SUBSTITUTED PHENYLACETYLENES. INFRARED SPECTRA

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ABSTRACT

A series of substituted phenylacetylenes has been prepared and their infrared spectra recorded. The C≡C and ≡C—H stretching frequencies are only slightly affected by substituents in the phenyl ring. Substituents in the 4-position cause a splitting of the ≡C—H band into two clearly resolved bands of similar intensity, about 10 cm^{-1} apart.

As part of an investigation into the formation of complexes between unsaturated organic molecules and transition metals, a series of substituted phenylacetylenes has been prepared and their infrared spectra recorded. Nuclear magnetic resonance spectra of these compounds have already been reported (1). In this paper we give the principal features of the infrared spectra of these compounds and the methods used for their preparation.

EXPERIMENTAL

A wide variety of substituted phenylacetylenes may be prepared by one of two general methods: (*a*) from the substituted acetophenone by chlorination followed by dehydrochlorination with alkali (2), and (*b*) from the substituted cinnamic acid by bromination followed by dehydrobromination with base.

Method (*a*) was used for the following compounds, the first four of which have not been reported previously, although Dessy (3) has described mercury acetylides derived from two of them (4-fluoro- and 3-methyl-phenylacetylene).

2-Methylphenylacetylene.—A mixture of 9.5 g phosphorus pentachloride and 5.5 g 2-methylacetophenone was maintained at 70–80° for 30 minutes. The resulting dark orange solution was distilled and the fraction boiling between 80–95° at 15 mm was collected (4.4 g). This fraction was refluxed overnight with 5 g potassium hydroxide in 15 ml absolute ethanol. After adding 150 ml iced water the solution was extracted with ether, and the extract was washed with iced water and dried over sodium sulphate. Distillation at reduced pressure gave the crude product, which was stored over potassium hydroxide pellets overnight at room temperature and then distilled from fresh pellets of potassium hydroxide. The product (1.8 g, 38%) was a colorless oil, b.p. 49–50° at 13 mm. Calc. for C_9H_8: C, 93.1; H, 6.9. Found: C, 93.0; H, 6.5.

2-Fluorophenylacetylene.—Prepared from 2-fluoroacetophenone (Pierce Chemical Co.) by the procedure used for 2-methylphenylacetylene. The product (5.8 g, 42%) was an oil, b.p. 31–32° at 10 mm. Calc. for C_8H_5F: C, 80.0; H, 4.2. Found: C, 80.0; H, 4.7.

4-Fluorophenylacetylene.—Prepared from 4-fluoroacetophenone (Pierce Chemical Co.) by the procedure used for 2-methylphenylacetylene. The product (7.5 g, 61%) was a solid, m.p. 25°, b.p. 34–35° at 10 mm, 140° at 758 mm. Calc. for C_8H_5F: C, 80.0, H, 4.2. Found: C, 80.1; H, 4.3.

3-*Methylphenylacetylene.*—Phosphorus pentachloride (83.5 g) was added to 50 g 3-methylacetophenone in 100 ml dry benzene. The mixture was cooled in ice during the initial vigorous reaction and then stirred overnight at room temperature, protected from moisture. The resulting solution was distilled at reduced pressure and the fraction boiling at 105–110° at 16 mm was collected (62 g). This fraction was refluxed for 5 hours with 75 g potassium hydroxide in 150 ml 95% ethanol. Dilution with 250 ml water, extraction with ether, drying and distillation of the ether extract gave the crude product, b.p. 75–80° at 23 mm, which was stored over potassium hydroxide pellets overnight. Distillation from fresh potassium hydroxide gave the product (16 g, 37%) as a colorless oil, b.p. 58–59° at 14 mm. Calc. for C_9H_8: C, 93.1; H, 6.9. Found: C, 92.1; H, 7.1.

4-Methylphenylacetylene.—Prepared from 4-methylacetophenone by the procedure used for 2-methylphenylacetylene. The product was an oil, b.p. 59–60° at 16 mm (lit. (2) b.p. 65–67° at 18 mm).

3-Methoxyphenylacetylene.—Prepared from 3-methoxyacetophenone by the method of Johnson *et al.* (4), b.p. 80° at 12 mm (lit. (4) b.p. 85° at 13 mm).

4-Bromophenylacetylene.—Prepared from 4-bromoacetophenone as described by Jacobs (5), m.p. 63° (lit. (2) m.p. 63.5°).

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4-Chlorophenylacetylene.—Prepared from 4-chloroacetophenone as described by Jacobs (5), b.p. 62–63° at 13 mm, m.p. 43° (lit. (2) m.p. 43.5–44°). This compound is best purified by sublimation.

2-Chlorophenylacetylene.—Prepared from 2-chloroacetophenone by the same method as was used for 2-methylphenylacetylene, b.p. 44–45° at 11 mm (lit. (2) b.p. 71° at 18 mm).

Method (*b*) was used for the following compounds.

2-Methoxyphenylacetylene.—The following procedure is a modification of those described by Manchot (6) and Smissman (7). A solution of 48 g bromine in 200 ml dry chloroform was added during 2 hours to 50 g 2-methoxycinnamic acid in 250 ml dry chloroform. During the addition the mixture was stirred vigorously and kept between 0° and 5°. After the addition the solution was stirred for a further 30 minutes and then cyclohexene was added to remove excess bromine. The solvent was removed in a stream of dry air and the resulting crystalline mass was washed with cold carbon tetrachloride. The yield of 2-methoxy-α,β-dibromocinnamic acid was quantitative. This product was heated on a steam bath for 2 hours with 600 ml 10% sodium carbonate solution. The cooled solution was extracted with ether, and the ether extract was washed, dried, and evaporated. The residue was refluxed for 4-hours with 400 ml tertiary butanol in which 8 g potassium metal had been dissolved. Most of the solvent was then removed by distillation at reduced pressure and the residue treated with 500 ml water. Ether extraction, followed by washing, drying, and distillation of the extract, gave the crude product, b.p. 88–92° at 8 mm. This was stored overnight over pellets of potassium hydroxide and then distilled from fresh potassium hydroxide, giving a colorless liquid (12 g, 33%), b.p. 89–90° at 8 mm (lit. (8) b.p. 93° at 10 mm).

4-Methoxyphenylacetylene.—Prepared from 4-methoxycinnamic acid by the procedure used for 2-methoxyphenylacetylene, b.p. 86° at 9 mm, m.p. 29° (lit. (7) b.p. 90–95° at 10 mm).

2-Nitrophenylacetylene.—2-Nitrocinnamic acid was converted into *cis*-2-nitro-β-bromostyrene by the method of Dann *et al.* (9). The product (11.5 g) was stirred for 30 minutes at room temperature with 20 g sodium hydroxide in 250 ml 95% ethanol. The resulting solution was neutralized with glacial acetic acid, and 200 ml solvent was removed by distillation at reduced pressure. The crude product was precipitated by adding 500 ml iced water. Recrystallization from aqueous ethanol gave the pure product (3.4 g, 45%) as colorless needles, m.p. 81° (lit. (10) m.p. 81–82°).

3-Nitrophenylacetylene.—Prepared from 3-nitrocinnamic acid by the procedure used for 2-nitrophenylacetylene, b.p. 118–120 at 20 mm, m.p. 27° (lit. (11) m.p. 27°).

4-Nitrophenylacetylene.—Prepared by the method of Cristol *et al.* (12), m.p. 149–150° (lit. (12) m.p. 148–149°).

Other methods were used for the following compounds.

2-Hydroxyphenylacetylene.—Coumarilic acid (benzofuran-2-carboxylic acid) was prepared from coumarin by the method of Fuson *et al.* (13). An intimate mixture of 20 g coumarilic acid, 20 g powdered calcium oxide, and 1 g copper bronze powder was heated in a small distilling flask with a free flame until distillation stopped. The crude benzofuran (14 g) was washed with 10% sodium hydroxide solution, dried over sodium sulphate, and distilled, b.p. 170°.* A mixture of 11.8 g benzofuran, 6.9 g sodium, and 94 g pyridine (freshly distilled from potassium hydroxide) was heated in an oil bath at 190° for 4 hours. The cooled mixture was treated with pyridine and water and then acidified (to congo red) with dilute hydrochloric acid. Extraction with ether, followed by drying and distillation of the ether extract, gave the crude product, which was then dissolved in 10% aqueous potassium hydroxide. The resulting solution was extracted with ether to remove any unreacted benzofuran, and the acetylene was regenerated by the addition of dilute hydrochloric acid to the alkaline solution. The resulting acidic solution was extracted with ether, and the ether extract was washed, dried, and distilled at reduced pressure to give the pure product (3.8 g, 32%), b.p. 63° at 7 mm (lit. (8) b.p. 73–74° at 11 mm).

2-Aminophenylacetylene.—Prepared by the reduction of 2-nitrophenylacetylene as described by Schofield and Swain (10). The product was purified by precipitating the amine hydrochloride from benzene solution, and recovering the free amine by treating the precipitate with aqueous alkali. Extraction with ether, followed by washing, drying, and distillation of the ether extract, gave the product as a yellowish oil, b.p. 99–101° at 13 mm (lit. (10) b.p. 98–100° at 12 mm).

4-Aminophenylacetylene.—Prepared by reduction of 4-nitrophenylacetylene, as described by Burawoy and Critchley (14), m.p. 99–100° (lit. (14) m.p. 100°).

Phenylacetylene.—The commercial material was distilled from pellets of potassium hydroxide and the fraction boiling between 140–144° was collected and stored over potassium hydroxide. Fractional distillation gave the pure material, b.p. 44° at 23 mm (lit. (15) b.p. 140°).

Infrared Spectra

The infrared spectra of dilute solutions (ca. 5%) of the compounds in carbon tetrachloride (Fisher 'Spectranalysed') were obtained using a Perkin–Elmer 221G prism-grating spectrometer. The instrument was calibrated against indene and routinely checked against polystyrene film. The spectra were recorded at 30±1°, at a scanning speed of approximately 1 cm^{-1}/sec, in the regions of interest. Standard 221G

**Details of this method for the decarboxylation of coumarilic acid, developed by H. Gilman, were kindly provided by Professor A. G. Brook.*

settings used were: slit schedule 927, attenuator speed 11.00, amplifier gain 4.5, and scan suppression at 4–5. A 0.1-mm sodium chloride fixed cell was used and the position of the weak band at 2100 cm^{-1} was checked if necessary by using scale expansion or a 0.5-mm cell. Reproducibility was ± 1 cm^{-1}, and the precision of the band maxima is estimated to be ± 2 cm^{-1}.

DISCUSSION

Table I shows details of the C≡C and ≡C—H stretching frequencies observed for these compounds.

TABLE I

Stretching frequencies ν for compounds X—$C_6H_4C_2H$

X	ν (cm^{-1}) ≡C—H	ν (cm^{-1}) C≡C	X	ν (cm^{-1}) ≡C—H	ν (cm^{-1}) C≡C
4-Amino	3328, 3313	2114	Hydrogen	3319, 3308 (sh)	2119
2-Amino	3316	2103	4-Fluoro	3319, 3305	2119 (w)
4-Methoxy	3324, 3310	2116	2-Fluoro	3320	2125, 2113 (sh)
3-Methoxy	3322	2118	4-Chloro	3317, 3310	2119 (w)
2-Methoxy	3320	2116	2-Chloro	3308	2112 (w)
2-Hydroxy	3310	2109	4-Bromo	3318, 3307	2119 (w)
4-Methyl	3323, 3307	2115	4-Nitro	3322, 3308	2122 (w)
3-Methyl	3313	2112	3-Nitro	3314	2126 (w)
2-Methyl	3312	2111	2-Nitro	3314	2119 (w)

The carbon–hydrogen stretching mode gives a strong absorption in all cases. The carbon–carbon stretching mode gives a much weaker absorption, the maximum observed for the series being about 10% of the ≡C—H absorption. Those compounds in which the C≡C absorption is markedly less than 10% of that of ≡C—H are shown as weak (w) in the table. It may be significant that such compounds all contain electron-withdrawing substituents.

It will be seen that there is little correlation between the electron-withdrawing or -donating ability of the ring substituent and the frequency of either stretching vibration. If the variations observed do indicate significant trends then these are that electron-withdrawing substituents tend to decrease the ≡C—H and increase the C≡C stretching frequencies.

A weak band showing up as a shoulder on the low-frequency side of the ≡C—H absorption has been reported for a variety of acetylenes by Brand *et al.* (16). They found this band to be most intense in the spectra of the aryl acetylenes studied and suggest that this absorption results from a combination tone intensified by Fermi resonance. Nyquist and Potts (17), in a more detailed examination of phenylacetylene, arrived at the same conclusion and propose that the absorption results from the summation of the first overtone of the ≡C—H bending mode (at about 1220–1250 cm^{-1}) and the C≡C stretching fundamental, the intensity being increased by Fermi resonance with the ≡C—H stretching fundamental. However recent work by West and Kraihanzel (15), which included a study of the spectrum of deuterophenylacetylene ($C_6H_5C_2D$), may invalidate the earlier proposals since these authors report that side bands also accompany the C—D stretching absorption at 2595 cm^{-1}.

We find that compounds with substituents in the 2- and 3-positions give a single, sharp band at about 3315 cm^{-1}, with perhaps a very weak unresolved shoulder, but that when the substituent is in the 4-position this band is split into two bands about 10 cm^{-1} apart. The lower-frequency band of this pair is usually of slightly lower intensity than the other,

but only in the unsubstituted phenylacetylene is it sufficiently poorly resolved to be described as a shoulder. These spectra are complex in the 1000–1500 cm^{-1} region and in many cases it is difficult to assign a band to the first overtone of the ≡C—H bending mode, but the suggestion of Nyquist and Potts is supported by the fact that the 4-substituted compounds usually have a strong band between 1220–1230 cm^{-1}, which may be attributed to this overtone, whereas the 2- and 3-substituted compounds usually do not.

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