

5% pyridine and 20% ethanol, melted at 202°. The mixed melting point with glucosazone (m. p., 207–208°) was 204–204.5°.

Summary

Rutin was isolated from the fresh flowers of two varieties of *Forsythia*, *suspensa* and *fortunei*, and

identified by chemical and spectrophotometric methods. Evidence was obtained that the rutin content diminishes with age in *F. fortunei* as it does in buckwheat.

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[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES, MONSANTO CHEMICAL COMPANY]

Unsaturated Nitriles. IV. Adducts of Dienes with Fumaronitrile¹

BY DAVID T. MOWRY

It has been well established that the cyano group confers considerable dienophilic activation upon a double bond in the α,β -position.² Acrylonitrile,³ crotononitrile⁴ and alkylidene malonitriles⁵ have been shown to condense with dienes. Recently Blomquist and Winslow⁶ have condensed cyclopentadiene and diphenylfulvene with dinitriles such as fumaronitrile, maleonitrile and acetylene dicarbonitrile.

ergosterol. In addition isosafrole and methyl abietate gave indications of having formed adducts but no well-defined crystalline or distillable products could be isolated from the reaction mixture.

3,6-Methano-1,2,3,6-tetrahydrophthalonitrile (from cyclopentadiene and fumaronitrile) was further characterized by the preparation of a dichloride.

TABLE I

1,2,3,6-Tetrahydrophthalonitrile	Yield, ^a %	M. p., °C.	Formula	Analyses, % ^a					
				Carbon		Hydrogen		Nitrogen	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
3,6-Methano-	98	98 ^b	C ₉ H ₈ N ₂
3,5-Dimethyl-	40	68 ^f	C ₁₀ H ₁₂ N ₂	75.0	74.8	7.50	7.43	17.50	17.66
3,3-Dimethyl-6-(α -methylpropenyl) ^c	23	98	C ₁₄ H ₁₈ N ₂	78.5	78.4	8.42	8.52	13.07	13.08
3,6-Endoxo-	25	111	C ₈ H ₈ ON ₂	65.7	66.0	4.13	4.52	19.30	19.11
3-Methyl-3,6-endoxo-	20	100	C ₉ H ₉ ON ₂	66.7	67.0	4.97	5.38	17.28	17.68
3,6-Dimethyl-3,6-endoxo-	24	72	C ₁₀ H ₁₀ ON ₂	69.0	69.0	5.75	6.04	16.08	16.19
3-Acetoxyethyl-3,6-endoxo-	23	113	C ₁₁ H ₁₀ O ₃ N ₂	60.6	60.5	4.63	4.76	12.83	12.93
3,6-Methano-1-methyl-	44	127 ^g	C ₁₀ H ₁₀ N ₂	76.0	75.8	6.38	6.67	17.74	18.06
Other adducts									
9,10-(α,β -Dicyanoethano)-9,10-dihydroanthracene	64	259	C ₁₈ H ₁₂ N ₂	84.4	84.3	4.72	4.87	10.94	10.96
5,8-(α,β -Dicyanoethano)-5,8-dihydroergosterol	40	210–212	C ₃₂ H ₄₆ ON ₂	81.0	80.7	9.75	10.10	5.91	5.71
3,6-Methano-4,5-dichlorohexahydrophthalonitrile	78	167	C ₉ H ₈ N ₂ Cl ₂	..	^d	12.96	12.95

^a Microanalyses by the Arlington Laboratories, Fairfax, Va. ^b Blomquist and Winslow, ref. 6, give m. p. 96°. ^c This structure is preferred to the alternative 3,4-dimethyl-6-isobutenyl-1,2,3,6-tetrahydrophthalonitrile because the analogous anhydride is obtained from allo-ocimene and maleic anhydride, see Alder, *Die Chemie*, **55**, 53 (1942), and Hultzsch, *Ber.*, **72B**, 1173–1187 (1939). ^d Calcd. for Cl, 32.8; found, 33.1. ^e No allowance made for unreacted reagents which were recovered. ^f B. p. 138° (3 mm.). ^g B. p. 158–160° (20 mm.).

The present paper reports an extension of the work with fumaronitrile in which a variety of dienes were used. Fumaronitrile has been found to form adducts with cyclopentadiene, 2-methylpentadiene, allo-ocimene, anthracene, furan, sylvane, 2,5-dimethylfuran, furfuryl acetate and

Cyclopentadiene was also condensed with mesaconitrile, which proved to be less reactive than fumaronitrile, to give 3,6-methano-1-methyl-1,2,3,6-tetrahydrophthalonitrile.

The compounds prepared are listed and described in Table I. The adducts of fumaronitrile with the lower diolefins were reasonably stable and could be distilled under reduced pressure. On the other hand, the compounds obtained from the furan derivatives decomposed at temperatures somewhat above their melting points. Thus, when 1,2,3,6-tetrahydro-3,6-endoxophthalonitrile was heated a short time at 115° a nearly quantitative dissociation into furan and fumaronitrile

(1) Preceding papers, *THIS JOURNAL*, **66**, 371 (1944); **67**, 926, 1050 (1945).

(2) See Norton, *Chem. Rev.*, **31**, 319 (1942); Alder, *Die Chemie*, **55**, 53 (1942).

(3) Wolfe, U. S. Patent 2,217,632 (1940); Miller and Bradley, U. S. Patent 2,382,803 (1945).

(4) I. G. Farbenindustrie A.-G., French Patent 37,498 (1929).

(5) Alder and Rickert, *Ber.*, **72B**, 1983 (1939), U. S. Patent 2,264,354 (1941).

(6) Blomquist and Winslow, *J. Org. Chem.*, **10**, 149 (1945).

occurred. Similar decomposition took place on refluxing in solvents such as ethanol so that it was necessary to exercise caution in recrystallization techniques.

Experimental

Reagents.—Fumaronitrile was prepared by the phosphorus pentoxide dehydration⁷ of fumaramide in 80–90% yields. The product was redistilled and crystallized from a mixture of benzene and hexane and melted at 96.8°. The dienoic compounds were obtained from Eastman Kodak Co. unless specified otherwise.

3,5-Dimethyl-1,2,3,6-tetrahydrophthalonitrile.—A method similar to that employed⁸ for the analogous condensation with maleic anhydride was used. A mixture of 78 g. of fumaronitrile (1.0 mole), 82 g. of 2-methylpentadiene (1.0 mole, Commercial Solvents Corp.) and 1 g. of hydroquinone was dissolved in 250 cc. of dioxane and allowed to stand at room temperature for five days. Distillation under reduced pressure through a 50-cm. Vigreux column gave 64 g. of the product, b. p. 177–182° (22 mm.). Redistillation gave a purer material, b. p. 138–139° (3 mm.), n_D^{20} 1.4852. The material was a viscous colorless oil which solidified when cooled in Dry Ice. The analytical sample was recrystallized five times from dilute ethanol.

3,3-Dimethyl-6-(α -methylpropenyl)-1,2,3,6-tetrahydrophthalonitrile.—Allo-ocimene (130 g., 1.0 mole, Newport Industries) and fumaronitrile (78 g., 1.0 mole) were dissolved in a mixture of 500 cc. of absolute ethanol and 100 cc. of dioxane. This was heated for two days at 50° before standing at room temperature for an additional three-day period. The product was poured into 2 liters of water, extracted with ether and distilled under reduced pressure. In addition to unreacted allo-ocimene and fumaronitrile, there was obtained a fraction, b. p. 160–165° (3 mm.), which solidified in the receiver, m. p. 90–92°. Recrystallization from dilute ethanol gave 48 g. of the adduct, m. p. 96–97°. The analytical sample after two more recrystallizations melted at 98°.

9,10-(α,β -Dicyanoethano)-9,10-dihydroanthracene.—The method used was similar to that employed by Clar⁹ who caused anthracene to react with maleic anhydride. Anthracene (125 g., 0.7 mole) and fumaronitrile (55 g., 0.7 mole) were dissolved in 500 cc. of xylene and refluxed for thirty minutes at which time precipitation of the product began. After fifteen minutes of further refluxing the material was cooled and filtered to give 143 g. (80%) of crude product m. p. 200–202° which a nitrogen analysis showed to be about 80% pure. It was purified by three recrystallizations from 90% dioxane.

3,6-Endoxo-1,2,3,6-tetrahydrophthalonitrile.—One half mole portions of fumaronitrile (39 g.) and furan (34 g., E. I. du Pont de Nemours & Co.) in 150 cc. of dioxane were heated at 40° in a closed container for two days. After cooling to room temperature, sufficient hexane was added to make the solution barely turbid and 18 g. (25% yield) of product, m. p. 111° (sealed tube), slowly precipitated in five days time. A second crop of 12 g., m. p. 81–88°, proved to be largely fumaronitrile and a third oily fraction was a mixture of the reagent and product. Cautious recrystallization from benzene and hexane did not raise the melting point.

A small sample was heated at 115° in an oil-bath and the decomposition products identified as a fluid liquid, b. p. 31.5° (furan has b. p. 32°) and a solid m. p. 96° which was not depressed by mixing with fumaronitrile. Similar thermal instability has been reported² for other Diels-Alder adducts of the furans.

Less satisfactory results were obtained when the reaction was run in a mixture of benzene and ether at room temperature and in benzene solution at 70°.

3-Methyl-3,6-endoxo-1,2,3,6-tetrahydrophthalonitrile.—One half mole portions of fumaronitrile (39 g.) and sylvane

(41 g., Quaker Oats Co.) were allowed to stand for five days in 200 cc. of dioxane. The product was precipitated by pouring into water and the crude product was recrystallized three times from dilute ethanol to give 16 g. of the pure adduct.

Attempts to run the reaction in a benzene or a benzene-ethanol mixture and to purify the product by recrystallization from benzene and hexane gave inferior results.

3,6-Dimethyl-3,6-endoxo-1,2,3,6-tetrahydrophthalonitrile.—One mole portions of fumaronitrile (78 g.) and 2,5-dimethylfuran (96 g., Carbide and Carbon Chemical Corp.) in 150 cc. of dioxane were allowed to stand for three weeks at room temperature. The solvent was removed at reduced pressures. The residue was recrystallized from dilute ethanol and 82 g. of a crude fraction, m. p. 57–64°, was obtained. Recrystallization gave 10 g. of impure reagent, m. p. 51–56° in the first crop and 42 g. of the adduct, m. p. 70–71°, in the second crop. The analytical sample was recrystallized two more times from ethanol.

3-Acetoxymethyl-3,6-endoxo-1,2,3,6-tetrahydrophthalonitrile.—One mole portions of fumaronitrile (78 g.) and furfuryl acetate (140 g.) in 150 cc. of dioxane were allowed to stand for ten days. The solvent was evaporated under reduced pressure and a crop (38 g.) of crystals was obtained by cooling and filtering. The operation was repeated twice on the mother liquor and two additional crops of crystals obtained. The first and third crops (54 g.) m. p. 106–108° were the desired product while the second crop (44 g. m. p. 94–97°) proved to be largely unreacted fumaronitrile. Two more recrystallizations from dilute ethanol raised the melting point to 113°.

5,8-(α,β -Dicyanoethano)-5,8-dihydroergosterol.—One-eighth mole portions of fumaronitrile (10 g.) and ergosterol (50 g.) were refluxed in 100 cc. of xylene for five hours. The material was diluted with hexane and cooled to give 24 g. of material, m. p. 198–205°. Three recrystallizations from ethanol raised the melting point of the adduct to 210–212°.

The structure of this compound was assigned by analogy with the corresponding known maleic anhydride adduct.¹⁹

1-Methyl-3,6-methano-1,2,3,6-tetrahydrophthalonitrile.—Half mole portions of mesaconitrile, b. p. 71° (15 mm.), n_D^{20} 1.4699, prepared in 89% yield by the phosphorus pentoxide dehydration¹¹ of mesaconamide, and cyclopentadiene were refluxed in benzene for two hours. The product was distilled under reduced pressure and a 32-g. fraction b. p. 158–160° (20 mm.) was obtained as waxy supercooled glass. Trituration gave a crystalline form, m. p. 127°. The material was extremely hygroscopic and all attempts to recrystallize it from dilute methanol or benzene and hexane failed.

Only traces of the material were formed at 30° in ethanol or benzene solution in two hours time. The more reactive fumaronitrile gives almost quantitative yields of 3,6-methano-1,2,3,6-tetrahydrophthalonitrile⁶ under these conditions.

3,6-Methano-4,5-dichlorohexahydrophthalonitrile.—Forty-three grams of 3,6-methano-1,2,3,6-tetrahydrophthalonitrile, m. p. 98°, obtained in 98% yield by the method of Blomquist and Winslow⁶ was dissolved in 150 cc. of glacial acetic acid. Chlorine was passed in at 14–20° until 21 g. had been absorbed. The solution was cooled, filtered and washed with acetic acid and water to give 28 g. of material m. p. 148–155°. Two recrystallizations from ethanol raised the melting point to 167°. An additional partially crystalline sirup of 22 g. of mixed isomers was obtained by addition of water to the mother liquor.

Summary

Fumaronitrile has been shown to form adducts of the Diels-Alder type with a variety of unsaturated compounds including 2-methylpentadiene,

(7) deWolf and Van de Straete, *Bull. Sci. acad. roy. Belg.*, **21**, 216 (1935).

(8) Bachmann and Goebel, *THIS JOURNAL*, **64**, 787 (1942).

(9) Clar, *Ber.*, **64**, 2194 (1931).

(10) Windaus and Lüttringhaus, *Ber.*, **64B**, 850 (1931).

(11) Van de Straete, *Bull. sci. acad. roy. Belg.*, **21**, 226 (1935).

allo-ocimene, anthracene, furan, sylvane, 2,5-dimethylfuran, furfuryl acetate and ergosterol. Mesacononitrile has been similarly condensed

with cyclopentadiene. The resultant compounds have been characterized.

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High-Boiling Hydrolytic Derivatives of Lignin

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A previous publication¹ described the hydrolysis of butanol lignin in 50% aqueous butanol, about 0.25 *N* with hydrochloric acid, at 160° for three hours. Products boiling below butanol, arbitrarily designated as volatile products, were isolated in the following yields

	Yield, %		Yield, %
Methanol	2.5	Allyl alcohol	2.5
Formic acid	11.4	<i>n</i> -Butyraldehyde	1.6
Acetone	1.9	β -Ethyl- α -methyl- acrolein	2.8
Propylalcohol	4.8	Total	27.5

The present study was undertaken to ascertain the nature and yields of additional less volatile substances found in the acidic hydrolysis of lignin from western hemlock.

Procedure.—The source and preparation of the lignin, the hydrolysis, and the fractionation were described in a previous publication.¹ The present study has required, in addition, the use of appropriate high-vacuum pumps and stills. The least volatile products were collected in a molecular still of the Washburn type at a pressure of 10^{-6} mm. of mercury, measured by a McLeod gage.

Results.—The following additional "high-boiling" substances were obtained

	Yield, %		Yield, %
Resorcinol mono- methyl ether	7.3	<i>n</i> -Butyric acid	1.0
<i>m</i> -Cresol	6.7	Guaiacol	0.3
		Vanillin	0.2
		Total	15.5

In addition to these compounds, 0.6% of complex phenols was obtained but the quantity was not adequate for characterization. A resinous, alkali-soluble fraction was also obtained.

Identification.—(1) **Resorcinol Monomethyl Ether.**—The *N*- α -naphthylcarbamate melted at 127–128° and the aryloxyacetic acid at 115–116°.

(2) ***m*-Cresol.**—The 3,5-dinitrobenzoate melted at 164°, mixed melting point of unknown and authentic sample of *m*-cresol showed no depression, and *N*-naphthylcarbamate melted at 125–126°.

(3) ***n*-Butyric Acid.**—The *S*-benzylthiuronium salt melted at 144° and the *p*-phenylphenacyl ester at 80–80.3°.

(4) **Guaiacol.**—The *p*-nitrobenzoate melted at 90–90.5° and the 3,5-dinitrobenzoate, crystallized from alcohol, at 140–140.4°.

(5) **Vanillin.**—The oxime melted at 115–115.7° and the 2,4-dinitrophenylhydrazone (from acetic acid) at 269°.

Discussion.—The total yield of products is of the same order as was obtained by Hibbert and co-workers in the hydrolysis of maple lignin in the presence of ethanol and hydrogen chloride, although the structures of the compounds obtained show less relationship. While benzene rings and short aliphatic chains have been found in both studies, Hibbert found them combined in compounds having the carbon skeleton of propyl benzene. This carbon skeleton has not been found in the present study although propyl compounds and benzene derivatives have been found. Hibbert used maple lignin while western hemlock lignin was used in these experiments.

The appearance of methoxyl in a resorcinol derivative was unexpected and suggests the presence of a structure of the meta configuration in the native lignin rather than the more common 1,2-substituted compounds such as guaiacol, the 1,3,4-substituted compounds such as vanillin, and the 1,4-substituted hydrogenation derivatives. The original methoxy appears to be satisfactorily accounted for in the yield of methanol, formic acid and resorcinol monomethyl ether. The occurrence of *m*-cresol in substantial quantities likewise suggests that the 1,3-substituted benzene nucleus should be considered in relation to constitution.

It is possible that the *n*-butyric acid should be regarded as derived from the butanol solvent rather than from the lignin.

Constitutional conclusions that might tentatively be drawn from the above experiments are these: hydrolysis (and perhaps mild oxidation as well) converts 40% of the lignin into identifiable compounds. About one-third are phenolic, and the remaining two-thirds are short-chain, aliphatic compounds. There is general similarity between these products and previously isolated derivatives of lignin. In view of the many products of reaction, and the 60% fraction of the lignin not converted to identifiable products, it does not appear justified to propose a constitutional model from the data of these experiments.

While the original intent was to learn the effects of acidic hydrolysis, the nature of the compounds identified suggests that mild oxidation also occurred.

The discussion in the previous paper,¹ relating to the more volatile products identified, does not appear to be in need of correction in the light of

(1) A. Bailey, THIS JOURNAL, 64, 22 (1942).