b.p. 75–80° (10 mm.). Purification by redistillation gave material melting at 24–25°.

The Rearrangement of 2,4,6-Trialkyl-*s*-triazines to 4-Aminopyrimidines.—A mixture of equal weights of 2,4,6-triethyl-*s*-triazine (I) and methanol was saturated with gaseous ammonia, and 7.58 g. of the resultant solution was held at 150° and 8500–8300 atm. for 17 hours. By distillation, 2.01 g. (53%) of the triazine was recovered. 4-Amino-2,6-diethyl-5-methylpyrimidine (VI, 1.21 g., 32% yield) was isolated by sublimation of the distillation residue. After recrystallization from ethanol it melted at 189–190°[18] alone or mixed with an authentic specimen prepared by the method of Larchar.[16]

A solution of 2.84 g. of 2,4,6-trimethyl-*s*-triazine in 4.80 g. of methanol was held at 150° and 8500 atm. for 18 hours. 4-Amino-2,6-dimethylpyrimidine (III, 0.35 g., 12% yield) and 2,4,6-trimethyl-*s*-triazine (1.9 g., 66% recovery) were separated from the reaction mixture by fractional sublimation.

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[18] R. Schwarze, *ibid.*, **42**, 1 (1890), reports m.p. 190°.

Wilmington, Delaware

[Contribution No. 299 from the Chemical Department, Experimental Station, E. I. du Pont de Nemours & Company]

The Reaction of Acetylene with Acrylic Compounds[1]

By T. L. Cairns, V. A. Engelhardt, H. L. Jackson, G. H. Kalb and J. C. Sauer

Received July 7, 1952

Reaction of acetylene with acrylic compounds was found to give high yields of heptatrienoic acid derivatives. The structures of these compounds were demonstrated and their reactivity in Diels–Alder and dimerization reactions investigated. Methyl 2,4,6-heptatrienoate was converted to the corresponding acid and alcohol.

A new reaction involving the condensation of two molecules of acetylene with one molecule of an α,β-unsaturated compound has been discovered during investigation of the behavior of acetylene in the presence of complex nickel-containing catalysts. Thus, interaction of acetylene and methyl acrylate gives in high yield a new compound proven to be methyl 2,4,6-heptatrienoate (I)

$$2C_2H_2 + CH_2{=}CH{-}CO_2CH_3 \longrightarrow CH_2{=}CH{-}CH{=}CH{-}CH{=}CH{-}CO_2CH_3$$

I

The reaction proceeds readily also with acrylonitrile to form 2,4,6-heptatrienenitrile (II). This synthesis provides a convenient new route to otherwise difficultly accessible, highly conjugated aliphatic compounds.

Proof of Structure.—The ester I and nitrile II absorbed three moles of hydrogen under mild conditions forming the well known corresponding saturated compounds and proving the linear arrangement of the seven chain carbon atoms. The nitrile failed to form a solid derivative with copper or mercury salts and this fact, coupled with the absence of absorption at 3 μ in the infrared, excludes the possibility of a terminal acetylenic function. Ozonization of the nitrile yielded hydrogen cyanide, formic acid and oxalic acid, indicating the presence of a double bond alpha, beta to the nitrile group[2] and the presence of terminal unsaturation. No higher dibasic acids, acetic acid or cyanoacetic acid, products to be expected from analogous compounds having allenic or acetylenic functions, were observed. Finally, the ultraviolet and infrared absorption spectra of the nitrile and the Raman and infrared spectra of the ester as well as reactivity in Diels–Alder condensations, Michael-type additions and polymerization are all in accord with the heptatriene structure.

Synthesis Conditions, Catalysts and Reaction Mechanism.—The most effective type of catalyst found for synthesis of these heptatrienes was a compound of nickel modified by the addition of a phosphine or a phosphite. The catalyst was ordinarily prepared by adding nickel carbonyl and triphenylphosphine to the acrylic compound. Such a mixture probably gives rise to the complexes, $Ni(CO)_2[(C_6H_5)_3P]_2$ and $Ni(CO)_3[(C_6H_5)_3P]$.[3] Other nickel compounds, such as nickel cyanide, in combination with triethyl phosphite were also active as catalysts.

The reaction was conducted by treating the acrylate containing nickel carbonyl and triphenylphosphine with acetylene at pressures up to about 15 atm. and temperatures of 70–90°. Yields of about 80% methyl heptatrienoate and about 70% heptatrienenitrile were regularly obtained. An induction period was frequently observed after which a smooth, exothermic reaction took place with absorption of approximately the theoretical amount of acetylene. The induction period could be reduced or eliminated by starting the reaction at temperatures around 100° followed by rapid cooling to about 70°. Great care must be exercised to prevent uncontrolled increases in temperature during these reactions since occasional violent decompositions have been encountered.

There is at present insufficient evidence on which to base a reaction mechanism for the synthesis of these heptatrienes. However, in postulating a probable mechanism the following must be taken into account. (1) One of the preferred catalysts for the synthesis of heptatrienes is the complex from nickel carbonyl and triphenylphosphine, the same catalyst reported to be effective for the conversion of acetylene to benzene.[3]

(2) We have found that nickel cyanide, which in the presence of inert solvents or weak electron

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(1) This paper was presented at the New York Meeting of the American Chemical Society, Sept., 1951. See abstracts page 14 M.

(2) A. van Dormael, *Bull. soc. chim. Belg.*, **52**, 100 (1943), shows that α,β-unsaturated nitriles yield hydrogen cyanide while β,γ-unsaturated nitriles form cyanoacetic acid when ozonized.

(3) W. Reppe and W. J. Schweckendieck, *Ann.*, **560**, 104 (1948).

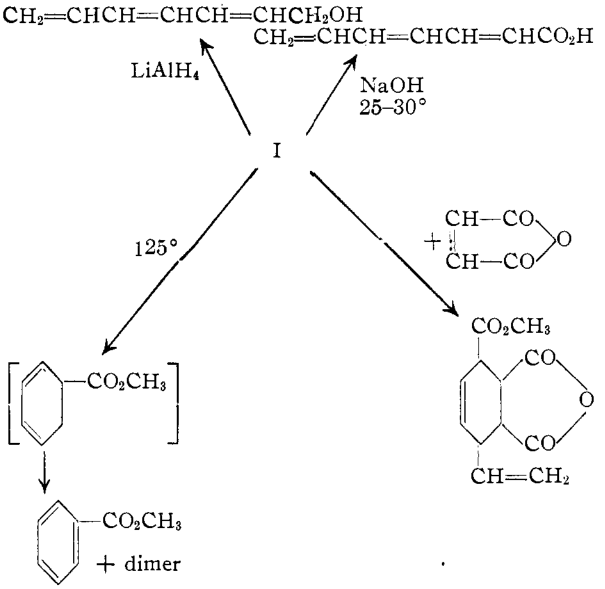
donors such as ethers is well known for the conversion of acetylene to cyclooötatetraene[4] under similar conditions, may be modified with triphenylphosphine to yield a combination active both for the synthesis of heptatrienes and benzene.

(3) It appears likely that all three of these reactions, namely, the preparation of benzene, cyclooctatetraene and heptatriene derivatives from acetylene takes place in homogeneous systems and that heterogeneous catalysis is not involved. Therefore, the indications are that the three reactions are related and involve intermediate formation of nickel–acetylene complexes.

Thus, unmodified nickel compounds, or nickel compounds in the presence of weak electron donors such as ethers, may be pictured as binding four acetylene molecules in such a manner that they can unite to form cyclooötatetraene. In the presence of stronger electron donors such as the phosphines, the nickel can hold only three molecules of acetylene or two of acetylene and one of acrylic compounds and, accordingly, this type of modified catalyst leads to benzene and the heptatrienes. Attempts were made to isolate possible intermediates in postulated, stepwise formation of the heptatrienes, but no indication of 1:1 or 1:2 acetylene/acrylonitrile adducts was obtained even when the reaction was run at very low conversion and in the presence of great excess of the acrylonitrile. The only compound formed under these conditions was heptatrienenitrile, the 2:1 acetylene/acrylonitrile adduct.

Chemical Reactions of the Heptatrienes.—Typical chemical reactions of methyl heptatrienoate, in addition to those mentioned in the section on proof of structure, are outlined in the chart. Hydrolysis of the ester to the free acid was found to take place with the theoretical amount of 10% sodium hydroxide at room temperature, conditions analogous to those used in the hydrolysis of methyl formate. More vigorous conditions tended to resinify the acid. Reduction of the methyl heptatrienoate to the unsaturated carbinol with lithium aluminum hydride proceeded readily. The ester reacted with maleic anhydride to form a Diels–Alder adduct whose structure was not demonstrated unequivocally. The formula shown represents one possibility.

The Reactions of Methyl Heptatrienoate.—At 125° the ester underwent a mild, exothermic, self-condensation resulting in the formation of a dimer and also a mixture of methyl benzoate and a compound that was almost certainly a methyl dihydrobenzoate.[5] The addition of methyl malonate to methyl heptatrienoate took place in the presence of sodium ethoxide but a mixture of products was obtained. The reaction was not as clean-cut as most cyanoethylation reactions or the analogous cyanobutenylation reaction.[6] Heptatrienenitrile underwent analogous dimerization and Diels–Alder reactions. Both the nitrile and the ester polymerized in the presence of typical free radical generators, such as aqueous persulfate–bisulfite, to yield rubber-like to hard materials, generally insoluble in common solvents.



The heptatriene derivatives would be expected to exist as four different geometric isomers corresponding to *cis–trans* isomerism about the two unsymmetrically substituted double bonds. In no case was a pure isomer isolated and characterized. The relatively wide boiling and melting ranges of these compounds are indicative of the presence of isomers.

Experimental[7,8]

2,4,6-Heptatrienenitrile.—To 150 g. of freshly distilled acrylonitrile was added 3 g. of triphenylphosphine and 1.5 g. of nickel carbonyl. After reaction between the phosphine and the carbonyl was complete, as evidenced by cessation of carbon monoxide evolution, the solution was transferred to a 500-ml. stainless steel rocker bomb. The bomb was flushed three times with nitrogen by alternate pressuring to 500 lb./sq. in. and bleeding to ordinary pressure and then was flushed once with acetylene. The equipment was installed behind a heavy barricade and all operations with acetylene were controlled from the outside. Finally, 50 lb./sq. in. acetylene pressure was applied and the reaction mixture heated to 75°. When this temperature was reached, 200 lb./sq. in. acetylene pressure was applied. After reaction was initiated (*ca.* 30 minutes) as indicated by a drop in acetylene pressure, the bomb was allowed to cool to 70°. Acetylene was added at least every half hour until approximately 2 moles of acetylene was absorbed for each mole of acrylonitrile (approximately 6.5 hours). Temperature "kicks" indicated the exothermic nature of the reaction. The tube was cooled to ordinary temperature, bled down, the contents removed, and the brownish reaction product (286 g.) distilled. Approximately 76 g. of recovered acrylonitrile was collected in a Dry Ice–acetone trap as a low boiling fraction. The main fraction, 2,4,6-heptatrienenitrile, amounted to 110 g. and boiled at 57–60° (2–3 mm.) (d^{25}_4 0.9089, $n^{25}\text{D}$ 1.5540). This amounted to a 74% yield of 2,4,6-heptatrienenitrile based on acrylonitrile consumed. The non-volatile residue weighed 82.5 g.

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(4) W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948); see also J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949, p. 191.

(5) W. Reppe and W. J. Schweckendieck (ref. 2) report the interaction of methyl acrylate and acetylene at 150° to form methyl dihydrobenzoate in very low yield. Other experiments reported by these authors were carried out at lower temperatures and the product was regarded as methyl dihydrobenzoate but they did not present structure proof except on the material made at 150°.

(6) J. L. Charlish, W. H. Davis and J. D. Rose, *J. Chem. Soc.*, 232 (1948).

(7) Analyses carried out under the direction of Dr. J. W. Stillman.

(8) G. H. Kalb and J. C. Sauer, U. S. Patent 2,540,736 (to E. I. du Pont de Nemours & Co., Inc., Feb. 6, 1951).

Anal. Calcd. for C_7H_7N: C, 79.97; H, 6.71; N, 13.32; mol. wt., 105.1; *MR*, 32.88; quant. hydrogenation, 0.0575 g. hydrogen/g. sample. Found: C, 80.12; H, 6.66; N, 13.18; mol. wt. (ebullioscopic in benzene) 106; *MR*, 37.08; quant. hydrogenation, 0.0588 g. hydrogen/g. sample.

Hydrogenation of a solution of 16 g. of unsaturated nitrile in 60 ml. of methanol at ordinary temperatures and 500–600 lb./sq. in. pressure employing palladium-on-charcoal as catalyst yielded on distillation 7 g. of a clear, colorless liquid boiling at 176–180°, redistilled b.p. 181°. This product was shown to be heptanenitrile. It reacted with mercaptoacetic acid and dry hydrogen chloride to form α-iminoheptylthioacetic acid hydrochloride, m.p. 131°, lit. m.p. 133°.[9] Acid hydrolysis of the nitrile yielded *n*-heptanoic acid, b.p. 223°, lit. b.p. 224°. An amide prepared from the acid melted at 94–96° after recrystallization from 1:1 ammonium hydroxide solution; a mixed melting point with a known sample of heptamide, m.p. 94°, showed no depression.

Ozonization of Heptatrienenitrile.—On one occasion the ozonide of heptatrienenitrile decomposed with explosive violence. The preparation and handling of this material was conducted behind a barricade.

A solution of 4 g. of heptatrienenitrile and 150 ml. of methylene chloride was cooled in a Dry Ice–acetone-bath and treated with a stream of oxygen containing ozone for a period of 18 hours. Immediately upon completion of the ozonization the methylene chloride was removed under water-pump pressure until the volume of the remaining solvent and gum-like ozonide was about 30 ml. To this mixture 150 ml. of 3% hydrogen peroxide solution was added. The reaction vessel was connected to a Dry Ice trap in order to collect all volatile reaction products. The ozonide was decomposed by heating the mixture in a water-bath for 6 hours. The system was swept with nitrogen, and the reaction vessel was removed from the barricade. The liquid which collected in the Dry Ice trap was extracted with 3% sodium hydroxide solution. This solution was shown by analysis to contain 0.51 g. of hydrocyanic acid (50% of theory).

The aqueous solution remaining from the decomposition of the ozonide was colorless and clear. No precipitate formed when it was treated with 20% sodium hydroxide. This solution was made acid with concentrated hydrochloric acid and then just alkaline with ammonium hydroxide. Addition of a solution of calcium chloride gave a precipitate of calcium oxalate. This precipitate was separated by filtration and dissolved in dilute sulfuric acid. The resulting acid solution decolorized potassium permanganate solution.

The clear filtrate from the calcium oxalate was made acid to litmus with hydrochloric acid and extracted in a liquid extractor for 40 hours with 150 ml. of ether. The ether extract was dried and ether was removed to yield a small liquid residue. Distillation of this residue at reduced pressure gave a colorless distillate with a distinct acid odor; micro boiling point, 103.5°. This distillate dissolved in sodium bicarbonate solution with evolution of carbon dioxide, reduced cold potassium permanganate solution and formed a crystalline derivative with *p*-bromophenacyl bromide, m.p. 134°, after one recrystallization from ethanol. A derivative prepared in the same manner from a known sample of formic acid melted at 134°; mixed melting point 133–134°. No other acids could be isolated.

Cold alkaline permanganate oxidation in acetone solution at 0° yielded copious quantities of oxalic acid. No β-cyanopropionic acid or succinic acid could be isolated.

Diels–Alder Reactions of 2,4,6-Heptatrienenitrile. (a) **Maleic Anhydride Adduct.**—3-Cyano-6-vinyl-4-cyclohexene-1,2-dicarboxylic anhydride (?). Treatment of the unsaturated nitrile with maleic anhydride in the presence of xylene at its boiling point gave a 54% yield of the 1:1 adduct, m.p. 181–186°.

Anal. Calcd. for $C_{11}H_9O_3N$: C, 65.02; H, 4.46; N, 6.89. Found: C, 65.45; H, 4.60; N, 6.72.

(b) **N-Phenylmaleimide Adduct.**—N-Phenyl-3-cyano-6-vinyl-4-cyclohexene-1,2-dicarboximide (?). A solution of heptatrienenitrile (5.8 g.) and 8.7 g. of N-phenylmaleimide in 28 ml. of xylene was refluxed for 22 hours. On cooling the solution to 0°, a crystalline product was obtained. After recrystallization from xylene, 6 g. (43% yield) of solid adduct melting at 210–212° was obtained. After two more recrystallizations, the melting point was raised to 222–224°.

Anal. Calcd. for $C_{17}H_{14}N_2O_2$: C, 73.76; H, 5.07; N, 10.0. Found: C, 73.75; H, 5.24; N, 10.18.

(c) **Acrylonitrile Adduct.**—Heptatrienenitrile reacts with acrylonitrile in the presence of copper powder at 125° to form a compound which boiled over considerable range. Three arbitrary fractions were taken and analyzed (Table I).

TABLE I

Dist. range, °C./0.15 mm.	Wt., g.	$n^{25}D$	C	H	N
155–162	3.1	1.5239	76.17	6.46	17.72
165–187	3.5	1.5393	77.08	6.58	15.75
187–199	3.1	1.5649	78.92	6.77	13.97
Calcd. for adduct of acrylonitrile, $C_{10}H_{10}N_2$:			76.0	6.3	17.7

The products of this reaction probably consist of a mixture of the acrylonitrile adduct and the dimer of the heptatrienenitrile.

Dimerization of 2,4,6-Heptatrienenitrile.—A mixture of 14.4 g. of heptatrienenitrile and 0.1 g. of copper powder was heated at 125° under nitrogen for 18 hours. Distillation gave 2.7 g. of low-boiling material and 4.9 g. (42% yield based on nitrile consumed) of the dimer as a clear, viscous liquid, b.p. 172–173.5° (0.4 mm.). At room temperature, the material soon became brown.

Anal. Calcd. for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32; mol. wt., 210. Found: C, 79.29; H, 6.96; N, 13.25; mol. wt., 214.

Quantitative hydrogenation of the dimer indicated that it contained an average of 2.66 double bonds per molecule.

Methyl 2,4,6-Heptatrienoate.—A 500-ml. stainless steel rocker bomb was cooled in ice and charged with a mixture of 1 g. of triphenylphosphine, 2 g. of nickel carbonyl and 100 g. of methyl acrylate which contained 0.25 g. of hydroquinone as stabilizer. The procedure for treating the reaction mixture with acetylene was exactly the same as that described above for the preparation of 2,4,6-heptatrienenitrile except that the reaction temperature was maintained at 70°. Forty-five grams of unreacted methyl acrylate was removed at a pressure of 1–2 mm. from the dark brown reaction mixture without application of heat. The residue was then distilled to give 73.6 g. of a clear product characterized by high refractivity and boiling over the range 55–80° (1–2 mm.). This represented an 83% yield of crude product based on methyl acrylate consumed; distillation of the crude product through a small Vigreux column gave the following fractions:

Fraction	Temperature, °C.	Pressure, mm.	$n^{25}D$	Weight g.
1	39.8	0.25	1.5363	5.2
2	38.0–37.8	.25	1.5552	13.3
3	39.4–38.0	.30–0.25	1.5503	29.0
4	45.5–57.8	.7–0.8	1.5429	12.8

Fractions 2 and 3 were the desired ester as shown by analysis.

An infrared spectrum showed that this product has a structure closely resembling that of 2,4,6-heptatrienenitrile.

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.99; H, 7.75.

Quantitative hydrogenation over palladium-on-carbon catalyst showed that each molecule of ester absorbed three molecules of hydrogen. When 7.0 g. of the unsaturated ester was hydrogenated in methanol solution over a palladium catalyst, the hydrogenation product, which was isolated by distillation, boiled over the range of 171.7–173.0°, and had a distinct ester-like odor; lit. b.p. for methyl *n*-heptanoate is 173°. Infrared analysis demonstrated that the hydrogenated ester was identical with a known sample of methyl *n*-heptanoate prepared from *n*-heptanoic acid and methanol.

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[9] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., pp. 206, 267.

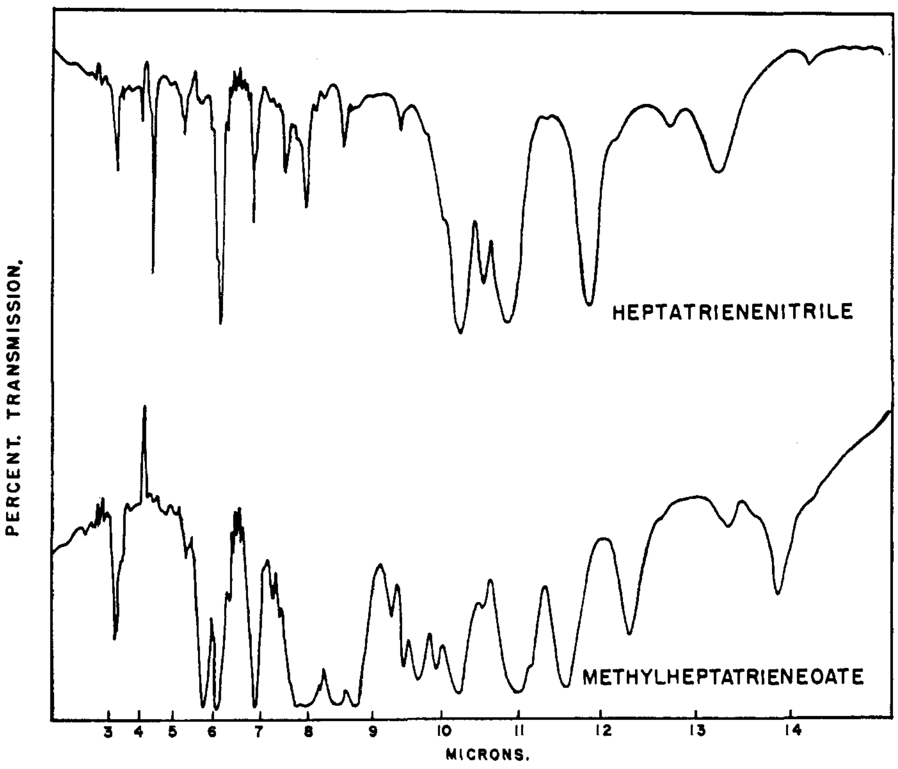


Fig. 1.

Maleic Anhydride Adduct of Methyl 2,4,6-Heptatrienoate.—3-Carbomethoxy-6-vinyl-4-cyclohexene-1,2-carboxylic anhydride (?).· A solution of the ester (12.5 g., 0.09 mole) and maleic anhydride (9.5 g., 0.095 mole) in xylene (23 ml.) was refluxed for 4.5 hours. Increasing the time of reflux to 12.5 hours did not increase the yield. After the solution had been kept at 0° for 5 days, the adduct separated as a sirupy mass. Xylene was decanted and the sirup was converted to a colorless solid (1.9 g.) on trituration with ether. Evaporation of the xylene filtrate on the steam-bath left a residual oil which was dissolved in an equal volume of ether. On standing, more of the adduct (4.8 g.) separated from the ether to give a total yield of 6.7 g. (31%). After recrystallization from ethyl acetate, the material melted at 92–95°.

Anal. Calcd. for $C_{12}H_{12}O_5$: C, 61.01; H, 5.12; sapn. equiv., 78.7. Found: C, 60.94; H, 5.00; sapn. equiv., 80.9, 81.1.

Methyl Malonate–Methyl 2,4,6-Heptatrienoate Adduct.—A solution of 0.78 g. (0.14 mole) of sodium methoxide in 3 ml. of methanol and 3 ml. of dry ether was added to a solution of 20 g. (0.145 mole) of unsaturated ester in 38.3 g. (0.29 mole) of methyl malonate. The solution was heated on a steam-bath for 17.5 hours. Four volumes of ether were added, and the ethereal solution washed with 5 ml. of 5% hydrochloric acid and then with water. After the solution had been dried over magnesium sulfate, the ether was removed by distillation. Distillation of the residual oil gave 35.4 g. of unreacted starting material and 7.4 g. of adduct, b.p. 138–153° (0.2 mm.). The recovered starting material was again treated with sodium methoxide and an additional 9.9 g. of adduct was obtained. The total quantities of adduct amounted to 17.3 g. (44% yield). Redistillation of the crude material gave a fraction boiling at 121–126° (0.1 mm.), $n^{25}D$ 1.4801.

Anal. Calcd. for $C_{13}H_{18}O_6$: C, 57.77; H, 6.71; sapn. equiv., 90.1. Found: C, 57.88; H, 6.51; sapn. equiv., 90.7, 91.7.

2,4,6-Heptatrienoic Acid.—To 150 g. (1.09 moles) of methyl 2,4,6-heptatrienoate was added an equimolar amount of aqueous 10% sodium hydroxide. The mixture was stirred under nitrogen for 6 hours at room temperature. The solution was acidified with concentrated hydrochloric acid (94 ml.) and the precipitated acid was removed by filtration. After washing the product with 150 ml. of ice-water, it was dissolved in 500 ml. of ether. The ether solution was dried over magnesium sulfate and then evaporated to dryness under reduced pressure. The residue was washed with 150 ml. of petroleum ether and then dried in a vacuum desiccator. The product amounted to 97 g. (72% yield). Due to the presence of geometric isomers, the product melted over the range 75–100°. Recrystallization of the material from petroleum ether gave colorless needles melting at 91–100°.

Anal. Calcd. for $C_7H_8O_2$: C, 67.72; H, 6.50; neut. equiv., 124.1; quant. hydrogenation, 0.0487 g. hydrogen/g. sample. Found: C, 67.59, 67.64; H, 6.79, 6.48; neut. equiv., 126.6, 125.3; quant. hydrogenation, 0.0456, 0.0447 g. hydrogen/g. sample.

It was necessary to store the free acid under nitrogen at Dry Ice temperature in order to prevent polymerization.

Hydrogenation of the 2,4,6-heptatrienoic acid in dioxane solution over palladium-on-carbon catalyst at 50° and 500–1500 lb./sq. in. pressure for 30 minutes gave a 91% yield of *n*-heptanoic acid. The saturated acid was identified by infrared measurements and refractive index.

Esterification of heptatrienoic acid with allyl alcohol in refluxing benzene using catalytic amounts of sulfuric acid gave allyl 2,4,6-heptatrienoate. This material was iso-

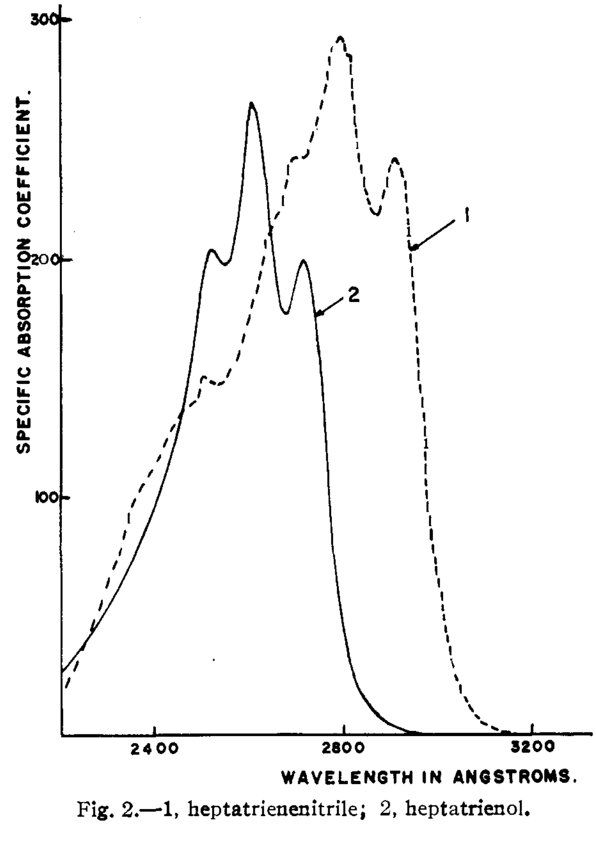


Fig. 2.—1, heptatrienenitrile; 2, heptatrienol.

lated in 12% yield and boiled at 46–49° (0.1 mm.). The heart-cut had a refractive index of 1.5520 at 25°.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37; sapn. equiv., 164.2; quant. hydrogenation, 0.0488 g. hydrogen/g. sample. Found: C, 72.78, 72.99; H, 7.30, 7.10; sapn. equiv., 161.1, 168.9; quant. hydrogenation, 0.0492, 0.0482 g. hydrogen/g. sample.

2,4,6-Heptatrienol.—Commercial lithium aluminum hydride (16.7 g.) in 300 ml. of anhydrous ether was stirred under nitrogen for 300 minutes and then filtered from 2.1 g. of insoluble material into a separatory funnel. The ethereal solution of 14.6 g. (0.38 mole) of lithium aluminum hydride was added dropwise with stirring at 0° to a solution of 95.3 g. (0.69 mole) of methyl 2,4,6-heptatrienoate in 300 ml. of anhydrous ether at such a rate that the temperature was kept below 10°. After the addition was completed (3 hours), the mixture was stirred for 30 minutes at 0–10°. A solution of 44 ml. of concentrated sulfuric acid in 185 ml. of water was then added with stirring so that the temperature did not exceed 15°. The ether layer was separated and the aqueous layer extracted several times with ether. The combined ether extracts were washed with aqueous 5% sodium bicarbonate and then with water. After drying over magnesium sulfate, the ether was removed by distillation under reduced pressure and the residual oil was stirred with a solution of 28 g. of sodium hydroxide in 160 ml. of water under nitrogen for 4 hours to remove any ester. The mixture was extracted with ether and the combined extracts dried over magnesium sulfate. After removal of the ether under reduced pressure, the residual oil was distilled through a helix-packed column. The main fraction distilled at 44–47° (0.02 mm.) and weighed 49.1 g. (65% yield).

Anal. Calcd. for $C_{10}H_{10}O$: C, 76.32; H, 9.15; quant. hydrogenation, 0.0549 g. hydrogen/g. sample. Found: C, 75.88, 76.13; H, 8.98, 9.20; quant. hydrogenation, 0.0502, 0.0512 g. hydrogen/g. sample.

Hydrogenation of 2,4,6-Heptatrienol to *n*-Heptyl Alcohol.—2,4,6-Heptatrienol (17.4 g.) in absolute alcohol (50 ml.) was hydrogenated using 5% palladium-on-carbon (1 g.) at 40–50° under 1000 lb./sq. in. of hydrogen for 2 hours. The solution was filtered from catalyst and alcohol was distilled from the filtrate. Distillation of the residual oil gave 12.7 g. of product, b.p. 82–84° (16 mm.). The N-phenylcarbamate was prepared by heating this compound (1 g.) with phenyl isocyanate (0.5 ml.) on the steam-bath for 5 minutes. Recrystallization of the carbamate from alcohol–water gave colorless crystals, m.p. 57.5–58°. In the same manner *n*-heptyl N-phenylcarbamate, m.p. 58–58.5°, was prepared from *n*-heptyl alcohol, b.p. 83–83.5° (16 mm.). There was no depression in melting point on admixture of the two carbamates. Therefore, the hydrogenated product is *n*-heptyl alcohol.

Absorption Spectra.—The infrared spectra of heptatrienenitrile and methyl heptatrienoate are given in Fig. 1 and the ultraviolet absorption spectra of the nitrile and heptatrienol in Fig. 2. These spectra show bands at 3.2, 6.1, 10.2 and 10.8 microns from the —CH=CH_2 group, slightly shifted from the position for this group in simple olefins such as 1-octene. The lack of absorption band for the —C≡C—H groups at 3.0 microns shows the absence of a terminal acetylenic CH bond. Absorption bands at 3.4 and 6.8 microns are not of sufficient intensity to allow CH_2 groups as a major constituent in either structure. The ultraviolet spectrum of the nitrile showed a series of strong bands about 2800 Å., while a similar absorption, shifted to the shorter wave lengths, is evident for the corresponding alcohol. The Raman spectrum of methyl heptatrienoate failed to show the characteristic lines near 2200 cm.$^{-1}$ for an internal triple bond. An exceedingly strong Raman line at 1630 cm.$^{-1}$, indicative of conjugated double bonds, was observed.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, FOUAD I UNIVERSITY]

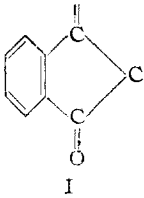
Some Adsorption Colors and Their Significance for Thermochromic and Tautomeric Effects. III. Experiments with Anthrone Derivatives, Nitrotoluenes, Spiropyrans and Xanthhydrols

BY ALEXANDER SCHÖNBERG, AHMED MUSTAFA AND WAFIA ASKER

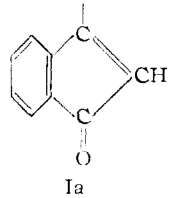
RECEIVED MARCH 17, 1952

Activated alumina acquires a deep orange color when added to a cold colorless solution of 10-nitroanthrone, presumably because of the formation of the colored 10-nitroanthranol. Similar results are obtained in the case of 10-anilinoanthrone (orange color). Adsorptiochromism was also observed with the colorless 10,10-bianthronyl and with 2,4-dinitrotoluene and 5-nitroacenaphthene. Benzene solutions (cold or hot) of dibenzospiropyran are colorless; a deep violet adsorption color is produced with activated alumina or dried silica gel. Adsorptiochromism, piezochromism and thermochromism are discussed in the case of some pyrans and pyrones and their sulfur analogs; replacement of the oxygen by sulfur is detrimental to the development of color.

Recently,[1] it has been shown that when activated alumina is added to a colorless cold solution of 1,3-diketohydrindene (I), the inorganic material acquires a violet color at once. The theory was advanced that the violet color was due to the enolic form; in the colorless benzene solution, there exists an equilibrium (I ⇆ Ia) which strongly favors the left-hand side, but the activated alumina preferentially adsorbs Ia, producing the adsorption color. It is also possible that the enol form (Ia) is produced by the action of the activated adsorbent. Ia has never been isolated as such, and it seems desirable to investigate the behavior of pairs of keto–enol tautomers toward activated alumina.



I



Ia

(1) **Experiments with (a) 10-Nitroanthrone.**—When to the colorless benzene solution of 10-nitroanthrone[2] is added a piece of activated alumina, a deep orange color is produced on the surface immediately. When the dried colored inorganic material is treated with aqueous ferric chloride solution, a green color is produced. 10-Nitroanthranol forms red needles; its yellow, alcoholic solution gives a green color with aqueous ferric chloride solution.

(b) **10-Anilinoanthrone (IIa).**—When the pale yellow benzene solution of IIa is treated with activated alumina, a yellowish-orange adsorption color is observed and the solution becomes yellow with a green fluorescence and then after

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[1] A. Schönberg, A. Mustafa and W. Asker, THIS JOURNAL, **73**, 2876 (1951).

[2] Meyer and Sander, *Ann.*, **396**, 133 (1913).