the *Crassulaceae* can be found in the review article by N. K. Richtmyer in "Advances in Carbohydrate Chemistry," Academic Press, Inc., New York, 1945, Vol. I, p. 47.

(3) LaForge, *J. Biol. Chem.*, **42**, 375 (1920); LaForge and Hudson, *ibid.*, **79**, 1 (1928).

(4) References concerning volemitol can be found in the review article by C. S. Hudson in "Advances in Carbohydrate Chemistry," Vol. I, p. 13 (1945).

(5) Ettel, *Collection Czechoslov. Chem. Commun.*, **4**, 504 (1932).

(6) LaForge, *J. Biol. Chem.*, **41**, 251 (1920).

(7) Richtmyer, Hann and Hudson, THIS JOURNAL, **61**, 343 (1939).

the older statements that β-sedoheptitol and D-gulo-L-*talo*-heptitol show no rotation should be revised; new data are required if a distinction between these enantiomorphs is to be established. If it should be possible to detect optical activity for these enantiomorphs, the values under like conditions of measurement should be equal in magnitude but opposite in sign. The first part of the research was performed several years ago by one of the authors (A.T.M.); it consists of a repetitoin of LaForge's synthesis of D-gulo-L-*talo*-heptitol from D-gulose. We have confirmed his value of its melting point (128–129°), but we find that the pure heptitol definitely possesses rotatory power, the value of $[\alpha]^{20}D$ being +0.95° (*c*, 4.5) in water and −4.6° (*c*, 3.5) in saturated borax solution.[8] The second part of the research was performed recently by a second author (W.T.H.); it deals with a repetition of the preparation of β-sedoheptitol by reduction of natural sedoheptulose (I) with sodium amalgam. This reduction of the ketose yielded as one product the α-sedoheptitol (II), which is unquestionably identical with natural volemitol and synthetic D-manno-D-*talo*-heptitol, as has been mentioned. The second product of the reduction of sedoheptulose was carefully purified through its crystalline benzylidene derivative, from which pure β-sedoheptitol was regenerated by acid hydrolysis. The pure heptitol melted at 128–129° and showed the rotation $[\alpha]^{20}D$ −0.75° (*c*, 4.10) in water and +4.3° (*c*, 4.08) in saturated borax solution, data[9] which establish that β-sedoheptitol is indeed L-gulo-D-*talo*-heptitol (III), the enantiomorph of the pure D-gulo-L-*talo*-heptitol (VI) that we have prepared from D-gulose (IV).

Having both enantiomorphs now available in pure condition, we have recently measured their rotations in an aqueous solution of ammonium molybdate and find the following $[\alpha]^{20}D$ values: D-gulo-L-*talo*-heptitol, −49.7°; L-gulo-D-*talo*-heptitol, +49.6°. These relatively large rotations of equal magnitude and opposite sign, confirm the enantiomorphous character of the two heptitols.

Experimental

D-Gulo-L-*gala*-heptonic and D-Gulo-L-*talo*-heptonic Phenylhydrazides.—The D-gulose sirup (equivalent to 106 g. of D-gulose) from the decomposition of 159 g. of D-gulose phenylhydrazone by benzaldehyde was converted to a mixture of the basic calcium salts of the epimeric D-gulo-L-*gala*-heptonic and D-gulo-L-*talo*-heptonic acids by the directions of Hudson, Hartley and Purves.[10] The solution (380 ml.) of free acids obtained by the decomposition of the calcium salts with sulfuric acid was heated with 32 ml. of acetic acid and 62 ml. of phenylhydrazine for four hours on the steam-bath; it was then diluted with 600 ml. of alcohol and allowed to cool to 25°. The precipitate which formed (32.2 g.) was separated by filtration and the filtrate was evaporated to a volume of 180 ml. and diluted with 200 ml. of hot alcohol. The precipitate (23.7 g.) which deposited from the solution on standing at 5° for eighteen hours was separated by filtration. Successive fractions of 25.0 g., 13.1 g. ($[\alpha]^{20}D$ +24.6°), 1.8 g. (+26.0°), 4.2 g. (+20.7°), 2.6 g. (−6.4°), 3.6 g. (+3.6°) and 37.0 g. (+10.1°) were obtained by progressive concentration and alcoholic precipitation of the filtrate. The total yield of D-guloheptonic phenylhydrazides was 143.2 g. (77%). The separation of D-gulo-L-*gala*-heptonic phenylhydrazide from D-gulo-L-*talo*-heptonic phenylhydrazide was based upon the relative insolubility of the former in 75% alcohol. In a typical fractionation, 50.5 g. of the combined first two fractions was dissolved in 12 parts of 75% alcohol; upon standing overnight at 25° nearly pure D-gulo-L-*gala*-heptonic phenylhydrazide (27.0 g.; m.p. 192–193°; $[\alpha]^{20}D$ −10.7° in water) crystallized; successive fractions obtained by concentration, dilution with alcohol, and filtration were 7.3 g. rotating −5.2°, 5.2 g. rotating −4.1°, 4.1 g. rotating +9.1°, showing increased concentration of D-gulo-L-*talo*-heptonic phenylhydrazide, and a final fraction of 3.5 g. of relatively pure D-gulo-L-*talo*-heptonic phenylhydrazide rotating +25.8°. By similar and repeated fractionation of the total yield of D-guloheptonic phenylhydrazides it was possible to isolate 66.4 g. (36%) of D-gulo-L-*gala*-heptonic phenylhydrazide and 62.5 g. (34%) of the epimeric D-gulo-L-*talo*-heptonic phenylhydrazide. The epimeric heptonic acids were thus obtained in approximately equal amounts in this cyanohydrin synthesis from gulose; in this respect the behavior of gulose resembles that of ribose, from which allonic and altronic acids are obtained in nearly equal amounts.

The D-gulo-L-*gala*-heptonic phenylhydrazide was readily purified by recrystallization from 12 parts of 75% alcohol. Its melting point varied somewhat with the rate of heating, but upon rapid heating it melted at 193–194°; it showed a specific rotation $[\alpha]^{20}D$ −11.2° in aqueous solution (*c*, 1.0).[11] LaForge[6] reported a melting point of 191–192° and a specific rotation of $[\alpha]^{20}D$ −15.38° in water (*c*, 8.3).

Anal. Calcd. for $C_{13}H_{20}O_7N_2$: C, 49.36; H, 6.37; N, 8.86. Found: C, 49.26; H, 6.37; N, 8.75.

The D-gulo-L-*talo*-heptonic phenylhydrazide was recrystallized from 6 parts of 75% alcohol. The pure substance melted at 156–157° and rotated $[\alpha]^{20}D$ +31.4° in aqueous solution (*c*, 1.2). Isbell[12] reported a melting point of 156° and a rotation $[\alpha]^{20}D$ +29.3° in water (*c*, 1.98). The directions of rotation of the epimeric phenylhydrazides agree with the phenylhydrazide rule of rotation.

Anal. Calcd. for $C_{13}H_{20}O_7N_2$: C, 49.36; H, 6.37; N, 8.86. Found: C, 49.28; H, 6.42; N, 8.85.

D-Gulo-L-*talo*-heptonic Lactone from D-Gulo-L-*talo*-heptonic Phenylhydrazide.—A solution of 12.2 g. of D-gulo-L-*talo*-heptonic phenylhydrazide and 10.6 g. (1.1 molecular equivalents) of copper sulfate pentahydrate in 500 ml. of water was boiled under a reflux condenser for five hours.[13] The reaction mixture was filtered to remove precipitated copper (2.0 g.), the filtrate was treated with hydrogen sulfide to remove excess copper and the copper-free solution was freed of sulfuric acid with the quantitative amount of barium hydroxide. The resulting solution was evaporated in a porcelain dish on the steam-bath to a crystalline mass of D-gulo-L-*talo*-heptonic lactone. The yield was 7.1 g. (89%).

D-Gulo-L-*talo*-heptitol.—The sirupy sugar that was obtained by the sodium amalgam reduction of 7.1 g. of D-

(8) These data were mentioned by one of us (C. S. H.) on p. 11 of ref. 4.

(9) It has been indicated that the measurements of rotation were made in the case of D-gulo-L-*talo*-heptitol by one of the authors (A. T. M.) several years ago and for the enantiomorphous β-sedoheptitol recently by another (W. T. H.). We regard the respective values for the enantiomorphs as equal in magnitude within the limits of error.

(10) Hudson, Hartley and Purves, THIS JOURNAL, **56**, 1248 (1934).

(11) All the crystalline compounds that are described were recrystallized to constant melting point and specific rotation $[\alpha]^{20}D$; *c* is the concentration in grams in 100 ml. of solution; the tube length was 4 dm. The melting points were determined with the stem of the thermometer immersed in the heated bath.

(12) Isbell, *J. Research, Natl. Bur. Standards*, **19**, 648 (1937).

(13) Hann and Hudson, THIS JOURNAL, **56**, 957 (1934).

gulo-L-*talo*-heptonic lactone was transferred to a bomb with 35 ml. of water and the solution was agitated for six hours at 98° with Raney nickel and hydrogen under a pressure of 133 atmospheres. The catalyst was removed by filtration and the filtrate was concentrated *in vacuo* to a dry residue, which was partially extracted with 50 ml. of hot alcohol. The D-gulo-L-*talo*-heptitol (2.7 g., m. p. 128–129°), which deposited from the extract as it cooled in the form of small, hard prisms, was recrystallized from 35 parts of alcohol and it melted at 127–129° and rotated +0.95° in aqueous solution (*c*, 4.54) and −4.6° in saturated aqueous borax solution (*c*, 3.54). LaForge[6] reported his D-gulo-L-*talo*-heptitol as melting at 128–129° and stated that it showed no rotation in borax solution. The undissolved portion of the residue (1.5 g.) was dissolved in 35 parts of alcohol and yielded a further 1.1 g. of pure D-gulo-L-*talo*-heptitol to make the total yield 3.8 g. (53%).

Anal. Calcd. for $C_7H_{16}O_7$: C, 39.62; H, 7.60. Found: C, 39.64; H, 7.46.

Sodium Amalgam Reduction of Sedoheptulose.—Thirty grams of a purified sedoheptulose sirup (prepared essentially by the method of LaForge and Hudson[1]) from 1200 g. of fresh *Sedum spectabile*, was dissolved in 150 ml. of water and reduced with sodium amalgam. The reduction was slow, much amalgam was required, and it was necessary at intervals to remove the accumulated sodium sulfate in the usual manner through precipitation with alcohol and removal of the alcohol by distillation *in vacuo*. Mechanical stirring for several days at 0° was necessary. The results from several such experiments showed that the yields of α- and β-sedoheptitols were nearly the same whether the reduction was carried out under mild acid or alkaline conditions. The final solution, which still reduced Fehling solution slightly, was concentrated under reduced pressure until sodium sulfate started to crystallize and then poured into one liter of alcohol; the precipitated salt was removed by filtration and the filtrate was concentrated to a dry sirup. This reduced sirup was mixed with 20 ml. of 90% alcohol and seeded with α-sedoheptitol (II); crystallization was fairly rapid and after standing three days at 5° the solid was removed by filtration and washed with 90% alcohol; the filtrate and washings were reserved for the preparation of tribenzylidene-β-sedoheptitol. The crude heptitol was recrystallized from 20 parts of 85% alcohol and gave nearly pure volemitol (α-sedoheptitol) melting at 147–150°; the yields were somewhat variable (5–9 g.). Two additional recrystallizations from the same solvent gave pure volemitol which melted at 152–153° and rotated +2.15° in aqueous solution (*c*, 4.0). Acetylation of the pure heptitol with acetic anhydride and fused sodium acetate in the usual way gave volemitol heptaacetate, m. p. 63–64°, and rotation +36.1° in chloroform solution (*c*, 0.82).[14]

Tribenzylidene-β-sedoheptitol.—(1) The filtrate from the α-sedoheptitol crystallization was concentrated *in vacuo* to a dry sirup which was dissolved in an equal volume of cold 70% sulfuric acid and there was added a volume of benzaldehyde equal to that of the sulfuric acid; upon shaking for a few minutes, the mixture set to a pasty mass and, after standing eighteen hours at room temperature, 50 ml. of ice-cold water was added and the solid removed by filtration and washed with dilute sodium bicarbonate solution, water, alcohol and ether. The yield was 6–12 g. of material, m. p. 150–160°. The crude benzylidene compound was refluxed for two hours with 100 parts of alcohol, which dissolved only a portion of it; the mixture was cooled and the solid recovered by centrifugation (4–8 g., m. p. 170–175°). This solid material was then recrystallized three times from 200 parts of methyl ethyl ketone and gave pure tribenzylidene-β-sedoheptitol (3–6 g.) which melted at 274–275° with slight darkening and rotated −22.5° in pyridine solution (*c*, 0.40). LaForge and Hudson[1] reported the m. p. of their pure tribenzylidene-β-sedoheptitol as 272–275°.

(14) Maclay, Hann and Hudson, *J. Org. Chem.*, **9**, 293 (1944), reported the m. p. of volemitol (α-sedoheptitol) as 153–154° and for its acetate m. p. 63°, $[\alpha]^{20}D$ +36.1° in chloroform solution (*c*, 2.0).

Anal. Calcd. for $C_{28}H_{28}O_7$: C, 70.57; H, 5.92. Found: C, 70.52; H, 5.85.

Concentration of the combined alcoholic extraction solution and the mother liquors from the methyl ethyl ketone recrystallizations to a sirup, followed by treatment with 70% sulfuric acid and benzaldehyde in the manner previously described, gave an additional 1–2 g. of the pure tribenzylidene compound.

(2) Starting with 2.0 g. of pure β-sedoheptitol, 5 ml. of 50% sulfuric acid and 5 ml. of benzaldehyde and following the above procedure, the same tribenzylidene compound was obtained in a yield of 3.4 g. (79%); it melted at 274–275° and rotated −22.3° in pyridine solution (*c*, 0.41).

We have not prepared the enantiomorphous tribenzylidene-D-gulo-L-*talo*-heptitol for lack of sufficient material, but it is not to be doubted that it can be made similarly and that it will show the same melting point and the same magnitude of rotation in pyridine in the opposite (*i. e.*, positive) direction.

β-Sedoheptitol (III).—Preliminary tests to determine the optimal conditions for the removal of the benzylidene groups from tribenzylidene-β-sedoheptitol showed that although the compound dissolved in boiling 60% acetic acid in about one hour, hydrolysis was not complete in twelve hours. Refluxing with 1.0 *N* sulfuric acid for eight hours produced no apparent reduction in the amount of undissolved benzylidene compound, but upon increasing the acid concentration to 2.0 *N* complete solution was obtained in six hours and a yield of 56% of β-sedoheptitol could be isolated. The best results were obtained by stepwise hydrolysis in the following manner. A suspension of 14 g. of tribenzylidene-β-sedoheptitol (m. p. 274–275°) was refluxed with 250 ml. of 60% acetic acid for three hours, and the reaction mixture was concentrated *in vacuo* to a thick sirup which was dissolved in 100 ml. of 0.1 *N* sulfuric acid, and the solution refluxed for five hours; the cooled solution was extracted with three 50-ml. portions of ether to remove the benzaldehyde, and the sulfuric acid was removed by the addition of an equivalent amount of saturated barium hydroxide solution; the filtered solution was concentrated *in vacuo* to a thin sirup which was dissolved in 50 ml. of warm alcohol; upon cooling the solution the product crystallized in a yield of 5.4 g. (87%). The heptitol was recrystallized from its solution in 1.5 parts of warm water by the addition of 10 parts of warm alcohol; it forms thick prisms which melted at 128–129° and rotated −0.75° in aqueous solution (*c*, 4.10) and +4.3° in saturated borax solution (*c*, 4.08), in good agreement with the values previously described for its enantiomorph. When the melting points of the enantiomorphs were measured simultaneously the value 128–129° was observed for both.

Rotations in the Presence of Ammonium Molybdate.—It is known[15] that in aqueous solutions containing molybdate ions the rotatory power of many polyhydric alcohols is greatly increased, the values for some alcohols being much larger than those in borax solutions. We find the following values for $[\alpha]^{20}D$ in an aqueous solution containing five per cent. of ammonium molybdate tetrahydrate (Mallinckrodt analytical reagent $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$): D-gulo-L-*talo*-heptitol, −49.7° (*c*, 0.4180); β-sedoheptitol (*syn.*, L-gulo-D-*talo*-heptitol), +49.6° (*c*, 0.4188); volemitol (*syn.*, D-manno-L-*talo*-heptitol), +57.0° (*c*, 0.41); D-mannitol, +16.9° (*c*, 0.41). The readings were observed in a 4-dm. tube and were −0.831 and +0.831 circular degrees, respectively, for the enantiomorphs. Their enantiomorphous character is very evident from these large and oppositely directed rotations of equal magnitude.

Summary

The records from the older literature indicate that β-sedoheptitol and D-gulo-L-*talo*-heptitol have the same melting point (127–129°) and that neither of them exhibits optical rotatory power. Later researches, which established the configura-

(15) Gernez, *Compt. rend.*, **112**, 1360 (1891).

tion of sedoheptulose, have made it almost certain that β-sedoheptitol is L-gulo-D-*talo*-heptitol, the enantiomorph of D-gulo-L-*talo*-heptitol. The older record of absence of rotation for both substances is not compatible with the view that they are enantiomorphs unless it be inferred that their rotations are so very low as to have escaped detection in the past. Since it must be assumed on theoretical grounds that optical activity of enantiomorphs should always be detectable by some method of observation, the two alcohols have been prepared again and carefully purified. The pure substances show the following properties: β-sedoheptitol, m.p. 128–129°, $[\alpha]^{20}D$ −0.75° (water), +4.3° (borax solution), +49.6° (molybdate solution); D-gulo-L-*talo*-heptitol, m.p. 128–129°, $[\alpha]^{20}D$ +0.95° (water), −4.6° (borax solution), −49.7° (molybdate solution). They have the same melting point and under comparable conditions they exhibit rotations which are equal in magnitude within the limits of measurement and are opposite in sign, as is to be expected for enantiomorphs. β-Sedoheptitol is L-gulo-D-*talo*-heptitol.

BETHESDA, MARYLAND RECEIVED AUGUST 28, 1946

[CONTRIBUTION FROM THE THOMPSON LABORATORY OF THE PHILLIPS EXETER ACADEMY]

o-Chlorophenylbenzoylacetylene

BY CHARLES L. BICKEL

A recent paper from this Laboratory described the preparation of *o*-chlorodibenzoylmethane by the reaction of alcoholic potassium hydroxide with the dibromide of *o*-chlorobenzalacetophenone.[1] The action of bases on α,β-dibromo ketones gives a variety of products and has been carefully studied by a number of investigators.[2] In no case, however, has an acetylenic ketone been obtained as a product of these reactions. In 1904, Watson[3] attempted without success to prepare phenylbenzoylacetylene from benzalacetophenone dibromide and also from α-bromobenzalacetophenone. From the dibromide he obtained β-ethoxybenzalacetophenone (a product one would expect) and from α-bromobenzalacetophenone he reported products which were presumably formed by the cleavage of the acetylenic ketone.

When the present author prepared *o*-chlorodibenzoylmethane for the first time, the residual oil, obtained by treating *o*-chlorobenzalacetophenone dibromide with alcoholic potassium hydroxide and by removing β-methoxy-*o*-chlorobenzalacetophenone, deposited a small amount of a substance which was not further investigated at the time. Subsequent analyses indicated that the substance was *o*-chlorophenylbenzoylacetylene, I. The reactions of the compound confirm this structure.

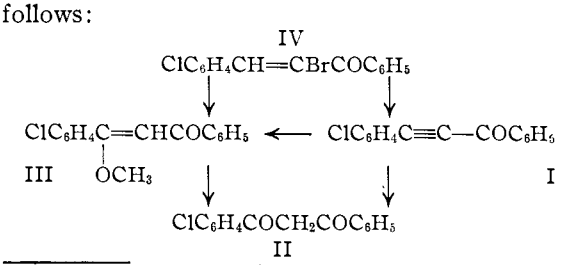
Compound I is converted quantitatively into *o*-chlorodibenzoylmethane II by the action of concentrated sulfuric acid followed by treatment with iced water, a method used by Nef,[4] Moureu[5] and Fuson[6] to confirm the structure of acetylenic ketones. Compound I adds methyl alcohol in an alcoholic solution of potassium hydroxide to give β-methoxy-*o*-chlorobenzalacetophenone III as the only product. The addition of alcohols to acetylenic ketones had previously been reported by Moureu and Brachin,[7] who found that phenylbutyrylacetylene and phenylpropionylacetylene gave addition products with ethyl alcohol in the presence of sodium ethylate.

Preparation of the acetylenic ketone I from a known substance was finally achieved by the removal of the elements of hydrogen bromide from α-bromo-*o*-chlorobenzalacetophenone IV, using potassium hydroxide in a mixture of acetone and water. The acetylenic ketone is the only product so far isolated from this reaction; there is no evidence of cleavage.

Moureu and Delange[8] found that phenylbenzoylacetylene is cleaved by alcoholic potassium hydroxide, giving acetophenone and potassium benzoate as products. *o*-Chlorophenylbenzoylacetylene reacts with alcoholic potassium hydroxide, but the reaction is one of addition rather than cleavage.

Watson[3] found that α-bromobenzalacetophenone reacted with solid potassium hydroxide, giving cleavage products. The *o*-chloro analog behaves similarly at the temperature of the water-bath, but is apparently unaffected when an ether solution of the compound is left in contact with solid potassium hydroxide for twenty-four hours.

The above transformations are summarized as follows:



(1) Bickel, THIS JOURNAL, **68**, 865 (1946).

(2) Kohler and Addinall, *ibid.*, **52**, 3728 (1930). This paper summarizes the action of bases on α,β-dibromo ketones and cites the most important references.

(3) Watson, *J. Chem. Soc.*, **85**, 1319 (1904).

(4) Nef, *Ann.*, **308**, 275 (1899).

(5) Moureu and Delange, *Bull. soc. chim.*, **25**, 303 (1901).

(6) Fuson, Ullyot and Hickson, THIS JOURNAL, **61**, 410 (1939).

(7) Moureu and Brachin, *Bull. soc. chim.*, **33**, 131 (1905).

(8) Moureu and Delange, *Compt. rend.*, **130**, 1259 (1900).