Synthesis of β-Methoxy-β-(*p*-nitrophenyl)-α-phenylacrylonitrile.—A solution of 10 g. (0.066 mole) of *p*-nitrobenzaldehyde and 12.2 g. (0.066 mole) of the sodium salt of phenylnitroacetonitrile in 200 cc. of methanol was refluxed for fourteen hours. The solution turned red and a copious precipitate formed as the reaction progressed. The mixture was cooled and filtered, and the crystalline mass was washed with cold methanol. Recrystallization from glacial acetic acid gave 13.5 g. (73%) of β-methoxy-β-(*p*-nitrophenyl)-α-phenylacrylonitrile in the form of long yellow needles melting at 176–177°. There was no depression of the melting point when the compound was mixed with the product from the reaction of *p*-nitrobenzyl chloride and the sodium salt of phenylnitroacetonitrile. The nitrile is only slightly soluble in ether, methanol, ethanol, and glacial acetic acid; it is somewhat more soluble in benzene and acetone. When exposed to the light, it turns light brown during the course of a week.

Action of *p*-Nitrobenzyl Bromide on the Silver Salt of Phenylnitroacetonitrile.—A mixture of 26.9 g. (0.10 mole) of the silver salt, 21.6 g. (0.10 mole) of *p*-nitrobenzyl bromide, and 80 cc. of dry benzene was refluxed with stirring for sixteen hours. The insoluble salts were then removed by filtration, washed with benzene, and dried *in vacuo*. Their total weight (20.2 g.) showed that complete conversion of the original silver salt into silver bromide had not occurred. The red benzene filtrate was concentrated by distillation, and the residue dissolved in alcohol. The solution deposited on cooling in an ice and salt mixture 0.1 g. of a light brown solid, which, after filtration and crystallization from methanol, melted at 174–175°. The analytical data agreed with the composition of 1,2-dicyano-1,2-dinitro-1,2-diphenylethane.

Anal. Calcd. for $C_{16}H_{10}O_4N_4$: C, 59.63; H, 3.13. Found: C, 59.89; H, 3.09.

The alcohol was removed by evaporation, the residue taken up in chloroform, and the solution extracted with a solution of sodium hydroxide. From the alkaline extract there was obtained by acidification and crystallization of the resulting precipitate from water 12.4 g. (0.0085 mole) of benzoyl cyanide oxime, while from the chloroform solution it was possible to isolate through the bisulfite addition product 12.2 g. (0.0081 mole) of *p*-nitrobenzaldehyde. The residual oil was found to contain 2.4 g. of unchanged *p*-nitrobenzyl bromide.

Summary

1. Benzyl chloride and *p*-cyanobenzyl chloride reacted in ethanol with the sodium salt of phenylnitromethane to yield the decomposition products of the nitronic esters formed by O-benzylation. When *p*-nitrobenzyl chloride and 2,4-dinitrobenzoyl chloride were used, C-benzylation likewise occurred, giving 1-nitro-2-(*p*-nitrophenyl)-1-phenylethane (36.8%) and 2,4-dinitrostilbene (46.6%) respectively. No reaction took place between *p*-nitrobenzyl chloride and the mercury derivative.

2. The action of benzyl chloride and of *p*-nitrobenzyl chloride on the sodium salt of phenylnitroacetonitrile in methanol solution and of *p*-nitrobenzyl bromide on a suspension of the silver compound in benzene gave only products resulting from intermediate nitronic ester formation.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

cis-Traumatic Acid and Related Compounds

BY WALTER M. LAUER AND WALTER J. GENSLER*

Traumatic acid, 1-decene-1,10-dicarboxylic acid (I, $n = 8$), has been isolated from string bean pods by English, Bonner and Haagen-Smit and

$$\underset{\text{I}}{\mathrm{HOOCCH{=}CH(CH_2)_nCOOH}} \qquad \underset{\text{II}}{\mathrm{HOOC(CH_2)_nCOOH}}$$

$$\underset{\text{III}}{\mathrm{HOOCCH_2CH{=}CH(CH_2)_7COOH}}$$

has been demonstrated to be active as a plant hormone.[1] In addition, related compounds such as 1,10-decanedicarboxylic acid (II, $n = 10$), sebacic acid (II, $n = 8$),[1a] 1-nonene-1,9-dicarboxylic acid (I, $n = 7$), 1-tridecene-1,13-dicarboxylic acid (I, $n = 11$) and 2-decene-1,10-dicarboxylic acid (III)[2] were shown to possess similar activity but to a lesser degree than traumatic acid. A synthesis of traumatic acid, which led to a product that was identical with the naturally occurring plant wound hormone, was accomplished by these same investigators by condensing the half aldehyde of sebacic acid with malonic acid in the presence of pyridine. The condensation of an aldehyde with malonic acid in the presence of pyridine has been shown to yield *trans* products in the cases of glyoxylic acid,[3a] benzaldehyde[3b] and acetaldehyde.[3c] Consequently, it is presumed that the naturally occurring traumatic acid is the *trans* form.

Biological systems show a high degree of specificity. An example which involves *cis–trans* isomers has been reported by Quackenbush, Platz and Steenbock.[4] These investigators demonstrated that although ethyl linoleate was active in curing acute dermatitis in rats in daily doses of one-half drop, the ethyl ester of elaidinized linoleic acid was inactive at a level of one drop daily.

In view of these considerations, the synthesis of the *cis* form of 1-decene-1,10-dicarboxylic acid

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[*] Abstract of Ph.D. thesis submitted August, 1942.

[1] (a) English, Bonner and Haagen-Smit, THIS JOURNAL, **61**, 3434 (1939); (b) English, Bonner and Haagen-Smit, *Science*, **90**, 329 (1939); English and Bonner, *J. Biol. Chem.*, **121**, 791 (1937); Bonner and English, *Plant Physiol.*, **13**, 331 (1938); English, Bonner and Haagen-Smit, *Proc. Nat. Acad. Sci.*, **25**, 323 (1939); Bonner and English, *Science*, **86**, 352 (1937).

[2] English, THIS JOURNAL, **63**, 941 (1941).

[3] (a) Doebner, *Ber.*, **34**, 53 (1901); (b) Knoevenagel, *ibid.*, **31**, 2602 (1898); Stoermer and Heymann, *ibid.*, **45**, 3099 (1912); (c) von Auwers and Wissenbach, *ibid.*, **56**, 715 (1923); Letch and Linstead, *J. Chem. Soc.*, 455 (1932).

[4] Quackenbush, Platz and Steenbock, *J. Nutrition*, **17**, 115 (1939).

was projected and completed.[5] An outline of the transformations which were involved follows.

$$CH_2BrCHBr(CH_2)_8COOH \longrightarrow \underset{IV}{HC{\equiv}C(CH_2)_8COOH} \longrightarrow \underset{V}{HOOCC{\equiv}C(CH_2)_8COOH} \longrightarrow \underset{cis,\ I}{HOOCCH{=}CH(CH_2)_8COOH}$$

Dehydrobromination of the bromine addition product of undecylenic acid was carried out either with alcoholic potassium hydroxide according to the method of Krafft[6] or more advantageously with sodamide in liquid ammonia. The disodium derivative of 1-decyne-10-carboxylic acid (IV) was prepared in liquid ammonia by means of sodamide. After replacement of the liquid ammonia with dry ether, carbonation with solid carbon dioxide produced 1-decyne-1,10-dicarboxylic acid (V).

Experiments on the semihydrogenation of V to I were carried out under one atmosphere of hydrogen using the following catalysts: palladium on starch,[7] palladium on calcium carbonate, palladium on barium sulfate, Raney nickel, and palladium on polyvinyl alcohol.[8] In all of these experiments the saturated compound (II, $n = 10$) was always present in the hydrogenation mixture along with the desired *cis*-olefinic acid. In no case was the *trans* compound, traumatic acid, detected. The last traces of the saturated compound were very difficult to remove, but by a process of fractional crystallization and fractional adsorption, *cis*-traumatic acid (I) was finally obtained pure.

The melting point of pure *cis*-traumatic acid was found to be 67–68°, which value is about 100° lower than that reported for traumatic acid (m. p. 165–166°). That the material has the structure assigned was shown by hydrogenating it to 1,10-decanedicarboxylic acid, (II, $n = 10$), and by cleaving it to sebacic acid by oxidation. The *cis* configuration was assigned by analogy with a large body of work which has shown that the catalytic half-hydrogenation of carbon to carbon triple bonds under controlled conditions results in the *cis* configuration of the ethylenic link formed.[7,9] To render less likely the possibility that the *cis*-traumatic acid was isomorphic instead of geometrically isomeric with traumatic acid, it was shown that the di-*p*-phenylphenacyl ester of *cis*-traumatic acid was different in melting point from the same ester of traumatic acid.

The diacetylenic hydrocarbon, 1,9-decadiyne (VI), was also treated with sodamide in liquid ammonia, and the resulting disodium derivative carbonated in dry ether with a large excess of crushed solid carbon dioxide.

$$\begin{tikzcd}
\underset{VI}{HC{\equiv}C(CH_2)_6C{\equiv}CH} \arrow[r] \arrow[dr] & VII\ \ HOOCC{\equiv}C(CH_2)_6C{\equiv}CCOOH \\
 & VIII\ \ HOOCC{\equiv}C(CH_2)_6C{\equiv}CH
\end{tikzcd}$$

The carbonation product contained the monobasic acid, 1,9-decadiyne-1-carboxylic acid (VIII), as well as the dicarboxylic acid (VII), and unreacted hydrocarbon.

The structure of VII was established by oxidation to suberic acid and by hydrogenation to 1,10-decanedicarboxylic acid. The 1,9-decadiyne-1-carboxylic acid was also cleaved to suberic acid by oxidation.

Experimental

1-Decyne-10-carboxylic Acid (IV).—The highest yield obtained in several experiments on the dehydrobromination of undecylenic acid dibromide[10] with alcoholic potassium hydroxide[6,11] was 49%; usually it was 30% or lower. Dehydrobromination with sodamide in liquid ammonia was found to be more satisfactory.

A 3-liter, three-necked flask was equipped with an efficient stirrer (glycerol seal) and a solid carbon dioxide cold finger reflux condenser having a moisture protected outlet. With the condenser empty, liquid ammonia (1.5 liters) was added to the flask. Stirring was started and a clean piece of sodium about the size of a pea was added to the ammonia followed by finely divided ferric nitrate (0.5 g. of $Fe(NO_3)_3 \cdot 9H_2O$).[12] The ferric nitrate should be added in one portion so that the material enters the liquid as quickly as possible. If ammonia vapors reach the crystals, the color changes and the solid tends to liquefy. The use of too large a portion of sodium here should be avoided, for as soon as the ferric nitrate is added, vigorous boiling and a strong evolution of gas accompanied by an immediate discharge of the blue color occurs. The above procedure yielded a very active catalyst for the conversion of sodium to sodamide.

The remainder of the sodium (total amount 27.2 g., 1.18 gram atoms) was added in small pieces during the course of twenty minutes and the solution was stirred for an additional thirty minutes. Finally 10,11-dibromoundecanoic acid (from 50.0 g. of undecylenic acid) dissolved in a small amount of absolute ether, was added over a period of about ten minutes. The condenser finger was then filled with a slush of methanol and solid carbon dioxide and the reaction mixture was stirred for six hours. After an additional five hours of stirring, during which time there was no refrigerant in the condenser and the ammonia evaporated, the reaction mixture was allowed to stand overnight.

Absolute ether was added to the dry, gray-colored solid in the flask and a cold concentrated aqueous ammonium chloride solution was then added with stirring. More water was added and stirring was continued until all the lumps were broken up. The whole mixture was filtered through a layer of Hyflo to remove any solid and after removing the organic layer from the filtrate, the water solution was washed once with ether.

The water solution containing the sodium salt of the

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(5) The results of a biochemical study of this material will be described separately by Professor Bonner.

(6) Krafft, *Ber.*, **29**, 2232 (1896).

(7) Bourguel, *Bull. soc. chim.*, [4] **41**, 1443 (1927); [4] **45**, 1067 (1929).

(8) Rampino and Nord, THIS JOURNAL, **63**, 2745, 3268 (1941); Taylor and Shenk, *ibid.*, **63**, 2756 (1941).

(9) Johnson and Johnson, *ibid.*, **62**, 2615 (1940); Zal'kind, *ibid.*, **63**, 2282 (1941); Johnson, *ibid.*, **63**, 2282 (1941); Campbell and Eby, *ibid.*, **63**, 216 (1941); Sherrill and Launspach, *ibid.*, **60**, 2562 (1938); Campbell and O'Conner, *ibid.*, **61**, 2897 (1939); Paal and Hartmann, *Ber.*, **42**, 3930 (1909); Ott and Schrötter, *ibid.*, **60**, 624 (1927); Paal and Schiedewitz, *ibid.*, **63**, 766 (1930); Gredy, *Bull. soc. chim.*, [5] **2**, 1029 (1935); Zal'kind, *et al.*, (No. XXXIII), *C. A.*, **35**, 6566 (1941); Borguel, *ibid.*, **19**, 2051 (1925).

(10) Myddleton and Bercham, *J. Chem. Soc.*, 1928 (1927).

(11) Oskerko, *Ber.*, **70**, 55 (1937).

(12) Vaughn, Vogt and Nieuwland, THIS JOURNAL, **56**, 2120 (1934).

product was acidified with sulfuric acid (6 *N*) and then extracted with ether. The combined ether extracts were washed with water until the washings showed a *p*H of approximately 5, and then dried over anhydrous sodium sulfate. After removal of the solvent, the red-colored residual oil was fractionally distilled through a packed column. The middle portion (26.3 g.) distilled at 124–130° at 3 mm. The fractions were crystallized separately from petroleum ether (28–38°). 1-Decyne-10-carboxylic acid (20.3 g., m. p. 42–43.5°,[13] and 2.7 g., m. p. 37–43°) was obtained.

1-Decyne-1,10-dicarboxylic Acid (V).—In a 1-liter, three-necked flask a solution of sodamide in liquid ammonia was prepared [sodium (14.5 g., 0.63 gram atom), ammonia (700 ml.), and ferric nitrate (0.5 g.)]. The reflux condenser was filled with a mixture of methanol and solid carbon dioxide, and the acetylenic acid IV (45.2 g., 0.248 mole) added as described below: A two-inch length of thin-walled wide rubber tubing was fitted to the mouth of the three-necked flask, and was closed with a clamp. A test-tube containing 5 g. of the acid was brought to ice-bath temperature, the cold tube was quickly fitted into the rubber, and with one motion the acid was shaken into the flask. The rubber tubing was then pinched off, the test-tube removed, and the process repeated. The pre-cooling was necessary to prevent melting of the acid in contact with ammonia vapor. The addition of all the acetylenic acid required thirty minutes.

Enough liquid ammonia was added to the reaction mixture to bring the volume to 700 ml. and the mixture was stirred under reflux for six hours, then for one hour with no refrigerant in the condenser. Finally the ammonia was allowed to evaporate.

To the residual material containing the desired sodium derivative, absolute ether (400 ml.) was added. The stirred mixture was then warmed to 50°, and the ether removed by distillation. More ether (500 ml.) was added to the ammonia-free solid. A large excess of crushed solid carbon dioxide was then added and after stirring the carbonation mixture for three and one-half hours, the flask was filled with crushed solid carbon dioxide. The stirring was continued for another four hours.

The mixture then was treated with concentrated aqueous ammonium chloride and stirred until all the large lumps had been broken up. After filtering the solution through a layer of Hyflo, the yellow aqueous portion of the filtrate was washed once with ether, and then acidified (6 *N* H_2SO_4). Ether extraction yielded a semi-solid residue which contained unchanged starting material and the desired product V. Separation was accomplished by treating the mixture of the acids with a large volume of petroleum ether (28–38°), in which the starting material was soluble but in which the dicarboxylic acid remained undissolved (light-colored solid, 23.2 g.). By working up the petroleum ether-soluble portion, 20.7 g. or 46% of the pure starting material IV was recovered.

The crude 1-decyne-1,10-dicarboxylic acid was purified by crystallization from carbon tetrachloride (yield, 18.5 g. (33%); m. p. 110–112°).

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.68; H, 8.02; neut. equiv., 113. Found: C, 63.66: H, 8.32; neut. equiv., 113.

The *p*-phenylphenacyl ester of V (m. p. 135–136°; crystallized from *n*-propyl alcohol) was prepared in the usual manner.

Anal. Calcd. for $C_{40}H_{38}O_6$: C, 78.15; H, 6.23. Found: C, 78.26; H, 6.19.

Dimethyl 1-decyne-1,10-dicarboxylate (b. p. 143–145° at 3 mm.) was prepared in 72% yield by refluxing V with absolute methanol in the presence of *p*-toluenesulfonic acid.

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.10; H, 8.73. Found: C, 65.86; H, 8.68.

Hydrogenation of the disodium salt in water using Raney nickel catalyst and one atmosphere of hydrogen resulted in the theoretical absorption of hydrogen. On extracting the acidified hydrogenation mixture with ether, pure 1,10-decanedicarboxylic acid was obtained. The melting point alone and mixed with an authentic sample was 127.5–129°.[14]

Oxidation of V, dissolved in dilute bicarbonate, at room temperature with dilute potassium permanganate yielded sebacic acid (m. p. and mixed m. p. 130–133°).

***cis*-Traumatic Acid (*cis* I, n = 8).**—1-Decyne-1,10-dicarboxylic acid (2.762 g., 0.0122 mole) was dissolved in an equivalent amount of 1 *N* sodium hydroxide solution and transferred to a hydrogenation bottle with 50 ml. of water. Raney nickel (about 1 g.) was added, the bottle was evacuated and filled with hydrogen at atmospheric pressure, and was shaken at room temperature. After thirty-five minutes a volume of hydrogen corresponding to 0.0122 mole was absorbed.

The nickel was removed by filtration through Hyflo and washed with water (25 ml.). The filtrate and washings were acidified (6 *N* H_2SO_4) and then extracted with ether. A semi-solid white residue (2.75 g.) was obtained.

A preliminary purification was effected by fractionally crystallizing this material from ethyl acetate containing increasing amounts of 28–38° petroleum ether. The material which separated from ethyl acetate and from ethyl acetate containing relatively small amounts of petroleum ether weighed 1.33 g. and melted at 95–125°. The *cis*-traumatic acid which separated from the ethyl acetate fractions containing relatively high proportions of petroleum ether, weighed 1.12 g. and showed a melting point of 59–91°. Several crystallizations of the higher melting material from ethyl acetate yielded pure 1,10-decanedicarboxylic acid.

The lower melting fraction was dissolved in 35 ml. of thiophene-free benzene and passed through an adsorption column of one-half inch diameter filled with a mixture of 3 g. of norit and 3 g. of Hyflo. Air pressure of a few centimeters of mercury was conveniently used to force the benzene through the tube. When the top level of the first 35 ml. of the solution had almost reached the top of the adsorption column, more benzene was added and the process continued until a total volume of 290 ml. of benzene had passed through.

The solution was collected in three portions. From the separate portions, the benzene was removed completely and the residues crystallized from a mixture of ethyl acetate and petroleum ether.

Most of the *cis*-traumatic acid came through in the first 110-ml. portion. After crystallization, there was obtained 0.71 g. of material most of which melted in the range 63–67° but still contained very small amounts of solid which persisted in the melt up to 77°. The second portion of benzene (100 ml.), contained 0.07 g. of material with m. p. 93–105°; and the third of 80 ml. contained 0.05 g. of material with m. p. 61–96°.

The 0.71 g. of material was again dissolved in benzene (25 ml.) and the adsorption and elution processes were repeated using a fresh column, and 300 ml. of benzene. After the benzene was removed completely, there remained a solid residue weighing 0.46 g. which, after two crystallizations from petroleum ether (28–38°) containing small amounts of ethyl acetate, yielded 0.37 g. (13%) of *cis*-traumatic acid, m. p. 66.5–67.5°. The melting point was raised to 67–68°, by further recrystallizations of the *cis*-traumatic acid from ethyl acetate and petroleum ether.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83; neut. equiv., 114.2. Found: C, 63.00; H, 8.85; neut. equiv. 114.7.

The di-*p*-phenylphenacyl ester of *cis*-traumatic acid was prepared and purified by recrystallization from absolute alcohol. The derivative melted at 91.5–92.5° to a cloudy liquid which persisted unchanged until 103° at which temperature the melt suddenly cleared.

Anal. Calcd. for $C_{40}H_{40}O_6$: C, 77.88; H, 6.54. Found: C, 78.04; H, 6.26.

For purposes of comparison, the di-*p*-phenylphenacyl

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(13) Krafft[6] reported m. p. 42.5–43°.

(14) Chuit. *Helv. Chim. Acta*, 9, 264 (1926).

ester of synthetic *trans*-traumatic acid was desired. This derivative possessed the totally different melting point of 144–145°.

Anal. Calcd. for $C_{40}H_{40}O_6$: C, 77.88; H, 6.54. Found: C, 77.60; H, 6.45.

Shaking the disodium salt of *cis*-traumatic acid in water under one atmosphere of hydrogen with Raney nickel yielded pure 1,10-decanedicarboxylic acid.

The position of the double bond in *cis*-traumatic acid was established by its cleavage to sebacic acid. The sodium salt in water at 0° was treated with a slight excess of dilute permanganate for two hours and finally warmed on the steam-bath for thirty minutes. An 83% yield of crude acid with a melting point of 120–130° was obtained. Decolorization and crystallization from water yielded pure sebacic acid, the identity of which was shown by melting point, mixed melting point, and neutralization equivalent.

1,9-Decadiyne (VI).—A 500-ml. three-necked flask was provided with a mechanical stirrer, a gas inlet (10-mm. tubing). and a cold finger reflux condenser. A solution of sodium acetylide in liquid ammonia was prepared by bubbling acetylene, passed through concentrated sulfuric acid and over soda-lime. into stirred liquid ammonia (300 ml.), while adding thin slices of clean sodium (8.8 g., 0.382 gram atom). Acetylene was passed into the solution for about five minutes after the last trace of deep blue color had disappeared. The inlet tube was then replaced with a dropping funnel, and the condenser finger, which was empty during the preparation of the acetylide, was filled with a slush of solid carbon dioxide and methanol.

1,6-Dibromohexane (46.4 g., 0.190 mole) was added over a period of one and one-half hours to the well-stirred and refluxing liquid ammonia solution; and finally to complete the reaction, the stirring was continued for two hours—keeping the volume of the mixture at approximately 300 ml. by adding more liquid ammonia. The ammonia was then allowed to evaporate.

The condenser was refilled with solid carbon dioxide and 50 ml. of saturated ammonium chloride solution was allowed to drop slowly into the reaction mixture. More water was added, and the organic material was taken up in ether. After washing and drying the extract, the ether was removed and the residual liquid fractionated. The yield of redistilled VI, b. p. 68–71° at 13–14 mm., was 11.2 g. (44%).

Anal. Calcd. for $C_{10}H_{14}$: C. 89.49; H, 10.51. Found: C, 89.32; H, 10.51.

1,9-Decadiyne is a water-white liquid with an unpleasant odor. It burns with a bright sooty flame, and forms a precipitate both with ammoniacal cuprous chloride and with silver nitrate in dilute ammoniacal alcohol solution.

The use of 1,6-dichlorohexane in the preparation of 1,9-decadiyne proved to be unsatisfactory.

1,9-Decadiyne-1,10-dicarboxylic Acid (VII).—The carbonation of the purified diyne to the dicarboxylic acid VII was accomplished; it was found much more convenient to prepare the acid, however, without isolating the intermediate diyne.[15]

In a 3-liter three-necked flask, a solution of sodium acetylide in 1–1.5 liters of liquid ammonia was prepared from one gram atom of sodium. 1,6-Dibromohexane (122.0 g., 0.50 mole) was added during a period of twenty minutes and the reaction mixture was stirred and allowed to reflux for a total time of six hours.

During this period a solution of sodamide in liquid ammonia was made up in a second 3-liter three-necked flask equipped with stirrer and reflux condenser. The conversion of the sodium (29.0 g., 1.26 gram atoms) to sodamide required one hour. Slightly more than one liter of ammonia for every mole of sodamide was used.

After the six-hour reflux period the sodamide solution was forced into the first reaction mixture through 10-mm. glass tubing by the use of controlled pressure of dry air. Stirring was continued in both flasks during the transfer, which required from five to ten minutes. The formation of the disodium derivative of VI in the stirred and refluxing liquid ammonia was allowed to proceed for six hours. Finally the ammonia was allowed to evaporate.

To the gray-colored solid material was added one liter of absolute ether and mechanical stirring was resumed. The ether was removed by distillation to effect a complete removal of any remaining ammonia. A second liter of absolute ether was added and carbonation was accomplished by the addition of a large excess of solid carbon dioxide. The flask was again filled with solid carbon dioxide after one and one-half hours and the carbonation allowed to continue for three hours.

The reaction mixture was then hydrolyzed with solid ammonium chloride and water, and the reaction mixture was filtered through a layer of Hyflo. The ether layer in the filtrate was separated and the light-yellow alkaline aqueous layer extracted with ether. After washing the combined ether solutions with water, dilute sulfuric acid. dilute bicarbonate solution, and finally water, it was dried over anhydrous sodium sulfate. Fractionation of the liquid residue yielded 1.9-decadiyne (b. p. 68–70° at 13 mm.; 19.8 g.).

The aqueous solution was acidified with dilute sulfuric acid and extracted thoroughly with ether. After the ether solution was washed with a small portion of water and dried, most of the ether was distilled off, dry benzene (200 ml.) was added, and the remaining ether removed completely by continuing the distillation. Cooling the benzene solution resulted in the separation of 21.4 g. of the 1,9-decadiyne-1,10-dicarboxylic acid melting at 146–149°.

The benzene filtrate was washed with water to remove any trace of sulfuric acid that may have remained. and then fractionated. The colorless distillate (b. p. 145–155° at 4–5 mm.; 20.8 g.) solidified (m. p. 39–40°) and proved to be monocarbonation product VIII.

The crude 1,9-decadiyne-1,10-dicarboxylic acid was purified by recrystallization from water to a constant m. p. of 148.5–149.5°.

Anal. Calcd. for $C_{12}H_{14}O_4$: C. 64.85: H, 6.35. Found: C. 64.85; H. 6.48.

The di-*p*-phenylphenacyl ester of VII was formed in dilute alcoholic solution and after recrystallization from *n*-propyl alcohol showed a m. p. of 152–153°.

Anal. Calcd. for $C_{40}H_{34}O_6$: C. 78.67; H. 5.61. Found: C, 78.50; H. 5.77.

Dimethyl 1.9-decadiyne-1.10-dicarboxylate (b. p. 160–161° at 3 mm.; m. p. 43–43.5°) was prepared in 72% yield by refluxing the acid with absolute methanol in the presence of *p*-toluenesulfonic acid.

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.16; H, 7.25. Found: C. 67.42; H. 7.14.

Hydrogenation of the sodium salt of the dibasic acid in water using Raney nickel under a small positive pressure of hydrogen resulted in the uptake of four moles of hydrogen per mole of material and the production of 1,10-decanedicarboxylic acid.

To prove the position of the two triple bonds, the acid. dissolved in dilute bicarbonate solution, was treated at room temperature with the theoretical amount of dilute permanganate. After one hour the manganese dioxide was removed by filtration and sodium bisulfite was added to discharge the very slight pink color. After acidifying the solution the suberic acid was removed by extraction with ether. The identity of the suberic acid (m. p. 139–141°[16]) was confirmed by its neutralization equivalent (calcd. 87, found 89), and the melting point. 146–146.5°[17] of its di-*p*-bromophenacyl ester.

1,9-Decadiyne-1-carboxylic Acid (VIII).—The acid was crystallized from petroleum ether (40–75°) and the crystals (m. p. 39–40°) dried *in vacuo* at room temperature. The melting point (39–40°) of the crystallized acid remained the same as that of the distilled product.

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[15] Zoss and Hennion. THIS JOURNAL, 63. 1151 (1941); Vaughn, Hennion. Vogt and Nieuwland, *J. Org. Chem.*. 2. 1 (1937).

[16] Verkade, Hartman and Coops. *Rec. trav. chim.*. 45, 373 (1926).

[17] Kelly and Kleff. THIS JOURNAL, 54, 4444 (1932).

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92; neut. equiv., 178. Found: C, 73.94; H, 8.02; neut. equiv., 178.

The *p*-phenylphenacyl ester of VIII (m. p. 59.5–60°) was prepared in the usual manner.

Anal. Calcd. for $C_{25}H_{24}O_3$: C, 80.62; H, 6.50. Found: C, 80.75; H, 6.38.

Oxidation of VIII with dilute permanganate according to the directions for the oxidation of VII and subsequent similar treatment yielded suberic acid (m. p. 139–141°; neut. equiv., 88; m. p. of *p*-bromophenacyl ester 146–146.5°).

Summary

The synthesis of 1-decyne-1,10-dicarboxylic acid, 1,9-decadiyne-1,10-dicarboxylic acid and *cis*-traumatic acid has been described.

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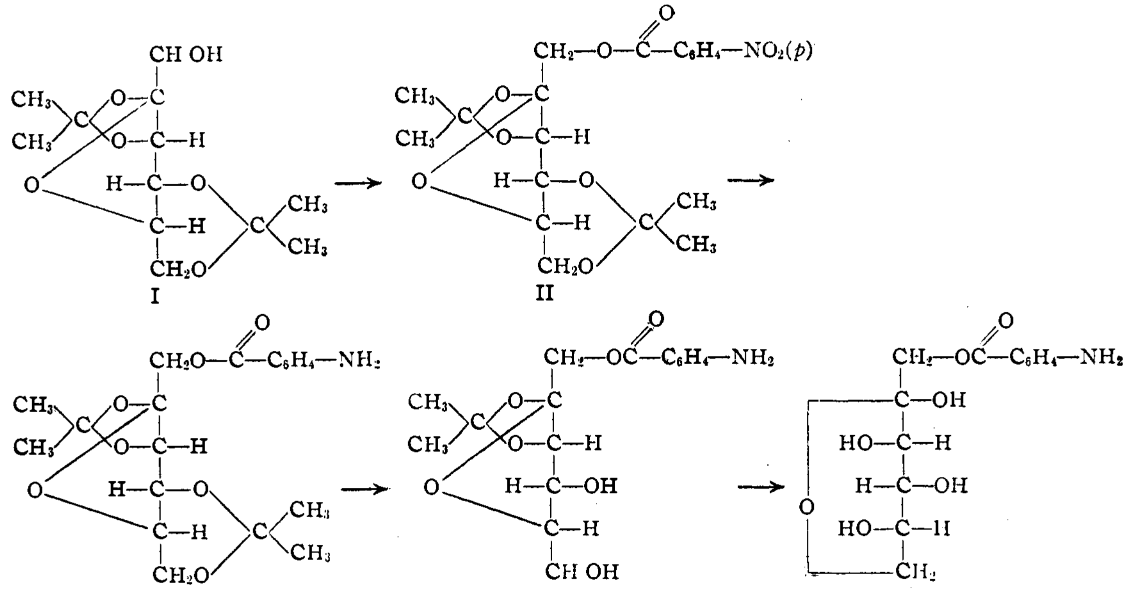
[CONTRIBUTION FROM THE RESEARCH LABORATORIES, MERCK & CO., INC.]

Synthesis of 1-(*p*-Aminobenzoyl)-*l*-sorbose

BY JACOB FINKELSTEIN[1] AND ERIC T. STILLER[2]

Many nitrobenzoyl esters of sugars are known, but so far, no analogous amino compound has been recorded. As a possible substance for measuring the rate of glomerular filtration,[3] we have prepared 1-(*p*-aminobenzoyl)-*l*-sorbose, the first of this class of sugar derivatives, by the following series of reactions


I II III IV V

This procedure, with certain modifications, may be applied as a general method for such types of compounds.

The preparation of 1-(*p*-nitrobenzoyl)-2,3-4,6-diacetone-*l*-sorbose was easily accomplished. The removal of both acetone groups, however, proved rather difficult and the yield of the final compound was poor.

When the diacetone compound was warmed with 50% acetic acid, it was converted into the monoacetone derivative (IV), whose structure is so formulated in accordance with the results obtained by Freudenburg and co-workers[4] from their studies on acetone sugars. This formulation was upheld by the fact that (IV) did not reduce Fehling solution while the completely hydrolyzed product did so quite readily. The method of hydrolysis used to obtain (V), as outlined below, was the only one, of the many tried, which produced small amounts of the desired product.

Experimental

2,3-4,6-Diacetone-*l*-sorbose (I).—This compound was prepared according to the method of Reichstein and Grussner.[5]

1-(*p*-Nitrobenzoyl)-2,3-4,6-diacetone-*l*-sorbose (II).—A solution of 45 g. of diacetone-*l*-sorbose was prepared in 200 cc. of dry pyridine and stirred while immersed in an ice–salt mixture. To this solution 35 g. of *p*-nitrobenzoyl

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(1) Present address: Hoffman–LaRoche, Inc., Roche Park, Nutley, N. J.

(2) Present address: Wyeth Institute of Applied Biochemistry, Philadelphia, Pa.

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(4) Freudenburg, *et al.*, *Ber.*, **61**, 1735 (1928).

(5) Reichstein and Grussner, *Helv. Chim. Acta*, **17**, 311 (1934).