trans-6-Octenoic acid. trans-3-Pentenoic acid[24] was prepared by condensing 5.20 moles of freshly distilled propionaldehyde with 5.20 moles of malonic acid in 5.20 moles of triethanolamine. The acid, obtained in a 13% yield, had a b.p. of 54° at 1 mm. and n_D^{20} 1.4357.

trans-3-Penten-1-ol[28] was prepared by the reduction of 1.28 moles of *trans*-3-pentenoic acid using 1.71 moles of lithium aluminum hydride. The alcohol, yield 81%, had a b.p. of 47° at 13 mm. and n_D^{20} 1.4334.

1-Bromo-*trans*-3-pentene was prepared in a 71% yield using 1.00 mole of *trans*-3-penten-1-ol, 0.41 mole of phosphorus tribromide, and 0.36 mole of dry pyridine in 75 ml. of carbon tetrachloride. The bromide, obtained in a 71% yield, had a b.p. of 80° at 152 mm. and n_D^{20} 1.4686.

trans-5-Hepten-1-ol was prepared by the reaction of the Grignard reagent from 0.70 mole of 1-bromo-*trans*-3-pentene and 0.94 mole of ethylene oxide. The procedure used was similar to that described by Huston and D'Arcy.[29] The alcohol was obtained in a 49% yield and had the following properties: b.p. 77° at 11 mm., n_D^{20} 1.4437, density 0.8536 g./ml. at 20°, m.p. of α-naphthylurethan, 79–80°.

Anal. Calcd. for $C_{18}H_{21}O_2N$: N, 4.95. Found: N, 4.98.

1-Bromo-*trans*-5-heptene was prepared in a 56% yield using 36.5 g. (0.32 mole) of *trans*-5-hepten-1-ol, 0.12 mole of pyridine, and 0.15 mole of phosphorus tribromide in 66 ml. of carbon tetrachloride. The bromide had a b.p. of 85° at 34 mm. and n_D^{20} 1.4691.

trans-6-Octenoic acid was prepared in a 52% yield by the carbonation of the Grignard reagent obtained from 30.1 g. (0.17 mole) of 1-bromo-*trans*-5-heptene.

ATLANTA, GA.

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(28) L. Crombie and S. H. Harper, *J. Chem. Soc.*, 873 (1950).

(29) R. C. Huston and H. M. D'Arcy, *J. Org. Chem.*, **18**, 16 (1953).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF DELAWARE]

β-Cyano-α-hydroxycinnamates from the Xylenes

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Received October 20, 1958

This paper describes the synthesis, separation, and characterization of β-cyano-α-hydroxycinnamates from the xylenes. The separated isomers from *o*-xylene and *m*-xylene have been used to obtain pure hydrolytic cleavage products.

It has been shown in previous reports[1] that isomeric monoalkylphenylacetonitriles could be separated through the intermediate β-cyano-α-hydroxycinnamates. We have accordingly applied this process to the nitriles from the xylenes and have also characterized the products.

The mixture of monochloromethylation products from *o*-xylene led to a mixture of ethyl β-cyanodimethyl-α-hydroxycinnamates. The lower melting isomer I was best separated from the mixture by crystallization from ethyl acetate. The less abundant higher melting isomer II could then be obtained from the non-volatile residue of the filtrate by crystallization from toluene. The relative amounts of I and II that have been isolated are in the ratio 9:4.

Mild alkaline hydrolysis[1] of I gave the pure nitrile which was further hydrolyzed to 3,4-dimethylphenylacetic acid and a small amount of the amide. 3,4-Dimethylacetophenone[2a,b] synthesized from *o*-xylene was converted successively to 3,4-dimethylbenzoic acid, the acid chloride, the diazoketone and the identical 3,4-dimethylphenylacetic acid, thus establishing that I is ethyl β-cyano-3,4-dimethyl-α-hydroxycinnamate, and that the methyl groups in this series are in positions 3 and 4.

The nitrile from II was found to be a solid which by similar refluxing with alkali gave almost entirely the corresponding amide. This was converted to the acid by saponification in diethylene glycol. The structure of the acid was established by oxidation[3] to hemimellitic acid. This was converted to trimethyl hemimellitate which was identical with an authentic sample.[4] These facts show that in this series the methyl groups are in the 2,3-positions and that II is ethyl β-cyano-2,3-dimethyl-α-hydroxycinnamate.

Likewise the ethyl β-cyanodimethyl-α-hydroxycinnamates expected from the chloromethylation products of *m*-xylene (III,IV) and *p*-xylene (V) have been isolated. The separation of the esters derived from *m*-xylene was tedious due to the small amount of IV. Some simplification was attained by the fact that the sodium salt of III crystallized well from the alcohol medium and IV could be obtained from the filtrate. The mild alkaline hydrolysis of III gave the nitrile. More vigorous hydrolysis of III gave the amide and the acid. This acid was oxidized to trimellitic acid which shows that the methyl groups in III and its degradation products are in positions 2 and 4. Similarly the structure of the 2,6-isomer (IV) was shown by hydrolysis to the amide and acid followed by oxidation of the acid to hemimellitic acid. The identity of the single

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[1] G. S. Skinner, J. A. Gladner, and R. F. Heitmiller, *J. Am. Chem. Soc.*, **73**, 2230 (1951).

[2] (a) K. v. Auwers, *Ber.*, **45**, 2780 (1912); (b) O. Grummit and E. N. Case, *J. Am. Chem. Soc.*, **64**, 880 (1942).

[3] W. P. Campbell and D. Todd, *J. Am. Chem. Soc.*, **62**, 1287 (1940).

[4] We are indebted to Professor Lee Irvin Smith, University of Minnesota, for this sample.

TABLE I

	Dimethyl-β-cyano-α-hydroxycinnamates			Dimethylphenylacetonitriles		Dimethylphenylacetamides		Dimethylphenylacetic Acids		
No.	Dimethyl	M.P.	N% Found[a]	B.P. (mm.)	N% Found[b]	M.P.	N% Found[c]	M.P.	C% Found	H% Found[d]
I	3,4-	89–90	5.87	63–65 (0.5)	9.54	174–175	8.54	93.5–94.5	73.15	7.66
II	2,3-	126–127	5.76	52–53[e]	9.59	166–167	8.56	116–117	73.08	7.59
III	2,4-	95–96	5.64	133 (9)	9.60	183–184	[f]	105–106	[f]	
IV	2,6-	113–114	5.72			180–181	8.61			
V	2,5-	118	5.67	113–115 (4)	[g]	154	[h]	128	[h]	

[a] Calcd. 5.72. [b] Calcd. 9.65. [c] Calcd. 8.59. [d] Calcd. C, 73.14; H, 7.37. [e] M.p. [f] P. Barbier and V. Grignard, *Compt. rend.*, **148**, 646 (1909). [g] W. Herz, *J. Am. Chem. Soc.*, **75**, 73 (1953). [h] M. Guerbet, *Compt. rend.*, **125**, 36 (1897).

ester from *p*-xylene was established by hydrolysis to the known nitrile, amide and acid (See Table I).

EXPERIMENTAL

Chloromethyl and cyanomethyl derivatives. The monochloromethylation of *o*-xylene (213 g., 2.02 moles) was effected by passing hydrogen chloride through a stirred mixture with 67 g. (0.82 mole) of formalin and 537 g. (5.47 moles) of hydrochloric acid (sp. gr. 1.19) for 6 hr. at 50°. The mixture of chloromethylxylenes (71.7 g.; 47%) had b.p. 46–49° (0.05 mm.). Similarly *m*-xylene (2.02 moles) in 3.75 hr. gave 111 g. (87%) of monochloromethyl derivatives, b.p. 87–90.5 (3–2 mm.). Similar monochloromethylation of *p*-xylene for 8 hr. gave 163.7 g. (72.5%), b.p. 79–85° (6.6 mm.). These products were converted to the nitriles as previously described.[1] The mixture of nitriles from *o*-xylene (70% yield) had b.p. 72–82° (0.27 mm.) and the mixture from *m*-xylene (82% yield) had b.p. 121–123° (3 mm.). The one product 2,5-dimethylphenylacetonitrile was obtained in 77% yield from *p*-xylene.

Preparation and separation of ethyl β-cyano-3,4-dimethyl-α-hydroxycinnamate (I) *and ethyl β-cyano-2,3-dimethyl-α-hydroxycinnamate* (II). A solution of sodium ethoxide from 13.6 g. (0.59 mole) of sodium and 215 cc. of alcohol was cooled to room temperature and quickly mixed with 87 g. (0.59 mole) of ethyl oxalate and 83.8 g. (0.58 mole) of the mixture of nitriles from *o*-xylene. After standing overnight the excess alcohol was removed under diminished pressure. The residue was shaken vigorously with a mixture of 300 g. of ice and water, 75 cc. of hydrochloric acid (sp. gr. 1.19) and 100 cc. of petroleum ether until all of the lumps were disintegrated. The ice cold product was filtered, washed with petroleum ether and iced water, and dried, yield 135 g. (95%), m.p. 74–79°.

Seven recrystallizations from toluene gave very small amounts of two isomers melting at 89–90° and 126–127°. Upon changing the solvent to ethyl acetate a relatively facile separation was obtained. From this solvent the lower melting isomer came out first and when the mother liquor was substantially free of it the solid residue from the removal of the ethyl acetate was crystallized from toluene to give the higher melting isomer.

Yield: I, m.p. 89–90°, 43.1 g. (29.6%). II, m.p. 126–127°, 18.4 g. (13.0%).

Preparation and separation of III *and* IV. The mixture of nitriles (186.7 g., 1.29 moles) from *m*-xylene was similarly added at once to the well stirred mixture of 203 g. (1.39 moles) ethyl oxalate with alcoholic sodium ethoxide prepared from 30.6 g. (1.33 moles) of sodium and 440 cc. of alcohol. Within a few minutes well formed crystals appeared and the mixture rapidly set to a semisolid mass. After 24 hr. the salt was filtered with the aid of a rubber dam and washed three times with alcohol. The salt was decomposed to the ester by stirring with a mixture of hydrochloric acid, ice, water, and petroleum ether. The collected air-dried product weighed 180 g., m.p. 85–89°. III had m.p. 95–96° when recrystallized from ethyl acetate.

The filtrate from the above salt was evaporated under diminished pressure. The glassy residue by treatment with hydrochloric acid, ice, and petroleum ether gave 59 g. more of product m.p. 85–93°. This was also crystallized from 60 cc. of ethyl acetate to give 29.5 g., m.p. 94–96°. The filtrate after concentration on the steam bath and allowing to stand overnight partly crystallized. The solid product was filtered and washed with petroleum ether, 12.5 g., m.p. 108–110°. Two crystallizations from toluene gave 5.8 g. of pure IV, m.p. 113–114°.

Alternate synthesis of 3,4-dimethylphenylacetic acid. A mixture of 3,4-dimethylbenzoic acid[5] (m.p. 166–167°, 3.00 g., 0.020 mole), thionyl chloride (2.40 g., 0.021 mole), 50 cc. of methylene chloride and 5 drops of pyridine was refluxed for 24 hr. The excess thionyl chloride was removed by evacuation for 5 hr. The solution of the residual oil in 200 cc. of ether was added slowly to a solution of 0.125 mole of diazomethane in 500 cc. of ether at 0°. After standing overnight at 0° the diazoketone was obtained as a viscous yellow oil by cautious distillation of diazomethane and ether. A solution of the oil in 50 cc. of dioxane was added dropwise to a mixture of 1.0 g. freshly prepared silver oxide, 2.5 g. sodium carbonate, 1.5 g. sodium thiosulfate and 100 cc. of water at 50–60°. The temperature was raised to 90° and heating and stirring were continued for 2 hr. The mixture was cooled, diluted with 100 cc. of water, filtered, and extracted with ether to remove oily material. The aqueous layer was acidified with nitric acid and extracted with ether. Evaporation of this extract gave 1.9 g. of yellow oil which slowly crystallized. The extraction of this residue with hot water and cooling of the aqueous solution gave 1.3 g. of white needles, m.p. 89–90°. Another crystallization from hot water raised the m.p. to 91–92°. The melting point was not depressed when admixed with the dimethylphenylacetic acid from I. The x-ray diffraction patterns were also superimposable.

Characterization of II. The hydrolysis of II in steps to the nitrile, amide, and acid proceeded less easily than in the case of I. A 2.00 g. (0.012 mole) sample of the amide (m.p. 166–167°) was suspended in 40 cc. of diethylene glycol containing 2 cc. of water and 1.50 g. (0.038 mole) of sodium hydroxide. The mixture was refluxed for 3 hr. The clear solution from dilution with 125 cc. of water was acidified with hydrochloric acid to give 1.75 g. (87%) of the acid, m.p. 116–117°.

This acid (500 mg.), 1 cc. of nitric acid (sp. gr. 1.42) and 2 cc. of water were heated[3] in a Carius tube (1″ × 36″) for 18 hr. by means of a salt bath at 195–205°. The tube was cooled carefully and gradually in a dry ice–acetone bath before opening. The contents were removed and the residue from evaporation was triturated with 1 cc. of nitric acid (sp. gr. 1.51), yield of crystals 38 mg. This material was esterified with diazomethane and the ester was crystallized from methyl alcohol, m.p. 99–100°. Mixed with an authentic

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(5) J. Cologne and L. Pechot, *Bull. soc. chim. France*, [5], **16**, 180 (1949).

sample of trimethyl hemimellitate the melting point was 99–100.5°.

Characterization of III. A suspension of 28.4 g. (0.116 mole) of III in a solution of 5.2 g. (0.13 mole) of sodium hydroxide in 200 cc. of water was slowly heated until dissolved (at 65°) and the nitrile began to separate (at 72°). The nitrile was extracted with petroleum ether. To the water layer was added 1.3 g. of sodium hydroxide and the heating process was repeated twice until no more nitrile separated. Yield 10 g. (61%). This nitrile (5.5 g.) was refluxed 10 hr. with a mixture of 2.25 g. of potassium hydroxide, 3.5 cc. of water and 25 cc. of alcohol to give 3 g. of the known 2,4-dimethylphenylacetamide and 3.1 g. of the known 2,4-dimethylphenylacetic acid (see *f* in Table). The acid was smoothly oxidized by alkaline permanganate to trimellitic acid, m.p. 226–227°, lit.[6] 228°.

III was further characterized by acidification of the ice-cold aqueous layer from the nitrile to yield 8.8 g. of shiny crystals. This product was dissolved in the minimum amount of hot 5% sodium hydroxide solution and reprecipitated by hydrochloric acid to give 6.5 g., m.p. 163–165°. It was necessary to dry the product in vacuo as the crystals underwent slow decomposition in the air.

Anal. Calcd. for $C_{11}H_{12}O_3$: Neut. equiv., 192; C, 68.71; H, 6.29. Found: Neut. equiv., 194; C, 68.50; H, 6.38.

The acid reacted readily with Tollen's reagent to produce a silver mirror. It also gave a 2,4-dinitrophenylhydrazone, m.p. 201–202°. One attempt to oxidize the substance with permanganate to another crystalline acid gave only a viscous oil. The acid by-product was not further investigated.

Anal. Calcd. for $C_{17}H_{16}O_6N_4$: N, 15.05. Found: N, 15.06.

Characterization of IV. A mixture of 2.7 g. (0.11 mole) of IV, 6.0 g. (0.11 mole) of potassium hydroxide, 30 cc. of water and 45 cc. of alcohol was refluxed for 48 hr. The alcohol was distilled and water was added to precipitate the amide which was crystallized from hot alcohol. The aqueous filtrate was acidified to give 1 g. of crude acid. This sample of acid was oxidized with an excess of aqueous permanganate with stirring under reflux for 12 hr. The excess permanganate was destroyed by addition of a few drops of methanol. The hot aqueous filtrate was concentrated to a small volume, filtered, acidified, and extracted with ether to give 0.2 g. hemimellitic acid, m.p. 186–188°, lit.[6] m.p. 190°.

NEWARK, DEL.

(6) Huntress and Mulliken, *Identification of Pure Organic Compounds I*, 116, 120 (1941). John Wiley and Sons, New York.

[CONTRIBUTION FROM THE HORMEL INSTITUTE, UNIVERSITY OF MINNESOTA]

Syntheses of Unsaturated Fatty Aldehydes[1]

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Received March 10, 1958

Oleyl-, linoleyl- and linolenyl-aldehydes were prepared by a modified Grundmann synthesis. The procedure can be used for the preparation of radioactive aldehydes on a milligram scale.

Most methods reported[2] for the synthesis of aldehydes are not applicable to the preparation of aliphatic aldehydes having methylene-interrupted systems of double bonds. In the present investigation, the procedures described by Brown and McFarlin,[3] Weygand,[4] and Grundmann[5] were selected as the most promising, and were compared by applying them to the synthesis of oleyl aldehyde. A modified Grundmann synthesis gave the purest product and satisfactory yields and therefore it is described in detail.

Grundmann treated the acid chloride with diazomethane to obtain a diazo ketone, which was converted with acetic acid into a ketol acetate. The latter, after reduction with aluminum isopropylate and subsequent saponification, yielded a diol which was split with lead tetraacetate to give the aldehyde of the same chain length as the initial acid.

In the case of highly unsaturated compounds, the use of aluminum isopropylate results in the formation of polymers and the yields of diols are very low. The present author used lithium aluminum hydride for the reduction of ketol acetates[2] to avoid excessive condensations. It is not necessary to purify the ketol acetates since lithium aluminum hydride reduces the expected contaminants such as acid, acid chloride, ester, and chloroketone to mono alcohols which can be separated from the glycol by distillation or by column chromatography. Prolonged treatment of the diol with lead tetraacetate in the final reaction produces a small amount of contaminating acid, which can be extracted easily with dilute sodium carbonate solution. Neutral compounds, which appear as

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[1] This research was supported by grants given to Dr. H. Schlenk by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. 18(603)18, by the U. S. Atomic Energy Commission (AT(11-1)-236), and by The Hormel Foundation.

[2] E. Mosettig, "The Synthesis of Aldehydes from Carboxylic Acids," in *Organic Reactions*, John Wiley & Sons, Inc., New York, 1954, Vol. VIII, Chapter 5, p. 218; O. Bayer, "Methoden zur Darstellung und Umwandlung von Aldehyden," in *Methoden der Organischen Chemie*, Thieme-Verlag, Stuttgart, 1954, Vol. 7, 1, p. 1.

The use of lithium aluminum hydride as reducing agent in the Grundmann synthesis was already suggested by Mosettig.

[3] H. C. Brown and R. F. McFarlin, *J. Am. Chem. Soc.*, **78**, 252 (1956).

[4] F. Weygand, *Angew. Chem.*, **65**, 525 (1953); S. S. Nigam and B. C. L. Weedon, *J. Chem. Soc.*, 3320 (1957).

[5] Chr. Grundmann, *Ann.*, **524**, 31 (1936).