Anal. Calcd. for $C_{14}H_{11}O_3NS$: C, 61.54; H, 4.03; N, 5.13. Found: C, 61.42; H, 4.18; N, 5.07.

8-Ethoxy-2-aminodibenzothiophene (VIII).—The nitro compound (VII) was reduced with stannous chloride and acetic acid; m. p. 109–110°.

Anal. Calcd. for $C_{14}H_{13}ONS$: C, 69.13; H, 5.35. Found: C, 69.27; H, 5.31.

The acetyl derivative (V), prepared with pyridine and acetic anhydride, melted at 196–196.5°, after recrystallization from ethanol. A sample mixed with the 195.5–196°-melting compound prepared from (IV) melted at 195.5–196.5°.

8-Ethoxy-2-acetamidodibenzothiophene-5-dioxide (IX).—The sulfide (V) was oxidized to the sulfone with 30% hydrogen peroxide in acetic acid, m. p. 313°, recrystallized from acetic acid.

Anal. Calcd. for $C_{16}H_{15}O_4NS$: C, 60.57; H, 4.73. Found: C, 60.43; H, 4.87.

8-Ethoxy-4-iodo-2-nitrodibenzothiophene-5-dioxide (X).—4′-Ethoxy-2,6-diiodo-4-nitrodiphenyl sulfide (5 g.) was oxidized in 100 ml. of acetic acid with 8 ml. of 30% peroxide as previoulsy described.[1] At the conclusion of the oxidation, but before diluting the reaction solution, 9 g. of potassium permanganate was added, very slowly with cooling at first, until the evolution of oxygen had practically ceased. The reaction mixture was stirred for 30 minutes, diluted with water, decolorized with sodium bisulfite, and the precipitate separated and dried. Recrystallization from dioxane yielded 1.5 g. of white microcrystals melting at 300°. From the dioxane solution, 2 g. of the yellow diphenyl sulfone was recovered. It was purified by recrystallization from amyl acetate.

Anal. Calcd. for $C_{14}H_{10}O_5NSI$: I, 29.5. Found: I, 29.1.

This compound was also prepared from the dibenzothiophene derivative (II) by oxidation with hydrogen peroxide and acetic acid; m. p. 300°, not lowered by admixture with the compound prepared directly from the diphenyl sulfide.

The product (X) could be converted into the acetamido sulfone (IX) by simultaneous reduction and deiodination with zinc and acetic acid, followed by acetylation with acetic anhydride and pyridine. Recrystallized from acetic acid, it had m. p. 313.5°.

8-Ethoxy-4-iodo-2-acetamidodibenzothiophene-5-dioxide (XI).—4′-Ethoxy-2,6-diiodo-4-acetamidodiphenyl sulfide[1] (XII) (1 g.) was heated under reflux for 20 minutes in 50 ml. of acetic acid to which had been added an excess of potassium permanganate. Water (50 ml.) was added, and sufficient sodium bisulfite to reduce the manganese dioxide. After standing in the refrigerator for several hours, the precipitate was filtered off, dried, and leached out thoroughly with hot ethanol. After recrystallization of the ethanol-insoluble residue from acetic acid, the material melted at 289°.

Anal. Calcd. for $C_{16}H_{14}O_4NSI$: C, 43.34; H, 3.16; N, 3.16. Found: C, 43.08; H, 3.27; N, 3.39.

Oxidation of the dibenzothiophene derivative (IV) with 30% hydrogen peroxide and acetic acid provided another route to the sulfone; m. p. 292–293°. A mixture of this with the product above melted at 291–292°.

Deiodination of (XI) with zinc dust and acetic acid gave (IX), m. p. 313°, recrystallized from acetic acid.

Acknowledgment.—The author wishes to record his appreciation to Dr. S. L. Bass, Dow Corning Corp., Midland, Mich., for making available a copy of his thesis as well as the unpublished notes of his work on diphenyl sulfides, and to Dr. R. Stuart Tipson, Mellon Institute, Pittsburgh, Pa., for his continuing interest and advice.

Summary

1. A substituted diphenyl sulfide, containing two ortho iodine atoms and one para nitro group in the same ring can be caused to cyclize to a substituted dibenzothiophene derivative with loss of the elements of hydrogen iodide.

2. Such a substituted diphenyl sulfide as well as one containing an acetamido in place of a nitro group was cyclized and oxidized simultaneously to a substituted dibenzothiophene-5-dioxide derivative.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XII. Preparation and Properties of *cis*- and *trans*-Cinnamyl Chloride

BY LEWIS F. HATCH AND HAROLD E. ALEXANDER[1]

Many investigators have reported the preparation and utilization of cinnamyl chloride but none has noted the geometrical configuration of the chloride involved. The present paper describes the preparation of both *cis*- and *trans*- cinnamyl chloride from the corresponding cinnamyl alcohols. Both alcohols have been prepared and characterized previously.[2]

The preparation of *trans*-cinnamyl alcohol presented no problem because the commercially available cinnamyl alcohol has the *trans* configuration. The synthesis of the *cis* isomer followed the method of Tchao Yin Lai[3] and Gredy[2b] which starts with phenylacetylene and has as the characterizing step the *cis* hydrogenation of 3-phenyl-2-propyn-1-ol. In an attempt to prepare 3-phenyl-2-propyn-1-ol by a more convenient method, cinnamyl alcohol was brominated to give 2,3-dibromo-3-phenylpropan-1-ol. This bromo alcohol was subsequently treated with alcoholic potassium hydroxide but no 3-phenyl-2-propyn-1-ol could be isolated from the reaction mixture.

trans-Cinnamyl alcohol was converted to *trans*-cinnamyl chloride using thionyl chloride,[4] while phosphorus trichloride in pyridine[5] was used in

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[1] Research Corporation Fellow 1947–1948; du Pont Fellow 1948–1949. E. I. du Pont de Nemours and Company, Arlington, New Jersey.

[2] (a) Bourguel and Ynon, *Compt. rend.*, **182**, 224 (1926); (b) Gredy, *Bull. soc. chim.*, [5] **3**, 1093 (1936).

[3] Tchao Yin Lai, *ibid.*, **53**, 682 (1933).

[4] Gilman and Harris, *Rec. trav. chim.*, **50**, 1052 (1931).

[5] Clark and Streight, *Trans. Roy. Soc.* (*Canada*), [3] **23**, III, 77 (1929).

the preparation of *cis*-cinnamyl chloride. Thionyl chloride apparently caused some rearrangement of the *cis* isomer to the *trans* isomer but did not cause a similar rearrangement of the *trans* isomer to the *cis* isomer.

The primary reason for the preparation of *cis*- and *trans*-cinnamyl chloride was to determine their relative reactivities with potassium iodide in acetone,[6] with sodium ethoxide in ethanol[7] and in the cuprous chloride-catalyzed acid hydrolysis.[8] It was hoped that the presence of the large phenyl group in these compounds would permit an evaluation of the influence, if any, of steric hindrance on these reactions. The results have been disappointing in this respect.

There is an increase in reactivity toward *potassium iodide* when a hydrogen atom on the number 1 carbon atom of 3-chloro-1-propene is replaced by a phenyl group. This increase in reactivity is greater than for a similar replacement by either a methyl group[9] or a chlorine atom,[6] but less than when both hydrogen atoms are replaced by methyl groups[10] or by a methyl group and a chlorine atom.[11] This would indicate that the replacement of hydrogen atoms is more important than the nature of the group which replaces the hydrogen atoms.

The reaction of both *cis*- and *trans*-cinnamyl chloride with *sodium ethoxide* was very rapid, and no data of value were obtained. The individual values for the velocity constant were widely scattered, even those calculated for the same reaction time but obtained in different runs. This indicated that either the reaction was not taking the normal course or that the method of analysis used in previous work was not applicable with cinnamyl chloride. This possibility will be investigated further.

The two isomers of cinnamyl chloride were hydrolyzed rapidly and at approximately the same rate in the *cuprous chloride-catalyzed acid hydrolysis* reaction. The two isomers are only very slightly soluble in water and the controlling factor in the rate of hydrolysis may have been the relative rates of solution rather than the relative reactivities of the isomers. All the other pairs of geometrical isomers studied, with the exception of the 1,3-dichloro-2-butenes, show an appreciable difference in reactivity.

Acknowledgment.—This investigation was supported in part by a grant-in-aid from the Research Corporation for "Research on Allylic Chlorides," and in part by a Fellowship granted to H. E. A. by E. I. du Pont de Nemours and Company. The authors wish to express their appreciation.

Experimental

All temperatures are corrected.

trans-Cinnamyl Chloride

***trans*-Cinnamyl Alcohol.**—Commercial cinnamyl alcohol (Eastman Kodak Co.) was distilled out of a 250-ml. Claisen flask having an 11-inch distillation arm packed with glass beads. A fraction boiling at 146.5–147.0° was obtained. This material had the following physical constants: m. p. 33°; $n^{36.1}$D 1.5755; 3,5-dinitrobenzoate m. p. 121–122° (lit., m. p. 33°[2a]; $n^{36.1}$D 1.5754[12]; 3,5-dinitrobenzoate m. p. 121°.[13])

***trans*-Cinnamyl Chloride.**—This chloride was prepared from *trans*-cinnamyl alcohol using thionyl chloride and the method of Gilman and Harris[4]; yield 76%.

***trans*-Cinnamyl Chloride**: b. p. 94° (2 mm.); m. p. 7–8°; d^{25}_{4} 1.0860; n^{25}D 1.5802 (lit., b. p. 102–103° (5 mm.)[4]; m. p. 7–8°[4]; d^{25}_{4} 1.08815[14]; n^{25}D 1.58065).[14]

cis-Cinnamyl Chloride

Preparation of 3-Phenyl-2-propyn-1-ol from Phenylacetylene.—The procedure used in this preparation followed closely a method reported by Tchao Yin Lai.[3]

Phenylacetylene (Farchan Research Laboratories, Cleveland, Ohio), 1.5 moles, was added to ethylmagnesium bromide (1.50 moles) in 750 ml. of diethyl ether over a period of 1.5 hours and the mixture was refluxed an additional hour. Formaldehyde was generated at 170–180° from trioxymethylene (100 g.) and passed into the reaction mixture resulting from the treatment of ethylmagnesium bromide with phenylacetylene. The contents of the reaction flask were rigorously agitated throughout the addition of formaldehyde.

When the addition of formaldehyde had been completed, the contents of the reaction flask were poured onto 450 g. of cracked ice. Sufficient 20% sulfuric acid was added to decompose all of the magnesium hydroxide and any acetal which may have formed. The organic layer was separated from the hydrolyzed reaction mixture and the aqueous layer was saturated with potassium carbonate. This solution was extracted with ether and the ether extracts added to the organic layer. The mixture was dried with anhydrous potassium carbonate.

The filtered mixture was distilled through a modified Claisen flask to give a yield of 131 g. (67%) of 3-phenyl-2-propyn-1-ol.

3-Phenyl-2-propyn-1-ol: b. p. 114–115° (3 mm.); d^{23}_{4} 1.061; n^{23}D 1.5837 (lit.,[2b] b. p. 136–138° (16 mm.); d^{23}_{4} 1.060; n^{23}D 1.5838.)

Preparation of *cis*-Cinnamyl Alcohol.—*cis*-Cinnamyl alcohol was prepared by the catalytic hydrogenation of 3-phenyl-2-propyn-1-ol in a manner similar to that used for the preparation of *cis*-crotyl alcohol from 2-butyn-1-ol.[15] The best yield was 73%.

***cis*-Cinnamyl Alcohol**: b. p. 115° (5 mm.); d^{22}_{4} 1.044; n^{22}D 1.5728; $n^{36.1}$D 1.5666 (lit.,[2b] b. p. 127–128° (10 mm.); d^{22}_{4} 1.041; n^{22}D 1.5710); 3,5-dinitrobenzoate m. p. 138°.

Preparation of *cis*-Cinnamyl Chloride.—*cis*-Cinnamyl alcohol was converted to *cis*-cinnamyl chloride using phosphorus trichloride in pyridine.[15,16] After the reaction was completed the reaction mixture was washed three times with 50-ml. portions of water and then dried over calcium chloride. The cinnamyl chloride was then obtained by distillation out of a modified Claisen flask at reduced pressure. Several runs were made with the best yield being 61%. When thionyl chloride was used in place of phosphorus trichloride a mixture of *cis*- and *trans*-cinnamyl chloride was obtained.

***cis*-Cinnamyl Chloride**: b. p. 85° (3 mm.); d^{25}_{4} 1.0891; n^{25}D 1.5746.

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(6) Hatch, Gordon and Russ, THIS JOURNAL, **70**, 1093 (1948).

(7) Hatch and Alexander, *ibid.*, **71**, 1037 (1949).

(8) Hatch, Brown and Bailey, *ibid.*, **72**, 3198 (1950).

(9) Hatch and Nesbitt, data presented before the 5th Southwest Regional Meeting of the American Chemical Society, Oklahoma City, December 9, 1949.

(10) Hatch and Gerhardt, THIS JOURNAL, **71**, 1679 (1949).

(11) Hatch and Ballin, *ibid.*, **71**, 1041 (1949).

(12) Nisini and Bernheimer, *Gazz. chim. ital.*, **15**, 84 (1885).

(13) McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1943, p. 196.

(14) Goebel and Wenzke, THIS JOURNAL, **60**, 698 (1938).

(15) Hatch and Nesbitt, *ibid.*, **72**, 727 (1950).

(16) Juvala, *Ber.*, **63B**, 1989 (1930).

Anal.[18] Calcd.: Cl, 23.23. Found: Cl, 23.31, 23.34.

Relative Reactivities

Reaction with Potassium Iodide in Acetone.—The same procedure was used as previously described.[6] The usual modified second order equation, $k = {}^1/_4bt \log (5 - z)/5(1 - z)$, was used and a plot of $\log (5 - z)/5(1 - z)$ *vs.* time gave a straight line between 26 and 77% reacted for *cis*-cinnamyl chloride and between 22 and 64% reacted for *trans*-cinnamyl chloride. The data are given in Table I.

TABLE I

RELATIVE REACTIVITIES OF *cis*- AND *trans*-CINNAMYL CHLORIDE

Reaction with Potassium Iodide in Acetone at 20°

cis, rel. reactivity 17.3[a]			*trans*, rel. reactivity 11.4[a]		
Time, hr.	% reacted	*k*, hr. mole l.	Time, hr.	% reacted	*k*, hr. mole l.
0.17	26.3	4.07	0.25	21.8	2.19
.50	55.4	3.73	.50	42.9	2.56
.67	65.0	3.69	.75	59.2	2.79
.75	70.2	3.81	1.00	63.6	2.38
1.00	77.1	3.53		Av.	2.48 ± 0.19
	Av.	3.77 ± 0.14			

Cuprous Chloride-Catalyzed Acid Hydrolysis at 20°

	cis				
Time, hr.		1.00	2.00	3.00	4.00
% reacted		25.1	52.8	70.8	74.4
	trans				
Time, hr.	0.50	1.00	2.00	3.00	4.00
% reacted	10.1	24.2	53.6	85.2	92.7[b]

[a] Allyl chloride as 1.00 with *k* = 0.218. [b] Average of two runs.

It was necessary, before titration with potassium iodate, to extract the reaction mixture with chloroform to remove the cinnamyl iodide because this iodide can be titrated with potassium iodate. This added step in the analysis adversely affected the precision of the data obtained.

Reaction with Sodium Ethoxide in Ethanol.—The same procedure and mole ratios were used as in previously reported work[7] with the exception of the temperature which was 20 ± 0.1°. Only anomalous results were obtained. The reaction for each isomer apparently was about 60% complete in 10 minutes and only about 65% complete after 40 minutes.

Catalytic Hydrolysis with Cuprous Chloride in Hydrochloric Acid.—The method used was essentially the same as the previously described.[11] It was necessary to introduce the organic chloride to the reaction flask from a weighing bottle instead of by use of gelatine capsules because at the temperature used (20°) the capsules would not melt and liberate the chloride. The data obtained are given in Table I.

Summary

Both *cis*- and *trans*-cinnamyl chloride have been synthesized and the boiling point, density and index of refraction of each isomer have been determined.

The relative reactivities of these two isomers have been determined for their reaction with potassium iodide in acetone. *cis*-Cinnamyl chloride is slightly more reactive than the *trans* isomer.

Attempts to obtain similar data for their reaction with sodium ethoxide in ethanol and for their cuprous chloride catalyzed acid hydrolysis gave anomalous results.

The phenyl group apparently increased the rate of reaction for all three of these reactions.

AUSTIN, TEXAS RECEIVED MARCH 24, 1950

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[18] Chablay, *Ann. chim.*, **1**, 510 (1914).

[CONTRIBUTION FROM THE RESEARCH DIVISION, STAMFORD RESEARCH LABORATORIES, AMERICAN CYANAMID CO.]

The Dimer of α-Phenylacrylonitrile

BY HERBERT A. NEWEY[1] AND JOHN G. ERICKSON

Walker[2] has recently described the preparation of α-phenylacrylonitrile (atroponitrile) and its spontaneous conversion to a crystalline dimer, m. p. 123°, for which he proposed a cyclobutane structure. He hydrolyzed this dimer with sodium hydroxide solution to obtain a dicarboxylic acid, m. p. 204–206°. Hydrolysis of the dimer with sulfuric acid yielded a diamide which was further hydrolyzed to a dibasic acid by means of alkali; the melting points and other properties of the diamide and dibasic acid so obtained were not stated. The dimeric nitrile has also been isolated by German workers,[3] who apparently made no effort to determine its structure. We have also obtained this dimer of α-phenylacrylonitrile, m. p. 123–124°, and wish to present our observations on its chemical properties and structure.

We have found that hydrolysis of the dimer with dilute sulfuric acid yields a dibasic acid, m. p. 238–240°, which, oxidized with potassium permanganate, yields *o*-benzoylbenzoic acid. This same dibasic acid appears to have been obtained by Fittig,[4] who found that α-phenylacrylic acid is dimerized by heating to two products, melting at 237–237.5° and 206°, which he called "α- and β-isatropic" acids, respectively. Fittig also noted that, when heated above its melting point, β-isatropic acid was converted to the higher melting α-isatropic acid. He reported that oxidation of either α- or β-isatropic acid with chromium trioxide in acetic acid yielded *o*-benzoylbenzoic acid and anthraquinone, but no benzoic acid. It appears to us that Walker's dicarboxylic acid, m. p. 204–206°, is identical

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[1] Shell Development Co., Emeryville, Calif.

[2] Walker, U. S. Patent 2,478,990, Aug. 16, 1949.

[3] Meisenburg, I. G. report, May 20, 1938; PB 13321, frame 245. Also PB 50455.

[4] Fittig, *Ann.*, **206**, 34 (1880).