[CONTRIBUTION FROM THE EASTERN[1] REGIONAL RESEARCH LABORATORY]

SYNTHESIS OF 4-(1-NAPHTHYL)-2-BUTYNOIC ACID

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Tincker and Unwin (1), Bausor (2), and Veldstra and Havinga (3) have shown that 1-naphthaleneacetic acid and other naphthalene compounds are active plant-growth regulators. Veldstra (4) has published a comprehensive review listing most chemicals tested up to that time, including many naphthalene compounds, and has since published additional work on naphthalene compounds. Mentzer (5) has made a number of naphthalene acids, including 4-(1-naphthyl)-3-butenoic acid, but did not prepare the acetylenic compounds.

During the course of our testing of various chemicals for plant-growth responses, it was brought to our attention by Dr. T. H. Harris that "4-(1-naphthyl)-2-butynoic acid" might be active. A small sample of the above compound prepared by Harris (6) in 1943 was made available to us. This compound proved to be an active plant-growth regulator and attempts were made to prepare additional material following the directions of Harris (6). Modifications of experimental conditions were found to be necessary during the course of the synthesis and a compound different from that reported by Harris (6) was obtained.

The key compound in the synthesis of 4-(1-naphthyl)-2-butynoic acid is 3-(1-naphthyl)-1-propyne. The preparation of acetylenic naphthyl hydrocarbons has been largely ignored by research workers and few preparations were found to be listed in the literature. Among the first to work with acetylenic naphthyl hydrocarbons was Leroy (7) who prepared the 1- and 2-naphthylacetylenes. Bert and Dorier (8) prepared 1-naphthyl-1-propyne, but as yet the preparation of 2-naphthyl-1-propyne has not been recorded in the literature. Harris (6) pointed out that Bert and Dorier (8) made no mention of the possibility of a *cis* or *trans* configuration in the 1,3-dichloropropenes and 3-(1-naphthyl)-1-chloro-1-propenes used in the preparation of 3-(1-naphthyl)-1-propyne. Harris found that when 1-naphthylmagnesium bromide was reacted with the two geometrical isomers of 1,3-dichloropropene, two different products were obtained; a solid, m.p. 50° and a liquid, b.p. 155–160°/6–7 mm. He concluded that the solid isomer of 3-(1-naphthyl)-1-chloro-1-propene had a *trans*-configuration and the liquid isomer a *cis*-configuration. The low-boiling (104°) and high-boiling (112°) isomers of 1,3-dichloropropene have since been assigned *cis*- and *trans*-configurations, respectively (9–12). We have found that the *cis*-1,3-dichloropropene gives the solid 3-(1-naphthyl)-1-chloro-1-propene and the *trans*-isomer the liquid product. Dipole moment measurements conducted by Maryott

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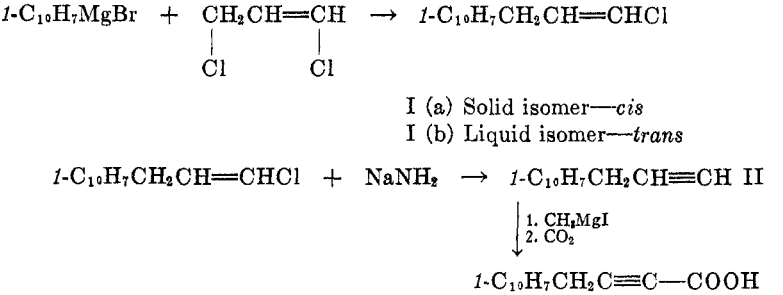
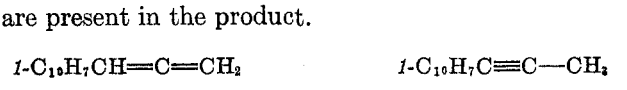
(13) indicated that the solid isomer would have a *cis* configuration. These assignments are opposite to those of Harris (6) but could not be called conclusive since they were run with benzene as a solvent. We have since substantiated Maryott's data by infrared analysis of these compounds and have assigned the *cis*-configuration to the solid 3-(1-naphthyl)-1-chloro-1-propene isomer (14).

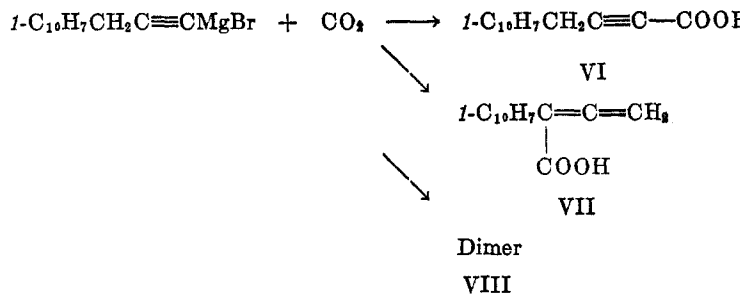


We found that the yield of 3-(1-naphthyl)-1-propyne obtained from the two isomers varied depending upon the isomer used. The *cis*-3-(1-naphthyl)-1-chloro-1-propene isomer (m.p. 50–51°) in general, gave twice the yield of 3-(1-naphthyl)-1-propyne as did the *trans*-isomer. The yields obtained with the solid isomer were comparable to those reported by Bert and Dorier (8) who had started with probably a 50% mixture of isomers and obtained a 50% yield of 3-(1-naphthyl)-1-propyne. These results indicate, in this case at least, that there may be a rearrangement such as $RCH_2—C{\equiv}CH \rightarrow R—C{\equiv}CCH_3$ as postulated by Faworsky (15) for acetylenic compounds heated with alcoholic alkali. On the other hand, Bourguel (16) and Guest (17) have indicated that when sodamide was used at temperatures above 100° with allenes or disubstituted acetylenes a monosubstituted acetylene was formed. Vaughn, Vogt, and Nieuwland (18) introduced the method of using sodamide in liquid ammonia as a dehydrohalogenation agent. They tested this method at −34° with ethylamylacetylene to determine if any rearrangement of the diacetylide would occur but found no evidence for this. Qualitative tests with the propyne by formation of metal derivatives such as the silver, copper, or mercury salts all indicated the presence of the active hydrogen. However, it was thought necessary to investigate the amount of active hydrogen present in a given sample of 3-(1-naphthyl)-1-propyne so produced. The method used was that in Siggia (19) and consisted of reacting the propyne with $AgNO_3$ to obtain the silver acetylide. Results of these tests showed that the propyne formed from mixed 3-(1-naphthyl)-1-chloro-1-propene isomers contained 72% mono-acetylenic compound and the propyne formed from the *cis* isomer contained only 48% mono-acetylenic compound. Although 3-(1-naphthyl)-1-propyne (II) is the normal product, some of the allene type (IV) and a small amount of the rearranged diacetylide, methyl-1-naphthyl acetylene (V) are present in the product.



The presence of the two contaminates was indicated by the infrared data, as shown in Figure 1, Curve 1, and is discussed later in the paper.

The method used to convert the 3-(1-naphthyl)-1-propyne to the acetylenic acid was by carbonation of the acetylenic Grignard. On following the directions given by Harris (6), an acidic compound was isolated but it did not contain an acetylenic bond on the basis of its infrared spectrum. This compound, however, gave the same melting point as Harris' compound. The carbonation of the acetylenic Grignard was then run at $-20°$ instead of at room temperature. A number of products were possible from this reaction, as follows:



However, the acid obtained gave the correct neutral equivalent and carbon and hydrogen analyses for 4-(1-naphthyl)-2-butynoic acid and its infrared curve showed the presence of an acetylenic bond. The melting point of this compound did not agree with that reported by Harris (6). Since no infrared curves of naphthalene unsaturated acid compounds were available, it was decided to prepare the 3-(1-naphthyl)-1-propynoic acid (20), a known compound, for comparison. The infrared data (Figure 1) showed conclusively that both compounds had an acetylenic bond present (Curves 3 and 4). Both compounds showed typical acetylenic absorption peaks at approximately 4.5 microns, whereas the compound made by Harris (6) did not show this absorption peak (Curve 2), nor did it show the allene peak at 5.16 microns as expected for VII. The butynoic acid was then converted to the corresponding butenoic acid using the method of Fischer (21). The infrared curve (Curve 5) of this butenoic acid was then compared with those of the butynoic acid and Harris' compound. The 4-(1-naphthyl)-2-butenoic acid did not show an absorption peak at 4.5 microns, indicating the absence of an acetylenic bond in the compound. The infrared curve of this butenoic acid, however, differed from that of Harris' compound. As further evidence that the carbon side chain was intact, the butenoic acid was converted by catalytic hydrogenation to the known 1-naphthylbutyric acid.

It was thought that perhaps 4-(1-naphthyl)-2-butenoic acid could be prepared by an alternative method. The method of Perkin whereby 1-naphthaldehyde would be condensed with an acid salt, such as sodium propionate, in the presence of the anhydride was considered but Rousset (22) observed that one obtains only 3-(1-naphthyl)-1-propene. Mentzer (23) reported the formation of 1-naphthylisocrotonic acid using anhydrous sodium succinate in the presence of acetic anhydride. The paraconic (dicarboxylic acid) first formed was decom-

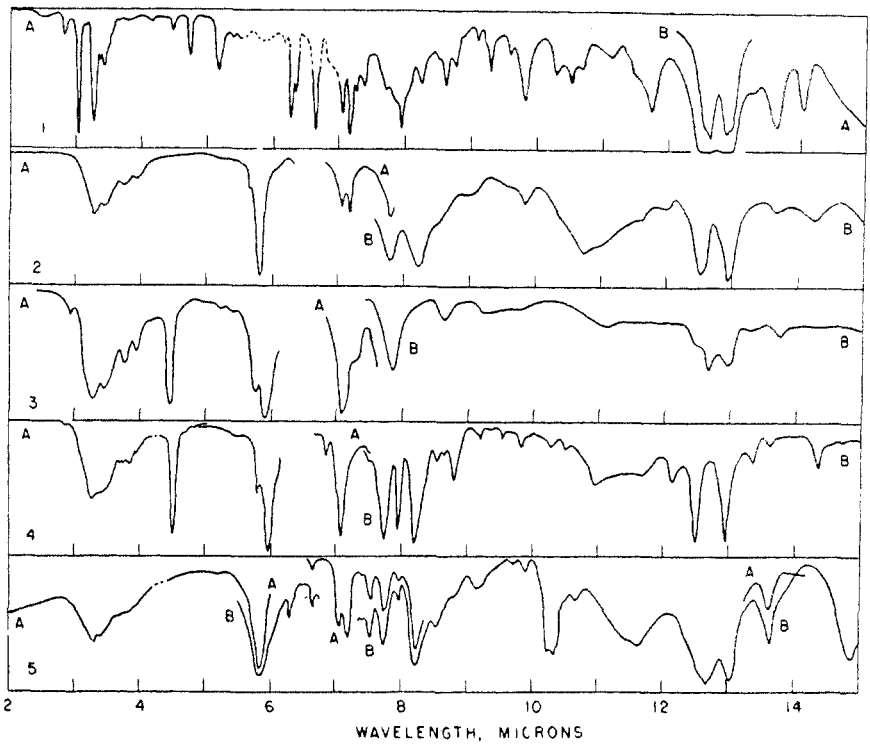


FIG. 1. INFRARED CURVES OF NAPHTHALENE COMPOUNDS. Curve 1. 3-(1-Naphthyl)-1-propyne, liquid state (72% pure, obtained by liquid ammonia method from a mixture of *cis-trans* isomers of 3-(1-naphthyl)-1-chloro-1-propene). A, 0.05 mm.; B, 0.01 mm. Curve 2. Compound from T. H. Harris (6), m.p. 110–111°, 0.45-mm. cell, A, 1% in CCl_4; B, about 2% in CS_2. Curve 3. 4-(1-Naphthyl)-2-butynoic acid. A, an approximately saturated solution in CCl_4, 3.2-mm. cell; B, an approximately saturated solution in CS_2, 0.45-mm. cell.

Curve 4. 3-(1-Naphthyl)-2-propynoic acid, 0.55-mm. cell. A, 0.76% in CCl_4; B, 1% in CS_2. Curve 5. 4-(1-Naphthyl)-butenoic acid, m.p. 108–110°, 0.04-mm. spaced mulls. A, in hexachlorobutadiene; B, in Nujol.

posed by heating at 200–250° to decarboxylate it, and yielded 1-naphthylisocrotonic acid or 4-(1-naphthyl)-3-butenoic acid. In an attempt to make the corresponding 2-butenoic acid which would compare with the hydrogenated butynoic acid, Mentzer observed that the product of 1-naphthylacetaldehyde condensed with malonic acid was not the α,β-unsaturated acid but the β,γ-unsaturated acid as prepared previously by the method of Perkin, thus indicating a migration of the double bond. This might be true of the hydrogenated product of the butynoic acid here since its melting point (110°) is very close to that reported by Mentzer (113°) for the β,γ-unsaturated acid. An attempt to show that the bond in the butenoic acid was α,β by oxidation tended to support the theory of the double bond shift to the β,γ position since the only product isolated was 1-naphthoic acid.

EXPERIMENTAL[4]

Apparatus. The Grignard reaction involving the 1-bromonaphthalene was conducted in a conventional type of Grignard apparatus using all glass-joint glassware and a Hershberg stirrer.

The Grignard apparatus for the formation of the 3-(1-naphthyl)-1-propyne magnesium bromide was also standard equipment except that smaller size glassware was used. A small Dewar flask containing Cellosolve-Dry Ice was used to cool the reaction to −20° during the carbonation.

For the preparation of the sodamide in liquid ammonia, a 3-neck 1-liter round-bottomed flask cooled to −50° (or less) by a Cellosolve-Dry Ice bath (contained in a large Dewar flask) was fitted with a mechanical stirrer, condenser, and gas-inlet tube.

REAGENTS

1-Bromonaphthalene. The commercial grade compound was stirred and heated with sodium hydroxide pellets at 90–100° for four hours. The mixture was filtered and distilled; the fraction distilling at 99–103°/2 mm. was collected and used, n_D^{20} 1.6561 (lit. 1.6582).

1,3-Dichloro-1-propenes. A commercial sample of the mixed isomers was distilled at a slow rate at atmospheric pressure and the *cis*- and *trans*-isomers boiling at 104° and 110°, respectively, were collected.

1-Chloromethylnaphthalene. This compound was prepared by heating, at 80–85°, with vigorous stirring, 320 g. (2.5 moles) of crude naphthalene, 138 g. of paraformaldehyde, 325 ml. of glacial acetic acid, 206 ml. of 85% phosphoric acid, and 452 ml. of concentrated hydrochloric acid for six hours, followed by distillation (24).

1-Naphthaldehyde. To a stirred solution of 237 g. (1.34 moles) of 1-chloromethylnaphthalene in 700 ml. of boiling acetic acid was added slowly 198 g. (1.34 moles) of hexamethylene tetramine. The mixture was heated until the solution became clear, then poured into 500 ml. of water. The oil which separated was purified through the bisulfite addition product and then distilled over nitrogen, b.p. 112–113°/11.9 mm. (25).

PREPARATION OF INTERMEDIATE COMPOUNDS

1. *The 3-(1-naphthyl)-1-chloropropenes.* The method developed by Bert and Dorier (8) was used for the synthesis of these isomers. *Cis*- and *trans*-isomers of 1,3-dichloropropene were reacted with 1-naphthylmagnesium bromide in hot toluene solution to yield *cis*- and *trans*-3-(1-naphthyl)-1-chloro-1-propenes. The yields and experimental details are reported elsewhere (14).

2. *3-(1-Naphthyl)-1-propyne.* This compound was prepared according to the method of Bert and Dorier (8) from the *trans*-3-(1-naphthyl)-1-chloro-1-propene isomer (b.p. 137–145°/2.5 mm.) in a 13% yield with solid sodamide suspended in an organic solvent and a 24% yield with liquid ammonia-sodamide, while the *cis*-isomer (m.p. 50–51°) gave a 21% yield with solid sodamide and a 46% yield with liquid ammonia-sodamide. Since both isomers react similarly only examples of the *cis*-isomer's reactions with the different sodamides will be discussed.

Sodamide (17 g., 0.43 mole) was finely pulverized in a mortar under dry xylene and transferred to a 250-ml. 3-neck flask fitted with a mercury seal stirrer, reflux condenser, and dropping-funnel fitted with calcium chloride drying tubes. A solution of 34.0 g. (0.167 mole) of solid 3-(1-naphthyl)-1-chloro-1-propene in 45 ml. of dry xylene (over sodium) was added dropwise, with stirring, and heated in an oil-bath at 140–150° for three hours. Ammonia was given off and the solution changed in color from red to purple-brown. The xylene was partially removed at atmospheric pressure when the reaction was complete and the remaining solution in the flask was then cooled in an ice-bath and cautiously acidified with a mix-

[4] All melting points were determined on a hot stage and are uncorrected.

ture of one part concentrated hydrochloric acid and two parts crushed ice. The xylene layer was washed with water and then distilled off under reduced pressure in an oil-bath heated to 140°. The product, a clear yellow oil, distilled at 104–105°/1.2 mm., yield 6.1 g. (22%), n_D^{13} 1.633.

In the second method used, the sodamide was prepared according to the directions of Vaughn, *et al.* (18). This method of preparation leads to a very fine suspension of very reactive sodamide in an organic solvent. The liquid ammonia was collected from a 25-pound cylinder resting on its side on a box above the level of the reaction flask, using a bubbler tube to introduce it into the flask.

Ammonia (450–500 ml.) was run into a liter 3-neck round bottomed flask, cooled in a Dry Ice-Cellosolve bath (in a large Dewar flask), and fitted with a stirrer and a reflux tube protected by a calcium chloride drying tube, and a gas inlet tube. Ferric nitrate (0.25 g.) and sodium (0.5 g.) were added to the ammonia and the mixture was stirred rapidly. A deep blue color resulted. Dry air was then bubbled in until the color became a dark-grey black, and then 20.5 g. of sodium was added. Stirring was continued until all the sodium had dissolved, then 70.0 g. (0.346 mole) of the *cis*-3-(1-naphthyl)-1-chloro-1-propene isomer dissolved in 100 ml. of anhydrous ether was added dropwise to the black suspension. A vigorous evolution of gas resulted which subsided by the end of the addition. The stirred solution was then allowed to warm up to room temperature with the addition of 300 ml. of dry toluene or xylene (over sodium) during this time to replace the ammonia evaporating off. The mixture was then poured into a 4-liter beaker and cautiously was acidified with a mixture of one part ice and one part concentrated hydrochloric acid. The acidified solution was separated into two phases and the organic layer was washed with water until neutral, dried over magnesium sulfate, and filtered. The solvents were removed under reduced pressure and the product was vacuum-distilled at 89–90°/0.6 mm., yield 26.08 g. (45.5%).

PREPARATION OF NAPHTHALENE ACIDS

4-(1-Naphthyl)-2-butynoic acid. Methyl iodide (4.78 g., 0.034 mole) in 25 ml. of anhydrous ether (over sodium) was added to 0.73 g. of magnesium and a crystal of iodine in the usual apparatus (100 ml. size). The rapidly stirred solution was refluxed for 15 minutes more after the refluxing caused by the reaction had ceased, cooled to room temperature, and 5.0 g. (0.03 mole) of 3-(1-naphthyl)-1-propyne (53% active hydrogen) in 25 ml. of anhydrous ether was added rapidly with rapid stirring. The solution was left standing overnight in a nitrogen atmosphere, then cooled to −15° in a Dry Ice-Cellosolve bath and dry, gaseous carbon dioxide was added with vigorous stirring. When the mixture became too sticky to stir, 20 ml. of anhydrous xylene was added and the reaction mixture was allowed to warm up to room temperature while the carbon dioxide addition was continued for 2-½ hours. The mixture was then acidified with 1:1 ice-water-concentrated hydrochloric acid. The separated organic layer was washed with water until neutral to Alkacid paper and then extracted with 75 ml. of 5% sodium bicarbonate. This extract was heated on the steam-bath until all of the ether had been removed. The bicarbonate solution was then acidified with a 1:1 mixture of ice-concentrated hydrochloric acid. The yield (recrystallized from toluene) was 42% on the basis of 53% of propyne having reactive hydrogen, m.p. 127–128°.

Anal. Calc'd for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79.
Found: C, 79.93; H, 4.87.

Amide of 4-(1-naphthyl)-2-butynoic acid. The amide was made according to the method of Wotiz (26). The acid (0.1 g.) was placed in a flask, protected with a drying tube, and dissolved in 15 ml. of CCl_4, followed by the addition of 0.15 g. of PCl_5. Aqueous ammonia was then added in excess and the amide was precipitated. The CCl_4 was distilled off and the aqueous layer was extracted with ether, washed with water until neutral, and the ether extract was evaporated to dryness. The product was crystallized from benzene; yield 0.092 g. (94%), m.p. 148–148.4°.

Anal. Calc'd for $C_{14}H_{11}NO$: C, 80.35; H, 5.30; N, 6.69.
Found: C, 80.34; H, 5.27; N, 6.75.

Conversion to 4-(1-naphthyl)-2-butenoic acid. The compound was converted to the ethylenic acid, employing the method used by Fischer (27) to convert phenylpropynoic acid to the *trans*-cinnamic acid. One gram (0.00475 mole) of 4-(1-naphthyl)-2-butynoic acid was placed in a 250-ml. Erlenmeyer flask containing 100 ml. of 1 *N* sodium hydroxide and 1.4 g. of powdered zinc. The flask was shaken for 24 hours, filtered to remove the zinc, and cooled in an ice-bath. The cooled solution was acidified to Congo Red paper with 1:1 ice-concentrated hydrochloric acid. The copious white precipitate was filtered off, dried, and the ethylenic acid was recrystallized from *n*-heptane; yield 0.68 g. (68%), m.p. 108–110°.

Anal. Calc'd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70.

Found: C, 79.18; H, 5.66.

Oxidation of 4-(1-naphthyl)-2-butenoic acid. Pickering and Smith (28) have shown that it is possible to oxidize an unsaturated (ethylenic) side chain on a naphthalene nucleus with the aid of barium permanganate in acetone. *Trans*-4-(1-naphthyl)-2-butenoic acid (100 mg., 0.00046 mole) was dissolved in 5 ml. of freshly distilled acetone and then added dropwise to a stirred solution of 250 mg. (0.00067 mole) of barium permanganate dissolved in 15 ml. of acetone. Manganese dioxide precipitated immediately. Water was added, the acetone was evaporated off, and the manganese dioxide was dissolved by passing in sulfur dioxide gas. The aqueous layer was extracted with ether and the ether extract was then washed with 10% sodium carbonate. Acidification of the basic washings, and extraction with ether, followed by concentration of the ether, gave white crystals, m.p. 156–157° (lit. m.p. 160° for 1-naphthoic acid). The results of this oxidation indicated the possibility that in the process of hydrogenation to the ethylenic acid, the α,β-unsaturated bond may have shifted to the β,γ-link, as shown by Mentzer (23).

The 3-(1-naphthyl)-2-propenoic acids. 1-Naphthaldehyde (22.0 g., 0.14 mole), 26.0 g. malonic acid (0.25 mole), 60 ml. of dry pyridine, and 2 ml. of dry piperidine were placed in a 200-ml. flask fitted with a reflux condenser, protected by a calcium chloride tube, and heated for two hours at 100°. The mixture was then cooled and poured into a mixture of 85 ml. of concentrated hydrochloric acid and 150 g. of ice. The precipitate was filtered, washed with water, and dried; yield 30 g. (88.4%), m.p. 203–205°. This was the 1-naphthylmalonic acid condensation product.

This dried product was heated in an oil-bath at 215–220°. The solid material melted and decomposed with the evolution of carbon dioxide. Heating was continued for one hour, then the material was cooled, dissolved in 2 *N* sodium hydroxide, and extracted with ether to remove any non-acidic organic matter, and then acidified; yield 20.8 g. (85%) of crude material; m.p. 190–202°, recrystallized from chloroform, m.p. 208.5–209.5°. According to Wojack (20), this propenoic acid has the *trans* configuration.

Anal. Calc'd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.09.

Found: C, 78.39; H, 5.14.

To prepare the *cis* propenoic acid, 1.5 g. of *trans*-3-(1-naphthyl)-2-propenoic acid was placed in a 250-ml. quartz round-bottomed flask containing 230 ml. of anhydrous benzene. The flask was fitted with a mechanical stirrer and the contents were heated to 64–70° and irradiated with ultraviolet light for 40 hours (29). The solution was cooled and extracted with 10% sodium carbonate. The sodium carbonate solution was acidified to Congo Red with 6 *N* hydrochloric acid and the *cis*-propenoic acid was extracted with ether. The ether solution after drying over calcium chloride was concentrated to dryness. The yellow crystals thus obtained were recrystallized from acetone. The *cis*-form is soluble in cold acetone while the *trans*-form is insoluble. The tan crystals were recrystallized from chloroform to yield white crystals, m.p. 144.8–146.2°.

Anal. Calc'd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.09.

Found: C, 78.31; H, 5.13.

3-(1-Naphthyl)-2-propynoic acid. The ethyl ester of *trans*-1-naphthyl propenoic acid was prepared, b.p. 122–124°/0.8 mm. The ethyl ester (10.0 g., 0.044 mole) was dissolved in 10 ml. of carbon tetrachloride and a carbon tetrachloride solution (70 ml.) of bromine (0.044 mole) was added dropwise over 40 minutes, while stirring continuously under ultraviolet

illumination. Stirring was continued for another two hours and the solvent was then removed under reduced pressure to give 16.7 g. of the dibromo ester as a red oil (98.8%). This compound was debrominated by refluxing for 6 hours with potassium hydroxide in 98% ethanol solution. The alcohol was removed at reduced pressure and the solid residue was dissolved in water, acidified with 20% sulfuric acid, and extracted with benzene. The benzene was distilled off at reduced pressure to give a quantitative yield of tan crystals, m.p. 128–130°. Recrystallization from carbon tetrachloride, using Norit to remove some color, gave tan crystals, m.p. 136–137° [lit. 137° (20)].

Anal. Calc'd for $C_{13}H_9O_2$: C, 79.57; H, 4.11.

Found: C, 79.37; H, 4.07.

This 3-(1-naphthyl)-2-propynoic preparation was used to obtain infrared data which was compared with the data obtained on 4-(1-naphthyl)-2-butynoic acid. The infrared data confirmed the presence of an acetylenic bond in both acids.

INTERPRETATION OF INFRARED DATA[5]

Published infrared data (30) on a few naphthalene compounds were used to assist in the interpretation of the curves shown in Figure 1. According to Wotiz, *et al* (31), the monoacetylenic type of link should give a strong peak at 3.06 microns, as shown in Curve 1, for 3-(1-naphthyl)-1-propyne, and a strong peak at 4.4–4.57 μ for the disubstituted acetylenic compounds, as shown in Curves 3 and 4. Allene formation of the propyne was demonstrated by a peak at 5.16 microns in Curve 1, as had previously been pointed out by Wotiz, *et al.* (32) in his work with acetylenic and allenic aliphatic acids, which substantiated the active hydrogen determinations reported in our paper.

The infrared curve of 4-(1-naphthyl)-2-butynoic acid (Curve 3) was compared with that of 3-(1-naphthyl)-2-propynoic acid (Curve 4) to establish the presence of an acetylenic bond. Both of these compounds showed an absorption peak at 4.5 microns, which is in agreement with the work of Wotiz, *et al.* (32) on aliphatic acetylenic acids. The carboxyl groups were also clearly shown and there was some evidence of dimer formation, as indicated by a small peak at 5.7 microns. The acid prepared by Harris (6) failed to show an acetylenic bond in the infrared spectrum (Curve 2), although the carboxyl group was clearly indicated by a peak at 5.8 microns. Chemical reduction of the butynoic acid resulted in disappearance of the acetylenic peak at 4.5 microns (Curve 5), although the carboxyl peak at 5.85 microns was unaffected. An ethylenic bond was not observed, however, possibly due to a shift from α,β to β,γ of the double bond and conjugation with the aromatic ring, which would tend to mask this effect.

PLANT-GROWTH REGULATING ACTIVITY OF THE NAPHTHALENE ACIDS

The compounds prepared in this investigation have been screened for plant-growth responses by Dr. J. W. Mitchell, Bureau of Plant Industry, Soils, and Agricultural Engineering, Beltsville, Maryland. 4-(1-Naphthyl)-2-butynoic acid in a Tween 20-Lanolin paste was applied as a smooth band about 6–8 mm. wide around the 1st internode midway between the 1st and 2nd nodes of Black Valentine variety of beans grown under greenhouse conditions. Treated plants showed slight curvature at treated area, local proliferation and root induction; all internodes were much shorter than those of the controls and a brown discoloration of tissue at the treated area was observed. The other acids gave similar results in this screening program.

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[5] We are indebted to Mr. J. S. Ard, of this Laboratory, for analytical and infrared data. The infrared curves were obtained with a Perkin-Elmer, Model 12-C, single beam instrument, using a NaCl prism.

SUMMARY

The synthesis of a new acetylenic acid, 4-(1-naphthyl)-2-butynoic acid, and some of its derivatives has been described. Infrared data have been used as an aid in establishing its structure.

PHILADELPHIA 18, PENNA.

REFERENCES

(1) TINCKER AND UNWIN, *J. Roy. Hort. Soc.*, **64**, 554 (1939).
(2) BAUSOR, *Am. J. of Botany*, **26**, 415 (1939).
(3) VELDSTRA AND HAVINGA, *Rec. trav. chim.*, **62**, 841 (1943).
(4) VELDSTRA, *Enzymologia*, **11**, 97 (1944).
(5) MENTZER, *Bull. soc. chim. biol.*, **30**, 384 (1948).
(6) HARRIS, M. S. Thesis, George Washington University, Washington, D. C., 1943.
(7) LEROY, *Bull. soc. chim.*, **6**, 385 (1891); *Bull. soc. chim.*, **8**, 644 (1892).
(8) BERT AND DORIER, *Bull. soc. chim.*, **37**, 1600 (1925); *Bull. soc. chim.*, **39**, 1610 (1926).
(9) HATCH AND ROBERTS, *J. Am. Chem. Soc.*, **68**, 1196 (1946); HATCH, GORDON, AND RUSS, *J. Am. Chem. Soc.*, **70**, 1093 (1948).
(10) ANDREWS AND KEPNER, *J. Am. Chem. Soc.*, **69**, 2230 (1947).
(11) SMITH AND KING, *J. Am. Chem. Soc.*, **70**, 3528 (1948); ORIANI AND SMYTH, *J. Chem. Phys.*, **16**, 930 (1948).
(12) HATCH AND PERRY, *J. Am. Chem. Soc.*, **71**, 3262 (1949).
(13) MARYOTT, National Bureau of Standards, private communication, 1949.
(14) WOLFE, DOUKAS, AND ARD, *J. Am. Chem. Soc.*, **76**, 627 (1954).
(15) FAWORSKY, *J. prakt. Chem.*, **37**, 382, 417 (1888).
(16) BOURGUEL, *Ann. chim. (Paris)*, [11] **3**, 191, 325 (1925); *Compt. rend.*, **179**, 686 (1925); *Compt. rend.*, **192**, 686 (1931).
(17) GUEST, *J. Am. Chem. Soc.*, **50**, 1744 (1928).
(18) VAUGHN, VOGT, AND NIEUWLAND, *J. Am. Chem. Soc.*, **56**, 2120 (1934).
(19) SIGGIA, *Quantitative Organic Analysis via Functional Groups*, p. 54, John Wiley, New York (1949).
(20) WOJACK, GLUPE, AND JATZKEWITZ, *Ber.*, **71**, 1372 (1938).
(21) FISCHER, *Ann.*, **394**, 350 (1912).
(22) ROUSSET, *Bull. soc. chim.*, **17**, 812 (1897).
(23) MENTZER, *Bull. soc. chim. France*, 943 (1948); MENTZER AND PILLON, *Bull. soc. chim. France*, 607 (1950).
(24) *Org. Syntheses*, **24**, 20 (1944).
(25) PRICE AND VOONG, *J. Org. Chem.*, **14**, 111 (1949).
(26) WOTIZ, *J. Am. Chem. Soc.*, **72**, 1639 (1950).
(27) FISCHER, *Ann.*, **386**, 374 (1912); *Ann.*, **394**, 350 (1912).
(28) PICKERING AND SMITH, *Rec. trav. chim.*, **69**, 535 (1950).
(29) LOCK AND GERGELY, *Monatsh.*, **79**, 521 (1948).
(30) RANDALL, FOWLER, FUSON, AND DANGL, *Infrared Determination of Organic Structures*, D. Van Nostrand Company, Inc., New York, 1949; COLTHUP, *J. Opt. Soc. Amer.*, **40**, 397 (1950).
(31) WOTIZ AND MILLER, *J. Am. Chem. Soc.*, **71**, 3441 (1949); WOTIZ, *J. Am. Chem. Soc.*, **72**, 1639 (1950).
(32) WOTIZ, MATTHEWS, AND LIEB, *J. Am. Chem. Soc.*, **73**, 5503 (1951).